Biomass Gasifier "Tars": Their Nature, Formation, and Conversion

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NOTICE

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PREFACE

This literature study was commissioned by the IEA Bioenergy, Biomass Utilization Task XIII, "Thermal Gasification of Biomass" activity. At the invitation of Dr. Suresh Babu, Institute of Gas Technology, activity leader, the authors agreed to compile the following information pertinent to one of the persistent problems in coupling gasifiers to energy conversion devices—the presence and modification or removal of the organics historically called "tars."

This report will be issued under the auspices of the IEA Biomass Utilization Activity and will be published as an NREL technical report and appear on the NREL/DOE Power Home Page.

*"When *I* use a word," Humpty Dumpty said in a rather scornful tone, "it means just what I choose it to mean—neither more nor less." *Through the Looking Glass*, Lewis Carroll.

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SUMMARY

The main purpose of this review is to update the available information on gasification "tar." "Tar" is the most cumbersome and problematic parameter in any gasification commercialization effort. For this reason the IEA Gasification Activity has commissioned this work, which aims to present to the community the scientific and practical aspects of (a) "tar" formation and (b) "tar" conversion or removal during gasification as a function of the various technological and technical parameters and variables.

Historically "tar" was an operationally defined parameter, based largely on organics from gasification that condensed under operating conditions of boilers, transfer lines, and internal combustion engine (ICE) inlet devices. Such a definition requires a more detailed chemical explanation in light of the greatly expanded uses proposed for both high- and low-energy gas from a variety of biomass and waste materials. At present the literature contains many data on the "destruction," "conversion," "removal," etc., of "tars," "condensibles," "heavy hydrocarbons," etc., without a consistent definition of these terms and a description of the sampling and analytical methods used for the organics of interest. Though the data presented are useful in the context of the system being studied, they are limited in their transfer to other systems because they are "apparatus dependent."

It is not within the mandate of this work to propose a widely accepted definition of "tar," but rather to report the varied use of the term. Hopefully this report will complement a recent effort of the IEA Gasification Task [BTG/UTWENTE 1998] to reach a consensus among its members regarding such an acceptable definition, as the first step in the adoption of a "tar" sampling protocol for the product from a variety of gasifiers, both high- and low-energy (producer) gas. Thus, within these limitations, this work suggests that "tar" is defined as follows:

"The organics, produced under thermal or partial-oxidation regimes (gasification) of any organic material, are called "tars" and are generally assumed to be largely aromatic."

Although this definition does not allow for distinction between classes and families of compounds, to be presented comprehensively in Chapter II of this report, it is a useful starting definition for gasification "tar."

Chapter III points out the main, and consequently the most practically important, differences in "tar" nature and quantities as a function of gasification conditions and applied technology. "Tar" nature also depends on gasified feedstock and degree of feedstock contamination. A summary of the known mechanisms of chemical formation and conversion during gasification regimes is presented and commented on in Chapter II.

Chapter IV undertakes a short presentation of "tar" sampling and analysis protocols used worldwide by workers and researchers in this field. A comprehensive report on this topic is available in the literature. Nevertheless, in this chapter the authors have undertaken a comparison of the technical details of a few of the sampling and analysis protocols, the aim being to relate facts with intrinsic difficulties and encountered errors, and thus provide an insight into the efforts to formulate widely accepted protocols for "tar" identification and quantitative measurement.

A very important, though not well studied, topic is the tolerance of gasifier gas end-use devices for "tar." Data are available from R&D activities and from field experience, mainly coming from manufacturers. In Chapter V there is a presentation of the gasifier-gas applications for energy and chemicals production, followed by a report of gas specifications for these processes. The reader has access to a large amount of information regarding the content and nature of contaminant "tar" in fuel gases, but their impact on a variety of energy conversion and process applications is only beginning to be documented. One should contact manufacturers and involve them in the process leading to commercial application as well as performance warrantees.

Chapters VI, VII, and VIII deal with raw-gas cleaning technologies. They focus on tar removal through physical processes (Chapter VI) and "tar" conversion through thermochemical and catalytic processes (Chapters VII and VIII). The physical processes are classified into wet and dry technologies depending on whether water is used. Cyclones, cooling towers/scrubbing columns, venturis, demisters/coalescers, cold and hot filters, baghouses, electrostatic precipitators, and wet-dry contactors/scrubbers are reported with sample literature coverage. Technologies available for treating wastewater coming from wet-scrubbing processes are also briefly presented. They concern organic solvent extraction, distillation, adsorption on activated carbon, incineration, biological treatment, and wet oxidation. The choice of cleaning train depends on the specific application and the results of technoeconomic evaluation that must be carried out before a process is selected.

The chemical "tar" conversion processes are divided into four generic categories: thermal, steam, partially oxidative, and catalytic processes. Because of their particular importance as well as the intensive R&D work dedicated to them, the catalytic processes are analyzed and reported separately in Chapter VIII. Among these processes, catalytic steam reforming using dolomites and, more efficiently, Ni-based catalysts seem of great importance and should lead to commercial applications in the near future, especially for gas use in gas turbines. It is widely accepted that physical cleaning technologies are suitable for gas use in boilers and ICEs (for downdraft gasifiers at least); high-temperature chemical "tar" conversion schemes may be required for gas turbine or high-temperature fuel cell applications.

The review is complemented with a selected bibliography on biomass gasifier "tars," with annotations relevant to formation, nature, analysis, removal, conversion, and end-use device tolerance. This bibliography is composed of some 400 publications. Comments/annotations are meant to help interested readers select papers for their specific needs.

In conclusion, we would like to reiterate our intention to provide the gasification community with an appropriately compiled resource regarding the important issue of "tar" presence in raw gas from the variety of gasifiers being developed.

CONCLUSIONS AND RECOMMENDATIONS

Composition, Formation, and Maturation of "Tar"

The characterization of "tars" as primary, secondary, and tertiary is a first step in classifying these materials and relating the composition of "tars" with formation conditions. Some gasifiers show the presence of primary and tertiary "tar" constituents in the same "tar" sample, and this raises the question of the importance of process upsets and large, residence-time distributions that could cause this occurrence. This could have important implications in the design and operation of gasifiers to ensure adequate control of reaction conditions. These "tar" constituents can be used as indicators of overall reactor performance and design (Brage et al. 1997b).

Although past work has shown the systematic nature of "tar" composition as a function of reaction temperature, more detailed study is needed to characterize the product at a higher level of detail. Some primary products will likely be more refractory to secondary thermal and oxidative cracking reactions than others, so an accepted method of characterizing the compound classes in each major group is desirable and a method of rapidly screening for this information is needed. For example, it may be possible to "train" spectroscopic techniques to provide the necessary analysis based on correlation with more detailed work on a test system with GC/MS and other techniques that give highly specific information, but are expensive to perform. Another approach is to identify "marker compounds," or predominant constituents, which are indicators of overall chemical composition and to use methods to monitor these representaitve indicators of overall "tar" composition (Brage et al. 1996).

This chemical characterization could be correlated with key physical property data and process operations, such as performance of wet scrubbing systems or catalytic cracking units. Primary, secondary, and tertiary classes are a starting point, but more detail is needed about the conversion of specific compound classes such as organic acids, which seem to persist beyond other primary products.

Kinetics and reaction pathways for primary to secondary and tertiary processes should be known so they can be included in the design of gasifiers and cleanup systems. The qualitative and quantitative effects of oxygen and steam on product distributions should also be better known. More quantitative studies are needed of primary, secondary, and tertiary products in fluid beds where residence time distribution affecting reaction severity must be considered.

Alternative feedstocks, such as herbaceous crops with high nitrogen content, raise questions about nitrogen-containing constituents. Analysis of these materials warrants more study.

Finally, the pathways to soot and particulates, from tertiary products, require quantitative study to better ascertain the importance of these processes. This may be critical in hot-gas cleanup technology.

Recommendations:

Once "tar" collection protocols are established, compound-class analysis methods and the analysis of predominant constituents should be established as standard procedures. Kinetic modeling of these groups should be attempted to help gasifier designers systematically address the relative importance of process upsets and residence-time distributions in accounting for mixed product slates.

"Tar" Levels from Gasifiers

The results reported for "tar" levels from the three main categories of gasifiers, tabulated in Table 3-1, show a bewildering array of values, in each case (updraft, downdraft, and fluid-bed) spanning two orders of magnitude! Three of many reasons for this have no relation to the gasifier performance per se, but are a result of the different definitions of "tar" being used; the circumstances of the sampling; and the treatment of the condensed organics before analysis. There is general agreement about the relative order of magnitude of "tar" production, with updraft gasifiers being the "dirtiest," downdraft the "cleanest," and fluid beds intermediate. A very crude generalization would place updraft at 100 g/Nm^3, fluid beds at 10 g/Nm^3, and downdraft at 1 g/Nm^3. It is also well established that well-functioning updraft gasifiers produce a largely primary "tar," with some degree of secondary character (assuming no oxygen is added in a second stage); downdraft gasifiers produce an almost exclusively tertiary "tar;" and fluid beds produce a mixture of secondary and tertiary "tars." In updraft gasifiers, the "tar" nature is buffered somewhat by the endothermic pyrolysis in the fresh feed from which the "tars" primarily arise. In downdraft gasifiers the severity of final "tar" cracking is high, due to the conditions used to achieve a significant degree of char gasification. In fluid-bed gasification a great variety of temperatures, environments, and circulation schemes are being tested, suggesting major improvements are coming. The nature of the feed material (for biomass) is only a secondary influence on the nature of the "tar."

The amount of "tar," not to mention the chemical making of the "tar," from a given gasifier is a function of the temperature/time history of the particles and gas; the point of introduction of feed in fluid beds; the thoroughness of circulation (in fluid beds); the degree of channeling (in fixed beds); the feed particle size distribution; the gaseous atmosphere (O_2, steam); the geometry of the bed; the method of "tar" extraction and analysis. In view of this, it did not seem worthwhile to try to rationalize the amounts of "tar" report in Table 2.1, except in the broadest terms.

Recommendations:

The two most helpful things that researchers and operators could do in reporting raw-gas "tar" levels would be to clearly highlight the condensation, sample preparation, and analytical methods used and the end use to which the definition of "tar" is being applied. As an example, in the context of operating ICEs, one might be collecting only organics condensing above, say, 100°C; weighing the condensate; and not considering light hydrocarbons and benzene or toluene. At the other extreme, in a projected use of the gasifier output for an internally reforming solid-oxide fuel cell, the entire suite of organics, particularly olefines and aromatics, might need to be specified. At the last IEA Gasification Task meeting (Brussels, March 1998), it was stated that *"all organics boiling at temperatures above that of benzene should be considered as 'tar.'"*

"Tar" Measurements

The biggest issue, which confuses the meanings people apply to "tar" and the intercomparability of results from various researchers, are: the conditions and solvents used for "tar" collection; and the subsequent solvent separation. The variety of analytical characterizations of the collected material gives different views of the makeup of the organics, but if clearly documented, does not mislead the reader. As detailed earlier, the temperatures, trapping schemes, and solvents used to capture organics vary extremely. Capture temperatures from -78°C to +190°C, with many temperatures in between, are reported. Single-to-multiple vessels are used, containing solvents such as acetone, methanol, dichloromethane, methylene chloride, and toluene. Solid sorbents such as cellulose, fiber glass, and amino-bonded silica (Brage et al. 1997a) are also used. Sometimes the collection of aerosols of "tar" is mentioned. The extraction of the organic fraction of ash, char, and soot is seldom considered. Losses of solvent during sampling is also a concern when "tar" is measured gravimetrically, especially for gases with low "tar."

Some measurements of the organics in the condensate do not require separation of the solvent or water. In most cases, however, a pre-separation or extraction is used, especially when weight is the measure. Solvent removal has been reported by distilling at 75°C to 150°C; by evaporating at 25°C to 105°C under ambient to 10-mm Hg pressure; by air-drying at room temperature or at 93°C overnight; and by organic partitioning; depending on the fraction of "tar" that is of interest to the end use being studied. As one example of the large difference in quantity of "tar" being reported, Aldén et al. (1996) note that the "total tar" can be six times the commonly measured "condensable tar."

There are issues in the probe design that are not always explicitly discussed. Probe and lines must be at a high enough temperature to prevent condensation of the least volatile tar component of interest, but not so high as to cause additional cracking or interaction with particulates of whatever nature. Because some of the tar can be in aerosol form or reside on ash, char, or soot particulates, isokinetic sampling would seem to be a prudent practice.

Recommendations:

A number of sampling methods, specific to biomass and the predominant measure of organics for categories of end use, need to be standardized. These should include probe conditions; collection geometry and conditions; and solvent use and removal. To support these standards, research needs to be carried out on the fractions of organics that are captured and removed from the solvents being used for primary, secondary and tertiary "tars." As noted earlier, and following the suggestions in the literature, a widely recognized standards organization, in collaboration with other standards groups and the IEA gasification task, should lead this activity (BTG 1995b; Kurkela et al. 1995a; Salzmann et al. 1996; Ståhlberg and Kurkela 1990; Brown 1996; Easterling et al. 1985; Techwest 1983; CRE 1997; Delgado et al. 1997).

This issue of standards is currently being addressed, as is documented in the University of Twente web site: http://bgt.ct.utwente.nl/projects/558/(BTG/TWENTE 1998) and by the IEA Gasification Task (Brussels, IEA 1998).

Tolerance of End-Use Devices for "Tar"

There are very few well-defined and long-term data on the tolerance to "tar" of the great variety of energy conversion devices now being considered for gasifier output (boilers excepted). The older literature focused primarily on ICEs for automotive use. More recently, applications of the gas to fire turbines have been in the forefront. In almost no applications, except close-coupled boilers, have endurance tests or operations been carried out long enough to give valid projections of maintenance and systems costs. When such tests are done it will be most valuable if the offending organics are clearly identified so the results can be generalized. The studies going on in coal gasification, with coupling to turbines, engines, fuel cells, etc., should provide valuable information, particularly when highly cracked or tertiary "tars" are involved. Such "tars" are remarkably similar for biomass and for coal.

Recommendations:

Governments and developers should support long-term, well-controlled tests on engines (industrial and automotive), internally and externally fired turbines, fuel cells, and the variety of externally fired systems such as Stirling engines, where heat transfer materials and geometry differ from simple boilers. The nature of the "tar" involved in these tests should be well defined.

Tar Removal through Physical Processes

Physical processes will continue to play a very important role for the successful commercial implementation of gasification. They constitute the basic arm for removing most of the raw gasifier contaminants, including "tar." "Tar" is removed mainly through wet or wet-dry scrubbing. Coalescers, demisters, and cold filtration are also necessary supplements. These well-known commercial methods are easily designed and applied, depending on the specific needs of any gasification process. The main problem arising from "tar" scrubbing is that condensed "tar" components are merely transferred into another phase (water or solids such as scrubbing lime), which then has to be disposed of in an environmentally acceptable manner. The problems associated with the management of these wastewater or solid residues are summarized as follows:

- "Tar" and "tar"-contaminated solid-waste streams are considered as a special waste; consequently, their disposal is usually cumbersome and costly.

- "Tar"-bearing wastewater is usually a bi-phasic mixture requiring various steps of treatment before final disposal.

- Most water-soluble "tar" components are refractory to the usual biological wastewater treatments.

The applied methods for "tar" and "tar"-containing waste streams include solid waste stabilization and landfilling, organic phase skimming off the bi-phasic wastewater-free surface, wastewater incineration, wet oxidation, adsorption on activated carbon, and final biological treatment.

Recommendations:

Although chemical (mainly catalytic) conversion of "tar" at high temperature for eventual use of the gas in gas turbines attracts more and more attention, it is expected that physical removal of "tar" will continue to be widely used because:

- Burners/boilers that are not close coupled, as well as ICEs, require cold-gas use; it is rather difficult to envision, without serious economic problems, the simultaneous use of high-temperature "tar" conversion reactors combined with cold-gas conditioning modules. Thus, wet or dry-gas cooling/scrubbing is the recommended method in such cases

- When high-temperature conversion of "tar" is used there remain in the producer gas some other contaminants (mainly acid gases and volatile alkali metals), which could be detrimental to gas turbines. Thus, cold-gas conditioning, or in-series guard columns, should be used for these contaminants.

Extensive development work in this field is recommended. Government and private funding should be devoted over the next 5 years, to improve scientific understanding and technical/technological knowhow on physical "tar" removal from raw producer gas. This work should focus on:

- Wet scrubber design for higher efficiencies

- Aerosol removal module design and efficiency measurement

- Water insoluble "tar" skimming

- Skimmed "tar" recycle back to the gasifier; reactivity as a function of the recycle stream nature and quantity; rules for calculating the steady-state conditions

- Use of carbon-rich ashes from the gasifier to supplement the adsorption of "tar" on activated carbon; scale-up of bench-scale systems and establishment of design parameters

- Optimization of wet-oxidation conditions for treating soluble "tar" containing wastewater. Study and optimization of deep-bed, cold filters for "tar" removal; life cycle analysis.

Thermal, Steam and Oxidative "Conversion" of "Tars"

Thermal

The consensus seems to be that temperatures in excess of $1,000°C$, at reasonable residence times, are necessary to destroy the refractory unsubstituted aromatics without a catalyst. Apart from the economics and materials problems, such thermal decomposition can produce a soot that can be even more troublesome for some processes than the aromatics. Benzene seems to be the least reactive, thermally, of the light aromatics.

Steam

The addition of steam, over and above that formed from the water and oxygen in the feedstock, has been reported to produce fewer refractory tars, enhance phenol formation, reduce the concentration of other oxygenates, have only a small effect on the conversion of aromatics, and produce "tars" that are easier to reform catalytically.

Partial Oxidation

Oxygen or air added to steam seems to produce more refractory "tars" but at lower levels, while enhancing the conversion of primaries. When oxygen is added selectively to various stages, such as in secondary zones of a pyrolysis-cracker reactor, "tars" can be preferentially oxidized.

The Catalytic "Destruction" of "Tars"

Many types of catalysts have been investigated to reduce "tars" to lower levels and at lower temperatures than by thermal, oxidative, or steam reforming alone. Non-metallic catalysts such as dolomites, and metallic catalysts such as nickel (Ni), have been extensively studied. When used in situ, the results have not been promising due to a combination of coking and friability. Secondary beds have been much more effective for both types of catalysts. Even more promising has been the use of guard beds of inorganic catalysts such as dolomite in front of steam-reforming catalysts such as supported Ni. The duration of most reported catalyst tests has been quite short, especially considering the long activity requirements for expensive catalysts such as Ni to be economical. Refer to the notes and the annotated bibliography for guidance as to the details of tests, and their relevance to the cleanup requirements for any particular end-use device.

Recommendations:

Funding should continue on the thermochemical and catalytic behavior of cheap inorganic, and expensive metal-based catalysts. The emphasis should now be on long-term tests and catalyst poisoning and regeneration, with due attention to the nature of the "tar" and the "destruction" or "conversion" sought in terms of the tolerance of the end-use device to organic materials. The high levels of sulfur, chlorine, and alkali present in many attractive herbaceous feedstocks bring new problems to be addressed in lifetime and poisoning tests.

We have put the word tar in parentheses ("tar") throughout this report (but not in the bibliography) to emphasize the ambiguity inherent in the word.

I. Introduction

Gasification of solid fuels is an old technology. Foley et al. (1983) reviewed the early history of gasifiers and noted that producer gas was first used to drive an internal combustion engine (ICE) in 1791! A classic book on early gasification is Rambush (1923): *Modern Gas Producers*. The early applications were mainly for coal or fossil residues; e.g., the use of "town gas" before natural gas distribution was widespread. Biomass gasification was practiced in the early decades of this century (see Weisgerber et al. 1979, which contains an extensive bibliography on gas cleaning for the years 1920–1970), but received a major boost during World War II. A reported million vehicles were kept running in Europe as documented in GENGAS (1979), a SERI translation to English of the Swedish original edited by Reed and Jantzen.

Another wave of development began, as shown in the annotated bibliography in Appendix IV, in the 1970s, following the drastic increase in world oil prices, and a growing awareness of possible climatic effects of continued use of fossil fuels. This new interest was accompanied by an expansion of the devices considered for use with biomass gasification, beyond firing boilers and fueling ICEs. In particular, several applications, such as direct firing of gas turbines and fuel cells, were expected to benefit from hot-gas cleanup of particulates and "tars," at gasifier pressures. Several reviews of gas cleanup have appeared recently, most notably a review for the IEA of *Biomass Gasification: Hot Gas Clean-Up* by Graham and Bain (1993).

Tom Reed (1998) offers the following insight as to his experience to date:

> *While a great deal of time and money has been spent on biomass gasification in the last two decades, there are very few truly commercial gasifiers, operating without government support or subsidies, day in, day out, generating useful gas from biomass. The typical project starts with new ideas, announcements at meetings, construction of the new gasifier. Then it is found that the gas contains 0.1-10% 'tars.' The rest of the time and money is spent trying to solve this problem. Most of the gasifier projects then quietly disappear. In some cases the cost of cleaning up the experimental site exceeds the cost of the project! Thus 'tars' can be considered the Achilles heel of biomass gasification. (In the gasification of coal, a more mature technology, the 'tars' (benzene, toluene, xylene, coal tar) are useful fuels and chemicals. The oxygenated 'tars' from biomass have only minor use. With current environmental and health concerns, we can no longer afford to relegate 'tars' to the nearest dump or stream.*

The purpose of this review is to update the available information on hot-gas cleanup, with particular emphasis on "tar." Historically "tar" was an operationally defined parameter, based largely on organics from gasification that condensed under operating conditions of boilers, transfer lines, and engine inlet devices. Such a definition requires a more detailed chemical analysis and description in light of the greatly expanded uses proposed for high- and low-energy gas from a variety of biomass and waste materials. At present the literature contains many data on the "destruction," "conversion," "removal," etc., of "tars," "condensibles," "heavy hydrocarbons," etc., without a consistent definition of these terms, as well as a description of the sampling and analytical methods used for the organics of interest. Though the data presented are useful in the context of the system

being studied, they are limited in their transfer to other systems because they are "apparatus dependent," to borrow a phrase from chemical kinetics. In the following sections and appendixes, we discuss and summarize the literature of the past 30 years regarding the nature, formation, analysis, and treatment of "tars" in the context of what gasifiers produce and what end-use devices require. Recommendations are then given as to the need for nomenclature, reporting, and analysis standards and research needs. Appendix IV contains a bibliography, with selective annotations relevant to "tar" issues. Appendixes I–III contain lists of the compounds reported frequently in so-called primary, secondary, and tertiary "tars." (References in the text refer to the Appendix IV bibliography, to avoid extensive duplication of entries.)

II. Composition, Formation, and Maturation of "Tar"

Biomass gasification is a complex combination of pyrolysis and oxidation reactions in the condensed and vapor phases. Evans and Milne (1987a) identified reaction regimes and characterized the gaseous constituents present and the nature of the major vapor- and solid-phase reactions. This scheme is shown in Figure 2.1 and the product distribution in each regime is a function of process variables, such as oxygen level, steam-to-biomass ratio, pressure, and the time and temperature history of the solid and gaseous materials. Under typical gasification conditions, oxygen levels are restricted to less than 30% of that required for complete combustion, and CO and H_2 are the major products. This section describes the organic products that typically are formed and presents the changes in product composition as as a function of reaction severity (a function of process temperature and time).

* This box is meant to include solid biomass, but also its plastic or rubbery forms prior to major rupture of covalent bonds to produce low molecular weight vapor or liquids.

** Only first-formed products are shown. All of these products could be condensed to liquids and solids.
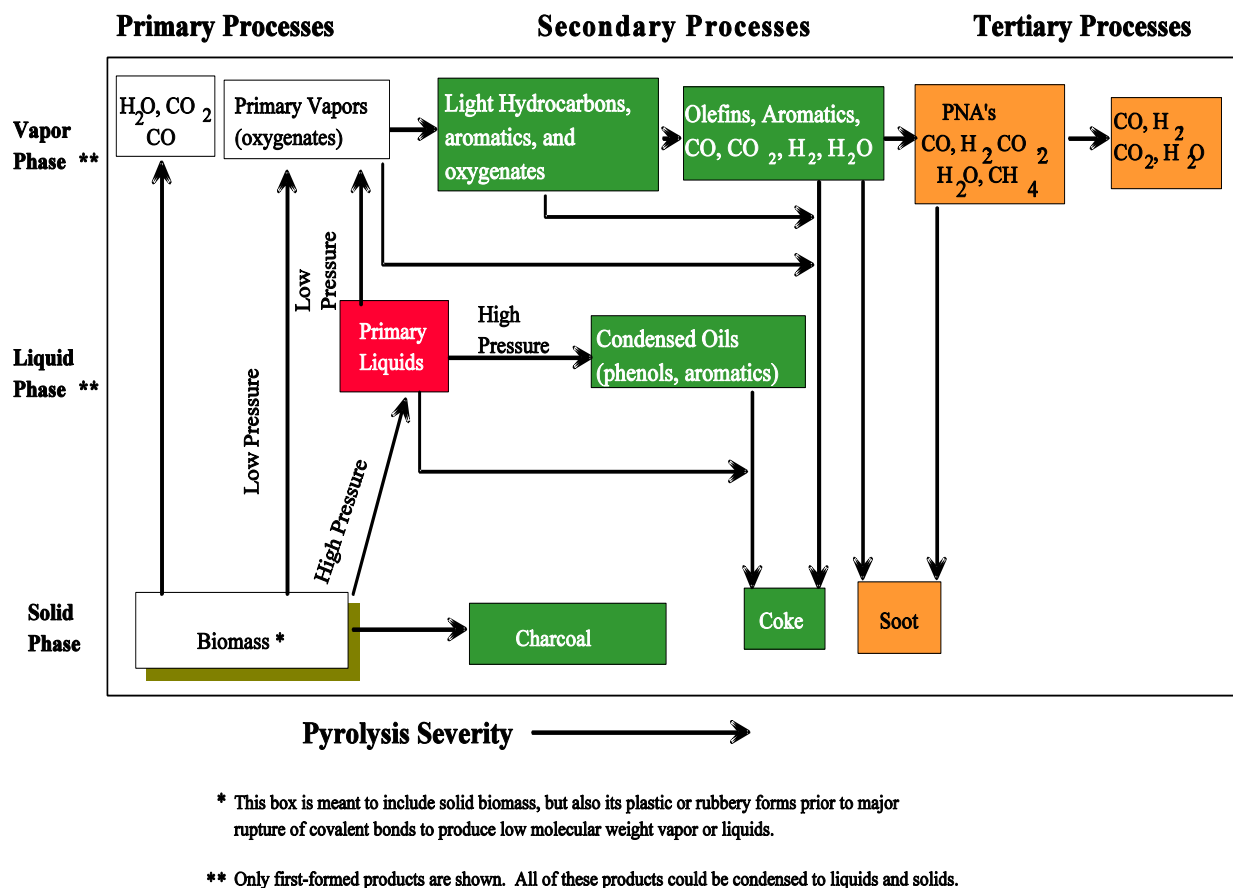
Figure 2.1. Pyrolysis pathways (Evans and Milne 1987c).

A. "Tar" Definition

"Tar" has been operationally defined in gasification work as the material in the product stream that is condensible in the gasifier or in downstream processing steps or conversion devices. This physical definition covers all the processes shown in Figure 2.1, although in most uses "tars" are generally

assumed to be primarily aromatic. However, this general usage is insufficient for modern gasification technology development because it loses the distinction between classes of compounds that originate under various reaction regimes, such as the primary pyrolysis products that may be in the gasifier effluent because of low-temperature operation or process upsets, and high molecular weight polynuclear aromatic hydrocarbons (PAHs), which are produced under high gas-phase reaction severity and are precursors of particulate matter "soot" (see Blackadder et al. 1994). One goal of this review is to propose a set of definitions for organic residuals in gasifier raw gas and to propose definitions for "destruction" or "conversion" for various contemplated end uses. At this time, laboratory and pilot results on "conversion" are often end-use specific. A goal might be for each study on "tar removal" to have an explicit definition of "tar" and of "conversion" so the results could be extended to other circumstances. This report uses the following starting definition of "tar" throughout:

(The organics produced under thermal or partial-oxidation regimes (gasification) of any organic material are called "tars" and are generally assumed to be largely aromatic.)

However, newly contemplated applications of gasifier gas, such as fuel cells, may be affected by "non-condensibles" such as ethylene, cyclopentadiene, and benzene.

B. "Tar" Composition and Maturation

Elliott (1988) reviewed the composition of biomass pyrolysis products and gasifier tars from various processes. Figure 2.2 shows the transition as a function of process temperature from primary products to phenolic compounds to aromatic hydrocarbons, and Table 2.1 shows the classes of chemical components in each major regime based on GC/MS analysis of collected "tars."

Mixed Oxygenates	Phenolic Ethers	Alkyl Phenolics	Heterocyclic Ethers	PAH	Larger PAH
400 °C	500 °C	600 °C	700 °C	800 °C	900 °C
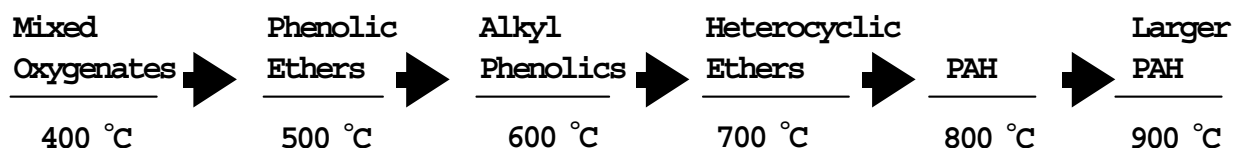
Figure 2.2. "Tar" maturation scheme proposed by Elliott (1988).

In a later publication, Baker et al. (1988) showed a conceptual relationship between the yield of "tars" and the reaction temperature as shown in Figure 2.3. They cited levels of "tar" for various reactors with updraft gasifiers having 12 wt % of wood and downdraft less than 1%. Steam-blown, fluid-bed gasifiers had tar levels of 15% at 600°C and 4% at 750°C. For oxygen-blown fluid beds, the levels of "tar" were 4.3% at 750°C and 1.5% at 810°C. The entrained flow gasifier of Battelle Columbus Laboratories, operated at 1,000°C, had "tar" levels of 1% (Baker et al. 1988). Table 3.1 tabulates the variety of reported levels of "tar."

Table 2.1. Chemical Components in Biomass Tars (Elliott 1988).

Conventional Flash Pyrolysis (450°–500°C)	High-Temperature Flash Pyrolysis (600°–650°C)	Conventional Steam Gasification (700°–800°C)	High-Temperature Steam Gasification (900°–1000°C)
Acids Aldehydes Ketones Furans Alcohols Complex Oxygenates Phenols Guaiacols Syringols Complex Phenols	Benzenes Phenols Catechols Naphthalenes Biphenyls Phenanthrenes Benzofurans Benzaldehydes	Naphthalenes Acenaphthylenes Fluorenes Phenanthrenes Benzaldehydes Phenols Naphthofurans Benzanthracenes	Naphthalene* Acenaphthylene Phenanthrene Fluoranthene Pyrene Acephenanthrylene Benzanthracenes Benzopyrenes 226 MW PAHs 276 MW PAHs
* At the highest severity, naphthalenes such as methyl naphthalene are stripped to simple naphthalene.			
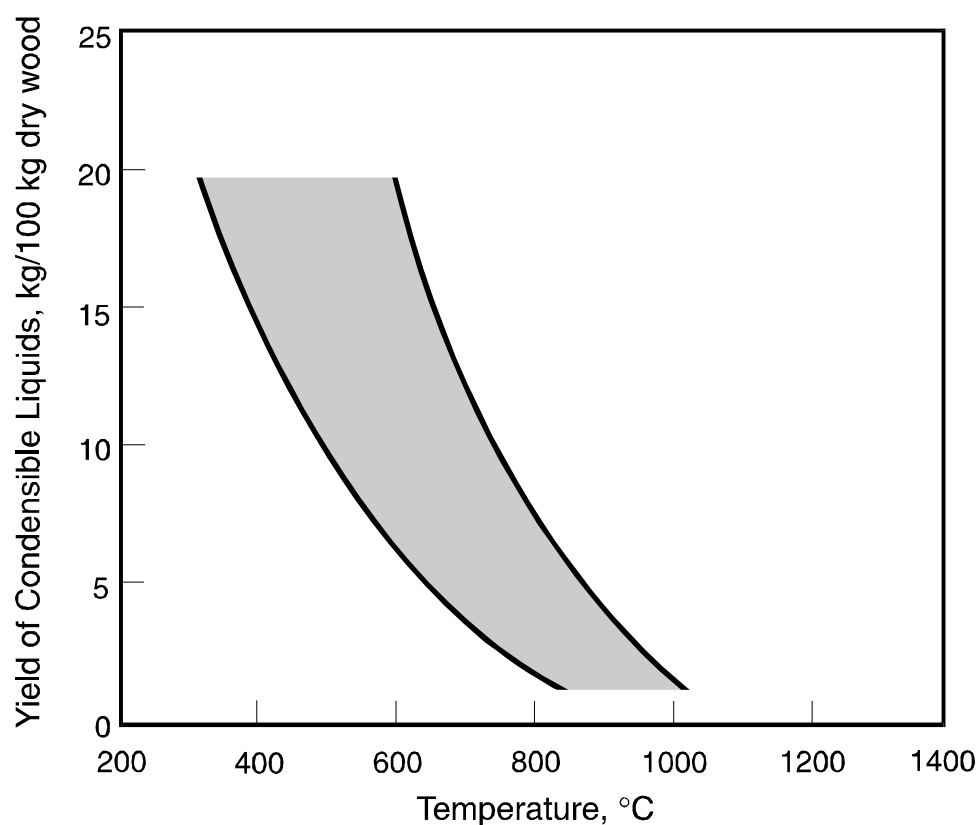
Figure 2.3. "Tar" yield as a function of the maximum temperature exposure (Baker et al. 1988).

The description of process changes should be seen as a function of reaction severity, which combines both temperature and time. Evans and Milne (1987a,b) show the trade-off in product distribution as a function of these two parameters by using multivariate analysis of product composition. Another important factor is the importance of gas-phase reactions leading to "tar" synthesis. Hydrocarbon chemistry, based on free radical processes, occurs in this thermal regime where olefins react to give aromatics. This process occurs at the same time that dehydration and decarbonylation reactions cause the transformations shown in Figure 2.2.

Evans and Milne (1987a,b) used molecular beam mass spectrometry (MBMS) to suggest that a systematic approach to classifying pyrolysis products as primary, secondary, and tertiary can be used to compare products from the various reactors that are used for pyrolysis and gasification. Four major product classes were identified as a result of gas-phase thermal cracking reactions (extensive tables are shown in the appendixes):

1. Primary products: characterized by cellulose-derived products such as levoglucosan, hydroxy-acetaldehyde, and furfurals; analogous hemicellulose-derived products; and lignin-derived methoxyphenols;

2. Secondary products: characterized by phenolics and olefins;

3. Alkyl tertiary products: include methyl derivatives of aromatics, such as methyl acenaphthylene, methylnaphthalene, toluene, and indene;

4. Condensed tertiary products: show the PAH series without substituents: benzene, naphthalene, acenaphthylene, anthracene/phenanthrene, pyrene.

The primary and tertiary products were mutually exclusive as shown by the distribution in Figure 2.4 (Evans and Milne 1997). That is, the primary products are destroyed before the tertiary products appear. The tertiary aromatics can be formed from cellulose and lignin, although higher molecular weight aromatics were formed faster from the lignin-derived products (Evans and Milne 1987a,b).

MBMS was also used to rapidly screen products from simulated gasifiers in the laboratory as well as on-line analysis of large-scale gasifiers. This technique allows the products to be placed in the primary, secondary, and tertiary product ranges shown by laboratory MBMS studies (Evans and Milne 1987a,b). Figure 2.5 shows a comparison of effluents from updraft and downdraft gasification. The MBMS was coupled to a 5-cm, insulated, quartz, fixed-bed gasifier that could be operated in either an updraft or a downdraft mode (Reed et al. 1986). The updraft gasifier effluent shows primary products from both lignin (m/z 168, 180, 194, 210) and carbohydrates (m/z 60, 73, 85, 98, 114, 126, 144). The downdraft product spectrum shows the near complete destruction of these compounds except for a trace of m/z 60. The tertiary aromatics are now predominant: benzene (78), naphthalene (128), phenanthrene (178), and pyrene (202). The tertiary alkyl aromatics are also present: toluene (92), indene (116); as well as phenol (94). Key compounds in this spectrum are the olefins, such as butene (56) and cyclopentadiene (66), which are likely intermediates in aromatic hydrocarbon formation, and are often overlooked in "tar" formation and maturation chemistry.
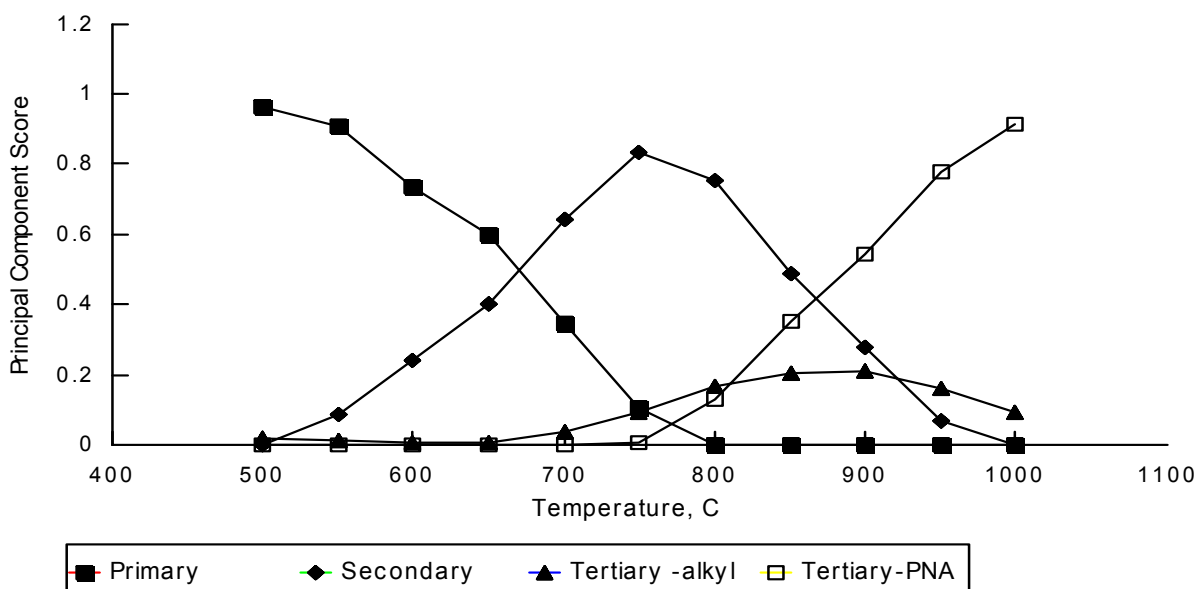
Figure 2.4. The distribution of the four "tar" component classes as a function of temperature at 300 ms (0.3 s) gas-phase residence time (reprinted from Evans and Milne 1997)

Some representative mass spectra of engineering-scale gasification products are shown in Figure 2.6 from the use of the transportable MBMS on-line with the Battelle Columbus Laboratory (BCL) indirect, circulating, fluidized-bed gasifier (Gebhard et al. 1994a,b) and the Institute of Gas Technology (IGT) pressurized, fluidized-bed gasifier (Ratcliff et al. 1995). These spectra show the effect of reaction severity, with the IGT product spectrum containing only condensed tertiary products and the BCL gasification product slate being largely secondary in nature with high levels of phenolics and alkyl aromatics as well as the olefins as discussed earlier.

Ion peak identification is as follows: 55-fragment ion; 66-cyclopentadiene; 78-benzene; 91/92-toluene; 94-phenol; 108-cresols; 128-naphthalene; 142-methylnaphthalene; 152-acenaphthalene; 178-phenanthrene; 202-pyrene/fluoranthene/benzacenaphthalene; 228-chrysene et al; 252-benzo[a] pyrene, etc.; 276-anthanthrene, etc.; 302-unknown.

Hence, these examples show that pyrolysis "tar" maturation pathways are relevant to gasification, and understanding the maturation pathway can help characterize and optimize reactor performance. For example, primary and tertiary "tars" in the same "tar" sample would indicate nonuniform conditions, such as channeling or process upsets. This might explain evidence of primary products in fixed-bed, downdraft effluents. Aiken and McDonald (1983), found the "tars" from a downdraft gasifier to have 21%–25% oxygen and found acids and formaldehyde in the condensate, which indicate the survival of primary products. Elliott (1987) found that the downdraft gasifier operated by Syngas Inc., had an oxygen content in the "tar" of 25–31 wt %, which was the highest level for the gasifiers studied.

Upddraft gasifier
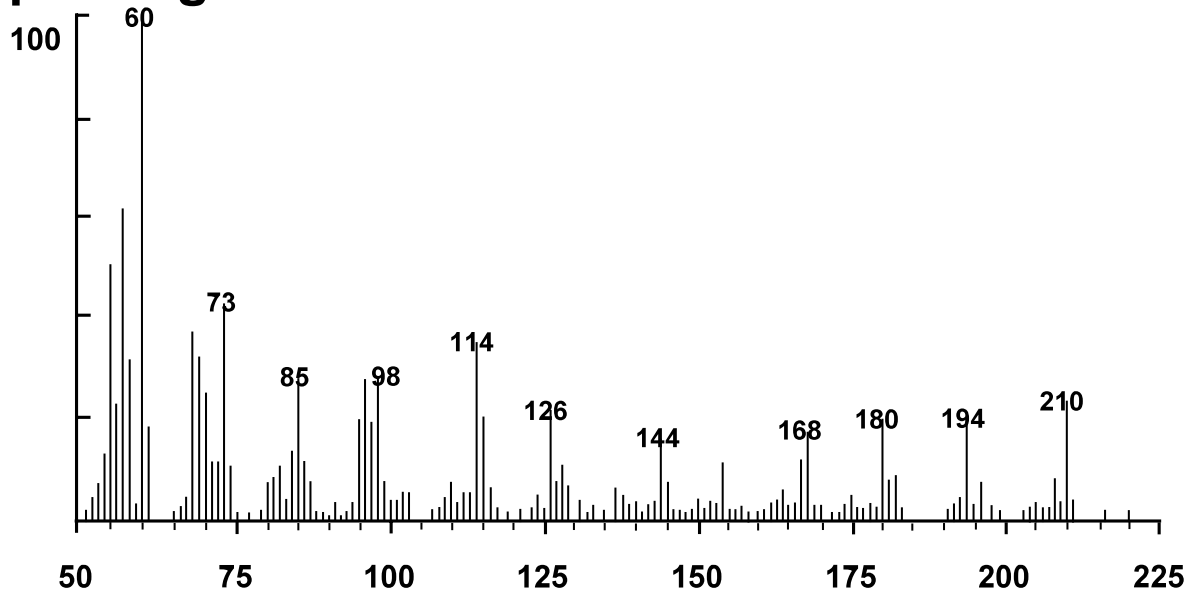
Downdraft gasifier
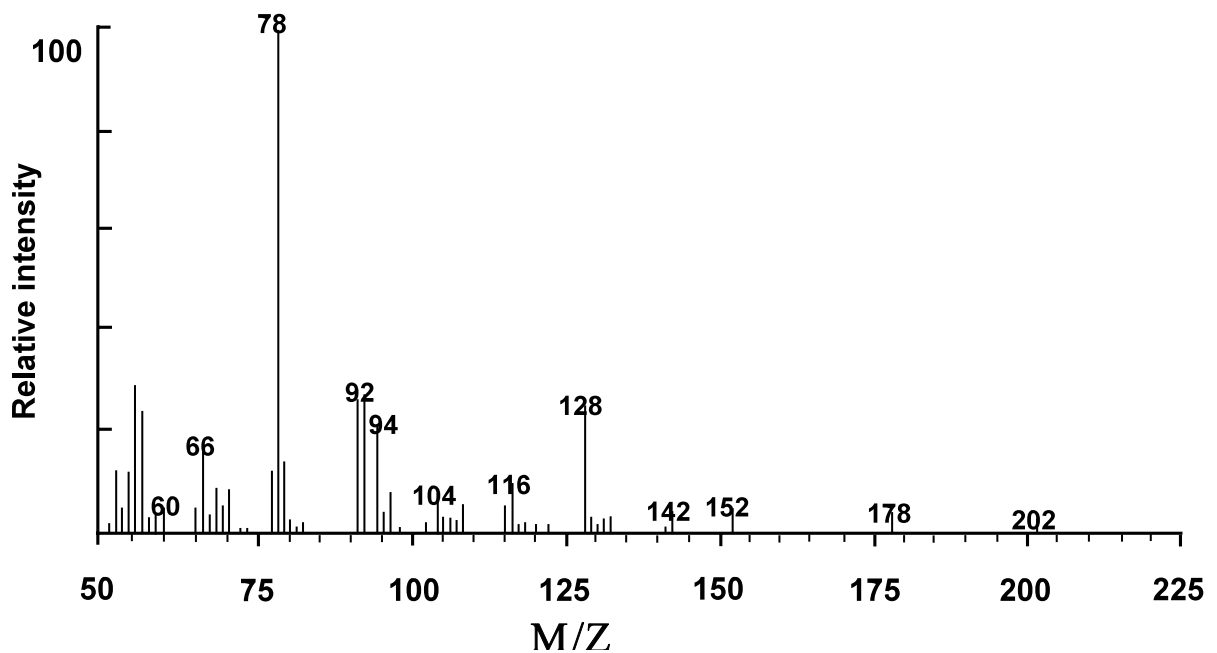
Figure 2.5. MBMS sampling of gasifier effluents run in the updraft and downdraft modes (Reed et al. 1986).

(See appendixes for ion peak identification.)

TMBMS On-Line Analysis of IGT Gasifier Process Stream

TMBMS On-Line Analysis of Batelle Columbus Gasifier Process Stream
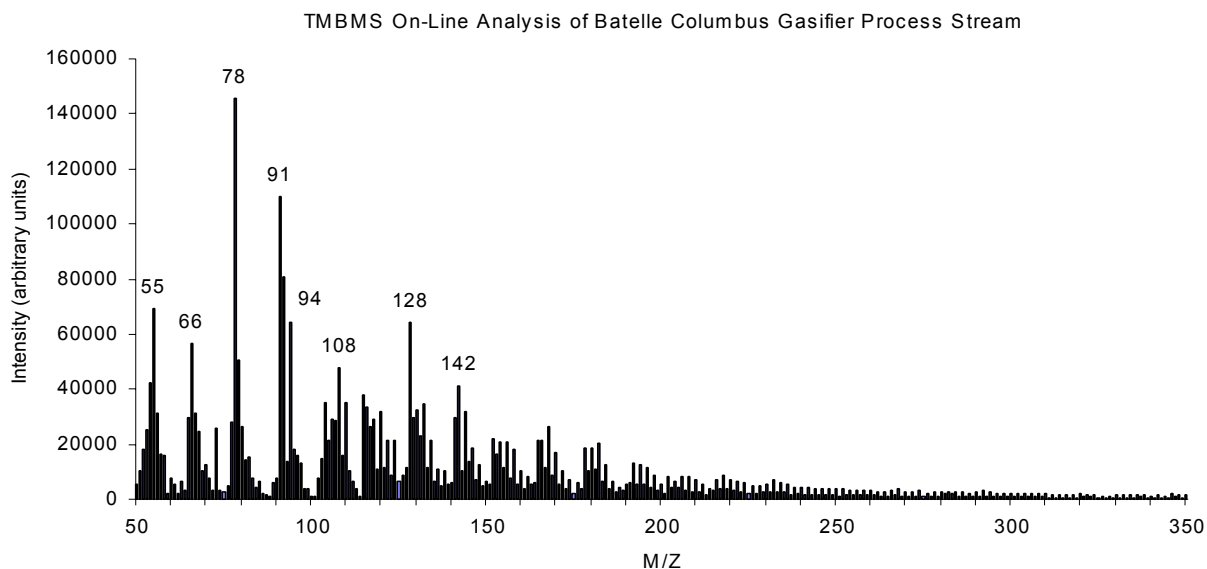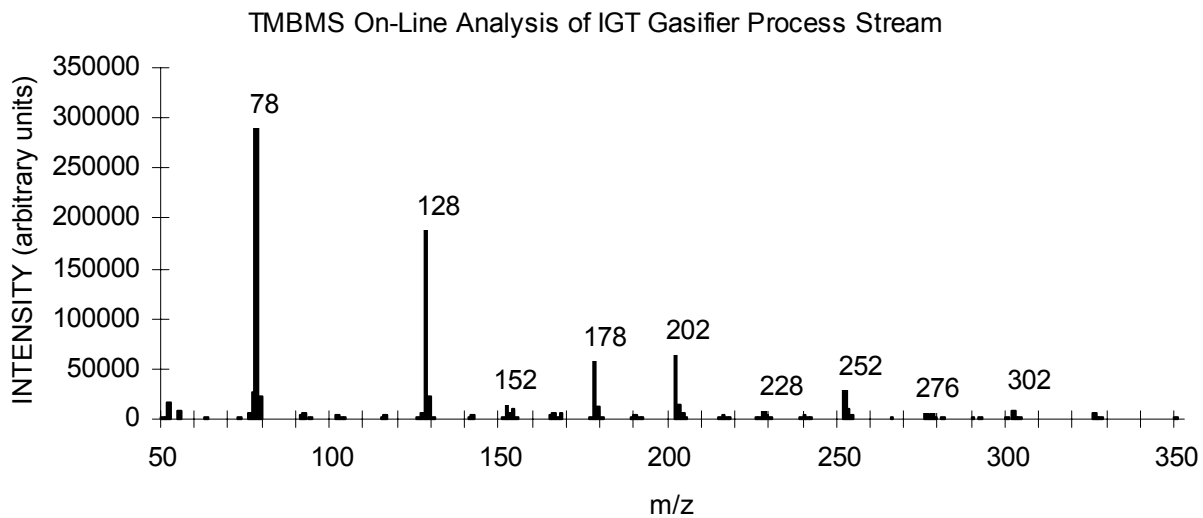
Figure 2.6. TMBMS on-line analysis of Battelle Columbus (Gebhard et al. 1994a) and IGT (Ratcliff et al. 1995) gasifier tars.

Ekstrom et al. (1985) showed the catalytic effects of char on "tar" cracking. Gas was passed over a char bed resulting in reduced yields of "tar" and increased yields of methane, CO_2, and H_2. These and other results quoted by them indicate that the temperature and the type of wood are important factors in "tar" composition. These results lead to the conclusion that intra-particle phenomena are likely to be important and add complexity to the severity equation that governs "tar" amount and composition.

9

The assumption is often made that "tars" thermally crack to CO, H_2, and other light gases with temperature. This is true with primary product cracking, and yields of 50% by weight of CO are possible by thermal cracking. However, this is not true for the condensed tertiary products, which grow in molecular weight with reaction severity. For example, Evans and Milne (1997) show the ratio of benzopyrene to naphthalene (m/z 252/128) increasing with both temperature and gas-phase residence time. Simell et al. (1993) found the relative proportion of heavy PAH components in the "tar" to increase as the gasification temperature increases for high pressure, air-blown, fluid-bed gasification of wood. The decision to run a gasification system at high severity to crack "tars" should be balanced by a consideration of the remaining "tars" composition. Elliott (1986) pointed out this processing dilemma of high temperature favoring greater efficiency and rates but also leading to a more refractory nature of the "tar" that was left. The condensed aromatics in these tertiary "tars" may prove harder to remove by downstream catalytic cracking than the larger amount of primary or secondary "tars" produced under less severe gasification conditions. The molecular weight of PAHs increases through the tertiary cracking zone; hence, maturation of "tar" to soot should be kept in mind both in running gasifiers and in performing chemical analysis to determine the effectiveness of "tar" cracking.

Conventional analysis of "tars" from various gasifiers by GC/MS, shows the relationship of reaction severity and "tar" composition, but always with the caveat that incomplete product collection, post-condensation reactions, and the averaging of sample composition over time can mask the true underlying chemical processes. These analyses are particularly valuable for evaluating "tar" composition before and after catalytic and scrubbing operations. Bangala et al. (1997) published a representative GC of the "tars" from the atmospheric-pressure, fluidized-bed gasification of wood at 780°C shown in Figure 2.7. This shows a mixture of primary products such as furfural, secondary products such as cresols, and tertiary products such as phenanthrene. There are no correlations allowing a statistically valid quantification of the residence-time distribution as a function of the formed "tar" profile. This raises the question of changing process conditions, especially leading up to steady-state operation, versus the actual co-evolution of these product classes because of a residence-time distribution within the fluidized-bed gasifier such that some particles, and the resulting gases, have shorter residence times.

Aldén et al. (1988) developed a two-stage reactor system to study "tar" formation and thermal and catalytic cracking where the gas-phase cracking temperature can be independently varied. GCs of "tars" generated at temperatures from 400° to 900°C show the systematic maturation of the low-temperature "tars," which have many peaks at short retention times, to the high-temperature "tars," which have fewer peaks at short retention times, but more peaks in higher quantities at the longer retention times.

C. Effect of Partial Oxidation on "Tar" Composition

The effects of steam and oxygen on biomass gasification rates were reported by Wang and Kinoshita (1992) and by Narváez et al. (1996), among others. Equivalence ratios (ratio of oxygen in the mixture to that required for complete combustion) of .2 to .45 were explored. The thermal cracking of "tars" with steam and oxygen added in the cracking zone was reported by Jönsson (1985). Both additives increased the cracking rate over the temperature range studied (950°–1,250°C). The partial oxidation of the primary, secondary, and tertiary products has been studied by MBMS (Evans and

Milne 1997). Oxygen under these conditions can influence the cracking of these products before complete oxidation occurs. The effect of oxygen at 600°–700°C accelerates the destruction of primary pyrolysis products but has no significant effect on benzene destruction once it is formed. Secondary and tertiary products are generally less susceptible to oxidation than primary products, and each primary product appears to have its own reaction rate, which indicates a selective bimolecular process.

Tar composition from gasification of biomass

GC-MSD with HP-101/50 m x 0.20 mm x 0.20 capillary column

1- 2-Methyl-2-Propenal	10- Benzofuran	19- Naphthalene
2- Benzene	11- Phenol	20- 2-Methylnaphthalene
3- Cyclohexene	12- 1-Propynylbenzene	21- 1-Methylnaphthalene
4- Toluene	13- 1-Phenylethanone	22- 1,1'-Biphenyl
5- Cyclopentanone	14- o-Cresol	23- Acenaphthene
6- 2-Cyclopenten-1-one	15- m/p-Cresol	24- Biphenylene
7- Furfural	16- 1-Methyl-1H-Indene	25- Phenanthrene
8- 1,3,5,7-cyclooctatetraene	17- 1-Methylene-2-Propenylbenzene	
9- *Unknown*	18- 1,2-Dihydronaphthalene	

Figure 2.7. Composition of "tar" from atmospheric-pressure, air gasification of biomass at 780°C (Bangala et al. 1997).

D. Conclusions

The characterization of "tars" as primary, secondary, and tertiary is a first step at classifying these materials and relating the composition of "tars" with formation conditions. Some gasifiers show the presence of primary and tertiary "tar" constituents in the same "tar" sample; this raises the question of the importance of process upsets and large, residence-time distributions that could cause this occurrence. This could have important implications in the design and operation of gasifiers to insure adequate control of reaction conditions. These "tar" constituents can be used as indicators of overall reactor performance and design (Brage et al. 1997b).

Although past work has shown the systematic nature of "tar" composition as a function of reaction temperature, more detailed study is needed to characterize the product at a higher level of detail. Some primary products will likely be more refractory to secondary thermal and oxidative cracking reactions than others, so an accepted method of characterizing the compound classes in each major group is desirable and a method of rapidly screening for this information is needed. For example, it may be possible to "train" spectroscopic techniques to provide the necessary analysis based on correlation with more detailed work on a test system with GC/MS and other techniques, which give highly specific information, but are expensive to perform. Another approach is to identify "marker compounds," or predominant constituents, which are indicators of overall chemical composition, and to use methods to monitor these representative indicators of overall "tar" composition (Brage et al. 1996).

This chemical characterization could be correlated with key physical property data and process operations, such as performance of wet scrubbing systems or catalytic cracking units. Primary, secondary, and tertiary classes are a starting point, but more detail is needed about the conversion of specific compound classes, such as organic acids that seem to persist beyond other primary products.

Kinetics and reaction pathways for primary to secondary and tertiary processes should be known so they can be included in the design of gasifiers and cleanup systems. The qualitative and quantitative effects of oxygen and steam on product distributions should also be better known. More quantitative studies are needed of primary, secondary, and tertiary products in fluidized beds, where residence time distribution must be considered as it affects reaction severity.

Alternative feedstocks, such as herbaceous crops with high nitrogen content, raise questions about nitrogen-containing constituents. Analysis of these materials warrants more study.

Finally, the pathways to soot and particulates from tertiary products require quantitative study to better ascertain the importance of these processes. This may be critical in hot-gas cleanup technology.

Recommendations:

Once "tar" collection protocols are established, compound-class analysis methods and the analysis of predominant constituents should be established as standard procedures. Kinetic modeling of these groups should be attempted to help gasifier designers systematically address the relative importance of process upsets and residence-time distributions in accounting for mixed product slates.

III. The Dependence of "Tar" Nature and Amount on Gasifier Type and Conditions

A. General

In the preceding section we presented a summary of the main mechanisms (physicochemical phenomena) of "tar" formation during gasification reactions. In this section information is provided on the almost bewildering array of "tar" quantities reported in raw gas from the three main types of gasifiers being used.

B. "Tar" Quantities as a Function of Gasifier Type

Numerous publications report the quantities of "tar" produced by various types of gasifiers, under various geometries and operating conditions; e.g., Abatzoglou et al. 1997a; Bangala 1997; CRE Group, Ltd. 1997; Graham and Bain 1993; Hasler et al. 1997; Mukunda et al. 1994a,b; Nieminen et al. 1996. The lack of standard quantification procedures renders a successful comparison difficult (CRE Group, Ltd. 1997). However, the gathering of a significant numeric of measurements (although the latter are affected by different laboratories using various methods) gives statistical validation to the comparison undertaken. Generally it has been proven and explained scientifically and technically that updraft gasifiers produce more "tar" than fluidized beds and fluidized beds more than downdrafts. This generalization is apparent in Table 3.1.

It is useful at this point to provide some information on the mode of operation of the three main gasifier types tabulated in Table 3.1. Reed (1998) offers the following:

> *There are hundreds of gasifiers in the patent literature. However, they divide into four principle types that we will discuss from the point of view of the types of tar each produces: Pyrolytic; Updraft; Downdraft and Fluidized bed.*
>
> *Pyrolysis of biomass can start as low as 200 ℃ and is essentially complete by 500 ℃ (Fig. 2.1, 2.2). We will show that in this range the cellulose, hemicellulose and lignin of biomass (and rubber and plastics in MSW) produce oxygenated, primary organic condensible molecules, also called **primary tars**; wood oils; wood syrups. (See Figs. 2.2-2.5) Charcoal is a major product of slow pyrolysis, with smaller amounts produced with faster pyrolysis of small particles. As the temperature is raised above 500 ℃ the primary tars begin to rearrange to form more gas and a series of molecules called **secondary tars**. (See Figs. 2.2-2.5). **Pyrolytic gasification** uses external heat (sometimes from charcoal combustion) to produce these primary tars. **Fast pyrolysis processes** can produce up to 60% of the original weight as a primary tar liquid, very undesirable for gasification. For gasification the process must be taken to 700-900 ℃ to break these primary tars down to smaller amounts of secondary tars and much more gas, typically 1-5% secondary tar in the gas. Generally a catalyst will be required to lower this secondary tar level at these temperatures.*

*In **updraft (counterflow) gasification** air/oxygen/steam contacts charcoal on a grate, generating gas temperatures of 1000-1400 ℃. This hot gas rises through the downcoming biomass, pyrolysing it at successively lower temperatures and eventually drying it. All of the types of tar in Figs. 2.2-2.5 occur in the final gas, with primary tars dominating, typically at a level of **10-20%**. Updraft gasifiers are useful for producing gases to be burned at temperature, but the high tar level makes them difficult to clean for other purposes.*

*In **downdraft (coflow) gasification** air/oxygen and fuel enter the reaction zone from above and burn most of the tars to pyrolyse the fuel, in a process called "**flaming pyrolysis.**" The flame temperatures are 1000-1400 ℃, but the flame occurs in the interstices of the pyrolysing particles whose temperatures are 500-700 ℃, so that about **0.1%** of the primary tars are converted to secondary tars and the rest are burned to supply the energy for pyrolysis and char gasification. Very few of the compounds found in downdraft gasification are found in updraft tars and vice-versa. The low tar levels of downdraft gasifiers make them more suitable for uses requiring clean gas.*

*In **fluidized bed** gasifiers air/oxygen/steam levitate the incoming particles which recirculate through the bed. Some of the oxidant contacts biomass and burns the tars as they are produced as in a downdraft gasifier; some of the oxidant contacts charcoal as in an updraft gasifier. Thus the tar level is intermediate between updraft and downdraft, typically 1-5%.*

Different authors use different bases for "tar" quantity. Some relations reported, which differ for air, oxygen, or indirect gasification, are:

1 wt % feed equals about 5.0 g/m3 (Corella et al. 1988a)
1 wt % feed equals about 12.9 g/Nm3 (Corella et al. 1989a)
1 wt % feed equals about 3.3–6.7 g/m3 (Wallin and Padban 1996)
1 wt % feed equals about 5.5 g/Nm3 (Turn et al. 1997)
1 wt % feed equals about 11–13 g/Nm3 (Henriksen and Christensen 1995)
1 wt % dry wood equals about 5,000-10,000 ppmw in gas (Paisley and Overend 1994)
1 wt % carbon equals about 5,000 ppmw in gas (Reed 1998)
1 mgN/m3 equals about 1 ppmw in gas (Reed 1985; Das 1985)
1 mg/Nm3 equals about 0.9 ppmw in gas (Liinanki et al. 1994)

The "tar" loading in raw producer gases from updraft gasifiers, with an average value of about 50g/Nm^3, is higher than in any other gasifier. Fluidized beds and CFBs have an average "tar" loading of about 10 g/Nm^3. Downdraft gasifiers, when operated according to specifications, produce the cleanest gases with "tar" loading typically less than 1 g/Nm^3. However, in routine commercial operation downdraft units often have loadings in excess of 1 g/Nm^3 (Graham and Bain 1993; Sjöström et al. 1988).

Table 3.I. "Tars" Reported in Raw Gases for Various Types of Gasifiers

Updraft Gasifiers (All gasifiers are at atmospheric pressure and air-blown unless otherwise noted.)

Amount of "Tar"	Gasifier	Conditions	"Tar" is:	Reference
1-15 g/Nm3 12 wt % of feed		Reported max. Typical		Baker et al. 1988 Bain 1995
10-100 g/.Nm^3		Reported range	B.P. greater than 150°C	Baker et al. 1986, Brown et al. 1986b
To 100g/Nm^3		Reported range		Buhler 1994
58 g/Nm^3		Reported average	Higher hydrocarbons	Bui et al. 1994
10-100 g/Nm^3		Reported range		Pedersen 1994
2-30 wt % feed		Reported range		Philp 1986
10-20 wt % of gas		Reported range		Reed and Gaur 1988
10-100g/Nm^3		Reported range		Rensfelt and Ekstrom 1988
2-10 g/Nm^3		Reported range		Stassen 1995, Stassen 1993a
0.23 mol % gas 0.09 mol % gas	GE coal gasifier on wood chips.	290 psi 200 psi	Tars and oils	Furman et al. 1993
6.7 g/Nm^3	U.K.	Not specified		BTG 1995b
8 wt.% of feed	PNL	Steam/oxygen		Baker et al. 1984
25 wt % of lig.	Rome, Georgia		Condensates below 700°F	Hart 1983
7.0 g/Nm^3	Haarboore			Kristensen 1996
80-160 g/Nm^3 30-45 "	Bioneer		Distillation at 75°C Residue at 105°C	Kurkela et al. 1989a
41-43 g/Nm^3	Lab unit	peat		Leppälahti et al. 1992
58 g/Nm^3	Wellman		Collection at -50°C	McLellan 1996
50 g/Nm^3	Volund			Pedersen et al. 1996b
50-100 g/Nm^3	Bioneer			Salo 1990
9.8 g/Nm^3	Lab scale tube	900°-910°C		Simell et al. 1995a

Amount of "Tar"	Gasifier	Conditions	"Tar" is:	Reference
10-40 g/Nm3 50-100 g/Nm^3 10-20g/Nm3	Bioneer	Straw Chips, forest residue, sod peat. MSW		Ståhlberg et al. 1989
50 g/Nm^3		Typical	Condensibles measured gravimetrically	Susanto and Beenackers 1996
23-46 g/Nm^3	Hudson Bay		Condensible hydrocarbons	Weisgerber 1979
0.5 vol %	Proler	Rotary kiln	Benzene	Niessen et al. 1996
8.0 g/Nm^3	Coal	Variety of gasifiers		Ham et al. 1985
0.3-0.7 g/Nm^3	Coal		Total hydrocarbon analyzers	Nelson 1987

Downdraft Gasifiers (Air-blown and atmospheric pressure unless otherwise noted.)

0.5 g/Nm^3		Typical		Bain 1995
Less than 1 wt %		Reported range		Baker et al. 1988
0.05-0.5 g/Nm^3		Reported range		Baker et al. 1986
0.1-0.5 g/Nm^3 0.78 0.85-2.8 1.3	Wamsler HTV-JUCH Ensofor	Reported range, quoted from Buhler, 1994. for good DD.		Beenackers and Maniatis 1996
0.05-0.5 g/Nm^3		Reported range		Brown et al. 1986b
2 g/Nm^3		Average		Bui et al. 1994
0.5-5 g/Nm^3		Typical range		Kurkela et al. 1989a; Reed et al. 1987
0.2-0.4 %		Typical WW2	Heavy hydrocarbons	National Academy of Sciences 1983
0.1-5 g/Nm^3		Reported range		Pedersen 1994
0.1-1 g/Nm^3	Stratified	Typical range		Reed 1997b
0.3-1 g/Nm^3	Running well	Normal range		Rensfelt 1985
0.01-4 g/Nm^3	Small 3rd world	Reported range		Stassen and Knoef 1995
0.1-3 g/Nm^3		Typical small		Stassen 1995;
0.4-1.4 g/Nm^3		Typical		Susanto and Beenackers 1996

1.4-1.8wt% feed 7.4-9.2	Forintek prototype		Tar Total condensate	Aiken and McDonald 1983
6.1 wt % feed	BC research		Evaporate acetone at 30°C, weigh	Aiken et al. 1983
0.6-1.3 g/Nm^3	Reed lab gasifier			Babu 1991
0.025 g/Nm^3	CEMAGREF		Condensibles	Becker 1988
1.0-2.4 g/Nm3				Borisov et al. 1998
0.3-0.6 g/Nm^3	Imbert			GENGAS 1979
7,700-23,000 ppmw	NREL 1t/d	Oxygen. wood chips		Reed et al. 1987
20,000 ppmw	Syngas Inc.	Oxygen, wood.		Reed et al. 1987
0.61 g/Nm^3	Gotland Gengas			Liinanki et al. 1985
.04-0.1 g/Nm^3	Open core			Mukunda et al. 1994b
0.8 g/Nm^3	Buck Rogers			Reed and Gaur 1998

Fluidized Gasifiers

0.4 vol %		Typical		Bain 1996
4 wt % feed 15 4.3 1.5 less than 1 wt %		Literature Steam-blown " Oxygen-blown " Entrained	600-750°C 600°C 750°C 850°C 1000°C	Baker et al. 1988
2-10 g/Nm^3	Fluid-bed, entrained-bed	Reported range		Baker et al. 1986
2-10 g/Nm^3 8-30 g/Nm^3	Entrained	Reported range Reported range		Brown et al. 1986b
10 wt % feed	Typical	Typical Steam		Corella et al. 1991b
8.5 g/Nm^3 5		Typical Tar Benzene		Kurkela et al. 1993b
4.7-5.4 g/Nm^3	Typical	Peat		Leppälahati 1992
7-10 g/Nm^3		Literature, CFB		Rensfelt and Ekström 1988

0.32-6 g/Nm^3		Typical range		Susanto and Beenackers 1996
0.7-2.9 wt % feed 4-35 g/Nm3	Biosyn Atmospheric	Typical Tar plus VOC		Abatzoglou 1996
5 g/Nm^3 5 g/Nm3 3 g/Nm3	Biosyn AFBG Atmospheric Biosyn	 Wood RDF		Abatzoglou et al. 1997a Abatzoglou 1997b
4 wt. feed	3rd generation, Zaragosa	Bottom fed		Aznar et al. 1995a
Greater than 30 g/Nm^3	Zaragosa	Steam only		Aznar et al. 1990
35-195 g/Nm^3	Zaragosa	Steam only, top fed	Total organic carbon analyzer	Aznar et al. 1992
7 g/Nm^3	3rd generation, Zaragosa	Turbulent-bed		Aznar et al. 1997b
21.2 g/Nm^3	3rd generation Zaragosa	Fast-fluidized		Aznar et al. 1995b
30-50 g/Nm^3	3rd generation Zaragosa			Aznar et al. 1996a
30-70 g/Nm^3	Greve		CxHy	BTG 1994
0.5-1 wt % fuel	Battelle PDU		Condensibles	Bain and Overend 1996
67 g/Nm^3 84	Greve, circulating	Sorghum RDF	Condensate	Barducci et al. 1996
2 g/Nm^3 or more	KTH	Optimized		Corella 1996
8-10 g/Nm^3	Biosyn , air	200kPa, 800C		Black 1989

1.9 mg/l
2.4
1.8
2.6
	Top fed	700°C, 0.4 MPa
		        1.5
		900°C, 0.4
		        1.5
				Brage et al. 1995

21 g/Nm^3 21.2	Lund Complutense	Literature		Brown 1996
100 g/Nm^3	Top-fed, steam	750°C		Corella et al. 1989a
8-4 wt % feed	Steam	650°C-780°C 780°C		Corella et al. 1989b
15 wt % feed 3 wt %	Top-fed. Bottom-fed	750 C		Corella et al. 1988b

36-82 g/Nm^3	Bench scale, bottom-fed	Air-blown		Corella et al. 1995b
12.6 g/Nm^3 2.2 g/Nm^3	Biometh	Total tars Heavy tars Light tars	B.P. above 400°C B.P. 80°-400°C	DeSousa and Stucki 1997
0.4-2.0 g/Nm^3 0.5 g/Nm^3	ATEKO, air	Typical 850°C		Dittrich 1995
9.3 wt % feed	Bench , steam	Pyrolysis		Elliott and Baker 1986
1.2-2.6 wt %feed 0.5-3 wt % feed	IGT IGT	Pressurized Pressurized	"Oils" Total tars	Evans et al. 1985 Evans et al. 1988
10 wt % feed 7.5 wt % feed	Indirect	620°C 760°C	Total carbon in scrub water	Flanigan et al. 1988
46 wt % feed 39 wt % feed	Waterloo-type	650°C 700°C	liquid by weight	Garcia et al. 1996b
0.2 mol % of gas	Batelle-Columbus	M.W. 100 assumed	MBMS	Gebhard et al. 1994a
2-50 g/Nm^3 5 g/Nm3	Pilot-scale	Variable steam-O2 mixtures 800°-900°C		Gil et al. 1997
18.2 wt % feed 10.7 9.2 24 6	Laboratory	600°C, Top-fed, inert gas 790° " 990° " 700° Steam 900° "		Gulyurthu et al. 1994
.16-1.05 g/Nm^3	Lurgi CFB	Urban wood waste		Hasler and Bühler 1994
1.6-23 g/Nm^3	VTT	1-20 bar 800°-950°C		Hepola et al. 1994
1 g/Nm^3 or less	FICFB		Condensibles at 10°C, GC	Hofbauer et al. 1997
2.3 wt % dry feed 0.8	Paia/IGT, air	841°C, 2.9 bar 835°C, 4.2bar		Kinoshita et al. 1997
4.3 wt % feed 5.4 2.5	HNEI , indirectly heaated	700°C 750°C 900°C		Kinoshita et al. 1994
8.0 g/Nm^3 7-11 2-5 2.4	8 bars. Wheat straw, 800°-900°C	Benzene M. W. 79-202 Pyridine-indene Naphthalene		Kurkela et al. 1996

3-4 wt % feed 0.7-1.2 " 0.5 "	Air-blown, pressurized, 900°C	Wood Peat Brown coal	Benzene plus tars	Kurkela and Ståhlberg 1992
4-8 g/Nm^3	Pressurized peat	830°C-870°C	Tar dominated by BTX	Kurkela et al. 1989b
30 -12 g/kg dry feed	800°-910°C freeboard temperature.	Peat		Leppälahti and Kurkela 1991
21 g/Nm^3	Lund	Internally circulating	Condensates	Mårtensson and Lindblom 1995
0.5 g/Nm^3 42 g/Nm3 12 8.2 1.6	Stuttgart BFB Stuttgart BFB	 600°C 700°C 800°C 900°C	Tar meter based on FID Total tar by wt. and GC	Moersch 1997a Moersch et al. 1997
~3% of fuel C	MTCI, indirect			MTCI 1990
2-10 g/Nm^3	Bubbling bed	One atm.		Narváez et al. 1996
12 g/Nm^3		Steam/oxygen		Olivares et al. 1997
0.5-1wt % wood	BCL	Typical	Condensible materials	Paisley 1995a
16 g/Nm^3	BCL	Typical		Paisley et al. 1997
1-3 g/Nm^3	Typical	700°-1000°C	Compounds lighter than toluene	Pedersen 1994
2.2-42 g/Nm^3	Steam.oxygen	800°-850°C		Perez et al. 1997
3% dry feed Below 1g/Nm3	IGT-PDU Lurgi			Reed and Gaur 1998
0.1-.5 wt % feed	Top-fed, BFB	To 3 MPa and 900°C		Rosén et al. 1997
1.5 g/Nm^3				Simell et al. 1995a
6% of feed or 20- 40 g/m^3	Lund	Pressurized	3-4 ring PNAs are dominant	Wallin and Padban 1996
5.4 wt % feed	Bench	800°C, no steam		Wang et al. 1994b
2 g/acf	IGT Paia	Up to 982 C and 2 sec residence time.	40% of PNAs are heavier than 3-rings.	Wiant et al. 1994

C. Nature of "Tar" as a Function of Gasifier Type (See Section II)

D. Conclusions

The results reported for "tar" levels from the three main categories of gasifiers, tabulated in Table 3-1, show a bewildering array of values, in each case (updraft, downdraft, and fluidized-bed) spanning two orders of magnitude! Three of many reasons for this have no relation to the gasifier performance per se, but are a result of the different definitions of "tar" being used, the circumstances of the sampling, and the treatment of the condensed organics before analysis. There is general agreement about the relative order of magnitude of "tar" production, with updraft gasifiers being the "dirtiest," downdraft the "cleanest," and fluidized beds intermediate. A very crude generalization would place updraft at 100 g/Nm^3, fluidized beds at 10 g/Nm^3, and downdraft at 1 g/Nm^3. It is also well established that well-functioning updraft gasifiers produce a largely primary "tar," with some degree of secondary character (assuming no oxygen is added in a second stage); downdraft gasifiers produce an almost exclusively tertiary "tar;" and fluid beds produce a mixture of secondary and tertiary "tars." In updraft gasifiers, the "tar" nature is buffered somewhat by the endothermic pyrolysis in the fresh feed from which the "tars" primarily arise. In downdraft gasifiers the severity of final "tar" cracking is high, due to the conditions used to achieve a significant degree of char gasification. In fluidized-bed gasification a great variety of temperatures, environments, and circulation schemes are being tested, suggesting major improvements are coming. The nature of the feed material (for biomass) is only a secondary influence on the nature of the "tar."

The amount of "tar," not to mention the chemical makeup of the "tar" from a given gasifier, is a function of the temperature/time history of the particles and gas, the point of introduction of feed in fluid beds, the thoroughness of circulation (in fluid beds), the degree of channeling (in fixed beds), the feed particle size distribution, the gaseous atmosphere (O$_2$, steam), the geometry of the bed, and the method of "tar" extraction and analysis. In view of this, it did not seem worthwhile to try to rationalize the amounts of "tar" report in Table 3.1, except in the broadest terms.

Recommendations:

The two most helpful things researchers and operators could do in reporting raw-gas "tar" levels would be to clearly highlight the condensation, sample preparation, and analytical methods used and the end use to which the definition of "tar" is being applied. As an example, in the context of operating ICEs, one might be collecting only organics condensing above, say, 100°C; weighing the condensate; and not considering light hydrocarbons and benzene or toluene. At the other extreme, in a projected use of the gasifier output for an internally reforming solid-oxide fuel cell, the entire suite of organics, particularly olefines and aromatics, might need to be specified. At the last IEA Gasification Task meeting (Brussels 1998), it was stated that *"all organics boiling at temperatures above that of benzene should be considered as 'tar.'"*

IV. The Dependence of "Tar" Measurement on Sampling, Treatment Protocols, and Chemical Analysis Methods

A. "Tar" Measurements

A description of the development of gasifier sampling systems can be found in Ståhlberg et al. (1998). They state that the EPA Method 5 for sampling particulate emissions from flue gas is the basis for most gasifier sampling trains. Modifications have been necessary because of the higher tar and particulate loading of gasifier streams. Hence, cyclones have been added before hot filtration elements to remove dust. Temperatures of the front end of the system, which prevent organic condensation causing plugging, but low enough to prevent (or minimize) thermal alteration of the tar, must be selected. Early work in the modification of EPA Method 5 was performed in Canada (McDonald et al. 1983, Esplin et al. 1985), and has been the basis of current isokinetic sampling approaches. Ståhlberg et al. (1998) describe the development and rationale of non-isokinetic sampling systems when high gas flow rates are not possible and when particulate measurement is not to be performed simultaneously.

Usually sampling techniques have been used to simultaneously measure tar and particles. A typical example of these techniques is the sampling train used to evaluate the operation of the 10 tn/h Pressurized Bubbling Fluidized Bed BIOSYN Biomass Gasifier (Techwest Enterprise Ltd. 1983). The train is shown in Figure 4.1. It is an isokinetic sampler composed of the following modules:
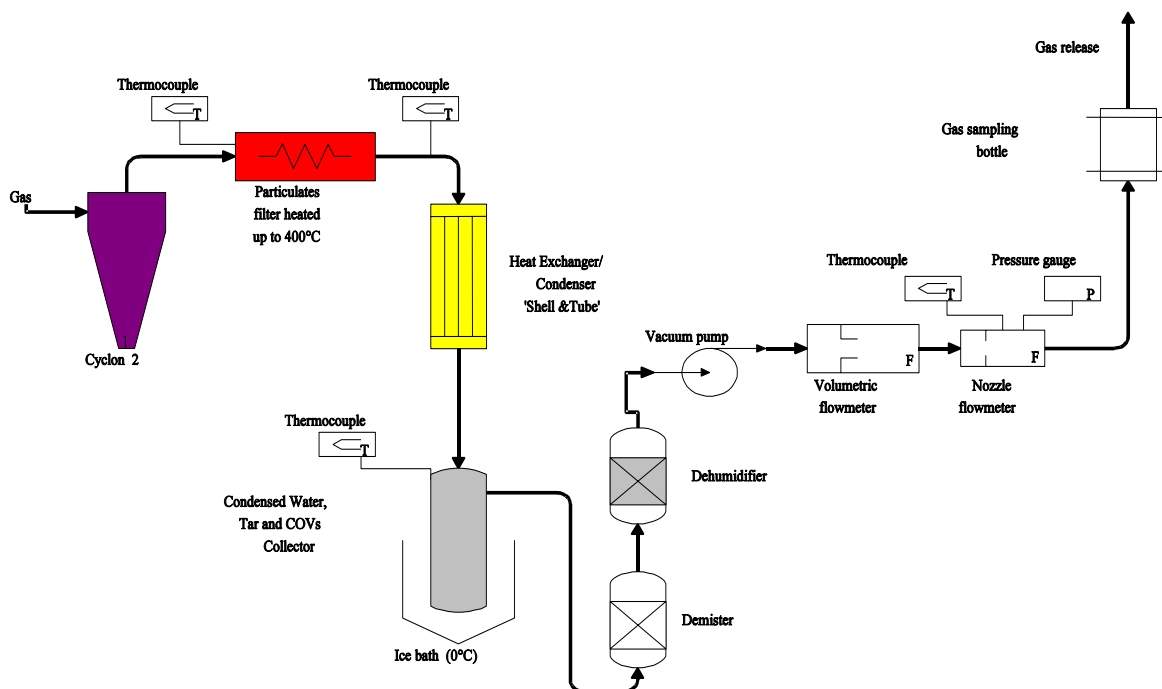

Figure 4.1. BIOSYN sampling train used in Canadian R&D activities.

- Automatically controlled sampling flow to ensure isokinetic conditions
- Heating element prior to the particles collector to avoid high molecular weight "tar" deposition; this is a point where the different methods used do not agree; a temperature range of 250°–400°C is used by various authors and systems
- A particle collector composed of porous metal filter elements and glass wool packings has also been used
- A "tar" condenser quenched continuously by a glycol air-cooled radiator
- A silica-gel filter-drier followed by a gas-rate counter and an automatically modulated valve.

Possible problems with this kind of sampler are:

- The difficulty in removing all condensed "tar" droplets and aerosols from the gas flow
- The possible condensation of heavier "tar" before and during filtration.

The Danish Technological Institute (see citations in CRE Group 1997), with the partial support of the JOULE Program of the EC, has developed a dust and tar measurement method, mainly based on the following standards: VDI 2066 Messen von Partikeln, Manuelle Staubmessung in Stromenden Gasen and VDI 3499 Messen von PCDD und PCDF, Filter/KŸhler-Methode. To some extent this method has been modified as measurements are often carried out in heavily polluted gases. The aim of this method is to measure dust and tar at the same time. The particles are separated in a heated filter and the gas is cooled to $100°C$ afterward, at which point the tar aerosol is separated in a glass filter with a pore size of 10–16 μm. Afterward, the gas is cooled to approximately $5°C$, when the remaining condensibles are separated. After having passed the cooling phase, the gas passes through an adsorbent XAD-2 (porous polymer of inert material) or polyurethane foam (PUF), in which very volatile components and extremely fine aerosols are retained. Finally, the gas is dried for the remaining the water content and the sample volume is measured by a gas meter. The sampling flow can be varied by means of a bypass to obtain isokinetic sampling. The dust and tar measurement method developed by DTI is shown in Figure 4.2.

According to the authors the method has the following advantages: Most dust and "tar" are retained by the two filters, which can be weighed on site allowing an immediate measurement result; depending on the degree of elaboration required, the sampling equipment can be configured, thus individual components can be omitted. The installation of a gas-tight lock system makes multiple sampling possible.

Significantly higher "tar" concentrations are measured by weighing procedures rather than by GC/MS analysis performance. This is due to the limited capacity of the GC/MS to identify and quantify all "tar" components. The heaviest components are rather retained and do not elute through the GC columns. Sampling precision, accuracy, and reproducibility are highly affected when applied to low "tar" and particulate content gases (i.e., post-cleanup gases).
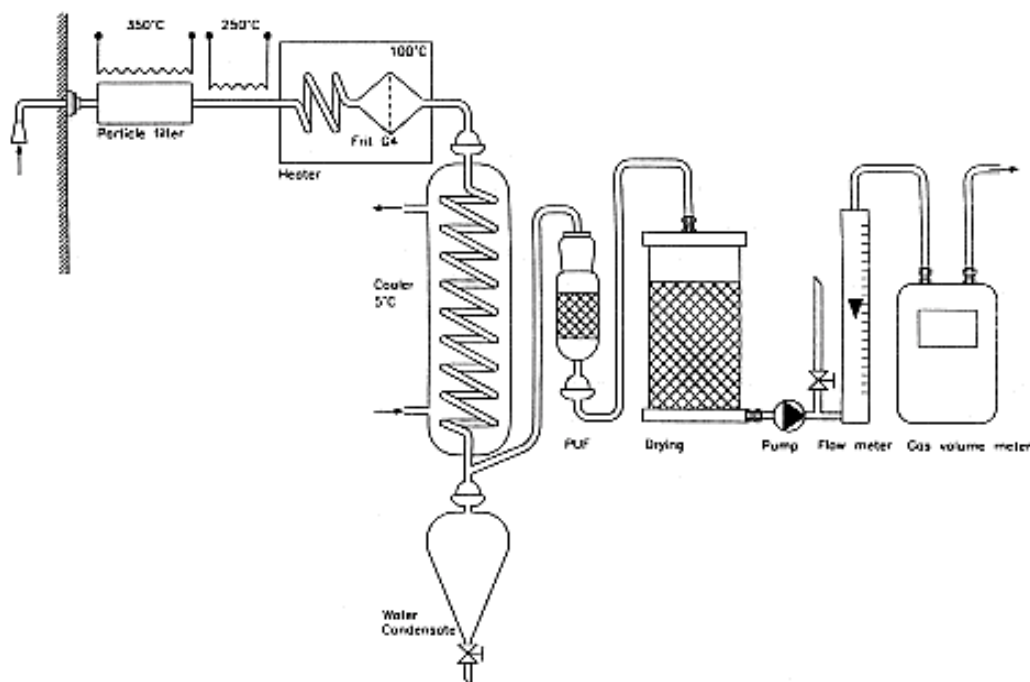
The dust and tar measurement method developed by DTI

Figure 4.2. The dust and tar measurement method developed by DTI.

B. Other Simultaneous "Tar" and Dust Measurements in the Producer Gas

Measuring the amount of "tar" and dust in the raw and clean gas should be done simultaneously to ensure similar process conditions. Isokinetic conditions should prevail during sampling. Several other isokinetic sampling systems have been conceived and applied so far: their common elements are a heated filter (glass fiber, cellulose, quartz-fiber, ceramic) for trapping the dust particles and a condenser for trapping the "tar."

BTG et al. (1995b) point out that a general problem of this type of sampling is that some of the particles collected by the sample filter may have been in gaseous form in the product gas. Besides, a special problem comes from the heaviest "tar" compounds. Some of these "tars" condense on the sample filter and some create soot particles in the sampling probe. Moreover, some of the heaviest "tar" compounds are insoluble in certain solvents or seem to polymerize on the filter paper to form insoluble "soot" particles. No clear solution is found to overcome this problem. The soot forming reactions are probably enhanced by the high temperature, so sampling at lower temperatures is recommended. This is in conflict with the need to sample at temperatures high enough (e.g., 400°C) to avoid "heavy-tar" condensation. A short description of different sampling systems is given in more detail later.

The stationary source sampling methods developed by EPA (Rules and Regulations, August 18, 1977—Method 5; February 13, 1991—Method 23) have been examined for their applicability to monitoring of gasifiers. Her Majesty's Inspectorate of Pollution and Warren Spring Laboratory (Department of Trade and Industry) in the UK were consulted for methods for sampling and analysis

of PAHs ("tar"). They considered that these EPA methods can be useful for this purpose. Techniques similar to these are being used by VTT and the University of Sherbrooke on an experimental and pilot gasification facility, respectively. In general, the various techniques may have to be adapted for different levels of contamination and systems. BTG et al. (1995b) is an excellent source for more details.

A summary of the advantages and disadvantages of key sampling elements are given below:

- Isokinetic sampling:
    + simultaneous sampling of tars and particulates
    - high gas flows make use of impingers difficult

- Non-isokinetic sampling:
    + design of probe can minimize plugging
    - not possible to sample particulates

- Hot gas filtration:
    + allows simultaneous determination of particulates and tars by gravimetry
    - reactivity of material is unknown, such as transformation of tars into particulate.

C. Sampling from Different Gasifiers

There are not enough data in the literature to undertake a comprehensive comparative study of "tar" nature as a function of the gasifier types. The reasons for this are: Full quantification of "tar" components is a difficult, expensive, and time-consuming task. Not all gasification technology developers and operators have access to the appropriate analytical equipment.

The work of ETSU/DTI (CRE Group, Ltd. 1997) brings some new light to this field. In this work the authors undertake an, as comprehensive as possible, identification of "tars" from various gasifiers accessible to them. The work is complemented by a thermal/catalytic cracking study using model compounds and "real tar." From this work we choose some very important points and conclusions to be reported here:

1. In-situ sampling and analysis have been affected, keeping in mind the following:

    Because biomass tars are complex materials, consisting of hundreds of compounds, varying widely in polarity and molecular mass, repolymerization reactions can occur in "aged" samples. Fresh sample analysis is recommended to ensure representativity of the "tar" present during the gasification process. Acetone cooled to approximately -55°C was used to condense and collect "tar." Low temperatures decrease the undesirable free radical reactions rates, which are responsible for the condensation reactions leading to high molecular weight compounds. The gaseous tar sample was collected using a sampling procedure depicted in Figure 4.3. A full description of the method as well as general sampling guidelines are presented in CRE Group, Ltd. (1997).

    For the latest developments in sampling protocols, see BTG/TWENTE (1998).
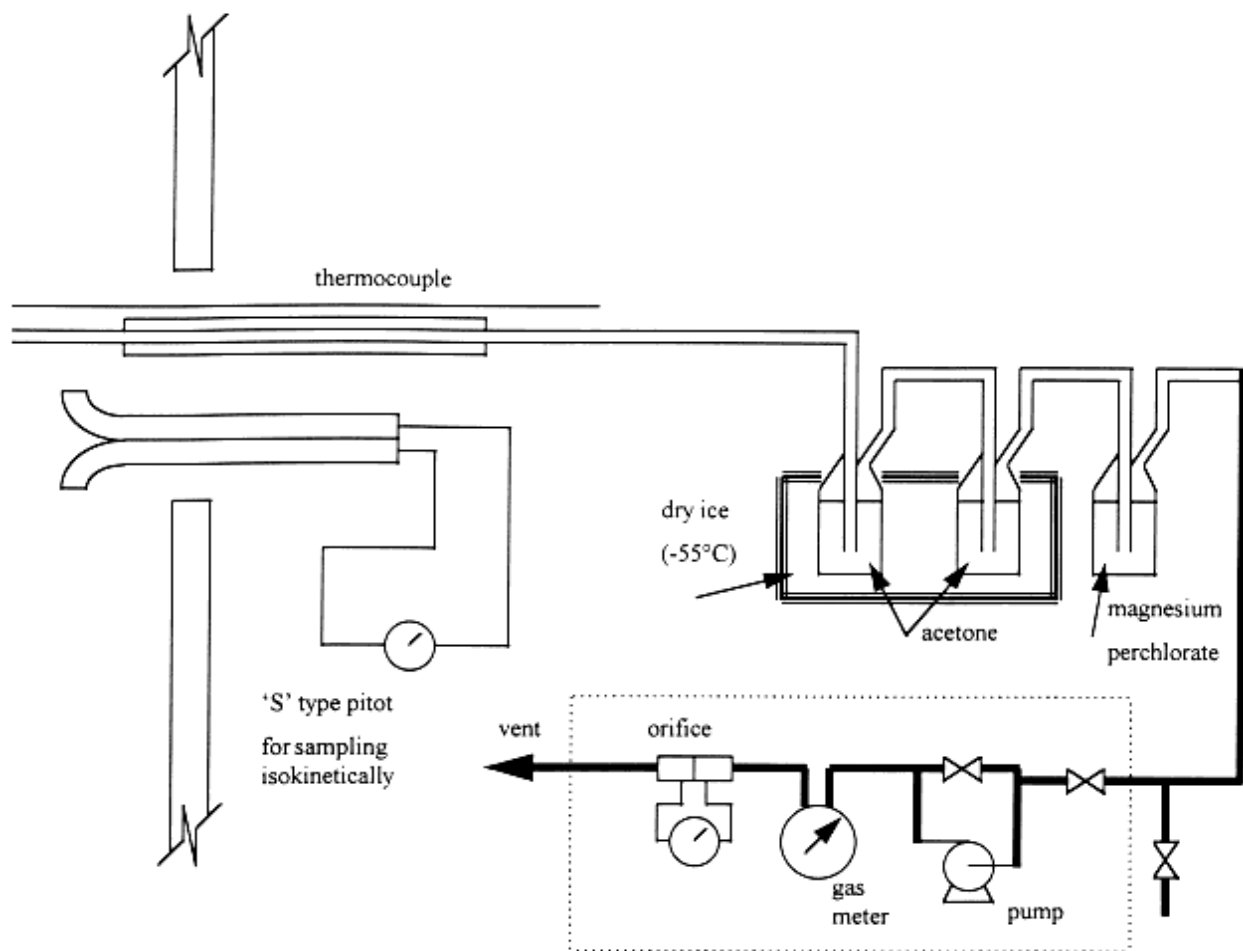
Figure 4.3. Sampling train used by CRE Group, Ltd. (1997)

2. Four gasifier "tars" are sampled, covering the range of technologies: updraft, downdraft, fluidized bed, and entrained flow gasifiers.

3. The analytical techniques for identifying and quantifying the "tar" components are varied and sometimes depend on the gasifier. They are generally adaptations of those employed in the petroleum industry. We can summarize them as follows:

   • Elemental analysis

   • Solvent fractionation and adsorption chromatography to separate the material into aliphatic, aromatic, and polar constituents

   • GC/MS

   • Probe MS techniques to provide molecular profiles of the original tar, aromatic, and polar fractions

- Size exclusion chromatography

- Ion chromatography.

4. General Results

"Fresh 'tar' sample yields almost 100% recovery whereas the 'aged' sample shows a recovery, off the chromatographic column, of 86%. This suggests that high molecular weight (>350 daltons) compounds are present in the 'aged' sample due to polymerization and bridging reactions" (CRE Group, Ltd. 1997). Most heteroatomic compounds decrease in concentration when comparing the "fresh'" and "aged" "tar" samples because they are more likely to polymerize and/or bridge. Most PAHs show very little change in concentration when comparing the "fresh'" and "aged" "tar" samples, indicating that these compounds are relatively stable. Specific comparative results between the various types of gasifiers, regarding the nature of tar are summarized in the Table 4.1; the data are obtained from CRE Group, Ltd. (1997):

Table 4.1. Comparative "tar" characterization, by gasifier type (CRE Group, Ltd. 1977).

Gasifier type Topic	Updraft	Downdraft	Fluid-bed	Entrained flow fluid-bed
Oxygen content	high	low	low	low
Concentration of high MW tar	high	low	low	low
Heteroatomic tar concentration (*)	low	high	low	low

(*) This point is rather a function of feedstock chemical composition

Upon reviewing the results of this unique study and taking into account all information contained in our literature review, we note the following:

The method, timing, and logistics of the sampling play very important roles in any attempt to evaluate qualitatively or quantitatively gasification "tar." Feedstock can be a very important parameter in gasification "tar" nature, though lignocellullosics behave similarly. Each type of gasifier, fed with the same feedstock, gives off "tar" with a characteristic chemical profile; however, even within a specific family of gasifiers (e.g., fluidized-bed), differences can be substantial. These differences result from varying geometries, configurations, and temperature profiles, residence times, and bed materials. Detailed analysis of this field has never been undertaken systematically, because (a) the availability in time and space of pilot units; (b) the need of a highly efficient coordination; (c) the adoption and use of a widely accepted tar sampling protocol; and (d) the time and expense required.

D. Some Further Notes on Sampling and Analysis, from the Literature (Appendix IV)

A quick perusal of the following notes will give the reader a feeling for the diversity of sampling and analysis methods that have been used.

1. Probe issues.

    As mentioned earlier, heated probes and isokinetic sampling are desirable if particulates and aerosols of "tar" are to be sampled:

    Isokinetic sampling of "tars" is recommended since *"these 'tar' compounds can form droplets and can then behave like particulates"* (BTG Biomass Technology Group 1995a).

    "There are some indications that 'tar' behaves like a particle, a droplet and/or an aerosol" (Brown 1996).

    Sampling considerations for high-"tar" gasifiers include aerosols discussion (Esplin and McDonald 1982).

    Gas is extracted through a stainless steel sample probe maintained at 250°C to prevent "tar" condensation (Leppälahti and Kurkela 1991).

    "Tars" present in gas will condense at less than 370°C (Miller 1983).

    Gas temperatures in probe and lines should be kept at temperatures higher than 350°C to prevent "tar" condensation (Mudge et al. 1988a).

    If product gas contains particulates, the sample should not be taken at temperatures higher than 700°C, because the "tar" components can be catalytically decomposed by the particles (Oesch et al. 1996).

    Some "tar" components may adsorb on carbonaceous particulate. "Tar" sampling should be done under quasi-isokinetic sampling conditions (Salzmann et al. 1996).

2. "Tar" condensation and collection issues.

    A great variety of "tar" condensation conditions have been used which, coupled with the operational definitions of "tar," make comparisons difficult:

    "Acetone was found to be the best solvent for sample recovery and cleanup of sampler components" (Aiken et al. 1983).

    Recovered the "tars" by washing in acetone, thus filtering the particulates (Allen et al. 1984).

    Condensers, traps, etc., are washed with methanol to give *"methanol solubles"* composed of "tar" and water (Arauzo et al. 1997).

"Tars" are collected in a four-condenser train, third-generation system (Aznar et al. 1997b).

"Tars" are collected in a cellulose filter followed by a water-cooled condenser (BTG 1995a).

"Tars" are collected by an impinger following the cyclone at 110°–190°C to prevent water condensation (Beck et al. 1982).

Various solvent systems for "tars" from four woodwaste gasifiers in Canada, showed a mixture of ether, tetrahydrofuran, and ethanol (1:8:1) was best (Beall and Duncan 1980).

"Tar" equals condensibles at 100°C (Boroson et al. 1989).

"Tar" was collected using water-cooled condensers and cold traps (ice-acetone and dry ice-acetone) (Brage et al. 1996).

"Tar" collected in ice water (Brown et al. 1986a).

Collect and analyze a water soluble and acetone soluble fraction (Corella et al. 1991a).

Condense "tar" vapor in acetone at -55°C (CRE Group, Ltd. 1997).

"Tars" are collected by a multi-stage condenser/absorber sampling train (De Sousa et al. 1994).

"Tars" are collected as condensate on a cotton filter at dry ice-acetone temperature (Donnot et al. 1985).

Decanted condensate; extracted aqueous phase with methylene chloride; and acetone rinse to remove adhering "tars" (Elliott and Baker 1986).

Acetone solutions of "tar" are analyzed (Esplin et al. 1985).

"The absence of toluene, benzene and other more volatile compounds is an operational characteristic of the BCL 'tar' collection technique" (Gebhard 1995a).

Collected "tar/liquids" at 0°C (Gulyurthu et al. 1994).

"Tar" sampling was facilitated by absorbing tar into dichloromethane (Hepola et al. 1994).

Defines "tars" as condensibles at 10°C (Hofbauer et al. 1997).

Condenses "tars" at -78°C in acetone (Jensen et al. 1996).

"Tar" condenser runs at 120°C to separate water (Jönsson 1985).

Condensation temperature of most "tar" species is less than 250°C (Kinoshita et al. 1994).

Condensed "tars" in dichloromethane in wash bottles at +5°C and -70°C (Leppälahti and Kurkela 1991).

Collected "tar/oil" in an ice bath quench (MTCI 1990).

Two "tar" scrubbers in series, filled with methylene chloride and maintained at 0°C and -20°C (Mudge et al. 1987).

Collect "tars" in a five-stage condenser to -5°C or -80°C (Narváez et al. 1996).

Sampled "tars" by controlled condensation at 150°C and dissolution in dichloromethane (Oesch et al. 1996).

"Tar" is toluene wash material from MM5 sampling train (Paisley 1995b).

"Tar" sampled in water cooled condensers and cyclone-shaped dry-ice traps (Rosén et al. 1996).

"Tars" are absorbed in dichloromethane at 0°C (Salo and Patel 1997).

Hydrocarbon "tars" are removed through a fiberglass filter submerged in ice water (Stobbe et al. 1996).

"Tars" are condensibles in an ice bath plus aerosols (Wallin and Padban 1996).

"Tars" are collected by a new solid-phase absorption method (Brage et al. 1997a; Yu et al. 1997).

"Tars" are collected in a water-cooled condenser. Remaining aerosol is removed in cyclone-shaped dry-ice traps and a cotton filter (Zanzi et al. 1993).

3. Treatment of collected "tars" before analysis.

Because researchers define "tar" for different practical reasons, there is no uniformity in how condensates are treated before analysis. The following notes indicate the extreme range of such treatments:

Acetone solvent for "tars" is evaporated at 30°C before weighing residue (Aiken et al. 1983)

Acetone wash for "tars" is rotary evaporated at 100°C and 10-mm Hg (Allen et al. 1984).

Dichloromethane "tar" solvent was rotary evaporated to constant weight at 50°C and 2 kPa (Brage et al. 1996).

"Tars" are collected in ice water and air dried at room temperature (Bui et al. 1994).

Collected a non-water soluble fraction in acetone and distilled at 80°C (Corella et al. 1991a).

Acetone solutions of tar are evaporated at 25°–30°C and tar determined by weight (Esplin et al. 1985).

Generally only determine the "heavy tars," which represent the distillation residue from an organic absorption solution at a temperature of 150°C (Hasler 1997).

"Tar" condenser runs at 120°C to separate water (Jönsson 1985).

Dichloromethane "tar" solvent distilled away at 75°C (Leppälahti and Kurkela 1991).

When methylene chloride dissolved "tars" are evaporated at 105°C for 1.5 hours, none of the C6-C20 hydrocarbons remain (Mudge et al. 1988a).

Sample "tars" by controlled condensation at 150°C (Oesch et al. 1996).

Acetone is very difficult to separate completely from "tar" by distillation (Olsen 1989).

"Tars" collected in toluene are dried overnight at 93°C and then weighed (Paisley 1993).

A few examples of how treatment may influence total "tars" reported: Aldén et al. (1993) note that under severe conditions, BTX can be much greater than naphthalene. At 800°–900°C and one atmosphere with dolomite, "total tar" was about six times the "condensible tar" (mainly naphthalene) (Aldén et al. 1996); Reed (1996c) assumes that "total tar condensate" at -40°C is five times the 100°C value.

4. A further impediment to comparing reported "tar" values is the great variety of analytical techniques that have been used to characterize "tars" collected by different methods and with different pre-analysis treatment as just noted. Some analytical techniques used are:

"Tar" is absorbed, extracted, and analyzed by GC (Aldén et al. 1997).

"Tar" condensate was removed and analyzed by LC and total organic carbon (TOC) assuming phenol as representative of the "tar" (Aznar et al. 1990).

"Tar" analyzed by a Dhormann DC-90 for TOC (Aznar et al. 1992).

The EPA methods for stationary source sampling seem appropriate for sampling and analysis of PAHs ("tars") (BTG 1995b).

"Tars" were fractionated by column chromatography (Beall and Duncan 1980).

"Tars" separated into polar and aromatic fractions for GC analysis (Beck et al. 1982).

Used chemical oxygen demand (COD) as the simplest and most reproducible measure of "condensates" (Black 1984).

"Tar" samples were analyzed by methods based on combined application of liq-liq partitioning, solid-phase extraction (SPE), and capillary GC with flame ionization detection (FID) (Brage et al. 1995).

Several techniques used for analysis, including TOC, were tested (Corella et al. 1992).

The "tar" sampling and analysis methods can significantly modify the number for the "tar" content (Corella et al. 1995b).

All products from partial oxidation of switchgrass were measured by direct MBMS (Dayton and Evans 1997).

Used GC/MS of ambient "tars" (Elliott and Baker 1986).

Direct MBMS with a portable system to detect "tar" components in the raw, hot gas (Gebhard et al. 1994a).

For distillation residue at 150°C from an organic condensate, determine 16 PAHs according to EPA list and methods (Hasler 1997).

Absorb "tar" into dichloromethane, followed by capillary GC (Hepola et al. 1994).

Same technique for "tar" analysis as in Sjöström et al. (1988) and Corella et al. (1991a) (Herguido et al. 1992b).

"Lighter tars" (to 180°C) measured by GC/MS (Hepola et al. 1994).

"Tars" measured with a quasi-continuous "tar meter" based on FID (Moersch 1997a,b).

Multi-step fractionation and analysis of condensates gives detailed compositions (Myrén et al. 1996).

Overall sample of condensates is diluted with water until a homogeneous phase is obtained, then do a TOC determination (Narváez et al. 1996).

"Tars" measured by a total hydrocarbon analyzer (Nelson 1987).

"Tars" collected in dichloromethane are analyzed by GC, high-temperature GC, pyrolysis GC, atomic emission detector, and gravimetric analysis of components above MW 302 (Narváez et al. 1997).

"Tars" are condensed in a solvent at 0°C and are estimated by a solvent method (Parikh et al. 1988).

"Tars" analyzed by TOC by the method in Narváez et al. (1996) and Perez et al. (1997).

Describes a simple "tar" measurement method based on EPA Method 5 (Das 1985).

Volatile organics measured by GC with MS identification (Rosén et al. 1997).

Dust and "tar" by THT dust and "tar" sampler. "Tar" by Soxhlet apparatus and THT. PAH and phenols by biological oxygen demand. Gas analysis by ORSAT (Stassen and Knoef 1995).

"Tar" analysis was performed by Capillary GC/MS, following pre-separation by liquid extraction (LE) or SPE on aminopropylsilane modified silica, and in some cases by preparative HPLC using a C18 reverse phase column and UV detection at 254 nd 280 n.m. (Brage and Sjöström 1991; Vassilatos et al. 1992a).

Gravimetric methods are widely used and cited. See the following references for examples: (Aiken et al. 1983; Brage et al. 1996; Brandt and Henrickson 1996; Bui et al. 1994; Corella et al. 1991a; De Sousa et al. 1994; Esplin et al. 1985; Garcia et al. 1997b; Gebhard 1995a; Jensen et al. 1996; Jönsson 1985; Myrén et al. 1997; Paisley 1993; Salzman et al. 1996; Sjöström et al. 1988, Vassilatos et al. 1992a).

5.   Standards and reviews of sampling and analysis methods.

"Development of a standard procedure for gas quality testing in biomass gasifier plant/power generation systems" (BTG 1995b). There are no uniform methods for monitoring and evaluating the performance of gasifier systems. This study reviews the methods proposed by the UNDP/World Bank and the Biomass Research Group of ITT, Bombay. For practical application, the THT (UNDP) World Bank sampling system is recommended because "the analysis is simple, low cost and easy to execute under field application. Other sampling techniques as developed by VTT and ETH/Verenum are more suitable for research applications." Further development of standards would be a suitable subject for future IEA Voluntary Standards Activity and through the CEC framework under Joule and/or Thermie. At Vienna "there was a general agreement that this subject will be included as a sub-activity or sub-task of future meetings on gasification" (BTG 1995b).

Strategies for Sampling and Analysis of Contaminates from Biomass Gasifiers. VTT Energy, Gasification Research Group, Espoo, Finland. Task Study Report prepared for the IEA Biomass Thermal Gasification Activity (1992-94) (Kurkela et al. 1995a).

Practical Achiements in Biomass Gasification. Cites problems in 1985 regarding sampling and definition of "tar" (organics) in lack of reliable and comparative tests with "tar" (Rensfelt 1985).

Guideline for Sampling and Analysis of Tars, Condensate and Particulate from Biomass Gasifiers. ETH/Verenum, Zurich, Switzerland: Institute for Energietechnik. No common or widely accepted composition of "tar." "Tar" is most widely measured gravimetrically. Can't intercompare results. In this guide the following definitions for "tar" components are used: "Heavy tars": the sum of high molecular weight polynuclear aromatics (PNA) determined gravimetrically by evaporating a solvent (e.g. methoxy benzene, B.P.=155°C, evaporated under vacuum. "PAH": Use the EPA list of 16 compounds. "Light Tars": Aromatic hydrocarbons with medium volatility, 80°–200°C (e.g., BTX). Does not include phenols. "Light

Hydrocarbons": Non-aromatic hydrocarbons up to about C5, gaseous at room temperature (e.g., methane, ethylene). "Phenols": Aromatic hydrocarbons with at least one OH group (e.g., phenols, cresols). Oxygenates: Organic, non-aromatic compounds with oxygen (e.g., acetic acid, methanol). Notes: 1. Non-chromatographable hydrocarbons are considered an important fraction of "heavy tars." 2. Some tar components may adsorb on carbonaceous particulate. "Tar" sampling should be done under quasi-isokinetic sampling conditions. 3. *"at the gasifier outlet, most of the organic compounds such as phenols or the PAHs will be present as aerosols."* 4. Reports schematics and discussions of their preferred sampling train for particulates and "tar." 5. List of 16 EPA compounds ranges from naphthalene through pyrene, to benzofluoranthene (most of these are seen in highly cracked, or "tertiary tars"). Procedures for tar analysis and definitions of "tar" have been proposed as standards, jointly worked out and verified with the Swiss Federal Laboratories for Materials Testing and Research (EMPA) in Dubendorf (Salzmann et al. 1996).

Sampling and Analytical Methods for Product Gases from Solid Fuel Gasifiers. In this reference are reviews of the methods developed at the Laboratory of Fuel and Process Technology of the Technical Research Centre of Finland (VTT), Finland, in the 1980s, and the method developed within the ENFOR Project C-172 at the Energy Research Laboratory CANMET, Canada, in the early 1980s (Ståhlberg and Kurkela 1990).

A Workbook for Biomass Gasifier Sampling and Analysis. Based on the two Aiken et al. reports for Techwest (Techwest 1983).

Producer Gas Quality Requirements for IGCC Gas Turbine Use. The definition of "tar" has mainly to do with the temperature at which "tar" compounds are condensed. There is no standard by which "tar" should be measured. *"There are some indications that 'tar' behaves like a particle, a droplet and/or an aerosol. An industry-standard gas quality measurement protocol for biomass gases must be defined and implemented. A program to do so could be funded by the energy departments of several interested countries pursuing IGCC. Care must be taken to sufficiently include the concerns of the turbine manufacturing industry; overall a commercial standards body such as ASTM could be consulted as well"* (Brown 1996).

Identifying the Barriers to Commercialization of Low-BTU Gasifiers: Proceedings of a Workshop. The panels called for controlled testing of the effects of "tar," char, and ash, as well as alkali, on turbines. Almost all the the panels called for standards development. In particular, ASTM, EPA-5 and other test methods should be modified to create new standards acceptable to the gasification industry (Easterling et al. 1985).

Identification and Processing of Biomass Gasification Tars. The authors call for the development of a European standard *"for the sampling and quantification of condensible compounds found in biomass thermochemical processes"* (CRE Group, Ltd. 1997).

Biomass Gasification with Steam in Fluidized Bed: Effectiveness of CaO, MgO, and CaO-MgO for Hot Raw Gas Cleaning. Refers to the tobacco companies' world-wide, standardized, methods for "tar" collection and analysis. Biomass gasifiers each use their own method. No equivalence between numbers for "tar" yields or composition (Delgado et al. 1997).

Sampling and analysis procedures are discussed in connection with a study of the gasification of wood chips and bagasse in the GE pressurized, air-blown, fixed-bed, updraft coal gasifier (Furman et al. 1993).

A "dry" "tar" sampling method, developed at the University of Stuttgart, is described in Moersch et al. (1997). The three main componants are: hot-gas filtration; tar probe to retain componants with high boiling points; and on-line analysis of the componants passing the filter (GC/FID).

An excellent web site documents an effort by several laboratories to provide their sampling and analysis experience, toward the establishment of one or more standard methods (BTG/UTWENTE 1998).

E. Conclusions

The biggest issue, which confuses the meanings people apply to "tar" and the intercomparability of results from various researchers, are: the conditions and solvents used for "tar" collection; and the subsequent solvent separation. The variety of analytical characterizations of the collected material give different views of the makeup of the organics, but if clearly documented, do not mislead the reader. As detailed earlier, the temperatures, trapping schemes, and solvents used to capture organics vary greatly. Capture temperatures from $-78°C$ to $+190°C$, with many temperatures between, are reported. Single-to-multiple vessels are used, containing solvents such as acetone, methanol, dichloromethane, methylene chloride, and toluene. Solid sorbents such as cellulose, fiberglass, and amino-bonded silica (Brage et al. 1997a) are also used. Sometimes the collection of aerosols of "tar" is mentioned. The extraction of the organic fraction of ash, char, and soot is seldom considered. Losses of solvent during sampling is also a concern when "tar" is measured gravimetrically, especially for gases with low "tar."

Some measurements of the organics in the condensate do not require separation of the solvent or water. In most cases however, a pre-separation or extraction is used, especially when weight is the measure. Solvent removal has been reported by distilling at from $75°C$ to $150°C$; by evaporating at $25°C$ to $105°C$ under ambient to 10-mm Hg pressure; by air-drying at room temperature or at $93°C$ overnight; and by organic partitioning; depending on the fraction of "tar" that is of interest to the end use being studied. As one example of the large difference in quantity of "tar" being reported, Aldén et al. (1996) note that the *"total tar"* can be six times the commonly measured *"condensible tar."*

There are issues in the probe design that are not always explicitly discussed. Probe and lines must be at a high enough temperature to prevent condensation of the least volatile tar component of interest, but not so high as to cause additional cracking or interaction with particulates of whatever nature. Because some of the tar can be in aerosol form or reside on ash, char, or soot particulates, isokinetic sampling would seem to be a prudent practice.

Recommendations:

A number of sampling methods, specific to biomass and the predominant measure of organics for categories of end use, need to be standardized. These should include probe conditions, collection geometry and conditions, and solvent use and removal. To support these standards, research needs to be carried out on the fractions of organics that are captured and removed from the solvents being used for primary, secondary, and tertiary "tars." As noted earlier, and following the suggestions in the literature, a widely recognized standards organization, in collaboration with other standards groups and the IEA gasification task, should lead this activity (BTG 1995b; Kurkela et al. 1995a; Salzmann et al. 1996; Ståhlberg and Kurkela 1990; Brown 1996; Easterling et al. 1985; Techwest 1983; CRE 1997; Delgado et al. 1997).

This issue of standards is currently being addressed, as is documented in the University of Twente web site: http://bgt.ct.utwente.nl/projects/558/ (BTG/UTWENTE 1998) and by the IEA Gasification Task (Brussels 1998).

V. The Tolerance of End-Use Devices for "Tar"

A. Gasifier End Use

For selecting an optimal integrated clean-up strategy, the intended end use (gas application) for the gasifier gas is a key consideration. The most important end uses, so far practiced commercially or under research study, can be summarized as follows:

- Close-coupled combustion (kilns, ovens, furnaces, dryers, "town gas" for local distribution, and boiler firing)

- Hydrogen fuel production

- External combustion for power: externally fired turbines, Stirling engines, steam engines, thermo-photovoltaic cells, catalytic oxidation, and thermo-electric systems

- Internal combustion (IC) diesel and Otto engines

- Compressors

- Gas turbine internal combustion

- Fuel cells: molten carbonate, solid oxide, proton exchange membrane, and phosphoric acid

- Chemical synthesis: methanol, ammonia, methane, Fischer-Tropsch liquids, other oxygenates.

Specifications for contaminant levels that can be tolerated in these end-use applications are given in Table 5.1. Since Graham and Bain's (1993) report published specifications have changed very little, but several new applications are under investigation, which require short- and long-term tests of contaminant toleration. The reader should view this information as representing a range of likely values, with the realization that few long-term tests with modern devices have been reported, and almost no studies in which the "tar" is well characterized. For specific applications the constructor of the engine or conversion device is the most reliable source of information. Close-coupled combustion applications for process heat are relatively insensitive to gas quality, and therefore the main concern is that the final combustion gas product (stack gas) meet emissions regulations. Aside from environmental considerations, the gas must be maintained above the "tar" dew point so that no condensation occurs in transport lines. Brown, quoted in Graham and Bain (1993), reports that maximum "tar" levels should be in the range of 60 to 600 mg/Nm^3 (site-specific range) for successful compression and piping of producer gas.

Table 5.1. Contaminant Constraints

Gas Application/ End Use	"Tar" Loading mg/Nm^3, ppmw	Reference
Close-Coupled Combustion	Limits are large	Baker et al. 1986
"Town-Gas" for local distribution (a few miles)	50-500 ppmw	Reed et al. 1987
Externally Fired Stirling Engines	Higher than for ICE Tolerates raw producer gas	Cuda and Ziak 1995 Johansson et al. 1996
Steam engines	Similar to boilers	
Thermo-photovoltaic cells	Unknown	Broman and Marks 1995; Coutts and Benner 1994
Thermo-electric systems	Unknown	
Catalytic oxidation	Unknown	Järås and Johansson 1996
Externally fired turbines		Kuehn 1995 Evans and Zaradic 1996
Internal Combustion Systems		
SI and diesel	Max of 100 mg/Nm^3	BTG 1995a
	50-100 mg/Nm^3	BTG 1995b
	10-50 mg/Nm^3	Baker et al. 1986
	Less than 100 mg/Nm^3 Preferably 50 mg/Nm^3	Beenackers and Maniatis 1996
	Less than 20-500 mg/Nm^3	Corella 1996
	Up to 30 mg/Nm^3	Bridgwater 1995
	10-50 mg/Nm^3	Brown et al. 1986b
	Less than 10 mg/Nm^3	Bui et al. 1994
	Less than 30 mg/Nm^3	Das 1985
	Total contaminates less than 10 mg/Nm^3	Kaupp 1984

Gas Application/ End Use	"Tar" Loading mg/Nm^3, ppmw	Reference
	Assumes less than 50 mg/Nm^3 advisable	Mukunda et al. 1994a
	Condensates that can be consumed by engines need not be named "tars"	Parikh et al. 1987
	World War II experience favors less than 10 mg/Nm^3	Reed 1985
	Less than 100 mg/Nm^3 OK but less than 50 preferable	Stassen and Knoef 1995
	(A direct comparison of "tar" tolerances for spark ignition versus diesel has not been found.)	
Direct-Fired Aero Gas Turbines	Unknown	
Direct-Fired, Industrial Gas Turbines	Compression is biggest problem. Tars OK if in vapor phase. Engines have higher tolerance to tars than turbines.	Bridgwater 1995
	Tolerance for condensing tars 0.05–0.5 ppm	Brown 1996
	Tars may not be of concern for BIG/BT. Keep in vapor phase.	Williams and Larson 1996
	Tar and naphthalene, 0.5 mg/Nm^3	Aigner 1996
	Tar less than 5 mg/Nm^3, C7+less than 0.01 vol % of gas.	BTG 1995b
Compressors	50–500 mg/Nm^3	Reed et al. 1987
Ceramic Filters	Unknown	
Fuel Cells		
MCFC-external reforming	C_2H_6-tolerant; C_2H_4-less than 0.25 vol.%; C_2H_2, less than 0.2 vol.%; benzene -0.5%; aromatics, 0.5 vol %.	Klinger and Kennedy 1987

Gas Application/ End Use	"Tar" Loading mg/Nm^3, ppmw	Reference
MCFC-internal reforming	Total contaminants less than 80 ppb.	Anonymous 1997
	Temperature is high enough to reform hydrocarbons.	Bain 1995
	Saturated HC, less than 12 vol %; olefins less than 0.2 vol %; aromatics less than 0.5 vol %; cyclics less than 0.5 vol %.	Bossart et al. 1990
	Tars are typical catalyst poisons.	Heinzel et al. 1996
	Benzene less than 1 vol.%, naphthalene less than 0.5 vol.%.	Ratcliff and Czernik 1997
	Steam/carbon for the reformer to be set at 3.5 to avoid carbon formation.	Yasue et al. 1998
	"Some external pre-reforming may be desirable to remove high molecular weight hydrocarbons from the fuel gas, which would otherwise crack to produce elemental carbon."	Dicks 1988
Solid-Oxide, external reforming	Unknown	Clark et al. 1997
Solid-Oxide, internal reforming	Unknown	Clark et al. 1997 EPRI 1997
	"Complete internal reforming can lead to . . . carbon formation in the anode chamber." Partial pre-reforming can avoid this problem.	Meusinger et al. 1998
	Carbon deposition was a problem unless air was added to the biogas.	Staniforth and Kendall 1998
Phosphoric Acid	Unknown	

Standard technology is available to ensure that a modern biomass gasifier coupled to a modern kiln or boiler (with a well-designed burner) will meet stringent environmental emissions guidelines and regulations. Therefore, there is no urgent need to further address close-coupled combustion in terms of gas cleanup.

ICE and methanol synthesis applications require that the gas be cooled before final use; therefore, it seems that gas cleaning would be greatly simplified by the use of proven, commercially available "cold" unit operations (filtration, direct scrubbing). However, there are many technical and economic reasons (thermal efficiency, environmental emissions compliance, non-condensible hydrocarbon gas removal, "tar"/effluent treatment costs) to justify catalytic cracking and reforming of the "tars" before cooling. However, if hot chemical conversion processes are adopted for gas conditioning, hot removal of particulates and aerosols must also be included. These constituents can cause catalyst fouling and poisoning, and deactivation in the cracking/reforming operations, and can result in excessive compressor erosion. Hot-gas cleanup (filtration and chemical conversion) is therefore relevant to "cold-gas" ICE and syngas end uses. Cold-gas cleanup unit operations may then be used in the final cleanup stages to ensure that technical specifications are fully met (CRE Group, Ltd. 1997).

ICE applications require that particles and "tars" be reduced before the producer gas can be effectively utilized. Limits of about 30 mg/Nm^3 for particulate and 100 mg/Nm^3 for "tar" are representative. For a turbo-charged engine the "tar" limit drops somewhat. Historically, gasifier/ICE/ generator sets (i.e., non-utility power plants as large as 1 MWe) have used direct scrubbers, versus filtration, and cracking, as a reliable, inexpensive means to condition gas. However, environmental considerations have rendered scrubbing largely unacceptable because these small non-centralized plants cannot afford to have individual water treatment and "tar" disposal facilities. Lately a new wet scrubbing option has been proposed to effectively clean the gas while reducing the wastewater consumption and final treatment needs by a factor of 20–30 (Abatzoglou et al. 1997a). The system has been developed at bench scale, scaled up to the pilot level, and tested with success. Commercial applications are under development.

Ideally, gas turbine fueling applications require that the hot gas be fully cleaned and remain hot (and under pressure) before use. It is not practical, or thermodynamically efficient, to cool down the gas at any point after production in the biomass gasifier. Because of the stringent gas quality requirements for turbine firing, any gas suitable for turbine applications, in terms of particulate removal, will be suitable for ICE applications. The range of the particulate concentration limit for gas turbines is 0.1 to 120 mg/Nm^3, depending on the design and the operating conditions. Alkalis are also critical contaminants, and the reduction of these to acceptable levels (usually below 0.1 mg/Nm3) remains one of the greatest challenges for successful commercialization. Very little has been published with respect to tolerable "tar" concentrations in gas turbine applications. A table of the latest information is provided in Nieminen et al. (1996). Alkali removal from hot gas is also possible. Various adsorpotion and absorption systems have been developed for coal gasification.

According to Graham and Bain (1993), synthesis gas applications have high gas cleaning requirements. Before the gas enters the final synthesis loop, particulates should be less than 0.02 mg/Nm^3, and the "tar" concentration less than 0.1 mg/Nm^3. Hydrocarbons also pose potential problems for methanol synthesis processes. If the methane concentration is greater than 10%, the entire syngas stream must be reformed to CO and H$_2$. If less than 3%, no reforming is necessary. In the intermediate range, reforming of a recycle stream is required. To preclude catalyst poisoning (particularly copper/zinc-based catalysts), total olefin content should be less than 6 mg/Nm^3 and the ethylene concentration should be below 4 mg/Nm^3. Synthesis catalysts are also very intolerant to the presence of sulfur and chlorine, normally present in MSW-derived gas and some herbaceous species-derived gas, with a concentration limit of about 0.1 mg/Nm^3 reported for both species.

B. Conclusions

There are very few well-defined and long-term data on the tolerance to "tar" of the great variety of energy conversion devices now being considered for gasifier output (boilers excepted). The older literature focused primarily on ICEs for automotive use. More recently, applications of the gas-to-fire turbines have been in the forefront. In almost no applications, with the exception of close-coupled boilers, have endurance tests or operations been carried out long enough to give valid projections of maintenance and systems costs. When such tests are done it will be most valuable if the offending organics are clearly identified so the results can be generalized. The studies going on in coal gasification, with coupling to turbines, engines, fuel cells, etc., should provide valuable information, particularly when highly cracked or tertiary "tars" are involved. Such "tars" are remarkably similar for biomass and for coal.

Recommendations:

Governments and developers should support long-term, well-controlled tests on engines, industrial as well as automotive; internally and externally fired turbines; fuel cells; and the variety of externally fired systems such as Stirling engines, where heat transfer materials and geometry differ from simple boilers. The nature of the "tar" involved in these tests should be well defined.

VI. The Removal of "Tars" through Physical Processes

A. General Overview of Gas Cleanup Technologies

In Figure 6.1 we present schematically the various gas cleaning strategies and available technologies. All have been used commercially or in demonstration plants. In this report we will not attempt a thorough comparison of these technologies. First, this would be a diversion from the main target of the report; second, there are few universally acceptable, technoeconomic comparison criteria. More information about the possibilities of the various technologies are already published in the literature. References are provided for each technology (Abatzoglou et al. 1977a,b; Bangala et al. 1997; Chowdhury et al. 1992; Levelton 1983; Fernandez 1997; Fenske and Schulz 1994; Graham and Bain 1993; Seville 1997; Taralas et al. 1996; Simell et al. 1996; Vassilatos et al. 1992b; Van de Beld et al. 1997; von Wedel 1994; Zielke 1997).

Gas Cleaning Technologies
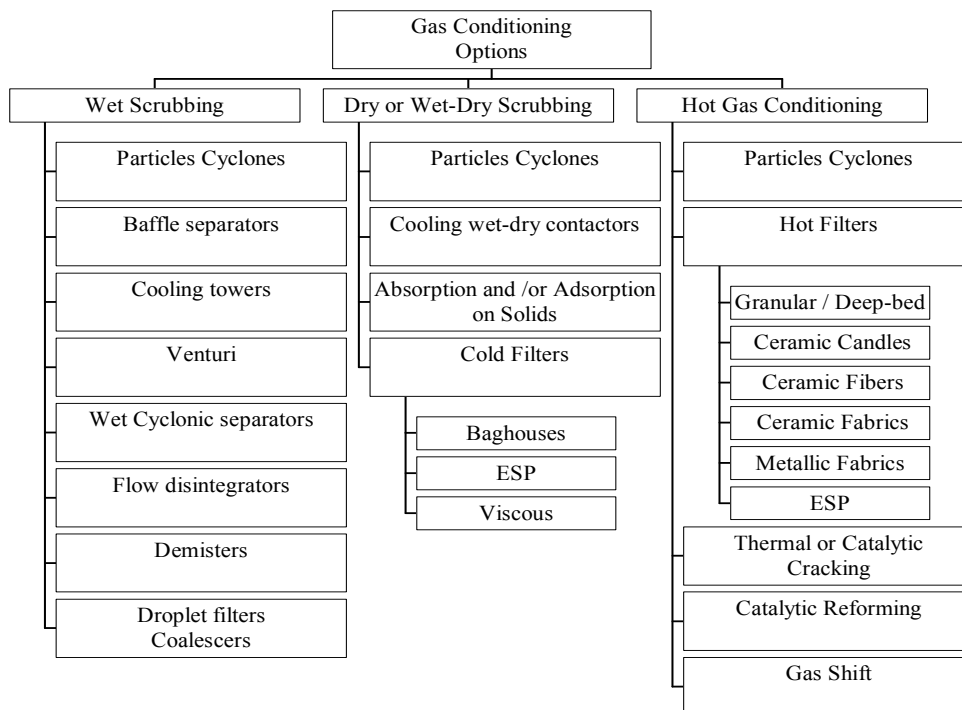
Figure 6.1. Gas cleaning technologies.

B. Gas Cleaning through Physical Removal of "Tar"

With regard to gas "tar" content, in the previous chapters, we have presented the raw gas "tar" content as a function of the gasification technology, the maximum "tar" content that can be tolerated in the gas as function of its intended use, the general unit operations available for a rational gas ("tar") cleanup as a function of the emission regulations, and final intended use.

We will complete our effort by attempting to provide information and data allowing the establishment of rationales for selecting integrated cleanup strategies and identifying the key considerations in the selection process. We point out a recent publication (Hasler et al. 1997), which efficiently covers this field.

1. *General Considerations for Internal Combustion Engines*

In most cases, the gas quality requirements are based on estimates because engine manufacturers cannot determine the engine specifications, due to lack of practical experience. Hasler et al. (1997) pointed out that it is doubtful that the values given above express a general trend; other parameters may be as important or even have a greater influence. They gave the following examples:

> Phenols and cresols, as acidic compounds, are corrosive in IC engine applications. It is not well established if the phenols/cresols are included in the various tar determination methods. Some of the "light tars" (such as benzene or toluene) are not considered as harmful components in the gas since these compounds are found in important quantities in gasoline. High performance "new generation" power units may display a higher sensitivity to impurities than old engines. High speed ICEs are more delicate than low speed engines.

We can add the following considerations: "Tar" particles or droplet; size would play an important role during combustion. Heavier "tar" content: premature condensation is of great concern and its percentage is a function of temperature (in the various parts of the engine) as well as of the component boiling point.

2. *Wet Technologies for Physical Removal of Tar*

Wet and wet-dry gas cleaning cycles remove tar using physical methods: Gaseous "tar" condensation, gas/liquid mixtures separations, and droplet filtration.

The specific energy consumption of wet gas cleaning systems is indirectly proportional to the particle diameter (Hasler et al. 1997). (Solid particulates and "tar" droplets are covered by the term *particles*.) The separation of small particles requires high specific energy inputs in the form of pressure drop over the system.

 a. Cooling towers and venturi scrubbers

Cooling/scrubbing towers are usually used after cyclones as the first wet scrubbing units. All "heavy tar" components condense there. However, "tar" droplets and gas/liquid mists are entrained by the gas flow, thus rendering the "tar" removal rather inefficient. Venturi scrubbers are usually the next step. Hasler et al. (1997) report that in venturi scrubbers, typically 2 kWh/1,000 m^3 are consumed, corresponding to a pressure drop of approximately 7,000 Pa. The combined cooling tower/venturi scrubber closed-loop system used by the new BIOSYN gasifier (Abatzoglou et al. 1997a) operates under slight vacuum and the total pressure drop is estimated at about 1,400 Pa. Fernandez (1997) has shown that under these conditions and at a gas/liquid ratio of 1/1, particle (both solid and "tar" droplets) concentrations at the exit of the venturi were lower than 10 ppmv.

The correct selection and dimensioning of wet gas cleaning systems requires information on the particle size distribution in the gas. There are no reliable sets of tar droplet size distributions from biomass producer gases.

Data on "tar" separations are very scarce in the literature. "Tar" separation efficiencies have been reported ranging from 51% to 91% in a venturi scrubber used to purify the producer gas from a countercurrent rice husk gasifier (Hasler et al. 1997). *"The gasifier generates a gas with approximately 80g/Nm³ of 'tars.' Before the venturi scrubber, the raw gas is mixed with (clean) recycle gas at a ratio of approximately 20:1. With this dilution, the 'tar' content at the venturi inlet decreases to 4 g/Nm³ approximately. The gas velocity at the entrance is maintained at 56 m/s. The pressure drop over the venturi is estimated to be 4,000 Pa. For the venturi scrubber investigated, an equation calculating the 'tar' separation efficiency has been found for gas to liquid flow ratios (Q_g/Q_l) between 4000 and 8000."*

From a work published lately (Abatzoglou et al. 1997c), the following scrubbing efficiency data for a combination of cooling tower + venturi + demister (new BIOSYN wet gas conditioning module) are available:

Parameters Feed	"Tar" load before scrubbing (mgCOD/Nm³)	"Tar" load after scrubbing (mgCOD/Nm³)	Retention efficiency *(%)*	Particles load before scrubbing (g/Nm³)	Particles load after scrubbing (g/Nm³)	Retention efficiency (%)
Rubber	291.6	4.2	98.5	19.5	0.003	99.99
RDF	448.4	30.7	93.0	4.2	0.004	99.91
Average	370	17.5	95.8	11.9	0.004	99.95

For the venturi scrubber alone, unpublished results from the new BIOSYN runs show a "tar" retention of more than 95% at G/L ratios of 1/1.

b. Demisters

Demisters are centrifugal flow units designed to coalesce mist droplets from their gas flow. They resemble cyclones and hydro-cyclones and are usually used as a secondary stage in conjunction with classical wet scrubbing units. Their design depends on mist liquid phase properties and gas flow load. Although design data are proprietary, such demisters and their operation are reported in Abatzoglou et al. (1997a). "Tar" and water are largely removed from producer gas at the exit of the second stage venturi scrubber. Wastewater containing "tar" is settled out for insoluble "tar" skimming, then recycled back to the scrubbing loop.

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c. Granular filters

Granular filters can be used for cold and hot gas filtration. Inorganic beds, usually consisting of silica or alumina sand, are used as impact or surface filtration media. Static and mobile granular bed configurations have been used or are under development. When hot filtration is used, the filter operates usually at temperatures higher than 500°C so that only particulates are removed while "tar" remains at the gas phase. Sands are nonporous materials, characterized by low specific surface area. Thus, when static beds are used, the surface filtration mechanism prevails, while the impact (deep-bed) filtration mechanism is favored with mobile beds. The most important development work in the field of hot gas filtration has been linked with coal gasification. An R&D program for the development of a granular, hot gas filtration unit coupled with a "tar" catalytic reformer is under way in Sherbrooke, Canada.

When cold filtration is used, particulates and condensing "tar" droplets are removed. Typical cold gas granular bed filtration configurations are static beds of sand or even organic substrates such as sawdust. Very few construction and operational data are available in the literature. Such a system has been extensively tested both in India and Switzerland for the IISc/DASAG open top gasifier (Mukunda et al. 1994b).

Sharan et al. (1997), as reported in (Hasler et al. 1997) state: *"With native wood, the particle separation efficiency has been found to be 80% to 95%w/w whereas the 'tar' separation efficiency is 60% to 95% w/w. The phenols could be reduced by 95%. This deep-bed filtration mechanism is essentially based on the impact separation phenomenon which is enhanced by the sticky 'tar' simultaneous removal."* From another such system in Denmark, reported also by Hasler et al. (1997) we learn that: *"The Danish experience with the sawdust filter after the Martezo gasifier in Hogild showed that cleaning intervals are in the range of 200h of operation. The cleaning requires very rigid safety precautions since the 'tar' loaded sawdust is toxic."* It is eventually possible to gasify this material, together with the feedstock, at the end of its cycle. A similar method is used by the new BIOSYN gasification cold gas conditionning cycle where "tar" skimmed off the scrubbing wastewater is recycled back to the gasifier

d. Wet electrostatic precipitators

Electrostatic precipitators (ESPs) are widely used to remove fine solids and liquid droplets from gas streams. Although effective with liquid droplets, they prove inefficient when "tar" is in the gaseous phase. This means that, when the target is the "tar" removal, high-temperature operation should be avoided. In such a case gas should be quenched before ESP use. The operation of an ESP is based on the passage of the gas stream through a high-voltage, negatively charged, area. Particles are thus charged and led to a collection area where opposite charge plates remove them from the stream. Very high, as well as very low, conductivities are detrimental to ESP operation. An appropriate balance is required for efficient operation. This means that the nature of "tar" can influence considerably the design of an ESP.

Only wet ESP can be used to remove "tar" from biomass gasifier gas, because "tar" condensation on dry ESPs precipitation electrode would progressively inhibit particle removal. With ESPs, particle removal efficiencies of more than 99% are possible for particles as small as 0.05 μm. Very few data are available in the literature regarding the application of this method for gasification. Hedden et al.

(1986) (reported in Hasler et al. 1997), have performed preliminary tests with a wet ESP to clean the producer gas from a co-current Imbert gasifier. The performance is cited here: *"The gas moisture after the ESP was 50 to 80 g/m³ and the ESP was operated in the corresponding dew point range from 38 ℃ to 46 ℃. The particle separation efficiency was found as 99% whereas much less 'tar' could be removed. 'Tar' separation efficiencies were determined between 0% and 60%. With the ESP some operational problems have been encountered (spark-over; 'tar' and solid deposition). Single test runs were made which lasted for several hours. The longest test period of uninterrupted operation was 14 hours."* A wet ESP has also been used during long term gasification tests without operational problems (Wellmann gasifier in Birmingham, UK). The operators claim to have obtained good "tar" separation efficiencies. However, no data are available.

e. Wastewater treatment

All wet gas cleaning systems generate wastewater that is contaminated with inorganic and organic pollutants. The concentration of the pollutants is always significant even for gasifiers with low "tar" production. Wastewater contaminants include dissolved organics, inorganic acids, NH_3, and metals. Typical values of COD, BOD, and phenols for wastewater from fixed-bed gasifiers are given in Hasler et al. (1997). Recycling/reuse of these wastewaters, as proposed in Abatzoglou et al. (1997a), leads to higher contaminant concentrations. Regarding the dissolved organic compounds and most of the metal oxides, there are saturation points beyond which separation of phases occurs. The new BIOSYN design proposes a continuous skimming-off of insoluble "tar" from the surface of the wastewater. Experimental data from runs with various feedstocks showed difference in organics concentration at equilibrium as a function of feedstock used. RDF runs gave an equilibrium value of 1,500 ppm for COD and 350 µS/cm for conductivity; for rubber-rich stream gasification the numbers are 1,000 ppm and 3,300 µS/cm, respectively (Fernandez 1997).

Various technologies are proposed in the literature for these wastewater treatments before their final disposal. In Hasler et al. (1997) there is a short description of the available technologies that comprise extraction with organic solvent, distillation, adsorption on activated carbon, wet oxidation, oxidation with hydrogen peroxide (H_2O_2), oxidation with ozone (O_3), incineration, and biological treatment.

Recent works at Sherbrooke (Abatzoglou et al. 1997a) focused on wet oxidation and adsorption on mixtures of activated carbon and carbon-rich ashes produced during gasification. These techniques, together with biological treatment, seem to offer the best potential for eventual application at an industrial/commercial level (CRE Group 1997). We summarize below the findings of the Sherbrooke works in wet oxidation and adsorption:

Wet Oxidation	Conditions	T:310°C		P:13.8 MPa
		Initial	Final	Efficiency
RDF Gasification Wastewater TOC	(mgC/1)	555	222	60%
Rubber Gasification Wastewater TOC	(mgC/1)	336	122	63%

Higher temperatures can improve the efficiency, but the heating cost will increase proportionally.

Source	Adsorption media	Load (g of solids per L of wastewater)	Efficiency TOC removal (%)
Wastewater from RDF gasification	Carbon-rich ashes	100	46
	Active carbon	10	56
Wastewater from rubber gasification	Carbon-rich ashes	100	74
	Active carbon	10	83

Based on ashes produced and wastewater generated during gas wet scrubbing, such loads of 100 g/L are technically possible

3. Dry Technologies for Physical Removal of "Tar"

The raw gas leaves gasifiers at temperatures between 400°C and 800°C. If hot gas filtration and "tar" cracking and/or reforming conversion follows, the temperature should be as high as possible. This is the case of physicochemical conversion of "tar," which will be covered in another chapter of this report. The use of dry, medium temperature, technologies for the physical removal of "tar" is not yet envisaged. Fabric, ceramic, and metallic filters can remove near-dry "condensing tar" particles from gasifier gas. They are based on the principle that "liquid tar" condensing at a relatively high temperature will rapidly react to form solid species behaving as particulates rather than "tar." The reasons they have not been used are the following:

They will be only partially effective at temperature higher than 150°C ; an important amount of "tar" will remain at the gas phase and pass through the filter without being retained. If a near-liquid layer is formed on the surface of the filtering material, its stickiness will cause considerable mechanical problems and frequent failures. Both operating and capital costs seem very high.

An alternative could be the use of relatively high temperature adsorption on activated carbon granular bed filters. The method is proposed in (Hasler et al. 1997). They mention that *"Charcoal or activated carbon are thermally stable up to 300 ℃. Since conventional fabric filters are expected to exhibit a limited 'tar' separation efficiency, an activated carbon filter can be installed after a fabric filter unit to remove high boiling hydrocarbons and possibly phenols. The filter is preferably made as a fixed bed with granular charcoal or activated carbon. The temperature should be as low as possible (e.g. 120 ℃), but above the gas dew point. The 'tar' laden activated carbon can be recycled in the gasifier as an extra feedstock. However, no information has been found in the*

literature for the 'tar' adsorption characteristics of carbonaceous adsorbents from biomass producer gas." The idea of recycling back to the gasifier the activated carbon or even the carbon-rich ashes after their use is mentioned by Abatzoglou et al. (1997), in a similar context. In this case the active carbon and the carbon-rich ashes were used in an adsorption column to treat the scrubbing wastewater.

4. Evaluation of the Physical Methods for "Tar" Removal

It is not feasible to imagine different physical systems for separate "tar" and particles removal. The cost would be prohibitive. Consequently the design of such systems is based on the optimization of the simultaneous removal of these two entities. Based on the results reported in the literature, as well as the hands-on experience of one the authors (N.A.), we can conclude the following:

- Wet scrubbing is already optimized and the efficiency of "tar" removal allows us to assume that gasifier gas end-use device specifications are fulfilled satisfactorily. Since available results come from various sources, the use of pilot tests could be necessary for applications in which feedstocks and in general gasification technologies vary considerably. Demisting is classified within wet scrubbing.

- The amount of wastewater generated from a wet scrubbing system is relatively important. The contamination level is important because of the toxicity of particulates and "tar," so the treatment cost is considerable and probably prohibitive in many cases.

- There are already available technologies minimizing the production of wastewater. Nevertheless, there is an absolute minimum in terms of wastewater production: it is the condensible water contained naturally in the producer gas.

- Wastewater treatment technologies are available. They comprise wet oxidation, adsorption on active carbon and/or carbon-rich ashes from gasification, and biological treatment. Although not yet fully optimized, these systems offer good possibilities and it can be postulated that their combination with a sewer wastewater treatment facility is possible for commercial applications.

- Wet ESP are significantly more expensive than any of the other systems. Moreover, the available data are scarce and we could not ensure that they will meet the required separation efficiencies.

- Wet, dry, and adsorptive filtering are eventual alternatives, but they require intensive R&D and piloting.

C. Conclusions

Physical processes will continue to play a very important role for the successful commercial implementation of gasification. They constitute the basic arm for removing most raw gasifier contaminants, including "tar." "Tar" is removed mainly through wet or wet-dry scrubbing. Coalescers, demisters, and cold filtration are also necessary supplements. These are well-known commercial methods and are easily designed and applied depending on the specific needs of any

gasification process. The main problem arising from "tar" scrubbing is that condensed "tar" components are merely transferred into another phase (water or solids such as scrubbing lime), which then has to be disposed of in an environmentally acceptable manner. The problems associated with the management of these wastewater or solid residues are summarized as follows:

- "Tar" and "tar"-contaminated solid-waste streams are considered as special wastes; consequently, their disposal is usually cumbersome and costly.

- "Tar"-bearing wastewater is usually a bi-phasic mixture requiring various steps of treatment before final disposal.

- Most water-soluble "tar" components are refractory to the usual biological wastewater treatments.

The applied methods for "tar" and "tar"-containing waste streams include solid waste stabilization and landfilling, organic phase skimming off the bi-phasic wastewater-free surface, wastewater incineration, wet oxidation, adsorption on activated carbon, and final biological treatment.

Recommendations:

Although chemical (mainly catalytic) conversion of "tar" at high temperature for eventual use of the gas in gas turbines attracts more and more attention, it is expected that physical removal of "tar" will continue to be widely used for the following reasons:

- Burners/boilers that are not close-coupled, as well as ICEs, require cold-gas use; it is rather difficult to envisage, without serious economic problems, the simultaneous use of high-temperature "tar" conversion reactors combined with cold-gas conditioning modules. Thus, wet or dry-gas cooling/scrubbing is the recommended method in such cases

- When high-temperature conversion of "tar" is used there remain in the producer gas some other contaminants (mainly acid gases and volatile alkali metals), which could be detrimental to gas turbines. Thus, cold-gas conditioning, or in-series guard columns for these contaminants, should be used.

Extensive development work in this field is recommended. Government as well as private funding should be devoted over the next 5 years, to improve both scientific understanding and technical/technological knowhow on physical "tar" removal from raw producer gas. This work should focus on the following:

- Wet scrubber design for higher efficiencies

- Aerosol removal module design and efficiency measurement

- Water insoluble "tar" skimming

- Skimmed "tar" recycle back to the gasifier reactivity as a function of the recycle stream nature and quantity rules for calculating the steady-state conditions.

- Use of carbon-rich ashes from the gasifier to supplement the adsorption of "tar" on activated carbon, scaleup of bench-scale systems, and establishment of design parameters.

- Optimization of wet-oxidation conditions for treating soluble-"tar" containing wastewater, study and optimization of deep-bed, cold filters for "tar" removal, life cycle analysis.

VII. The Thermal, Steam, and Oxidative "Conversion" of "Tars"

A. Introduction

In addition to the ambiguities in the literature concerning the definition, collection, and analysis of "tars" discussed earlier, we must now contend with meanings of the terms involved in mitigating "tars." These include: "destruction," "removal," "cracking," "conversion," "elimination," "reforming," "modification," . . . The term used and its meaning are influenced by the anticipated end use of the gas, and authors do not always clearly state which residuals are tolerable. A prime example is the emphasis on conversion of condensibles to non-condensibles in many studies, where organics like ethylene, benzene, toluene, and even naphthalene are tacitly assumed to be tolerable (e.g., boilers, turbines, engines). The references must be consulted to clarify the degree of molecular modification of "tars" in the discussion to follow.

B. Thermal "Destruction"

The evolutionary sequence of "tar" organics, from primary products of pyrolysis to intermediates to the very stable aromatics, has been detailed earlier. A number of references are given in the literature to the very high temperatures and reaction severities required to reduce these underivatized mono-, di-, and polynuclear aromatics to light gases under reducing conditions (ring opening). It is true that steam, CO_2, H_2, and CO will always be present during the final stages of organic destruction, though the proportions will be altered depending on the overall gasification stoichiometry. Some statements from the literature follow (see bibliography for details).

- Thermal destruction of tar and CH_4 requires steam and 1,300 °C (Beenackers and Van Swaaij 1984).

- *"Thermal cracking at high temperatures in the gasifier generates soot"* in pressurized gasifiers (Blackadder et al. 1994).

- Thermal stabilities and Arrhenius parameters for a number of aromatic compounds found in biomass gasifier "tars" are given in a flow-tube study of coal compounds (Bruinsma et al. 1988).

- The cross-draft gasifier, though used only with charcoal feedstocks, has operating temperatures in excess of 1500 °C (Cuda and Ziak 1995).

- *"We have determined 'tar' residence times for almost complete conversion (at a ratio of 10-4) and we found rather high values, from 15s at 800 °C to 5 s at 1000 °C. These values confirm that it is not possible to decompose 'tar' in the fluid bed gasifiers"* (Deglise et al. 1985).

- Converting "tar" completely to gas requires greater than 1,100 °C without catalyst (Donnot et al. 1985).

- Thermal cracking of "tar" is defined as conversion to gas. Thermal cracking data are reported to 1,000 °C (Fernandez et al. 1993).

- Results for the kinetics of thermal conversion of naphthalene, toluene, and benzene, in the presence of hydrogen and steam, are given. Order of reactivity is toluene greater than naphthalene greater than benzene. Besides organic gaseous products such as methane and ethylene, condensed products and soot are formed, principally from naphthalene (Jess 1996).

- Temperatures higher than 900°C are needed for thermal cracking in downdraft gasifiers in the context of ICEs (Kaupp et al. 1983).

- In the pressurized, fluid-bed gasification of peat, *"freeboard temperatures of 830-870°C seem to be high enough to crack the heavy 'tars' to benzene, naphthalene and other light components, which should not be detrimental to high-temperature gas filtration"* (Kurkela et al. 1989b).

- Temperatures lower than 1,000°–1,100°C are inadequate for thermal "tar" cracking and elimination (Parikh et al. 1987).

- Thermolysis of benzene, toluene, phenols, cresols, and polycyclic aromatics at 350°–1,000°C is reviewed (Poutsma 1987).

- The Lurgi gasification system produces very few "tars" (less than 1 g/Nm^3) because of the high gasification temperatures (Reed and Gaur 1998).

- Thermal "tar" cracking to acceptable levels requires temperatures higher than 1,100°C and produces soot (Rensfelt and Ekstrom 1988).

- Thermal cracking of "tar" might yield non-wettable and extremely fine soot (Rensfelt 1985).

- Research is needed on soot formation from "tar," and soot reactions leading to soot destruction (Studsvik 1992).

- Soot formation during isothermal pyrolysis of naphthalene, anthracene, and pyrene was studied. Sooting tendencies relative to methane at 1,350°C are methane, 1; ethylene, 4; acetylene, 7.6; diacetylene, 50; benzene, 7.4; toluene, 5.5; p-xylene, 4; naphthalene, 112; anthracene, 91; and pyrene, 74 (Tesner and Shurupov 1997).

- At 900°C, naphthalene is the major single component in "tar." Phenols are relatively stable at 700°C, but at 900°C they are significantly decomposed. The yields of the two major aromatics (indene and naphthalene) increase considerably between 800° and 900°C, although the total tar yield decreases (Vassilatos et al. 1992a).

- In coal gasification severe conditions obviate the need for "tar" cracking. Tertiary compounds are not expected to deposit carbon (Westinghouse 1995).

- Results from a reaction severity study of gasification in a flow reactor showed a temperature at which secondary tars are maximum and primary and tertiary "tars" are minimum, which may be

a useful balance between decreasing the amount of material and controlling the composition so catalytic materials can function effectively (Evans and Milne 1997).

- Oja and Suuberg (1998) give vapor pressures and enthalpies of sublimation of PAHs.

C. Steam Reforming or Cracking

Steam is present in all methods of gasification, so the issue is: What are the effects of added steam on "tar" behavior? A few notes on specific steam effects follow:

"Tars" produced in air gasification are more refractory than those produced in steam (Corella 1996). "Tars" produced in the gasification of biomass with steam are different than those produced in spruce gasification of biomass in air or with steam+O_2 (Corella et al. 1995a). "Tar" yields decrease with increasing gasification temperature and with steam/biomass ratio (Herguido et al. 1992b). It is postulated that steam gasification "tars" have more phenolics and C-O-C bonds, which are easier to reform, viv-a-vis air gasification" tars" (Orio et al. 1997b). Pure steam produces a more phenolic "tar," which is easier to catalytically convert than "tar" from steam+O_2 gasification (Perez et al. 1997).

- In the partial oxidation of pyrolysis vapors the addition of steam tends to enhance the formation of benzene and toluene. Steam also enhances phenol formation (Dayton and Evans 1997). Steam reduces the concentration of oxygenates in a fluid-bed gasifier (Evans et al. 1988).

- In steam gasification of naphthalene *the gas yields at temperatures up to 950 °C and residence times up to 60s are low because polymerization and condensation reactions are favored, whereby 'tar' and a carbonaceous residue are formed* (Garcia and Huttinger 1989).

- *"The yield of naphthalene and polycyclic aromatic hydrocarbons (PAH) in tar seem to increase in the presence of dolomite and/or steam"* (Guanxing et al. 1994b).

- Steam has only a small influence on the conversion of the aromatics (Jess 1996).

D. Partial Oxidation

All gasifiers involve heat and steam, but indirect gasifiers can function without any added oxygen to the gasification section. This is accomplished by either heat transfer through walls or tubes from an external combustor or by circulating a solid heated by external combustion into the gasifier section. A third method, which has not been much studied, involves a cyclic system of heating a bed through combustion of char followed by partial gasification. Some observations about the effects of partial oxidation on "tars" are reported in this section. (See bibliography for details.)

- The "tar" content when gasifying with steam plus oxygen is much lower than gasifying with pure steam. Gasifying with air gives comparable "tar" yields to O_2 gasification (Aznar et al. 1997b).

- "Tars" produced in air gasification are more refractory than those produced in steam (Corella 1996).

- In cocurrent gasifiers one can add O_2 to pyrolysis vapors to achieve "tar" contents as low as 300–500 mg/Nm³ (Beenackers and Van Swaaij 1984).

- A throat-less two-stage gasifier with air injected in the upper flaming pyrolysis zone and in the lower reduction zone can achieve "tar" loadings of 92 mg/Nm³ (Bui et al. 1994).

- "Tars" produced in the gasification of biomass with steam are different than those produced in spruce gasification in air or with steam+air (Corella et al. 1995b).

- In a flow reactor, with oxygen added downstream of the pyrolysis zone, more benzene was formed at higher pyrolysis temperatures and lower oxygen concentrations (Dayton and Evans 1997).

- The effect of oxygen at temperatures of 600°C to 700°C accelerates the destruction of primary pyrolysis products but has no significant effect on benzene. Hydrogen appears to be more reactive to partial oxidation than CO (Evans and Milne 1997a).

- "Tars" are studied in a fluidized-bed reactor as a function of steam/oxygen ratio, steam-oxygen/biomass ratio, and temperature (Gil et al. 1997).

- When oxygen is added to the second stage of a pyrolysis/cracker system, the "tar" is preferentially oxidized vis-a-vis CO (Jensen et al. 1996).

- Partial oxidation could effectively reduce "tars," but contact of oxygen and tar is limited in gas producers (Kaupp et al. 1983).

- As equivalence ratio is increased, "harder tars" are produced in air, but at lower levels (Orio et al. 1997b).

- Pure steam produces a more phenolic "tar," which is easier to catalytically convert than "tar" from steam +O_2 gasification (Perez et al. 1997).

- Behavior of light hydrocarbons with residence time, equivalence ratio, temperature, and steam/biomass ratio is reported (Wang and Kinoshita 1992).

E. Conclusions and Recommendations

Thermal.

The consensus seems to be that temperatures in excess of 1,000°C, at reasonable residence times, are necessary to destroy the refractory unsubstituted aromatics, without a catalyst. Apart from the economics and materials problems, such thermal decomposition can produce a soot that can be even more troublesome than the aromatics for some processes. Benzene seems to be the least reactive, thermally, of the light aromatics.

Steam.

The addition of steam, over and above that formed from the water and oxygen in the feedstock, has been reported to produce fewer refractory tars, enhance phenol formation, reduce the concentration of other oxygenates, have only a small effect on the conversion of aromatics, and produce "tars" that are easier to reform catalytically.

Partial Oxidation.

Oxygen or air added to steam seems to produce more refractory "tars" but at lower levels, while enhancing the conversion of primaries. When oxygen is added selectively to different stages, such as in secondary zones of a pyrolysis-cracker reactor, "tars" can be preferentially oxidized.

VIII. The Catalytic "Destruction" of "Tars"

A. Introduction

A great variety of approaches have been tried in the catalytic "conversion" of "tars." As with other aspects discussed earlier, the interpretation and comparison of results are made difficult by the frequent lack of specification of what the composition of the "tars" is and what is meant by "destruction," "removal," etc. In the summary of results that follows, the results as presented in the papers cited are given briefly and incompletely; the reader should consult the original papers. The research on catalytic, hot-gas cleanup has involved (a) incorporating or mixing the catalyst with the feed biomass to achieve so-called catalytic gasification or pyrolysis; and (b) treatment of gasifier raw gas in a second bed or beds. Two main classes of catalyst have been studied: non-metallic and metallic oxides. More recent work has included dual systems with catalysts such as dolomite serving as a guard bed for highly active catalysts such as Ni-based reforming catalysts.

B. Catalysts Used in-situ to Alter the Pyrolysis Step in Gasification

1.   Non-metallic catalysts

   •   Baker et al. (1985a) and Baker and Mudge (1984b) tested the reaction of biomass with steam in the presence of alkali carbonates. Loadings of up to 10 wt % K_2CO_3 in bagasse reduced "tars" to a "trace" level.

   •   Mehrling and Reimert (1985) tested wood-char, sand and Al_2O_3 as bed materials in an air-blown Lurgi CFB gasifier. Tests produced a "tar free gas" (Mäkinen et al. 1995).

   •   Corella et al. (1988a) tested an "in equilibrium" spent FCC and a dolomite catalyst in a fluidized-bed gasifier. The FCC catalyst was quickly elutriated from the bed, while dolomite was quickly eroded.   Both are very active in cracking. They *do not recommend dolomite use in a fluid bed unless harder forms can be found* (Corella et al. 1988a). Corella (1996) notes that in-bed use of dolomite leads to troublesome elutriation of fines. At pressurized conditions dolomite is deactivated by carbonate formation. At 10 bar it may need to operate at greater than 920°C. Under some conditions, dolomite has remained active for 16 hours (Olivares et al. 1997). In-bed calcined dolomite changes the product distribution at the gasifier exit. Gasifying with steam-O_2 mixtures, the "tar" content in the exit gas decreases from 12 to 2–3 g/Nm3. The dolomite is continuously fed to the gasifier, mixed with biomass at 2–3 wt %. Herguido et al. (1992a) tested an in-equilibrium spent FCC catalyst in a 15-cm i.d. riser-gasifier with a stable fluidized bed of sand at its bottom. With catalyst, recirculation and continuous regeneration of catalyst, "tar" was reduced from 78 to 9 g/Nm^3, but lifetime was not stated.

   •   Rensfelt and Ekström (1988) reviewed past work at Studsvik on gasification with dolomite as an active bed material.

   •   Leppälahti and Kurkela (1991) looked at effects of dolomite in the atmospheric, fluidized-bed, air gasification of peat. Dolomite beds cut the "tar" levels in half at

around 820°C. Kurkela et al. (1993b) report that dolomite was not particularly effective in catalytic "tar" reduction when used in the primary fluid bed of a gasifier. Much better results were obtained with a secondary bed of dolomite. Palonen et al. (1995) describe the Bioflow IGCC system at Varnamo. Fluidized solids are ash, char, sand, dolomite, and limestone. Operation at 950°–1000°C minimizes "tar." No other "tar" removal used.

- Guanxing et al. (1994a) fed a mixture of wood and dolomite catalyst to a pressurized fluidized-bed gasifier. The yield of H_2, as well as the yield of naphthalene and polycyclic hydrocarbons in "tar" seem to increase in the presence of dolomite and/or steam.

- Salo and Keränen (1995) say that "'tar' cracking occurs in the gasifier at high temperature and pressure using dolomite as a long residence time catalyst." Salo and Patel (1997) describe the use of dolomite as an absorbent in the Enviropower/Carbona pressurized fluidized-bed gasification tests. From a 360-hour run: heavy "tars" (condensible) 25–160 mg/Nm³; light "tars" (including benzene) 5–10 g/Nm³; benzene and naphthalene are 55% of the light "tars;" the sum of the light "tars" from pyridine to pyrene was 1.2–2.5 g/Nm³; benzene was 4.1–7.9 g/Nm³.

- Joseph et al. (1996) note that an entrained-flow vortex gasifier, with re-injection of char, *"ensures a larger proportion of the 'tar' and higher molecular weight hydrocarbons are cracked and undergo reduction."*

2. Metal-Based Catalysts

- Deglise et al. (1992) describe TNEE's fast pyrolysis-gasification process in a dual fluidized-bed system. The temperature level of the heat carrier entering the pyrolysis reactor had to be over 900°C for *"good de-tarring action."*

- Arauzo et al. (1997) tried modified Ni-Mg aluminate and stoichiometric $NiAl_2O_4$ catalysts for greater physical strength in catalytic pyro-gasification. K was added as a promoter. Partial replacement of Ni by Mg improved strength but significantly increased char production. Catalyst lifetime and coking not discussed. In 1994 catalytic pyrolysis and reforming in a fluid bed of $NiAl_2O_4$ achieved "tar" levels less than 100 ppmw of feed at 600°C (Arauzo et al. 1994).

- Baker et al. (1985a) note that previous studies of catalytic gasification of bagasse showed quite rapid deactivation of Ni-based catalysts in the presence of bagasse. Both sulfur poisoning and carbon deposition are blamed. Brown et al. (1985) state that biomass/catalyst contact leads to rapid deactivation.

- Garcia et al. (1997a) used a Ni/Al (1:2) catalyst in a Waterloo-type gasifier at a ratio of sawdust-to-catalyst from about 11 to 0.2. Increase of steam/biomass ratio lowered the rate of catalyst deactivation at 700°C. Garcia et al. (1997b) studied the effect of Ni-Al$_2$O$_3$ catalysts on pyrolysis gasification in a Waterloo fast pyrolysis process-type fluid bed. Liquid ("tar") yield was reduced from 46 to 3.4 wt % of feed under the best conditions.

With total sawdust fed to catalyst in the bed ratio of 1.6, noticeable deactivation occurred. "Liquid tars" are reduced from 46 and 39 wt % of feed to 11 and 8 wt % at 650° and 700°C, respectively (Garcia et al. 1996b).

- Many catalysts were tested for use in a fluidized-bed gasifier to produce clean synthetic gas for CH_3OH. Many catalyst combinations, including several exotic metals (e.g., Ni-Cu-Mo/alumina) and Ni deposited on silica/alumina were placed in the bed. Catalysts increase gas at the expense of "tar" and "oil" formation (Robertus et al. 1981).

C.   Catalysts Used in Secondary Beds to Alter "Tar" and Gas Composition

The generally unsatisfactory performance of catalysts placed in contact with biomass has led to much more emphasis and study of separate catalyst bed or beds following the gasifier.

1.   Non-metallic catalysts.

   a.   Model compounds. A number of simple molecules, chosen as surrogates for "tar," have been passed through a variety of non-metallic catalysts.

   - Aldén et al. (1993) passed naphthalene, in various atmospheres, over dolomite. Mechanisms were studied. At 800°C BTX can be much greater than naphthalene.

   - Espenäs (1996) looked at the kinetics of the conversion of naphthalene into H_2 and CO, catalyzed by dolomite, as a function of of gas composition and temperature.

   - Lammers et al. (1996, 1997) studied naphthalene as a model compound for tar. Secondary air effectively reduces naphthalene and other "tar" compounds with dolomite and keeps the dolomite active. Microreactor tar cracker outlet was analyzed for naphthalene, toluene, and CH_4 using mass spectrometry. Air introduces an extra, parallel naphthalene decomposition reaction.

   - Ellig et al. (1985) passed benzene over CaO, from calcining $CaCO_3$ and $Ca(OH)_2$. At 860°C, 2 mol %, and a 1-s residence time, 75%–85% of the benzene was converted. Lai et al. (1986) passed m-cresol over CaO at 350°–600°C. 60%–80% destruction to toluene was seen, with the reaction going through a calcium m-cresolate salt. Ellig et al. (1985) passed benzene, toluene, 1-methyl naphthalene, and n-heptane over packed beds of CaO/quartz and quartz, at 550°–950°C. The CaO significantly increased the rates of pyrolysis. Coke was the major product.

   - Simell et al. (1995b) tested calcined and carbonated dolomites, limestones, and SiC (as an inert reference) using toluene as a model for "tar," recognizing that it is easier to crack than benzene, naphthalene, etc. Typical tar from fluidized-bed gasification of wood at 850°–950°C contains 50%–60% benzene, 10%–20% naphthalene, and 10%–20% of other polynuclear aromatic compounds. Carbonated rocks decomposed PNA (PAH) more easily than benzene. At 900°C exposure of calcined dolomite to 300 kPa of CO_2 produces rapid deactivation. Most recently, Simell et al. (1997b) compared the tar and

ammonia decomposition (toluene was used as a tar model compound) activities of dolomite, alumina, SiC, and Ni catalysts. Tests were carried out in a fixed-bed tube reactor at 900°C under 2 and 5 MPA pressure of different atmospheres. A gasification gas mixture containing all the components was also used. CO_2 reforming reactions were faster than steam at 900°C. "Tar" decomposition on dolomite is strongly inhibited by the presence of CO. The main reaction products of toluene are benzene and methane.

- Jacoby et al. (1995) passed a synthetic mixture of benzene, toluene, and naphthalene over a gamma-alumina bed, followed by a bed of UCI G690B Ni-based catalyst. The catalysts remained active for more than 585 hours.

- Taralas (1997) chose cyclohexane as a model compound for "tar." Dolomite, quicklime, and dolomitic magnesium oxide were studied. The order of increasing effectiveness was: MgO, CaO, $CaCO_3$, $CaMg(CO_3)_2$. "Calcined dolomite and limestone have also been found to decompose 'tar' nearly as effectively as commercial nickel-containing catalysts, which are more costly and intolerant to oxygen breakthrough." ("Tar" conversion defined as conversion to light gases, up to C_6H_{14}, and benzene.) Taralas (1996) and Taralas et al. (1991, 1994) used n-heptane as a model compound *"to avoid the difficulties in using a complex raw material as 'tar'."* Catalysts studied included CaO, MgO, and dolomite. Various gaseous products, up to benzene and toluene, were produced (1991). For dolomite, in the absence of steam at 800°C the surface of the catalyst is covered by carbonaceous material. The water-to-heptane ratio must be above one to remove the carbonaceous material from the surface (1994). The effects of H_2O and H_2 levels on catalytic cracking were studied at 973° and 1,073°C (Taralas et al. 1996).

b.   Full gasifier output tar slates.

Some 50 references to the use of dolomite and related non-metallic catalysts in secondary beds are given in Appendix IV. Some observations on its effectiveness and behavior follow. In most cases actual numbers for "tar" content are not given, partly because of the ambiguities in the use of the term "tar." The reader is referred to Appendix IV.

- Corella and co-workers at the University of Zaragoza and University "Complutense" of Madrid have studied dolomites extensively. (See articles by Aznar et al., Corella et al., Delgado et al., Orio et al., and Perez et al. 1989–1997.) In steam gasification of biomass in a fluidized bed, a secondary bed of dolomite reduced "tar" from ~21 g/Nm³ at 600°C to 1 g/Nm³ at 910°C. Under the conditions used, substantial deactivation was seen in 10 min at 780°C and 50 min at 840°C (Aznar et al. 1989). Studies by Corella et al. (1991) tested the behavior of the porous Inconel filter and calcined silica sand on gas and "tar" from fluidized-bed gasification of cellulosics at temperatures to 850°C. *The hot filter chamber, the silica sand in the second bed and the carbonaceous solids formed are not inerts, but they crack the produced tars---."* Calcined stones such as dolomites, calcites, and magnesites were shown to crack tars at 800°–880°C. All the catalysts tested so far deactivate seriously in 1–8 h because of coke deposition (Corella et al. 1991b). In 1995 Delgado et al. reported that under proper porosity and particle size conditions, dolomites can clean raw gas to 0.5 g/Nm³ at gasification temperatures of

780°C and ratios of steam/biomass of 1. Catalyst deactivation is negligible under these conditions. Corella et al. (1996d) reported on six different dolomites and the effect of the "tar" sampling and analysis methods on results. The effectiveness of CaO, MgO, and CaO-MgO in cleaning tars from a steam fluidized-bed gasifier is reported in Delgado et al. (1997). Orio et al. (1997a,b) report on four dolomites with Fe_2O_3 varying from 0.01 to 0.75 wt % and K_2O from 0.01–0.24. The dolomites were used in a fixed bed (to avoid its erosion if fluidized) following the bubbling air-fluidized bed. The four were about equal in "tar" reduction. No deactivation of the four dolomites was seen in 5–10 h at steady state. Less moisture in feed or lowering the equivalence ratio increases the "tar." Perez et al. (1997) looked at the effects of space-time, and variable steam/O_2 and steam-O_2/biomass on the behavior of dolomite in a secondary fluidized-bed operating on a slipstream from a steam fluidized-bed gasifier. *"Calcined dolomite is quite soft and it might erode very much if the bed were fully fluidized."* No deactivation was observed over 4–10 h runs. Tar conversion increases with space-time and decreases as H_2O+O_2/(biomass) increases. Pure steam produces a more phenolic "tar," which is easier to catalytically convert than "tar" from steam/O_2 gasification. Dolomite is 8–9 times more effective for "tar" conversion than for methane conversion. Dolomite activity is diffusion controlled, so particle diameter is a variable. Corella (1996) gives a summary of results for Ni catalysts and dolomites tested on the output from the KTH gasifier. Under pressurized conditions, dolomite is deactivated by carbonate formation. At 10 bar it may need to operate at temperatures higher than 920°C. Under some conditions dolomite has remained active for 16 hours.

- Aldén et al. (1988) studied the effect of dolomite on "tars" from wood-chip pyrolysis. Almost all components of "tar," after catalytic cracking, were non-polar. At 800°C the "tar" was mainly mono- and polynuclear aromatics. At 900°C, alkyl groups were removed and naphthalene was dominant, as it was at 800°C. At 900°C catalyst temperature the amount of naphthalene indicated 99.9% conversion. *"Actually the "non-tar" components benzene and toluene were dominate aromatics from 800°–900°C. Our experimental data indicates that conversion (excluding BTX) using Glanshammar dolomite is sufficient to meet engine specifications at temperatures about 860°C."* In closely related papers, Aldén et al. (1996, 1997) studied the effect of dolomite on "tars" from atmospheric and pressurized pyrolysis-gasification. The emphasis was on conversion of condensibles to non-condensibles. With pyrolysis at 700°C and the catalyst at 800°–900°C in a fixed catalyst bed at one atmosphere, "total tar" was six times the "condensible tar" (mainly naphthalene). At 20 bar and 900°C "condensible tar" was several/fold less but "total tar" was reduced by only one-half. Steam suppressed cracking for dolomite.

- Simell and Bredenburg (1990) carried out several studies of catalytic "tar" removal from updraft gasification of peat. Gas was sampled from an industrial, updraft peat gasifier and passed over a variety of catalysts. These included dolomite, activated alumina, silica-alumina, and silicon carbide (essentially inert) in order of decreasing activity. Carbon deposition was observed for silica-alumina only, with the bed at 900°C and a residence time of 0.3 s. No catalyst lifetimes are reported. In a continuation of tests (Simell et al. 1992), high activity catalysts ankerite and dolomite; intermediate catalysts

limestone, calcitic dolomite, and dolomitic limestone; and low activity sintered iron ore and pelletized iron ore were studied. With dolomite, total "tar" drops from 3% to near zero as temperature increases from 800°–900°C at 0.2–0.3 s residence time. *It is likely that the primary 'tar' decomposed mainly thermally with the tested catalysts as well as with the inert material and that the catalysts affected the secondary 'tar' formation step.* "Tars" from the updraft gasifier are thermally quite unstable, unlike "tars" from the fluid-bed gasifier and thus decomposed easily, even with the reference material SiC (Simell et al. 1995a). Simell et al. (1996) review studies with dolomites, limestones, alumina, alumina silicate, iron sinter, and Ni monolith catalysts (see below). Leppälahti et al. (1991) tested SiC, iron sinter, limestone, Fe-dolomite, and Ni-0301 on the gas from an updraft heat gasifier. The latter two were the most efficient over the range 800°–900°C.

- Vassilatos (1990) and Vassilatos et al. (1992a,b) measured the effect of dolomite on "tars" from the pyrolysis of mixed hardwoods at 700°C. With the the catalyst at 700°–900°C the steam to biomass ratio and WHSV were varied. Under optimum catalyst and steam conditions, "tar" was reduced to 164 mg/kg dry biomass and naphthalene to 13 mg/kg. At 900°C the ability to facilitate the "tar" cracking decreases in the following order: steam, no additive, ceramic material, Inconel shaving. Myrén et al. (1996, 1997) tested dolomite (Sala) at 800°–900°C in a secondary reactor following the pyrolysis of straw, miscanthus, and mixed hardwoods at 700°C. The "tar" conversions reported here are rather large because benzene has been calculated as belonging to the gas, which is not done by all researchers. At 900°C "tars" are reduced to 107, 138, and 1825 mg/100 g feed for miscanthus, straw, and mixed hardwoods, respectively. C1-C3, benzene, and naphthalene dominate in all cases. Phenols are less than 1% of aromatics. With Sala dolomite, Sjöström et al. (1988) report that it is easy to bring "tar" content from biomass down to 6,000 mg/m^3.

- Donnot et al. (1985) looked at the effect of Fontainbleau silicious sand, dolomite, and carbonated dolomite on the "tar" from pine bark dropped on a grid at 650°C. Decarbonated dolomite is effective, but is too soft to use in a fluidized bed. Donnot et al. (1991a,b,c) measured the g "tar"/g salt catalyst for Ca salt deposited on graphon and decarbonated dolomite. Catalyst deactivation is mainly due to the deposition of a thin layer of carbon on the catalyst surface. Magne et al. (1990) tested charcoal from the CEMAGREF gasifier, charcoal from pine bark, bentonite (best silica-alumina tested), natural sand, silica gel, Zeosil 125, dolomite, and recarbonated dolomite. CEMAGREF charcoal was the best, followed by decarbonated dolomite. With cycling, decarbonated dolomite loses activity irreversibly.

- Gebhard et al. (1994a) applied direct MBMS to the Battelle Columbus dual fluidized-bed gasifier, allowing a semi-quantitative measure of the entire slate of raw-gas hydrocarbons with and without the catalyst DN-34. The raw syngas contained about 0.2 mol % tar (average MW of 100 assumed). Major compounds identified were benzene, toluene, phenol styrene, cresols, indene, naphthalene, methylnaphthalene, and phenanthrene/anthracene. With DN-34 the phenols and substituted aromatics were greatly reduced but the more stable aromatics were only slightly reduced, remaining at a few hundred ppmv range. Battelle tested slip-stream, fluidized-bed, secondary reactors with DN-35, DN-60,

DN-40, DN-36, and DN-50 catalysts on "tar" from the 9-ton/d process research unit (Gebhard 1995a). All the catalysts showed some activity but variability was too great to permit ranking. *"The absence of toluene, benzene and other more volatile compounds is an operational characteristic of the BCL 'tar' collection technique"* (then in use) (Gebhard 1995a). Bain and Overend (1996) described the Battelle-based FERCO gasifier project. Gas cleanup with a secondary fluid bed containing the catalyst DN-34 is expected to "essentially eliminate all 'tars' from the gas." Raw gas from the Battelle PDU can contain 0.5–1 wt % of the dry wood feed as condensable "tar." Paisley (1993), based on tests of catalytic cracking in a secondary bed, using ICI-Katalco and DN-34, saw little reduction in NH_3 and HCN. In some tests, the empty cracker was as good as the catalysts for "tar" but not for C_2H_4. DN-34 was better than ICI for "tars." DN-34 and several alumina-based catalysts were reported (Paisley 1995b). Severe DN-34 attrition was noted. Only DN-40 showed coke formation; DN-36 and 37 lost activity with time. DN-50 and fused alumina may have promise at 870°C. DN-34 destroys C_2H_2 more effectively than C_2H_4. C_2H_4 drops a factor of 2-3. DN-38 seems much better than DN-34 for C_2H_4 destruction. In the patent for DN-34 is a summary or previously reported DN-34 results. DN-34 *"is essentially alumina"* (Paisley 1996). Paisley (1997) summarizes "tar" destruction from studies in 1993 and later. Even wet scrubbing can leave a "mist" of "tars" of the order of 0.1% of the original "tar." DN-34 is a proprietary catalyst described in U.S. Patent 5,494,653 (Paisley et al. 1997).

- Wiant et al. (1994) describe tests of Ni-based, various alumina and alumina-silicate, and DN-34 catalysts in a secondary reactor. IGT gasifier projected to contain oils and "tars" at ~2 g/acf. Gas temperature must be kept above about 540°C to avoid condensation on ceramic filters.

- Van de Beld et al. (1997) achieved 98% "tar" conversion with dolomite (from 20,000 mg/Nm³ to as low as 100 mg/Nm³).

- Ekström et al. (1985) and Karlsson et al. (1995) report that from pyrolysis of salix, hardwoods, and peat at 700°–750°C, dolomite and carbon black at 750°C reduce "residual tar" from 50 g to 0.1 and 3 g, respectively. Rensfelt and Ekström (1988) note that at 800°C with dolomite, *"only lower quantities (100-400mg/Nm³) of stable compounds like phenanthrene, biphenyl and naphthalene are present."* At 900°C the only remaining heavy hydrocarbons are minor quantities of naphthalene.

- A two-stage gas cleaning system for Cl and "tars," using calcium carbonate, followed by dolomite, extends the lifetime of the dolomite for "tar" cracking (Barducci et al. 1997).

- Black (1984) looked at the reforming behavior of sand, alumina, limestone, and Ni catalysts on the output of "tar" from the batch-fed Forintek gasifier. Limestone, alumina, and Ni, at 830°C, reduced COD to 1,000, 1,000, and 320, respectively from the input value of 45,000 mg/L. In 1989, Black reported results from the on-line treatment of "tar" from the Biosyn gasifier, operated at 200 kPa and 800°C with air. Catalyst activity was ranked as: Ni/Co/Fe>Co/Mo limestone>Fe/Mo>alumina>MgO>Mo>LZ-Y52> activated carbon>SK500>Co>Ni>silica gel>LZ-Y53>mol sieve 3A. All catalysts

decayed at an exponential rate due to carbon buildup. Inlet "tar" concentrations ranged from 8–10g/m^3.

- Olsen et al. (1989) measured the effects of dolomite on "tar" from the continuous and batch mode steam gasification of straw.

- CRE Group, Ltd. (1997) have studied dolomite and a Ni/Mo catalyst for reducing "tars" from an updraft gasifier. The Ni/Mo was more active but the dolomite produced a more favorable cracking pattern and no coke. Ni/Mo produced no coke at 400–600°C.

2. Metal-Based Catalysts.

   a. Model compounds.

- Bangala et al. (1997) report on the reforming of naphthalene and orthodichlorobenzene, as surrogates for "tar," using UCI GB-98 and a novel Ni-based, robust formulation (UdeS) that incorporates a rare earth oxide in the alumina matrix. UdeS catalyst (U.S. and Canada patented) showed excellent activity after 60 hours on stream. Bangala et al. (1998) studied naphthalene reforming over a Ni-Cr/Al$_2$O$_3$ catalyst doped with MgO, TiO$_2$ and La$_2$O$_3$, at 750°C and GHSV of 19,080.

- Wang et al. (1997, 1998) have tested a great variety of metal-based catalysts, using model compounds, to maximize hydrogen production from pyrolysis oils. Model compounds include acetic acid, syringol/MeOH, and a three-component mixture plus a poplar oil aqueous fraction. Catalysts tested include UdeS (contains NiO, Cr$_2$O$_3$, MgO, La$_2$O$_3$, and Al$_2$O$_3$); a University of Zaragosa catalyst of stoichiometric nickel aluminate of a spinel lattice structure, with 20% NiO replaced by MgO; UCI G-9C; Ni/Al/Ca; ICI25-4M; Ni/Al/Cu/K; ICI 46-1; Ni/refractory carrier/K; UCI 6-90B; Ni/ceramic carrier/Al/Ca; UCI C$_{18}$HC; Cu/Zn/Al; BASF G1-255; Ni/ceramic carrier; ICI 46-4; Ni/Cu/Al/Zr; UCI G-91; Ni/ceramic carrier/Al/Ca/K; Ni/Mg/Al. Gephard (1992) reports on the use of toluene in a synthetic syngas to observe the effects of five catalysts: UCI G90C, UCI C150-1-3, ICI 46-1, ICI 506, and BASF GF1-2GS. Best performers were the ICI 46-1, a potassium-promoted, supported Ni catalyst; UCI G90C; and 15% Ni supported on ceramic.

- Simell et al. (1997b) looked at tar and ammonia decomposition over a Ni catalyst using toluene as a model compound for "tar." Various gas atmospheres of H$_2$, H$_2$O, CO, CO$_2$, and mixtures were used. Steam and CO$_2$ reforming were the predominant reactions for Ni catalysts. Hepola et al. (1994) chose toluene as a "tar" surrogate for tests with Ni catalysts.

- Taralas (1996, 1997) has studied Ni/Mo-gamma alumina catalytic destruction of cyclohexane and n-heptane as model compounds for "tar."

- Pedersen (1994) used a surrogate for "tar" of 0.3% phenol to study catalytic "tar" cracking of Co/Mo, Ni/Mo, NiW, Mo, Pt, Ru, and Pd.

- Lammers et al. (1997) used naphthalene as a surrogate for "tar" in the study of BASF G-22 and BASF G1-25S.

b. Full gasifier product slates.

- As with the non-metal-based catalysts, much work has been done by Corella and associates. In 1990, the methanation catalyst Harshaw Ni-3288 was used after the steam gasification of biomass. "Tar" in real gasifiers deactivates the methanation catalyst by coke formation that exceeds that from $2CO=CO_2 + C$. One needs to limit "tars" before the methanation catalyst (Corella et al. 1990). In 1991 a metal filter of porous Inconel was tested on condensibles from pine steam gasification. The hot filter chamber was not totally inert (Corella et al. 1991a). Aznar et al. (1992) studied Topsoe Ni catalysts R-67 and RKS-1. Temperatures in the second (catalyst) bed were $670°–780°C$. At the start, 99.99% destruction has been achieved but deactivation occurs in a few hours (Aznar et al. 1992). Deactivation is the major problem with commercial steam-reforming catalysts following steam gasification (in a matter of hours) (Aznar et al. 1993a, 1995a).

- Aldén et al. (1996) used a commercial Ni-based catalyst to reduce "tar" from pyrolysis at $700°C$. At $800°–900°C$ and pressurized and atmospheric conditions, steam increased the cracking for Ni, but Ni catalyst use is questionable because of its cost. A 1997 report also covered Ni-based catalysts. Conversion was defined as changing condensibles to non-condensibles.

- Abatzoglou (1996) found GB98-United Ni-based catalyst unsuitable for the BIOSYN gasifier. The UdeS proprietary catalyst gave excellent results under the same conditions.

- Baker and Mudge (1984a) reported using Ni and other transition metals on supports such as silica-alumina, in a secondary fixed-bed. *"With an active catalyst, equilibrium gas compositions are obtained and all liquid pyrolysis products are converted to gases." Elliott and Baker (1986) treated the gas from steam pyrolysis in a fluidized-bed, with supported Ni catalysts. After the Ni catalyst, the largest component was benzene, followed by toluene and naphthalene. Ni has a strong tendency to demethylate aromatics. Mudge et al. (1985) report that the best secondary catalyst is a Ni-Co-Mo on silica-alumina doped with 2 wt.% Na. This catalyst appears to retain its activity "indefinitely" at 750°C and 1 atmosphere."* Mudge et al. (1988a) reported that the best catalysts for "tars" from pyrolysis-gasification are GB90C, G98B, and ICI-46-1. These catalysts, and a special Ni/Co/Mo catalyst from Grace, remained active indefinitely at $600°C$ and higher. Catalytic destruction of "tars" from air-steam gasification was easier than from pyrolysis-gasification at the same temperature.

- Ham et al. (1985) studied siderite, ankerite, pyrite, magnetite, hematite, and jarosite to clean up coal gasification product gases containing heavy hydrocarbons that are mainly aromatic. Fixed-bed gasifiers can reach "tar" levels of 8,000 ppm. Aromatic hydrocarbons included benzene, toluene, and xylenes, polycyclic hydrocarbons, phenolic compounds, and organic sulfur heterocyclics. Combined, these are referred to as "tars."

Iron in a reduced state is thought to be the most effective catalyst for aromatic hydrocarbon destruction.

- Hepola (1993) gives a good review of past work on Ni-based catalysts for "tar" reforming. *"Nickel-based catalysts have proved to be efficient for 'tar' and ammonia decomposition in laboratory-scale gas purification experiments, in which biomass, peat and coal gasification was applied. Long-term tests using a gas stream from an operating gasifier are likely the best way to test catalyst deactivation. The probability of carbon formation decreases when the moisture content of the gas increases."* Some 40 references are discussed. Sulfur poisoning with Ni catalysts was studied from 800°–900°C, under 1–20 bar pressure, with real and simulated gasification gas mixtures containing various amounts of H_2S (Hepola et al. 1994). When H_2S was removed, any deactivation was rapidly reversed. Leppälahti et al. (1991) tested iron sinter, Fe-dolomite, and Ni-0301 on the gas from a 5-MW updraft gasifier The latter two were the most efficient over the range 800°–900°C. Simell and Bredenberg (1990) tested a commercial Ni catalyst on gas from an industrial updraft peat gasifier. It was more effective than the non-metal catalysts tested. In 1992 ankerite, sintered iron ore, and pelletized iron ore were added. The ankerite showed high activity (Simell et al. 1992). In 1995, ceramic monoliths of $Ni/Al_2/O_3$, having square channels, were tested in an updraft biomass gasifier. For temperatures of 900°C and 0.2–0.3 s at 1 bar, tar from wood was reduced from 9,800 ppmv to less than 10 ppmv. For a fluidized bed, tar was reduced from 1,000 ppmv to less than 10 ppmv. Biomass-derived gasification gas contains about 100 ppm H_2S, a known poison for Ni catalysts. This deactivation can be compensated for by going to 900°–950°C (Simell et al. 1995a). Studies showing the efficacy of Ni monoliths for tar and NH_3 were reviewed by Simell et al. (1996). Temperatures of 900°C were needed for *"complete"* "tar" destruction at five bars, without coke formation or sulfur poisoning. "Tar" from an updraft gasifier was thermally quite unstable, containing phenolic and aliphatic compounds, allowing even SiC to be effective. Fluidized-bed "tars" were thermally quite stable, requiring Ni catalysts for high destruction (90%–100%). In 1997, further results of testing the ceramic Ni monolith catalysts (manufactured by BASF AG) were presented by Simell and co-workers (Simell et al. 1997c). "Tars" from wood, bark, forest waste wood, eucalyptus chips, and fuel peat were reduced from ranges of 160 to 590 ppm to less than 1 ppm. *"If the lifetime of the catalyst exceeds 3-5 years in an IGCC process, the monolith catalyst is economically competitive, when compared to NOx removal by SCR."*

- Lammers et al. (1996) noted that the combination of catalyst lifetime and catalyst costs is unfavorable for use of Ni catalysts in large scale "tar" cracking. Lammers et al. (1997) tested BASF G1-25S for tar removal from the University of Madrid, bench-scale, bottom-fed, fluidized-bed gasifier, with and without air addition to the bed.

- Myrén et al. (1997) used Ni catalysts at 700°–900°C to upgrade crude gasification product gas (pyrolysis at 700°C). Paper contains a large table of "tar" compounds. Naphthalene is the most stable.

- Pedersen (1994) studied the following metallic catalysts: Co/Mo, Ni/Mo, Ni/W, Mo, Pt, Ru, and Pd for catalytic "tar" cracking of gas from the Kyndby updraft gasifier plant. (Synthetic gas with 0.3% phenol was also studied.) Compounds heavier than toluene were not addressed in this paper. The best catalysts were Ni/Mo and the Pt-catalytic system, which obtained nearly total conversion (99%) at 500°C. "Tars" exiting the catalytic beds from downdraft and fluidized-bed gasifiers were 0.1 g/Nm^3. In updraft gasifiers, aerosols of "tar" build up coke on the catalysts. At 400°C "tar" sticks to the filter. At 500°C most of the "tar" is in the gas-phase (Pedersen et al. 1996a). Tests of Co/MoO, Ni/MoO, Fe/MoO, and Cr/MoO, were made on the raw gas from the Volund updraft gasification plant, which contained 50g/m^3 of "tar" (Pedersen et al. 1996b).

- Wiant et al. (1994) tested Ni-based catalysts in a secondary reactor. See this reference under non-metallic catalysts.

- In connection with gas cleanup for coal gasification/molten carbonate fuel cell systems (METC 1986), Pacific Northwest Laboratory is developing catalysts for fixed-bed "tars" containing sulfur. Y-zeolite and CoMo-impregnated zeolites. MCFC needs sulfur levels less than 10 ppm.

- Milne et al. (1990) used MBMS of a batch pryolysis system to look at the effect of catalysts on the whole slate of "tar" species (methane-to-pyrene). The system could be operated to create primary, secondary, or tertiary "tar" slates. Pt, Pd, Rh, and Ni catalysts were examined. The real-time "tar" spectra by MBMS agree, in major features, with the flash re-pyrolysis of collected, actual gasification "tars."

D. The Use of Guard Beds for Metal Catalysts

- Narváez et al. (1997) show that a guard bed of calcined dolomite at 800°–850°C decreases "tar" to below 2g/Nm^3, a value that greatly extends the life of following catalysts such as BASF G1-25-S Ni-based catalyst. Aznar et al. (1990) used a dolomite guard bed in front of a Topsoe R-67-7H steam-reforming catalyst. At 700°–800°C the rate of coke deposits exceeds the rate of the steam-reforming catalyst to remove it. "Tar" concentrations from the dual bed were as low as 600 mg/Nm^3, representing 99% tar conversion. Severe deactivation was experienced for the Topsoe catalyst. In 1995, dolomite in front of UCI 3540S reduced "tar" from 21.2 g/Nm^3 to 0.33 g/Nm^3 (Aznar et al. 1995b). Finally, reports in 1996 show that a dolomite bed in front of BASF G25–15 cleaned raw gas from a fluidized bed to 1.1–1.3 g/Nm^3 from 30–50 g/Nm^3 (Aznar et al. 1996a). UCI, Topsoe, and ICI catalysts were also tested with a guard bed. *"With a small throughput of 'tar' to the catalytic bed, the catalyst does not deactivate in 100 hours"* (Aznar et al. 1996b). Corella et al. (1990) cautioned that one needs to limit tars before the methanation catalyst Harshaw Ni-3288. Work reported in 1996 shows that a dolomite guard bed in front of steam-reforming catalysts eliminates 90% of the "tar" and sulfur present. They tested BASF, ICI, Topsoe, Englehard, and UCI. Some catalysts reduced "tars" to 1 mg/Nm^3 (Corella et al. 1996a). Corella et al. (1995b) showed that gas from a bottom-fed, fluidized-bed gasifier gave "tars" at the 36–82 g/Nm^3 level. After a

dolomite or magnesite guard bed the "tar" was reduced to 0.9–1.3 g/Nm^3 and was further reduced to 10–100 mg/Nm^3 by a G1-25-S steam-reforming catalyst fluidized bed.

- Gebhard et al. (1994c) used the MBMS to study the reforming of a complex mixture of phenols, cresols, and polynuclear aromatics passed over a DN-34 guard bed followed by a bed of ICI-46-1. In 1995 it was reported that a dual bed of alumina upstream of UCI G90B was effective in "tar" cracking but did not significantly increase the Ni catalyst lifetime. Catalyst lifetime and water-gas shift activity are improved by going from a steam mole fraction of 0.3 to 0.4 (Gebhard 1995b). Jacoby et al. (1995) passed a mixture of benzene, toluene, and naphthalene over a gamma-alumina guard bed before a UCI G90B catalyst. The combination remained active for more than 585 hours.

E. Conclusions

Many types of catalysts have been investigated to reduce "tars" to lower levels and at lower temperatures than by thermal, oxidative, or steam reforming alone. Non-metallic catalysts such as dolomites, and metallic catalysts such as Ni, have been extensively studied. When used in-situ, the results have not been promising due to a combination of coking and friability. Secondary beds have been much more effective for both types of catalysts. Even more promising has been the use of guard beds of inorganic catalysts such as dolomite in front of steam-reforming catalysts such as supported Ni. The duration of most reported catalyst tests has been quite short, especially considering the long activity requirements for expensive catalysts such as Ni to be economical. Refer to the notes and the annotated bibliography for guidance as to the details of tests, and their relevance to the cleanup requirements for any particular end-use device.

Recommendations:

Funding should continue on the thermochemical and catalytic behavior of cheap inorganic, and expensive metal-based catalysts. The emphasis should now be on long-term tests and catalyst poisoning and regeneration, with due attention to the nature of the "tar" and the "destruction" or "conversion" sought in terms of the tolerance of the end-use device to organic materials. The high levels of sulfur, chlorine, and alkali in many attractive herbaceous feedstocks bring new problems to be addressed in lifetime and poisoning tests.

REFERENCES (See Appendix IV).

APPENDIX I: **List of Compounds Found in Primary Organics**

APPENDIX II: **List of Compounds Found in Secondary Organics**

APPENDIX III: **List of Compounds Found in Tertiary Organics**

Appendix I

Primary "Tar" Organics

M.W.	Formula	Chemical Names	ACS Registry Number
Acids			
46	CH_2O_2	Formic (Methanoic)	64-18-6
60	$C_2H_4O_2$	Acetic (Ethanoic)	64-19-7
74	$C_3H_6O_2$	Propanoic (Propionic)	79-09-4
76	$C_2H_4O_3$	Glycolic (Hydroxyacetic)	79-14-1
88	$C_4H_8O_2$	Butanoic (Butyric)	107-92-6
102	$C_5H_{10}O_2$	Pentanoic (Valeric)	109-52-4
116	$C_5H_3O_3$	4-Oxopentanoic	123-76-2
116	$C_6H_{12}O_2$	Hexanoic (Caproic)	142-62-1
122	$C_7H_6O_2$	Benzoic	65-85-0
130	$C_7H_{14}O_2$	Heptanoic	111-14-8
254	$C_{16}H_{30}O_2$	Hexadecanoic	52406-67-4
Sugars			
150	$C_5H_{10}O_5$	D-Xylose	58-86-6
162	$C_5H_{10}O_5$	1,6 - Anhydroglucofuranose	
162	$C_6H_{10}O_5$	Levoglucosan (1,6-Anhydro-beta-D-Glucopyranose)	498-07-7
180	$C_6H_{12}O_5$	alpha-D-Glucose (alpha-D-Glucopyranose)	492-62-6
180	$C_6H_{12}O_5$	Fructose	57-48-7
260	$C_{12}H_{20}O_6$	Cellobiosan	35405-71-1
Alcohols			
32	CH_4O	Methanol	67-56-1
46	C_2H_6O	Ethanol	64-17-5
Ketones			
70	C_4H_6O	2-Butenone	78-94-4
72	C_4H_8O	2-Butanone	78-93-3
84	C_5H_8O	Cyclopentanone	120-92-3

M.W.	Formula	Chemical Names	ACS Registry Number
96	C_6H_8O	2-Methyl-2-Cyclopenten-1-One	1120-73-6
98	$C_6H_{10}O$	3-Methylcyclopentanone	1757-42-2
98	$C_6H_{10}O$	Cyclohexanone	108-94-1
112	$C_7H_{12}O$	2-Ethylcyclopentanone	4971-18-0
112	$C_7H_{12}O$	Dimethylcyclopentanone	Several isomers
124	$C_8H_{14}O$	Trimethylcyclopentenone	106544-45-0
126	C10H8O	3-Methylindan-1-one	22303-81-7
Aldehydes			
30	CH_2O	Methanal (Formaldehyde)	50-00-0
44	C_2H_4O	Ethanal (Acetaldehyde)	75-07-0
56	$C_3H_4O_2$	2-Propenal (Acrolein)	107-02-8
84	C_5H_8O	2-Methyl-2-Butenal (Crotonaldehyde-2-methyl	1115`11-3
Phenols			
94	C_6H_6O	Phenol	108-95-2
108	C_7H_8O	2-Methyl Phenol o (o-Cresol)	95-48-7
108	C_7H_8O	3-Methyl Phenol m (m-Cresol)	108-39-4
108	C_7H_8O	4-Methyl Phenol p (p-Cresol)	106-44-5
122	$C_8H_{10}O$	2,3-Dimethylphenol (2,3-Xylenol) 3,4 3,5	526-75-0 95-65-8 108-68-9
122	$C_8H_{10-}O$	2,4-Dimethylphenol (2,4-Xylenol)	105-67-9
122	$C_8H_{10}O$	2,5-Dimethylphenol (2,5-Xylenol)	95-87-4
122	$C_8H_{10}O$	2,6-Dimethylphenol (2,6-Xylenol)	576-26-1
122	$C_8H_{10}O$	2-Ethylphenol	90-00-6
136	$C_8H_{12}O$	2,3,5 Trimethylphenol	697-82-5
Guaiacols			
124	$C_7H_8O_2$	Guaiacol (2-Methoxyphenol)	90-05-1
138	$C_8H_{10}O_2$	4-Methyl Guaiacol	93-51-6
152	$C_9H_{12}O_2$	4-Ethylguaiacol	2785-89-9
164	$C_{10}H_{12}O_2$	4-Propenyl Guaiacol (Isoeugenol)	97-54-1

M.W.	Formula	Chemical Names	ACS Registry Number
166	$C_{10}H_{14}O_2$	4-Propylguaiacol	2785-87-7
		Pyrolytic Lignin, Water Insoluable	Common designation

Syringols

M.W.	Formula	Chemical Names	ACS Registry Number
154	$C_8H_{10}O_3$	Syringol (2,6-Dimethoxy Phenol)	91-10-1
168	$C_9H_{12}O_3$	4-Methylsyringol	6638-05-7
182	$C_{10}H_{14}O_3$	4-Ethylsyringol	14059-92-8
182	$C_9H_{10}O_4$	Syringaldehyde/Benzaldehyde, 4-hydroxy-3,5, dimethoxy	134-96-3
194	$C_{11}H_{14}O_3$	4-Propenylsyringol (4-Allylsyringol)	6635-22-9
196	$C_{10}H_{12}O_4$	4-Hydroxy-3,5-Dimethoxyphenyl Ethanone	2478-38-8

Furans

M.W.	Formula	Chemical Names	ACS Registry Number
68	C_4H_4O	Furan (Furfuran)	110-00-9
82	C_5H_6O	2-Methylfuran (furan; 2-methyl, 5-methyl furan)	534-22-5
84	$C_4H_4O_2$	2(5H)-Furanone	497-23-4
96	$C_5H_4O_2$	Furfural (2-Furaldehyde 2-furancarboaldehyde)	98-01-1
98	$C_5H_6O_2$	3-Methyl-2(3H) Furanone	25414-24-8
98	$C_5H_6O_2$	Furfural Alcohol (2-Furanmethanol)	98-00-0
110	$C_6H_6O_2$	5-Methylfurfural (2-furaldehyde-5-methyl)	620-02-0
126	$C_6H_6O_3$	5-Hydroxymethyl-2-Furaldehyde	67-47-0

Mixed Oxygenates

M.W.	Formula	Chemical Names	ACS Registry Number
58	$C_2H_2O_2$	Glyoxal (Ethanedial, 1-2 Ethanedione)	107-22-2
60	$C_2H_4O_2$	Hydroxyethanal (Hydroxyacetaldehyde; Glycoaldehyde)	141-46-8
62	$C_2H_6O_2$	1,2-Dihyroxyethane (Ethylene Glycol)	107-21-1
72	$C_3H_4O_2$	Propanal-2-One (Methyl Glyoxal, 2-Oxopropanal)	78-98-8
74	$C_3H_6O_2$	1-Hydroxy-2-Propanone (Acetol)	116-09-6
74	$C_3H_6O_2$	2-Hydroxypropanal (Methanolacetaldehyde)	2134-29-4
86	$C_4H_6O_2$	Butyrolactone (gamma or beta); (2,3-Butanedione)	96-48-0
100	$C_5H_8O_2$	2,3-Pentenedione	1341-45-3
110	$C_6H_6O_2$	1,2-Dihydroxybenzene (Catechol)	120-80-9

M.W.	Formula	Chemical Names	ACS Registry Number
110	$C_6H_6O_2$	1,3-Dihydroxybenzene (Resorcinol)	108-46-3
110	$C_6H_6O_2$	1,4-Dihydroxybenzene (Hydroquinone)	123-31-9
112	$C_6H_8O_2$	2-Hydroxy-3-Methyl-2-Cyclopentene-1-One	68882-71-3
126	$C_6H_6O_3$	2-Methyl-3-Hydroxy-2-Pyrone	118-71-8
152	$C_8H_8O_3$	4-Hydroxy-3-Methoxybenzaldehyde (Vanillin)	121-33-5

Note: Literally hundreds of other compounds have been identified in pyrolysis, many derived from extractives and other non-lignocellulosic constituents of "biomass." This list includes those that have been reported and quantified in biomass fast pyrolysis oils (Milne et al. 1997a).

Appendix II

Secondary "Tar" Organics

M.W.	Formula	Chemical Names	ACS Registry Number
16	CH_4	Methane	74-82-8
28	C_2H_4	Ethene	74-85-1
30	C_2H_6	Ethane	74-84-0
40	C_3H_4	Propyne	74-99-7
42	C_3H_6	Propene	115-07-1
54	C_4H_6	Butyne	107-00-6
54	C_4H_6	Butadienes	106-99-0
56	C_4H_8	1-Butene 2-Butene	106-98-9 107-01-7
66	C_5H_6	Cyclopentadiene	542-92-7
67	C_4H_5N	1H-Pyrrole	109-97-7
78	C6H6	Benzene	71-43-2
79	C_5H_5N	Pyridine	110-86-1
92	C_7H_8	Toluene	108-88-3
93	C_6H_7N	Methylpyridine	1333-41-1
93	C6H7N	2.3.4 Picoline	109-06-8; 108-99-6; 108-89-4
94	C_6H_6O	Phenol	108-95-2
104	C_8H_8	Styrene	100-42-5
102	C_8H_6	Ethynlbenzene	536-74-3
106	C_8H_{10}	Xylene, o, m, p.	95-47-6 108-38-3 106-42-3
106	C_7H_6O	Benzaldehyde	100-52-7
107	C_7H_9N	Dimethylpyridine	27175-64-0
107	C7H9N	o,m,p-Ethylpyridine	100-71-0; 536-78--7; 536-75-4
107	C7H9N	2,4-Lutidine	108-47-4
108	C_7H_8O	p-Cresol	106-44-5

M.W.	Formula	Chemical Names	ACS Registry Number
108	C_7H_8O	o-Cresol	95-48-7
108	C_7H_8O	m-Cresol	108-39-4
110	$C_6H_6O_2$	Dihydroxybenzene	12385-08-9
116	C_9H_8	Indene	95-13-6
116	C_9H_8	1-Ethynal-4-methylbenzene (indene)	95-13-6
118	C_9H_{10}	Methylstyrene	98-83-9
118	C_9H_{10}	Indan	496-11-7
118	C_9H_{10}	Ethylbenzene	100-41-4
118	$C_8H_6O_{2,3}$	Benzofuran	271-89-6
120	C_8H_8O	Vinylphenol	31257-96-2
121	$C_8H_{11}N$	Trimethylpyridine	29611-84-5
122	$C_8H_{10}O$	Dimethylphenol	1300-71-6
124	$C_7H_8O_2$	Dihydroxytoluene	Many isomers, e.g. 488-17-5
128	C10H8	Naphthalene	91-20-3
129	C_9H_7N	Isoquinoline	119-65-3
129	C9H7N	Quinoline	91-22-5
130	$C_8H_6N_2$	Quinazoline	253-82-7
132	C_9H_8O	Vinyl Benzaldehyde	43145-54-6
132	$C_{10}H_{12}$	Methylindane	27133-93-3
132	C_9H_8O	Methylbenzofuran	25586-38-3
132	C_9H_8O	1-Indanone	83-33-0
134	$C_9H_{10}O$	Propenylphenol	Several isomers
135	$C_9H_{13}N$	Dimethylethylpyridine	37451-76-6
136	$C_9H_{12}O$	Propoxybenzene	622-85-5
136	$C_9H_{12}O$	Methylethylphenol	2-Methyl-3-Ethylphenol 1123-73-5 etc. for 7 isomers
142	$C_{11}H_{10}$	2-Methylnaphthalene	91-57-6
142	$C_{11}H_{10}$	1-Methylnaphthalene	90-12-0
142	$C_{11}H_{10}$	1,1-Dimethyl-1H-indene	18636-55-0
143	C10H7N	Quinaldine	91-63-4

M.W.	Formula	Chemical Names	ACS Registry Number
144	$C_{11}H_{12}$	1,2-Dihydro-3-methylnaphthalene	2717-44-4
146	$C_{10}H_{10}O$	Methyl-1-indanone	87259-53-8
146	$C_{12}H_{10}O$	Dimethylbenzofuran	25586-39-4
148	$C_8H_{10}O_2$	Creosole	93-51-6
150	$C_{10}H_{14}O$	Dimethylethylphenol	2-Ethyl, 3, 4-Methylphenol is 66/42-77-6 etc. for 10 isomers
154	$C_{12}H_{10}$	Vinylnaphthalene	26588-32-9
154	$C_{12}H_{16}$	Biphenyl	92-52-4
156	$C_{12}H_{12}$	Dimethylnaphthalene	28804-88-8
156	$C_{12}H_{12}$	2-Ethylnaphthalene	27138-19-8
166	$C_{13}H_{12}$	Methyl acenaphthalene	36541-21-6
168	$C_{13}H_{12}$	Methylbiphenyl	28652-72-4
168	$C_{12}H_8O$	Dibenzofuran	132-64-9
168	$C_{12}H_8O$	Naphthofuran	64083-16-5
168	$C_{13}H_{12}$	Diphenylmethane	101-81-5
170	$C_{13}H_{14}$	Propylnaphthalene	27378-74-1
179	$C_{13}H_9N$	Benzoquinoline	85-02-9
180	$C_{14}H_{12}$	Methylflourene	26914-17-0
182	$C_{13}H_{10}O$	Phenylbenzaldehyde (4-Phenyl carboxaldehyde)	3218-36-8
182	$C_{14}H_{14}$	Dimethylbiphenyl	Many isomers
190	$C_{15}H_{10}$	Methylenephenanthrene	203-64-5
192	$C_{15}H_{12}$	Methylphenanthrene	31711-53-2?
202	$C_{16}H_{10}$	Acephenathrylene	201-06-9
204?	$C_{16}H_{12}$	Phenylnapthalene	31711-53-2
204?	$C_{15}H_{10}$	4H-Cyclopenta [def]phenanthrene	203-64-5
216	$C_{17}H_{12}$	Methylpyrene	27577-90-8
216	$C_{17}H_{12}$	11H-Benzo [a,b] fluorene	a, 238-84-6; b, 243-17-4
226	$C_{18}H_{10}$	Benzo [ghi] flouranthene	203-12-3
228	$C_{18}H_{12}$	Benzo [c] phenanthrene	195-19-7

Note: Some of these compounds appear in the other two categories, demonstrating the evolutionary development and the somewhat arbitrary boundaries for the three types.

Appendix III

Tertiary "Tar" Organics

M.W.	Formula	Chemical Names	ACS Registry Number
16	CH_4	Methane	74-82-8
26	C_2H_2	Acetylene	74-86-2
66	C_5H_6	Cyclopentadiene	542-92-7
78	C_6H_6	Benzene	71-43-2
92	C_7H_8	Toluene	108-88-3
104	C_8H_8	Styrene	100-42-5
116	C_9H_8	Indene	95-13-6
128	$C_{10}H_8$	Naphthalene	91-20-3
152	$C_{12}H_8$	Acenaphthalene	208-96-8
154	$C_{12}H_{10}$	Acenapthene	83-32-9
166	$C_{13}H_{10}$	Fluorene	86-73-7
178	$C_{14}H_{10}$	Anthracene	120-12-7
178	$C_{14}H_{10}$	Phenanthrene	85-01-8
202	$C_{16}H_{10}$	Pyrene	129-00-0
202	$C_{16}H_{10}$	Fluoranthene	206-44-0
202	$C_{16}H_{10}$	Benzacenaphthalene	76774-50-0
216	$C_{17}H_{12}$	Methylpyrene	27577-90-8
216	$C_{17}H_{12}$	Benzo [a,b,c] fluorene	a, 238-84-6; b. 30777-18-5,30777-19-6; c, 205-12-9, 30777-20-9
226	$C_{18}H_{10}$	Benzo [ghi] fluoranthene	203-12-3
228	$C_{18}H_{12}$	Chrysene	218-01-9
228	$C_{18}H_{12}$	Benz [a] anthracene	56-55-3
228	$C_{18}H_{12}$	Triphenylene	217-59-4
228	$C_{18}H_{12}$	Benzoanthracene	56-55-3
228	$C_{18}H_{12}$	Benzo [c] phenanthrene	195-19-7
230	$C_{18}H_{14}$	2H-Benzo [d] phenathrene	68238-65-3

M.W.	Formula	Chemical Names	ACS Registry Number
228	$C_{18}H_{12}$	Naphthacene	92-24-0
240	$C_{19}H_{12}$	Methylbenzo [ghi] fluoranthene	51001-44-6
252	$C_{20}H_{12}$	Benzo [b] fluoranthene	205-99-2
252	$C_{20}H_{12}$	Benzo [a] pyrene	73467-76-2, 50-32-8
252	$C_{20}H_{12}$	Benzo [k] fluoranthene	207-08-9
252	$C_{20}H_{12}$	Perylene	198-55-0
276	$C_{22}H_{12}$	Anthanthrene	191-26-4
276	$C_{22}H_{12}$	Benzo [ghi] perylene	191-24-2
276	$C_{22}H_{12}$	Indeno [1,2,3-cd] pyrene	193-39-5
278	$C_{22}H_{14}$	Dibenzo [a,h] anthracene	53-70-3
300	$C_{24}H_{12}$	Coronene	191-07-1

Note: The frequent references to even higher molecular-weight materials (refractories, residues, undistillables), may be largely due to reactions that occur during condensation, solvent separation and the process of re-mobilization to the gas phase. We find that even in "flash analytical pyrolysis," and direct insertion into the mass spectrometer ion source (using MBMS), refractory residues of 10%–20% can obtain from material originally sampled entirely in the high-temperature gas phase (Milne et al. 1984).

A Selected Bibliography on Biomass Gasifier Tars with Annotations Relevant to Formation, Nature, Removal and End Use Tolerance

(Prepared by Thomas A. Milne, who assumes sole responsibility for any errors, misinterpretations, or omissions).

Corrections and additions to this bibliography would be greatly appreciated. Please send to: Thomas A. Milne, NREL, 1617 Cole Blvd., Golden, Colorado, USA. 80401. e-mail: Milnet@NREL.gov.

APPENDIX IV

A Selected Bibliography on Biomass Gasifier Tars with Annotations Relevant to Formation, Nature, Removal, and End-Use Tolerance

Abatzoglou, N.; Fernandez, J.-C.; Laramee, L.; Jollez, P.; Chornet, E. 1997a. "Application of Gasification to the Conversion of Wood, Urban and Industrial Wastes," in *Developments in Thermochemical Biomass Conversion,* Vol. 2. Edited by A.V. Bridgwater and D.G.B. Boocock. London: Blackie Academic & Professional, pp. 960–972.

Tar Definition: Organic residue when gas quenched to ambient. Describes the BIOSYN AFBG. Use wet scrubbing. 50 kg/h. Wood, tar level (air at 748°C) is 5 g/Nm^3, HC 6.2 vol % dry. Goal is gas clean enough to be co-burned with natural gas using commercial burners/boilers.

Abatzoglou, N.; Legast, P.; Delvaux, P.; Bangala, D.; Chornet, E. 1997b. "Gas Conditioning Technologies for Biomass and Waste Gasification," in *Proceedings of the 3rd Biomass Conference of the Americas, Volume 1.* Edited by R.P. Overend and E. Chornet. Canada: Montréal, August 24–29, 1997, pp. 599–606.

A BIOSYN gasifier pilot plant in Sherbrooke will be used to test a two-step, hot-gas cleanup: granular-bed filtering plus twin fixed-bed catalytic reformers using a proprietary catalyst, UdeS. This catalyst has been developed and optimized on naphthalene, dichlorobenzene, and real slip streams from the BIOSYN Process Development Unit (50 kg/h). Tar and VOCs for the BIOSYN gasifier are reported as follows: wood, 5,3; PE, 6,5; rubber, 5,4, and RDF, 3,4 g/Nm^3.

Abatzoglou, N.; Fernandez, J.-C.; Laramee, L.; Gasso, S.; Chornet, E. 1997c. "The BIOSYN Waste Biomass Gasification: Environmental Performances," in *Biomass Gasification and Pyrolysis.* Edited by M. Kaltschmitt and A.V. Bridgwater. CPL Scientific Ltd., Newbury, UK pp. 259–268.

The emphasis is on heavy metals, but air gasification runs on wood and RDF yielded tar and VOC levels of 3–5 and 3–4 g/Nm^3, respectively.

Abatzoglou, N. 1996. "R&D Demonstration & Commercialization Gasification Activities in Canada." *Analysis and Coordination of the Activities Concerning a Gasification of Biomass* (AIR3-CT94-2284), Second Workshop. Espoo, Finland.

Overview of "BIOSYN" gasifier R&D at Sherbrooke. (The only gasifier R&D in Canada.)
* Typical tar yields are 0.7%–2.9% dry feed. Tar and VOC range from 4–35 g/Nm^3.
* GB98-United Ni-based catalyst found unsuitable. Now using UdeS proprietary catalyst.
* Sampling procedures discussed.

Aigner, M. 1996. "LCV Gas Turbines—Requirements, Status, Results." *Analysis and Coordination of the Activities Concerning a Gasification of Biomass* (AIR3-CT94-2284), Second Workshop. Espoo, Finland.

Gives gas requirements for E and Single combustors for gas turbines:

	E Combustor	Single Combustor
LHV Range	11.2 MBTU	2.2–4
Dust	2–1 ppm	2
Max possible size	5 μm	5
Na + K	0.05–22 ppm	0.05
Ca 0.02–1 ppm	0.2	
Other metals	0.02– ppm	0.2
Tar and Naphthalene	0.5 ppm	0.5

Shows a graph of dust loading tolerances versus particle size, PFBC pushing the envelope.

Aiken, M.; McDonald, D.C. 1983. ENFOR Project C-172(2). "Testing the Prototype Sampler on a Downdraft Biomass Gasifier," Contractor's Report DSS Contract 41SS.KL229-1-4114, Vancouver, BC: Techwest Enterprises Ltd.

Prototype gasifier sampler was tested on the Forintek downdraft gasifier in Ottawa. Tar and condensate analysis are shown. Tar was 1.4–1.8 wt % of feed and condensate was 7.4–9.2 wt %.

Aiken, M.; McDonald, E.; Esplin, G. 1983. "Development of Sampling and Analytical Procedures for Biomass Gasifiers," ENFOR Project No. C172, DSS Contract No. 41SS.KL229-1-4114, Vancouver, BC: Techwest Enterprises Ltd.

"Acetone was found to be the best solvent for sample recovery and cleanup of sampler components." In this analysis, the acetone is evaporated at 30°C to weigh tar residue. Results from BC research gasifier gave tar at 6.1 wt % of feed, particulates at 0.4, and condensate at 0.3. "Conventional sampling trains have proven ineffective in sampling these high-temperature gases which are laden with condensible, tarry residues."

Aldén, H.; Espenäs, B-G.; Rensfelt, E. 1988. "Conversion of Tar in Pyrolysis Gas from Wood Using a Fixed Dolomite Bed," in *Research in Thermochemical Biomass Conversion.* Edited by A.V. Bridgwater and J.L. Kuester. London: Elsevier. pp. 987–1001.

Catalysts: Dolomite from the Glanshammar quarry. Tar in: From wood chip pyrolysis at 400°C to 900°C and ~3 s R.T. identified and quantified 70 compounds. Benzene, toluene, and xylene are not considered to be condensible tars. At low temperature (400°–600°C) compounds at <150 MW are dominant. Tar out: Almost all the components of tar, after catalytic cracking, were non-polar. At 800°C the tar was mainly mono and polynuclear aromatics. At 900°C, alkyl groups were removed and naphthalene was dominant as it was at 800°C. At 700°C pyrolysis and 900°C catalyst temperatures, the amount of naphthalene indicated 99.9% tar conversion. Actually, the "non-tar" components benzene and toluene were dominant aromatics from 800°–900°C. "There is no generally accepted definition of tar, but our interest is related to fouling problems that may arise from viscous or solid substances that condense even at low partial pressures and ambient temperature." Tar "conversion" was measured by excluding product benzene, toluene and xylene. "Our experimental data indicates that conversion using Glanshammar dolomite is sufficient to meet engine specifications at temperatures about 860°C. Naphthalene can be easily lost in sampling due to its high vapor pressure. Pyrolysis or gasification temperature (800°–900°C) give large fraction of PAH in the tar, but total amount of tar is low (1-2 wt % of dry fuel)."

Aldén, H.; Hagstrom, P.; Hallgren, A.; Waldhelm, L. 1997. "Investigations in High Temperature Catalytic Gas Cleaning for Pressurized Gasification Processes," in *Developments in Thermochemical Biomass Conversion,* Vol. 2. Edited by A.V. Bridgwater and D.G.B. Boocock. London: Blackie Academic & Professional, pp. 1131–1143.

Tar definition: Condensibles. Tar is absorbed, extracted, and analyzed by GC. Destruction Method: Dolomite and Ni-based catalysts. Study conversion of condensibles to non-condensibles (not specified).

Aldén, H.; Hagström, P.; Hallgren, A.; Waldheim, L. 1996. "High Temperature Catalytic Gas Cleaning for Pressurized Gasification Processes," in *Biomass for Energy and Environment: Proceedings of the 9th European Bioenergy Conference, June 1996*. Edited by P. Chartier et. al. Pergamon, pp. 1410–1415.

Catalysts: Dolomite and commercial Ni-based catalyst. Tar in: Pyrolysis at 700°C. Tar out: Mainly aromatics. How measured: GC. Conditions studied: Atmospheric and pressurized conditions, 800°–900°C in catalyst fixed bed. Used 700 g/h pyrolysis reactor with continuous feeding of aspen chips. At 800°–900°C and 1 atm with dolomite "total tar" was ~6 times the condensible tar (mainly naphthalene) at 20 bar and 900°C condensible tar severalfold less but total tar was reduced by only one-half. Steam suppressed cracking for dolomite but increased cracking for Ni. The use of Ni is questionable because of its cost.

Aldén, H.; Björkman, E.; Carlsson, M.; Waldheim, L. 1993. "Catalytic Cracking of Naphthalene on Dolomite," in *Advances in Thermochemical Biomass Conversion, Vol. 1.* Edited by A.V. Bridgwater. London: Blackie Academic, pp. 216–232.

Catalysts: Dolomite. Tar in: Model compound in various atmosphere (naphthalene). Tar out: Mainly aromatics. How measured: GC. Conditions studied: Mechanistic studies of naphthalene decomposition over dolomite. At 800°C BTX can be much greater than naphthalene.

Aldén H.; Bjorkman, E.; Espenas, B-G.; Waldheim, L. 1991. "Laboratory and Pilot Scale Gasification - Hot Gas Clean-Up Process for RDF Disposal and Energy Recovery." Studsvik Energy. S-611 82. Nykoping, Sweden.

RDF pellets have been successfully gasified, using air, in a CFB pilot gasifier. "One possible method is thermal cracking, but it requires high temperatures (greater than 110°C) and produces soot." Tar analysis methods are given in Alden et al. (1988). After sampling, acetone washing and extraction with dichloromethane, the two phases were analyzed and individual tar components were identified by GC/FID. "Tar" reductions with a dolomite catalyst are shown. The dolomite is not as effective with RDF as with wood, presumably because of deactivation of the dolomite by $CaCl_2$ on the surface. "Tar" levels of 20,000–25,000 mg/kg of dry RDF, and 18,000–22,000 mg/kg of dry wood, were observed. Using a secondary circulating fluid bed of Dolomite in the Studsvik CFBG pilot plant, tar reductions of 95% were achieved. With wood, 700 hours of operation of a dual-fuel diesel engine were logged. With a pilot fuel addition of 7% or more, the diesel performed satisfactorily, with this high speed, standard motor, "the exhaust gas contained hydrocarbons and CO in the excess of what the emissions regulations for stationary boilers stipulated."

Allen, D.T.; Gray, M.R.; Le, T.T. 1984. "Structural Characterization and Thermodynamic Property Estimation for Wood Tars: a Functional Group Approach," *Liq. Fuels Technol.* 2 (3), pp. 327–353.

Menard et al. have identified as many as 250 compounds in primary oils. Allen defines the tar fraction of the pyrolysis products as those condensed in the top of the pyrolysis reactor at about 200°C. They recovered tars by washing in acetone thus filtering the particulates, and removing the acetone by rotovaping the solution at 100°C and 10 mm Hg. The number of functionalities in wood tars is not great. Their functional groups, in a very primary "tar," number only 13, not counting polynuclear aromatics.

Andries, J.; Hein, K.R.G. 1996. "Co-Gasification of Biomass and Coal in a Pressurized, Fluidized-Bed Gasifier," NRI-DK-2627, pp. 1306–1311.

Plans for a 3-year program (1996–1998) are given. Pelletized straw and miscanthus will be the feed. Partners include KTH, TPS, and Imperial College. The Delft PFBC/G reactor will be used. The application will be for gas turbines.

Anonymous 1997. News item.

EPRI developed a new gas cleanup system based on hydro-treating landfill gas for use in a molten carbonate fuel cell. A 1,000-h test was recently completed. The objective is to get total contaminants down to a range less than 80 ppb.

Appleby, A.J. 1996. " Issues in Fuel Cell Commercialization," *J. Power Sources* 69, pp. 153–176.

Discusses the major types of fuel cells but no indication of fuel cell hydrocarbon tolerances.

Arauzo, J.; Radlein, D.; Piskorz, J.; Scott, D.S. 1997. "Catalytic Pyrogasification of Biomass. Evaluation of Modified Nickel Catalysts," *Ind. Eng. Chem. Res.* <u>36</u>, pp. 67–75.

Catalysts: Modified Ni-Mg aluminate and stoichiometric ($NiAl_2O_4$) catalyst for greater physical strength; addition of K as a promoter. Partial replacement of Ni by Mg improved strength but caused a significant increase in char production. How measured: Condensers and traps etc. washed with methanol to give "methanol solubles" composed of tar and water.

Arauzo, J.; Radlein, D.; Piskorz, J.; Scott, D.S. 1994. "A New Catalyst for the Catalytic Gasification of Biomass," *Energy and Fuels* <u>8</u>, pp. 1192–1196.

Catalytic pyrolysis and reforming in a fluidized-bed of $NiAl_2O_4$ achieved tar levels less than 100 ppmw of feed at 650°C Fast pyrolysis, followed by catalytic reforming, seems to be the mechanism. Catalyst lifetime and coking not discussed. Char, coke, and soot ranged from 6% to 24% over range of conditions studied.

Asplund, D.A.; Helynen, S.A. 1996. "Results on Bioenergy Use and Conversion in the Finnish Bioenergy Research Programme," in *Biomass for Energy and Environment: Proceedings of the 9th European Bioenergy Conference, June 1996*. Edited by P. Chartier et al. Pergamon, pp. 1074–1079.

A new CFB gasifier test rig has been constructed to test the effects of operating conditions on reduction of tar content, e.g., for small engine use.

Aznar, P.M.; Caballero, M. A.; Gil, J.; Martin, J.A.; and Corella, J. 1998. "Commercial Steam Reforming Catalysts to Improve Biomass Gasification with Steam Oxygen Mixtures. 2. Catalytic Tar Removal," *Ind. Eng. Chem. Res*. <u>37</u> (7), in press.

Contains details of "tar" reduction by eight commercial catalysts. "98% "tar" removal is easily obtained with space velocities of 14,000/h. No catalyst deactivation is found in 48-h on-stream tests when the catalyst temperature is relatively high (780°–830°C). The commercial catalysts for naphtha reforming are more effective than those for light hydrocarbon reforming. Incoming "tar" to the Ni catalysts must be in the range of 2 g/Nm^3 or less, "to avoid catalyst deactivation by coke."

Aznar, M.P.; Caballero, M.A.; Olivares. J.; Corella, J. 1997a. "Hydrogen by Biomass Gasification with Steam-O_2 Mixtures and Steam Reforming and CO-Shift Catalytic Beds Downstream of the Gasifier," in *Proceedings of the 3rd Biomass Conference of the Americas*. Edited by R.P. Overend and E. Chornet, 10 pp.

Studies are carried out in a fast-fluidized bed with bottom feeding. Inlet tar concentrations to the shift catalyst vary from 9–96 mg/Nm^3, after passage through an upstream steam-reforming catalyst (Ni-based).

Aznar, M.P.; Corella, J.; Gil, J.; Martin, J.A.; Caballero, M.A.; Olivares, A.; Perez, P. Frances, E. 1997b. "Biomass Gasification with Steam and Oxygen Mixtures at Pilot Scale and with Catalytic Gas Upgrading. Part I: Performance of the Gasifier," in *Developments in Thermochemical Biomass Conversion,* Vol. 2. Edited by A.V. Bridgwater and D.G.B. Boocock. London: Blackie Academic & Professional, pp. 1114–1128.

Collect in four-condenser train. Third generation, 15-cm i.d. turbulent-bed gasifier typically produces about 7 g/Nm^3 tar. The tar content when gasifying with steam +O_2 is much lower than gasifying with pure steam. Gasifying with air gives comparable tar yields to O_2 gasification.

Aznar, M.P.; Gil, J.; Martin, J.A.; Francés, E.; Olivares, A.; Caballero, M.A.; Pérez, P.; Corella, J. 1996a. "Recent Advances in AFB Biomass Gasification Pilot Plant with Catalytic Reactors in a Downstream Slip Flow," *New Catalyst for Clean Environment*, 2nd VTT Symposium in Espoo. Edited by A. Maijanen, and A. Hase. Espoo, Finland: VTT. pp. 169–176.

Tar cracking results presented for a 15-cm i.d. fast-bubbling fluidized bed with BASF G25-15 reforming catalyst. Typical results shown for the fluidized bed, followed by a dolomite bed and then a bed with BASF G25-15 reforming catalyst. Results show that raw gas with 30–50 g/Nm^3, is cleaned to 1.1–1.3 g/Nm^3 after the catalytic bed. No details on tar composition.

Aznar, M.P.; Corella, J.; Delgado, J.; Lahoz, J. 1993. "Improved Steam Gasification of Lignocellulosic Residues in a Fluidized Bed with Commercial Steam Reforming Catalysts," *Ind. Eng. Chem. Res*. <u>32</u>, (1), pp. 1–10.

See earlier papers. Deactivation is the main problem for these and other catalysts studied. Deactivation in a matter of hours.

Aznar, M.P.; Martin, J.A.; Gil, J.; Francés, E.; Caballero, M.A.; Olivares, A.; Pérez, P.; Corella, J. 1996b. "New Developments in the Pilot Plant for Biomass Gasification in Fluidized Bed with a Downstream Slip Flow for Testing Catalysts," in *9th European Bioenergy Conference and 1st European Energy from Biomass Technology Exhibition*. June 1996. Edited by P. Chartier et. al. Pergamon, p. 68.

Tested BASF, United Catalyst, Topsoe, and ICI catalysts in a 15-cm i.d. fast-fluidized bed followed by a dolomite guard bed and a slipstream-fed 4.0-cm id fixed catalytic bed. With a small throughput of tar to the catalytic bed, the catalyst does not deactivate (in 100 h).

Aznar, M.P.; Borque, J.A.; Campos, I.J.; Martin, J.A.; Francés, E.; Corella, J. 1995a. "New Pilot Plant for Biomass Gasification in Fluidized Bed and for Testing of Downstream Catalysts," in *Bionass for Energy, Environment, Agriculture and Industry, Volume 2, Proceedings of the 8th European Biomass Conference*, October 1994. Pergamon, pp. 1520–1527.

Third-generation gasifier produces 6.5% char and 4% tar. Raw gas C_2s were 3.0 vol % of gas. Typical clean gas reduced to 0.1 vol %.

Aznar, M.P.; Francés, E.; Campos, I.J.; Martin, J.A.; Gil, J.; Corella, J. 1995b. "Testing of Downstream Catalysts for Tar Destruction with a Guard Bed in a Fluidized Bed Biomass Gasifier at Pilot Plant Scale," Espoo, Finland: *Seminar on Power Production from Biomass II,* 6 pp.

Dolomite, United Catalysts 3540-S and BASF G 25 1S. This third generation gasifier (capacity 3–50 kg/h) is a fast-fluidized bed with two cleanup beds in series, operating on a slip stream. Typical results with United 3540-S and dolomite guard bed are: Tar in raw gas = 21.2 g/Nm^3 and cleaned gas = 0.33 g/Nm^3.

Aznar, M.P.; Delgado, J.; Corella, J.; Borque, J.A.; Campos, I.J. 1993. "Steam Gasification in Fluidized Bed of a Synthetic Refuse Containing Chlorine with Catalytic Gas Cleaning at High Temperature," in *Advances in Thermochemical Biomass Conversion.* Edited by A.V. Bridgwater. London: Blackie Academic, pp. 325-337.

Dolomite and calcite. Tests of tar destruction and chlorine sequestering in a secondary bed, when a wood-PVC mixture was gasified (1 and 10 wt % PVC). Tar concentrates in exit gas rises continuously with time because of coke formation and $CaCl_2$, $MgCl_2$ formation and slagging. Tar levels, with fresh catalyst, were in the range of 1–8 g/Nm^3. Authors conclude that gasification with air is preferable to steam alone.

Aznar, P.; Delgado, J.; Corella, J.; Lahoz, J.; Aragues, J.L. 1992. "Fuel and Useful Gas by Steam Gasification of Biomass in Fluidized Bed with Downstream Methane and Tar Steam Reforming: New Results," in *Biomass for Energy, Industry and Environment*, E.C. Conference 6th. Edited by G. Grassi, A. Collins, and H. Zibetter. Elsevier, pp. 707–713.

Topsoe Ni catalysts R-67 and RKS-1. Tar analyzed by Dhormann DC-90 TOC analyzer. Temperature in second (catalyst) bed 670°–780°C. Tar yields range from 35–195 g/Nm^3 when no oxygen is added to the steam. Deactivation of catalysts occurs in a few hours. At start, have achieved 99.99% destruction, but only gases to C_3 seem to have been measured.

Aznar, M.P.; Corella, J.; Delgado, J.; Lahoz, J. 1990. "Steam Gasification of Biomass in Fluidized Bed with a Secondary Catalytic Bed. Use of Methane Steam Reforming Catalysts," *Biomass for Energy and Industry (5th E.C. Conference)*, Vol. 2. Edited by G. Grassi et al. London: Elsevier Applied Science, pp. 2.798–2.803.

Tar condensate was removed and analyzed by LC and TOC. Assumed phenol as the representative of tar. Best results obtained with a dolomite bed upstream of the steam reforming catalyst. At 700°–800°C rate of coke deposits exceeds rate of steam gasification. Tar concentrations (from duel bed) were as low as 600 mg/Nm^3. This represented 99% tar conversion. Severe deactivation was experienced for the Topsoe R-67-7H catalyst, even when used in a fluidized bed. (Faster deactivation than with PVC reported.)

Aznar, P.; Delgado, J.; Corella, J.; Lahoz, J. 1989. "Steam Gasification of Biomass in Fluidized Bed with a Secondary Catalytic Bed—II. Tar Cracking with Dolomite(s) in the Secondary

Reactor," in *Pyrolysis and Gasification*. Edited by G.L. Ferrero, K. Maniatis, A. Buekens, and A.V. Bridgwater. London: Elsevier, pp. 629–634.

Using the same techniques and gasifier as in Part I, tar destruction by dolomites is presented as a function of temperature and time-on-stream. Tar was determined from total condensed liquid (mainly water) by TOC determination, assuming the tar was equivalent to phenol, M.W. 94. Tar levels decreased from ~21 at 600°C in the dolomite bed, to 1 g/Nm³ at 910°C. Under the conditions used substantial deactivation was seen in 10 min at 780°C and in 50 min at 840°C.

Babu, S.P. 1995. "Thermal Gasification of Biomass Technology Developments: End of Task Report for 1992 to 1994," *Biomass and Bioenergy* <u>9</u> (1–5), pp. 271–285.

Review of IEA activities and known demonstration projects. See key references. HC in fuel gases preferable except for chemical synthesis. Cites UK-Wellman work, with novel thermal tar cracker for diesel (no reference). Cites UK, DMT, Lund cooperative research program to study mechanisms of tar formation and catalytic removal. Ref. 13 therein has strategies for sampling gasifiers.

Babu, S.P.; Bain, R.L.; Craig, K. 1995. "Thermal Gasification of Biomass Technology Development in U.S.A.," Seminar on Power Production from Biomass II, Espoo, Finland: VTT.

Tar Definition: Distinguishes oils from tars. Discusses product treatment matched to end use. See p. 3 for categories of cleanup.

Babu, S.P. 1991. "Task VII. Biomass Conversion - Activity 4: Thermal Gasification, Participating Countries Report," *IEA Bioenergy Agreement*. Chicago, IL: Institute of Gas Technology.

Bühler states that for engines, need clean gas; tar and particulates at a few mg/m³. Reed, in 0.89 ton/downdraft gasifier, sees 600–1300 ppm tar. Graboski in 21 ton/d downdraft gasifier sees C_2H_2 0.26 mol %; C_2H_4 0.42; C_2H_6 1.5; C_3 0.24; with no tar reported. See Appendix for typical coal tar composition, and gas composition and for PNL oil degradation scheme.

Babu, S.P. 1990. "Task VII. Biomass Conversion - Activity 4: Thermal Gasification, Summary Report for Hot-Gas Cleanup," *IEA Bioenergy Agreement*. Chicago, IL: Institute of Gas Technology.

Deals with H_2S, COS, H_2 separation, CO_2 as well as tar reforming (coal). Reviews high-temperature desulfurization (deS) experience for coal, effect of Cl on deS. With coal tar, could have substantial S in tar. Could be a pollution problem. At 580°C and 2.2 s, get ~60% tar decomposed by catalyst.

Badger, G.M. 1995. "Pyrolysis of Hydrocarbon," in *Progress in Physical Organic Chemistry*, Vol. 3. Edited by S. Cohen et al., pp. 1–39.

A chemical/mechanistic review of pyrolysis of many tar-related compounds such as BTX, naphthalene, and pyrene.

Bain, R.L. 1997. "Milestone Completion Report—Center for Renewable Chemicals Technology and Materials," Biomass Power Fuel Cell Testing (BP712130).

Tolerances of molten carbonate fuel cells are:

H_2S	0.5 ppm
Chloride	0.1 ppm
Benzene	1 volume %
Naphthalene	0.5 vol %

The NREL thermal chemical PDU, an entrained-flow gasifier, yields 100 ppm H_2S and benzene at 1 vol %. Naphthalene was in the low ppm range (hybrid poplar).

Bain, R.L. 1996. "Biomass Gasification Activities in the United States," Country Report. Espoo, Finland: *Analysis and Coordination of the Activities Concerning a Gasification of Biomass* (AIR3-CT94-2284), Second Workshop.

"Tars may cause plugging of char filters and may form soot during combustion. If one gasifies at atmospheric pressure, must compress gas for turbine operation." "In this case a tar cracker will probably be used to minimize the amount of tar which must be handled during quenching." "The water and tar content must be low enough to ensure no condensation during quenching." Quotes typical gas composition from the Battelle gasifier as having 0.4 vol % tars, on a dry basis.

Bain, R.; Overend, R.P. 1996. "New Gasification Technology Offers Promise for Biomass Plants," *Power Engineering*, August, p. 4.

Description of the Battelle-based FERCO gasifier project. Gas cleanup with a secondary fluidized bed containing a new catalyst called DN-34 "essentially eliminated all tars from the gas." Raw gas from the Battelle PDU can contain 0.5–1 wt % of the dry wood feed as condensible tar.

Bain, R.L. 1995. Foreign Travel Trip Report Summary. Glasgow Scotland: IEA Biomass Gasification Working Group.

Table of gasifier demos by Maniatis. Refers to TPS final report on "loose-coupled" gasifier/turbine systems study. Design alkali levels after the scrubber: 14–37 ppb. Characteristic values for gasifiers: tar (g/m^3), downdraft 0.5, updraft 1–15, opencore 10–15, (crossdraft <0.1 for low-volatile fuels.)

	H_2S	SO_2	HCl	HF	NH_3	Zn
Fuel cell impurity tolerance	0.1–1	<1	0.1–1 ppm	0.1–1	1 vol %	5 ppm

In MCFC, T is high enough to reform hydrocarbons.

Baker, E.G.; Brown, M.D.; Elliott, D.C.; Mudge, L.K. 1988. "Characterization and Treatment of Tars from Biomass Gasifiers," Denver, CO: *AIChE 1988 Summer National Meeting*, pp. 1–11.

Tar yields are highest in fixed-bed, updraft gasifiers where they can reach 12 wt % of feed. Downdraft gasifiers, where tars pass through a hot zone, usually 900°C or higher, tar yields are less than 1 wt %. Steam-blown fluidized bed gasifiers have been reported to yield as low as 4 wt % at 600°–750°C and as much as 15 wt % at 600°C. In oxygen-blown fluid beds, tar ranged from 4.3 wt % at 750°C to 1.5 wt % at 810°C. An entrained-bed gasifier at 1,000°C reported < 1 wt % tar. Liquid products from gasifiers are often classified as primary tars (from pyrolysis) and secondary tars and oils are formed by further thermal reactions. Amount of tar that is acceptable in a gas depends on use. Uses include boilers, kilns, diesel and spark engines, gas turbines, synthesis gas and a pipeline gas. The limits on condensible hydrocarbons have been set as low as 8 mg/m^3.

Baker, E.G.; Brown, M.D.; Moore, R.H.; Mudge, L.K.; Elliott, D.C. 1986. "Engineering Analysis of Biomass Gasifier Product Gas Cleaning Technology," Richland, WA: Battelle Memorial Institute, Biofuels and Municipal Waste Technology Division, PNL-5534.

"Tar is a generic term for the higher boiling (>150°C) constituents of biomass gas which are formed during the pyrolysis reaction."

	Tars	**Particulates**	**Olefins**
Updraft	10–100 g/Nm^3	100–1000 mg/Nm^3	1–3%
Downdraft	50–500 mg/Nm^3	100–8000	0.2–0.4
Fluid bed, entrained bed	2–10 g/Nm^3	8,000–100,000	1–3

Evolution of tars as function of cracking severity follows:

mixed oxygenates→phenolic ethers→alkyl phenols→heterocyclic ethers→PAH→larger PAH

	Allowable Particulates (mg/Nm^3)	**mg/Nm^3 Tars**
Burners	200–1100 (Air Pollution)	Large
IC Engines	10–50	10–50
Gas Turbines	2–40	?
Synthetic Gas	2–30	?
Limits on tars are not well defined.		

Baker, E.G.; Mudge, L.K.; Brown, M.D. 1987. "Steam Gasification of Biomass with Nickel Secondary Catalysts," *Ind. Eng. Chem. Res.* $\underline{26}$ (7), pp. 1335–1339.

Summary and discussion of previously reported results. Three catalysts showed the most promise: NCM (W.R. Grace), G90-C (United Catalyst), and ICI-46-1. Catalyst deactivation is rapid when placed in the primary gasifier or in a secondary fixed bed. In a secondary fluidized bed, catalyst remains active for an extended time (one test was longer than 1,000 hours).

Baker, E.G.; Brown, M.D.; Robertus, R.J. 1985a. "Catalytic Gasification of Bagasse for the Production of Methanol," Pacific Northwest National Laboratory, prepared for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830. PNL-5100.

Previous studies of catalytic gasification of bagasse showed quite rapid deactivation of Ni-based catalysts in the presence of bagasse. Both sulfur poisoning and carbon deposition blamed. Tests at laboratory and PDU scale showed "K_2CO_3 doped on the bagasse to be a promising catalyst for converting bagasse to methanol synthesis gas." (Tests run at 10 wt % K_2CO_3 showed technical feasibility.)

Baker, E.G.; Mudge, L.K.; Wilcox, W.A. 1985b. "Catalysis of Gas-Phase Reactions in Steam Gasification of Biomass," in *Fundamentals of Thermochemical Biomass Conversion*. Edited by R.P. Overend, T.A. Milne, and L.K. Mudge. London and New York: Elsevier Applied Science Publishers, pp. 863–874.

Ni based. Summary of previously reported work. In steam gasification, pyrolysis, (1) CO_2, CO, CH_4, and some heavier hydrocarbon; (2) tar; (3) water soluble organics (acetic acid, methanol, acetone, esters, and aldehyde); and (4) char. A specially developed tri-metallic catalyst stayed active for 1,600 hours.

Baker, E.G.; Mudge, L.K. 1984a. "Catalysis in Biomass Gasification," Pacific Northwest Laboratory, Richland, WA. PNL-5030, DE84014555, 55 pp.

Using catalysts in a secondary fixed bed. Ni and other transition metals on supports such as alumina silica and silicon-alumina. "With an active catalyst, equilibrium gas compositions are obtained and all liquid pyrolysis products are converted to gases."

Baker, E.G.; Mudge, L.K. 1984b. "Mechanisms of Catalytic Biomass Gasification," *J. Anal. Appl. Pyrolysis* $\underline{6}$(3), pp. 285–297.

Reaction of biomass with steam in the presence of alkali carbonates and supported Ni catalysts. Primary catalyst (e.g., alkali carbonates) are doped in, or mixed with, the biomass. Secondary catalysts (Ni-based) are usually in segregated beds. Tar out: Typical levels of tar from fluidized-bed steam gasifier (PDU) at 1 atm: no catalyst, liquids are 7% of carbon; with Ni/Al_2O_3, 1% for wood and tires; with bagasse; 10 wt % K_2CO_3 + bagasse, trace.

Baker, E.G.; Mudge, L.K.; Mitchell, D.H. 1984. "Oxygen/Steam Gasification of Wood in a Fixed-Bed Gasifier," *Ind. Eng. Chem. Process Des. Dev.* $\underline{23}$, pp. 725–728.

Wood was gasified in an updraft gasifier with O_2/steam. Fractions of wood carbon converted to liquid products is about 20% and varies little with steam content of the blast or moisture content of feed. Under various cases, 2%–7% of energy is in the tars.

Bangala, D. N.; Abatzoglou, N.; Chornet, E. 1998. "Steam Reforming of Naphthalene on Ni-Cr/Al$_2$O$_3$ Catalysts Doped with MgO, TiO$_2$ and La$_2$O$_3$," *AIChE Journal* 44, pp. 927–936.

Steam reforming of naphthalene at 1,023 K, atmospheric pressure, water/naphthalene molar ratio of 16 and GHSV of 10,080, showed that *"the Ni-Cr catalyst supported on gamma-alumina doped with MgO and La2O3 has the best catalytic properties insofar as the activity and robustness are concerned."*

Bangala, D.N.; Abatzoglou, N.; Martin, J.P.; Chornet E. 1997. "Catalytic Gas Conditioning: Application to Biomass and Waste Gasification," *Ind. & Eng. Chem. Res. 36,* pp. 4184–4192.

Tar deposition can lead to improper functioning of compressors. This study covers reforming of naphthalene and orthodichlorobenzene, surrogates for biomass and waste tars, using UCI GB-98 and a novel Ni-based, robust formulation (UdeS) that incorporates a rare earth oxide in the alumina matrix. Defines the generic word "tar" to include a "heterogeneous group of organic compounds including phenol, naphthalene, polyaromatic hydrocarbons, chlorinated aromatic compounds and their substituted derivatives." Thermal cracking of tar requires T > 1,100°C with production of soot. GB-98 converted naphthalene "completely" (percent not given, products not given) at 850°C. UdeS catalyst showed excellent activity after 60 hours.

Bangala, D. 1997. "Reformage Catalytique de Naphtalene et Ai-chlos-benzene," Ph.D. Thesis, Universite de Sherbrooke, Faculte des Sciences Appliques, Department de Genie Chimque.

Barducci, G.L.; Ulivieri, P.; Polzinetti, G.C.; Donati, A.; Repetto, F. 1997. "New Developments in Biomass Utilization for Electricity and Low Energy Gas Production, on the Gasification Plant of Greve in Chianti-Florence," in *Developments in Thermochemical Biomass Conversion, Vol. 2.* Edited by A.V. Bridgwater and D.G.B. Boocock. London: Blackie Academic & Professional, pp. 1045–1057.

New developments include adding a two-stage gas cleaning system for Cl and tars. First a high-temperature dechlorination unit using calcium carbonate, followed by a dolomite bed for tar cracking. (The chlorine removal extends the lifetime of the dolomite.) The CaO reacts with HCl forming low-melting eutectics.

Barducci, G.L.; Ulivieri, P.; Polzinetti, G.C.; Donati, A.; Repetto, F. 1996. "New Developments in Biomass Utilization for Electricity and Low Energy Gas Production, on the Gasification Plant of Greve in Chianti-Florence," Bioenergy '96-The Seventh National Bioenergy Conference, *Partnerships to Develop and Apply Biomass Technologies*, pp. 296–303.

Gives composition of raw gas from the Greve circulating fluidized-bed gasifiers.

	Particulates	Condensate	CxHy	H_2S
Sorghum	42 g/Nm^3	67 g/Nm^3	1.4 vol %	76 ppm
RDF	48	84	4.9	47 ppm

Beall, K.; Duncan, D. 1980. "Characterization of Wood-Derived Tars," in *Proceedings of the 2nd Bioenergy R&D Seminar*. Edited by R. Overend. Ottawa, Canada: National Research Council, pp. 147–151.

Various solvent systems for tars from four wood waste gasifiers in Canada, showed a mixture of ether, tetrahydrofuran, and ethanol (1:8:1) was best. The tars were then fractionated by column chromatography into hydrocarbons, aromatic hydrocarbons and benzofurans, ethers, nitrogen compounds, and hydroxyl compounds.

Beck, S.R.; Bartsch, R.A.; Mann, U. 1982. "Applications of SGFM Technology to Alternate Feedstocks - Phase III. Final Report, September 1, 1979–March 31, 1982," Lubbock, TX: Texas Tech University, 190 pp.

Tar definition: Impinger residue after drying in vacuum. How collected: Impinger following the cyclone at 110°–190°C to prevent H_2O condensation. How measured: Condensation, GC. Tar separated into polar fraction and aromatic fraction. Quantitative analysis of PNA.

Gas compositions:	C_2H_4	2–4.5	Mole %
after scrub	C_2H_6	Trace to 1.0	
(oak sawdust)	C_2H_2	Trace to 0.3	
	C_3^+	Trace to 2.3	
	CH_4	10–14	
	tar	1 or 2	

Carcinogens seen in tar at micro g/g level. Polar fraction not discussed. Fewer PNA with O_2 gasification than air. Aromatics were 8%–19% of tar for wood. About half of organic fraction was in tar.

Becker, J.J. 1988. "Fixed Bed of Gasification Lignocellulosic: the CEMAGREF Process," in *Research in Thermochemical Biomass Conversion*. Edited by A.V. Bridgwater and J.L. Kuester. London: Elsevier, pp. 1016–1025.

Tar Definition: Condensibles. Describes the CEMAGREF fixed-bed gasifier. First set of experiments gave 1.3 vol % CH_4 and tars at 0.025 g/Nm^3 of dry gas.

Beenackers, A.A.C.M.; Maniatis, K. 1996. "Gasification Technologies for Heat and Power from Biomass," in *Biomass for Energy and Environment: Proceedings of the 9th European Bioenergy Conference, June 1996*. Edited by P. Chartier et al. Pergamon, pp. 228–259.

No gasifier produces as much tar as the updraft. For heat applications, blocking of pipes is main problem. Tar from downdraft gasifiers is more stable than updraft tar. Reports the following data on cocurrent (downdraft gasifier) from Bühler:

Gasifier	Raw gas dust (mg/Nm^3)	Raw gas tar (mg/Nm^3)
Wamsler	420	780
HTV-JUCH	2380 1880	85 2780
Ensofor	950	1300
"Good" Downdraft	100–1000	100–500
Engine Requires	<50; Pref. <5	<100, pref <50

Beenackers, A.A.C.M.; Maniatis, K. 1993. "Gas Cleaning in Electricity Production via Gasification of Biomass: Conclusions of the Workshop," in *Advances in Thermochemical Biomass Conversion, Vol. 1*. Edited by A.V. Bridgwater. London: Blackie Academic, pp. 540–546.

Tar cracking can be achieved by three main types of catalysts: dolomite, Ni-based, and multi-metallic. Tars can contain N and S and may cause environmental problems. Dr. Waldheim stated that tar is heavier than naphthalene.

Beenackers, A.A.C.M. 1989. "Gasification and Pyrolysis of Biomass in Europe," in *Pyrolysis and Gasification*. Edited by G.L. Ferrero, K. Maniatis, A. Buekens, and A.V. Bridgwater. London: Elsevier, pp. 129–157.

"A major problem is that minimum gas quality requirements for engines are still unclear." "For dust, values vary from <0.5 to <20 mg/m^3 whilst for tar a maximum value of 100 mg/m^3 is quoted."

Beenackers, A.A.C.M.; Van Swaaij, W.P.M. 1984. "Gasification of Biomass, a State of the Art Review," *Thermochem. Process. Biomass*. Edited by A.V. Bridgwater. London: Butterworths, pp. 91–136.

For direct heating, tars in low joule gas can generally be tolerated but may cause fouling problems in control equipment. Tars may increase luminosity and thus heat transfer. For Stirling engine jury is out on direct combustion versus gasification. For turbines 10–30 atm optimum. Cross-cut gasifier good for charcoal only. Fluidbed gasifier high in fine particulates. Co-current gasifier—can add O_2 to pyrolysis vapors to achieve tar as low as 300–500 mg/Nm^3. Entrained-flow gasifier (e.g., Texaco) virtually free of HCs but not suitable for wood. Thermal destruction of tar and CH_4 requires steam and 1,300°C. Catalytic post-destruction at 1,100°C.

Bennett, R. 1980. "Gas Conditioning," in *Survey of Biomass Gasification, Volume III—Current Technology and Research*. Edited by T.B. Reed. Golden, CO: Solar Energy Research Institute, SERI/TR-33-239.

Discusses five mechanisms of oil mist elimination. Applicable to a Purox gasifier to be coupled with an ICI methanol process. Various oil-mist elimination devices reviewed. Surprisingly little

information was found on catalyst tolerances for impurities, because there was not much experience with coal or biomass synthesis gas in 1980.

Cpd	Tolerance	Catalyst
C_2H_2	<3 ppm	ZnO
H_2S, COS, CS_2	<0.03 ppm <0.5 <0.7 <3 ppm	Cu-Zn-Cr ICI Cu-based ZnO
Chlorides	<0.03 ppm <0.2	Cu-Zn-Cr ICI

Separation processes for removing olefins are discussed, primarily C_2H_4. Detailed analysis of unit operations to clean the raw pyrolysis gas from wood in a Purox gasifier. Includes hydrocarbons from CH_4 to C_5H_{12}, acetic, propionic and butyric acid, methanol, ethanol, acetone, MEK, furfural, phenol, benzene, and "oil."

Berg, M.; Koningen, J.; Nilsson, T.; Sjöström, K.; Waldheim, L. 1996. "Upgrading and Cleaning of Gas from Biomass Gasification for Advanced Applications," in *Biomass for Energy and Environment: Proceedings of the 9th European Bioenergy Conference, June 1996.* Edited by P. Chartier et al. Pergamon, pp. 1056–1061.

Cites hydrocarbons in gasifier outlet (fluidized bed) as 3–6 vol %. Sulfur (as H_2S) gives strong deactivation of steam-reforming catalysts. Loss of activity due to 100 ppm H_2S can be compensated for by increasing the temperature 100°C or increasing the amount of catalysts.

Berg, M.; Waldheim, L.; Koningen, J.; Sjöström, K. 1997. "Steam Reforming with Nickel-Based Catalysts on Gas from Biomass Gasification," in *Developments in Thermochemical Biomass Conversion,* Vol. 2. Edited by A.V. Bridgwater and D.G.B. Boocock. London: Blackie Academic & Professional, pp. 1117–1130.

Catalysts: Commercial Ni-based. How measured: Gases by Balzers QMG421C quadruple MS. This study focused on steam reforming of methane in the presence of sulfur (H_2S) and tars. No tar conversion data. Application is for advanced conversion systems such as methanol synthesis and fuel cells, where hydrocarbon steam reforming will be necessary. Typical final tar loadings under conditions considered here for Ni are below 10 g/ton of dry fuel for condensible tars.

Black, J.W. 1989. "Catalytic Decomposition of Biomass Tar," in *Proceedings of the Seventh Canadian Bioenergy R&D Seminar.* Edited by E. Hogan, Ottawa, Canada: National Research Council, pp. 663–666.

On-line catalytic treatment of tar from the BIOSYN gasifier, operated at 200 kPa and 800°C with air. Catalyst activity ranked as Ni/Co/Fe > Co/Mo > limestone > Fe/Mo> alumina > MgO > Mo > LZ-Y52 > activated carbon > SK500 > Co > Ni > Silica gel > LZ-Y52 > mol sieve 3A. All catalysts decayed at an exponential rate due to carbon buildup. Inlet tar concentrations ranged from 8–10 g/m^3.

Black, J.W. 1987a. "Catalytic Tar Conversion, Interim Literature Report," Contract No. 2321-6-6088/01-SZ, 28 pp.

"Tars usually are defined as polycyclic aromatic hydrocarbons." In this work, tar is all of the organic material in the gasifier condensate stream. Includes BTX and simple phenols.

Black, J.W. 1987b. "Vapor Phase Destruction of Gasification Tars," Sixth Canadian Bioenergy R&D Seminar. Edited by Cecile Granger. Elsevier, pp. 430–434.

"Rather than conduct a detailed chemical analysis of each sample, the simpler COD test was utilized to evaluate the effectiveness of the catalyst." Studied sand, limestone, alumina, and a Ni catalyst. Alumina, Ni, and limestone all are capable of reducing gasifier tar content by 99.9%, thus permitting the condensate to be discharged to a sewage system.

Black, J.W. 1984. "Evaluation of Reforming as a Practical Technique for the Elimination of Water Pollution from Wood Gasifiers," Canada: *ENFOR Project C-166*, DSS Contract 42SS, KL229-0-4119, 112 pp.

From literature sources, gives a table of some 50 organic compounds in gasifier "condensates." Used COD as the simplest and most reproducible measure of condensates. Gases were measured up to pentanes and pentenes. Tar was quantitated for the batch-fed Forintek gasifier. Sand, alumina, limestone, and Ni all act as catalysts for the reforming reaction. Untreated condensate concentration in COD mg/L was 45,000. Limestone, alumina, and Ni, at 830°C reduced COD to 1,000, 1,000, and 320, respectively. Heavies C_6+ were of the order of 0.06 mol % and stayed level or increased with catalysts.

Blackadder, W.H.; Lundberg, H.; Rensfelt, E.; Waldheim, L. 1994. "Heat and Power Production via Gasification in the Range 5–50 MW_e," in *Advanced Thermochemical Biomass Conversion*, *Vol. 1*. Edited by A.V. Bridgwater. London: Blackie Academic & Professional, pp. 449–475.

Review of gasifiers for power in the 5–50 MW_e range. "Tars form in large amounts, 1%–10% by weight, from biomass. These are not a problem if they do not polymerize or condense. Fouling in the heat recovery train or permeability loss in the high temperature filter are reported in the literature." "Thermal cracking at high temperatures in the gasifier generates soot . . ." (pressurized gasifier).

Borisov, I.I.; Geletuha, G.G.; Khalatov, A.A. 1998. "Performance and Characteristics of Wood Downdraft Gasifier with Vortex Gas Cleaning System," in *Biomass for Energy and Industry*. Edited by H. Kopetz, T. Weber, W. Palz, P. Chartier, and G.B. Ferrero. 10th European Conference and Technology Exhibition, Würzburg, Germany. C.A.R.M.E.N., pp. 1826–829.

Boroson, M.L.; Howard, J.B.; Longwell, J.P.; Peters, W.A. 1989. "Heterogeneous Cracking of Wood Pyrolysis Tars over Fresh Wood Char Surfaces," *Energy & Fuels* 3, pp. 735–740.

Tar from pyrolysis of sweet gum hardwood. Tar $\equiv$ condensibles at 100°C. Found 15%–20% fraction that readily cracked.

Bossart, S.J.; Cicero, D.C.; Zeh, C.M.; Bedick, R.C. 1990. "Gas Stream Cleanup, Technical Status Report,"*Morgantown Energy Technology Center*, DOE-METC-91/0273, 66 pp.

Review, for coal systems, of PFBC, direct coal-fueled turbines (DCFT), IGCC, MCFC, SOFC, coal-fired diesel (CFD), and mild gasification.

"Tars, composed mostly of heavy aromatic hydrocarbons, can foul valves, piping, advanced particle filters, and heat exchange equipment. Tars can also deactivate sulfur sorbents and catalysts." For DCFT must have lower than 1 ppm for particles >5 microns. For IGCC no particles >5 to 12 microns. For MCFC, HCl, HF <0.1 ppmv; hydrocarbons: saturated, 12 vol %; olefins 0.2 vol %; aromatics 0.5 vol%; and cyclics 0.5 vol %. Particulate 10 ppmw HCl can cause electrolyte loss in the MCFC by reacting with the electrolyte to form lower boiling point compounds (e.g., KCl, NaCl). CFD, no particles larger than 5 microns.

Braekman, D.; Danheux, A.; Dhaeyere, A.; Fontana, A.; Laurent, P. 1998. "Upgrading of Waste Derived Solid Fuel by Steam Gasification," *Fuel* <u>77</u>, p. 55.

No tar data, but discussion and data on toxic metals Pd, Cu, Cd, and Mn.

Brage, C.; Yu, Q.; Chen, G.; Sjöström, K. 1998. "Tar Evolution Profiles Obtained from Gasification of Biomass and Coal," in *Biomass for Energy and Industry*. Edited by H. Kopetz, T. Weber, W. Palz, P. Chartier, and G.B. Ferrero. 10th European Conference and Technology Exhibition, Würzburg, Germany. C.A.R.M.E.N., pp. 1634–1637.

Evolution profiles of the main tar constituents, i.e., benzene toluene, indene, napthalene, and phenol, and coal in a pressurized fluidized bed at 700° and 900°C, 0.4 MPa.

Brage, C.; Qizhuang, U.; Sjöström, K. 1997a. "Use of Amino Phase Adsorbent for Biomass Tar Sampling and Separation," *Fuel* <u>76</u> (2), pp. 137–142.

"The tar sampling and separation method presented, based on solid-phase sorption/desorption on amino phase, has been shown to provide a much faster and accurate alternative to traditional cold trapping methods."

Brage, C.; Yu, Q.; Chen, G.; Rosen, C.; Liliedahl, Tl; Sjostrom, K. 1997b. "Application of Solid Phase Adsorption (SPA) to Monitoring Evolution of Biomass Tar from Different Types of Gasifiers," in *Biomass Gasification and Pyrolysis*. Edited by M. Kaltschmitt and T. Bridgwater. April. Stuttgart: CPL Press, pp. 218–227.

Brage, C.; Q., Yu; Sjöstrôm, K. 1996. "Characteristics of Evolution of Tar from Wood Pyrolysis in a Fixed-Bed Reactor," *Fuel* <u>75</u> (2), pp. 213–219.

"Tar" was collected in a series of traps, including ice-acetone and dry-ice acetone. Washed condensers and traps with dichloromethane and small amounts of acetone. Total tar determined gravimetrically from the crude tar extract by rotary evaporation of the solvent to constant weight at 50°C and 2 kPa. Tables of major condensible products and C_2S are given. "The term 'tar' as used here refers to a mixture of all the condensible, semivolatile and nonvolatile compounds, exclusive of water, with molecular weight ranging from pyridine (MW79) to heavy asphaltenes and pre-asphaltenes (M.W.>500) collected at room temperature." Hardwood chips were pyrolyzed in steam at 700°, 800°, and 900°C and several analytical techniques used to deduce correlations between C_2 gaseous species and principal tar components. Suggests use of these correlations for continuous monitoring of heavy tars.

Brage, C.; Qizhuang, Yu; Sjöström, K. 1995. "Characterization of Tars from Coal-Biomass Gasification," presented at the 3rd International Symposium on Coal Combustion, September 18-21, 1995, Beijing, China, pp. 45–52.

"Tar samples from gasification of coal, biomass, and their mixtures are analyzed in detail. Gasifier is a fluidized bed operated at 700°–900°C. "Tar samples were analyzed by methods based on combined application of liq-liq partitioning (LLP, solid-phase extraction, SPE, and capillary gas chromatography with flame ionization detection (CGC-FID). The selected tar compounds analyzed include phenol, cresols, C1-C3-benzene, indene, naphthalene, methylnaphthalene, acenaphthylene, fluorene, phenanthrene, anthracene, pyrene, and a number of minor N-organic compounds." The raw material was heart wood of birch, containing at most 1% bark, from a Swedish paper mill. The wood was fed into the top of the fluidized-bed reactor (144 mm id x 600 mm high). At 700°C phenols and cresols dominated naphthalene and 2-methyl-naphthalene, whereas the reverse was the case at 900°C Tar levels from biomass at 700°C and 0.4 Mpa and 1.5 Mpa were 1.9 and 2.4 mg/L (?) of product gas. At 900°C the values were 1.8 and 2.6 mg/L respectively. The basic N-organic compounds share of the total tar, range from 0.4–3.5 wt %.

Brage, C.; Sjöström, K. 1991. "Separation of Phenols and Aromatic Hydrocarbons from Biomass Tar Using Aminopropylsilane Normal-Phase Liquid Chromatography," *J. Chromatography* 538, p. 303.

Brandt, P.; Henriksen, U. 1998. "Decomposition of Tar in Pyrolysis Gas by Partial Oxidation and Thermal Cracking, Part 2," in *Biomass Energy and Industry*. Edited by H. Kopetz, T. Weber, W. Palz, P. Chartier, and G.L. Ferrero. 10th European Conference and Technology Exhibition, Würzburg, Germany, C.A.R.M.E.N., pp. 1616–1618.

"It was shown that it is posssible to acheive a significant reduction in tar content in the gas by partial oxidation. The minimum tar content measured was 0.5 g/kg (dry) straw giving a 98%–99% reduction at 900°C in the cracking reactor and with an excess air ratio of 0.5."

Brewer, M.K.; Brown, R.C.; Anderson, I.C.; Hall, R.B.; Woolsey, E.L. 1993. "Performance of a Downdraft Gasifier Coupled to an Internal Combustion Engine," in *Energy from Biomass Wastes*, XVI, pp. 957–978.

Tested a wood-chip filter on the Buck Rogers downdraft gasifier. Not sufficient to reach recommended 10–50 mg/Nm^3.

Bridgwater, A.V. 1995. "The Technical and Economic Feasibility of Biomass Gasification for Power Generation," *Fuel* 74 (5), pp. 631–653.

Destruction Method: Thermal, catalytic, and partial oxidation. Comprehensive review of all aspects of gasification and gasifiers. Estimates tar removal or cracking as 15% of plant cost. Lists tar and particulate propensity of the many types of gasifiers. Engines have higher tolerance to tars than turbines, up to 30 ppm tar. For turbine, compression is the biggest problem. Can tolerate high tars if they are in vapor phase. Turbine's tolerance quoted as < 1 ppm, whereas a biomass fuel with 0.1 wt % S will produce gas levels as high as 100 ppm.

Bridgwater, A.V. 1994. "Catalysts in Thermal Biomass Conversion," *Applied Catalysis A: General* 116, pp. 5–47. Elsevier Science Publishers.

Section on tars and methods of reduction for various end uses, with extensive references to past work.

Bridgwater, A.V.; Elliott, D.C.; Fagernas, L.; Gifford, J.S.; Mackie, K.L.; Toft, A.J. 1995. "The Nature and Control of Solid, Liquid and Gaseous Emissions from the Thermochemical Processing of Biomass," *Biomass and Bioenergy* 9 (1–5), pp. 325–341.

Review of environmental emissions, including gasification wastewaters. For pressurized gasification with a turbine, tend to use hot-gas cleaning to retain gas temperatures. For atmospheric gasification with an engine, water quenching to cool and clean the product gas is preferred. For atmospheric gasification with a turbine, water quench and scrub probably necessary to clean gas product before compression ahead of the turbine.

Bridgwater, A.V.; Evans, G.D. 1993. "An Assessment of Thermochemical Conversion Systems for Processing Biomass and Refuse," Aston University-DK Teknik-Denmark. ETSU B/T1/ 00207/REP.

Thorough review of 13 gasifiers, classified under 14 types. Fixed bed: co-current (down or up); countercurrent (down or up); cross-current; stirred bed; two stage. Fluidized bed: bubbling bed; circulating bed; entrained bed; twin reactor. Moving bed: multiple hearth, etc.; rotary kiln; cyclonic or vortex reactors. Lists general characteristics such as tar fractions for each. Cleanup options in use are tabulated.

Bridgwater, A.V.; van Swaaij, W.P.M.; Beenackers, A.A.C.M. 1987. "Thermochemical Biomass Conversion: Research Development and Demonstration Requirements," in *Biomass for Energy and Industry-4th E.C. Conference.* Edited by G. Grassi, B. Delmon, J.-F. Molle, and H. Zibetta. London and New York: Elsevier Applied Science, pp. 441–456.

Extensive list of R&D activities needed for large-scale gasification system (many tar issues) and for "Producer Gas" system. Status of recommendations and actions taken since 1985 is tabulated.

Broman, L.; Marks, J. 1995. "Co-Generation of Electricity and Heat from Combustion of Wood Powder Utilizing Thermophotovoltaic Conversion," in *AIP Conference Proceedings 321, The First NREL Conference on Thermophotovoltaic Generation of Electricity*. Copper Mountain, CO, 1994, pp. 133–139.

Describes a feeding mechanism and a combustion chamber for a 10-kW flame, burning at 1,400 K. Plans for developing other components of the converter are discussed. No tolerances of the heat transfer surfaces are given.

Brouwers, J.J.H. (1996). "Rotational Particle Separator: A New Method for Separating Fine Particles and Mists from Gases," *Chem. Eng. Technol*. <u>19</u>, pp. 1–10.

Brown, A.E. 1996. "Producer Gas Quality Requirements for IGCC Gas Turbine Use," NOVEM EWAB Report 9603, A state-of-the-art overview. The Netherlands: Delft University of Technology, BTG Biomass Technology Group BV.

An analysis of current and available biomass gas qualities, compared to current and available gas turbine requirements. From limited information from turbine manufacturers, tolerances for condensing tars should be 0.05–0.5 ppm, and tars should be <0.2–0.5 ppbw or same as particle limits. Gasifiers reviewed were Battelle, Bioflow Oy, U. of Lund, Enviropower, Thermie projects, EN Joule II, MTCI, VTT, DOE-Hawaii and D.U. Complutense, Zaragosa. Turbine manufacturers contacted were ABB, European Gas Turbines, GE, Solar Gas Turbines, Westinghouse. Tars, e.g., refractory aromatics, clog filters, are difficult to burn and deposit internally. In atmospheric gasification, the need for compression gives very strict cleanliness requirements. Manufacturers of turbine do not list tar in their specifications normally. The definition of tar has mainly to do with the temperature at which tar compounds are condensed. There is no standard by which tar should be measured. "There are some indications that tar behaves like a particle, a droplet and/or an aerosol." For gas turbine use, the gas must be cooled from the gasifier freeboard exit temperatures to 350°–600°C to protect turbine valve control components and process equipment.

Enviropower Oy (ABPBB) reports less than 1 g/Nm^3 total tar with 1% of this as heavy tars. The University of Lund reports 21 g/Nm^3 for CFB. Complutense (FB) reports 21.2 g/Nm^3 raw and 0.33 after catalytic cleanup. MTCI reports no tars. "An industry-standard gas quality measurement protocol for biomass gases must be defined and implemented. A program to do so could be funded by the energy departments of several interested countries pursuing IGCC. Care must be taken to sufficiently include the concerns of the turbine manufacturing industry; overall a commercial standards body such as ASTM could be consulted as well." A turbine performance standard should be developed, perhaps involving the IEA Bioenergy Group and standards organizations. A database on the Internet is recommended.

Brown, M.D.; Baker, E.G.; Mudge, L.K. 1986a. "Evaluation of Processes for Removal of Particulates, Tars, and Oils from Biomass Gasifier Product Gases," in *Energy from Biomass and Wastes*, X. Edited by D.L. Klass, London: Elsevier, and Chicago: Institute of Gas Technology.

See notes from Baker et al. (1986).

Brown, M.D.; Baker, E.G.; Mudge, L.K. 1986b. "Environmental Design Considerations for Thermochemical Biomass Energy," *Biomass* 11, pp. 255–270.

Allowable tar and particulate loading (mg/m^3)

	Particulates	Tar
IC Engines	10–50	10–50
Turbine	2–20	8

Overview of particulate and tar concentrations from gasification and combustion; and cleaning approaches. Cites following ranges for tar and particulate:

	Tar (mg/Nm^3)	Particulates (mg/Nm^3)
Updraft	10,000–100,000	100–1,000
Downdraft	50–500	100–8,000
Cross-flow	60–400	100–8,000
Fluid bed	2,000–10,000	8,000–100,000
Entrained bed	8,000–30,000	30,000–100,000

Distinguished two basic types of tars: Oxygenates and PNA.

Brown, M.D.; Baker, E.G.; Mudge, L.K.; Wilcox, W.A. 1985. "Catalysts for Biomass Gasification," in *Energy Biomass Wastes,* IX. Chicago: Institute of Gas Technology, pp. 505–521.

Catalysts: Contrasts single versus dual bed catalytic gasification. Biomass/catalyst contact leads to rapid deactivation. Two-stage, secondary catalysis (gas-phase) can lead to long-lived Ni-based catalysts (1,500 h or more). The most active secondary catalysts tested were:

Grace	SMR-1	NiCuMo/Al$_2$O$_3$
	SMR-2	NiCuMo/SiO$_2$-Al$_2$O$_3$
	SMR-3	NiCoMo/Al$_2$O$_3$
	SMR-4	NiCoMo/SiO$_2$-Al$_2$O$_3$
United Catalyst G90C		Ni/alpha alumina

Bruinsma, O.S.; Geertsma, R.S.; Bank, P.; Moulijn, J.A. 1988. "Gas Phase Pyrolysis of Coal-Related Aromatic Compounds in a Coiled Tube Flow Reactor," *Fuel* 67, pp. 327–333.

A flow reactor was used to obtain thermal stability of aromatic compounds. Included were the following wood-related compounds: benzene, toluene, ethylbenzene, styrene, phenol, methoxybenzene, xylenes, cresols, p-methoxytoluene. Arrhenius parameters are given.

Brussels 1988. IEA Thermal Gasification of Biomass Task, EC and USDOE Meeting on Tar Measurement Protocol. March 18–19, Brussels, Belgium. Meeting Presentation Information.

BTG Biomass Technology Group. 1996. "State of Small-Scale Biomass Gasification Technology." *Analysis and Coordination of the Activities Concerning a Gasification of Biomass* (AIR3-CT94-2284), Second Workshop, Espoo, Finland.

Reviews status of some 30 European and world gasifiers, "The VET concept with the reduction of hot combustion gases in the coal dust cloud is interesting, since the concept appears to solve the tar problem without applying a catalyst or a thermal cracking reactor."

BTG Biomass Technology Group. 1995a. "Cleaning of Hot Producer Gas in a Catalytic, Reverse Flow Reactor," Final Report, The Netherlands: EWAB 9605, NOVEM.

For engines, a maximum tar content of 100 mg/Nm^3 is acceptable. Catalytic cracking by chars and cokes is studied in a small-scale installation at 800°–1000°C and residence times up to 0.7 s. Only the charcoal had activity but it was slowly consumed. Dolomite was then tested. Used a pilot-plant, adiabatic and tar-cracker with periodic reversal of the feed flow. Added some air to maintain the desired temperature in the center of the reactor. At 99% tar conversion still had 200 mg/Nm^3 of tar. The heating value of the gas is hardly changed. A small fraction of the biomass is converted into "what is called 'tar'—a term without a generally accepted exact definition—i.e., a complex mixture of more or less easily condensible substances." In the context of fouling, "tar can be defined as a mixture of components which condense on surfaces at 20°C." Tar is collected in a cellulose filter followed by a water-cooled condenser. A downdraft gasifier produced tar levels of 30-60 g/Nm^3. Even an inert catalyst converted 80% of the "tar." Dolomite and charcoal each converted "tar" levels to less than 100 mg/Nm^3 (>99% conversion). (Tar presumably measured by weighing as no compound analysis was included.) Consumption of dolomite was negligible but longer-term tests are needed to determine mechanical strength. Economic analysis showed that "the tar cracking system only has a minor influence on the total investment costs as well as operational costs."

BTG Biomass Technology Group. 1995b. "Development of a Standard Procedure for Gas Quality Testing in Biomass Gasifier Plant/Power Generation Systems." Final report. The Netherlands: BTG Biomass Technology Group, JOU2-CT93-0408, NOVEM. EWAB-9608.

The major problem with gasification is the carryover of undesirable tars and particulates into engine or turbine. There are no uniform methods for monitoring and evaluating the performance of gasifier systems. This study reviews the methods proposed by the UNDP/World Bank and the Biomass Research Group of ITT, Bombay. The UNDP/World Bank methods served as the basis for developing a draft standard on gas quality testing. The EPA methods for stationary source sampling seem appropriate for "sampling and analysis of polyaromatic hydrocarbons (tars)." The most common solvents for tar trapping have been dichloromethane, cyclohexane,

and acetone. Isokinetic sampling of tars is recommended since "these tar compounds can form droplets and can then behave like particulates." For practical application, the THT (UNDP) World Bank sampling system is recommended because "the analysis is simple, low-cost and easy to execute under field applications. Other sampling techniques as developed by VTT and ETH/Verenum are more suitable for research applications." The draft standard procedures (based on UNDP/World Bank) were applied at three sites, two in the UK (fixed-bed up and downdraft) and one in Germany (downdraft). Tar contents are reported as follows:

Updraft UK	Downdraft UK	Germany Downdraft
Raw gas 6700 mg/Nm^3	n.m.	n.m.
Clean gas 627 mg/Nm^3	890 mg/Nm^3	1100–1800 mg/Nm^3

Further development of standards would be a suitable subject for further IEA Voluntary Standards Activity and through the CEC framework under Joule Thermie. Also at Vienna (1995), "there was a general agreement that this subject will be included as a sub-activity or sub-task of future IEA meetings on gasification." A survey of gas quality requirements for turbines gave the following range for tars: C_7+ lower than 0.01 vol % and tar, 5 ppm. For engines: C_5+, 0.0–0.4 mg/Nm^3 and tars; <400 mg/Nm^3; 50–100 mg/Nm^3. For gas engines Cl < 100 mg/Nm^3 has been specified.

BTG Biomass Technology Group. 1994. "Gasification of Waste. Evaluation of the Waste Processing Facilities of the Thermoselect and TPS/Greve," The Netherlands: BTG-94-NOVEM. Biomass Technology Group.

Tar Definition: CxHy. Thermoselect and TPS/Greve for MSW. Study tour of two Italian facilities, TPS uses fluid-bed tar cracker filled with dolomite. Greve: raw gas had 6-9 vol % CxHy, Tar 30-70 g/m^3.

BTG/TWENTE. 1998. "State of the Art: Tar Measurement Protocols," Available at http://btg.ct.utwente.nl/projects/558/

Bühler, R. 1994. "State of Technology in Wood Gasifying," Paper submitted to 3. Holzenergie—Symposium: Neue Erkenntnisse zur Thermischen Nutzung von Holz, Oktober, 27 pp.

Updraft can produce up to 100 g/m^3 of tar. Need thermal cracking at 1,000°C or catalytic at 300°C. Tar content: updraft > F.B. > downdraft. Engine needs ambient temperature gas for efficiency. Same engine specs quoted as by Stassen in World Bank study. Discussion of several gasifiers.

Bui, T.; Loof, R.; Bhattacharya, S.C. 1994. "Multi-Stage Reactor for Thermal Gasification of Wood," *Energy* 19, (4), pp. 397–404.

"Tar is a mixture of higher hydrocarbons which forms a very sticky condensate at normal temperatures." Average tar content reported for downdraft gasifiers is 2 g/Nm^3, for updraft 58 g/Nm^3. For engines, tar and dust loads must be lower than 10 mg/Nm^3. Use throatless two-stage gasifier with air injected in the upper flaming pyrolysis zone and in the lower reduction

zone. Collected tar in ice water. Air dried tar at room temperatures before weighing. Two-stage gasifier reduced tar from 3600 mg/Nm^3 to 92 mg/Nm^3.

Caballero, M.A.; Aznar, M.P.; Gil, J.; Martin, J.A.; Corella, J. 1998. "Co-Shift Catalytic Beds after a Biomass Gasifier and a Steam-Reforming Catalytic Reactor to Get New and Interesting Exit Gas Compositions," in *Biomass for Energy and Industry*. Edited by H. Kopetz, T. Weber, W. Palz, P. Chartier, and G.B. Ferrero. 10th European Conference and Technology Exhibition, Würzburg, Germany. C.A.R.M.E.N., pp. 1789–1793.

Caballero, M.A.; Aznar, M.P.; Gil, J.; Martin, J.A.; Frances, E.; Corella, J. 1997. "Commercial Steam Reforming Catalysts to Improve Biomass Gasification with Steam-Oxygen Mixtures. 1. Hot Gas Upgrading by the Catalytic Reactor," *Ind. Eng. Chem. Res*. <u>36</u>, pp. 5227–5239.

Eight Ni-based catalysts were tested for hot-gas cleaning in biomass gasification with steam-oxygen mixtures. A guard bed of calcined dolomite was used to keep the "tar" content of the gas entering the Ni catalyst bed below 2 g/Nm^3. The effects on the main gases: H_2, CO, CO_2, and CH_4, are studied as a function of temperature of the catalytic bed and the gas composition. "Tar" effects are reported in Azner et al. (1998). The gasifier is a small pilot plant based on an atmospheric and fast fluidized bed. Tar and gas sampling and analysis are as reported in Aznar et al. (1997b) and Narvaez et al. (1997). "If the tar sampling and analysis methods were varied, some results concerning tar could vary (by 10–20 wt %) but the trends and main conclusions would remain the same." Tar contents of 20–40 g/Nm^3 at the gasifier exit are lowered to 1–2 g/Nm^3 by the dolomite bed, and to 0.001–0.1 g/Nm^3 after the Ni bed. Phenols and cresols were the major components of the raw gas tars. (See Aznar et al. [1998] for details of tar elimination.)

Cahill, P.; Nieminen, M.; Dutton, M.; Rasmussen, G.; Kangasmaa, K. 1996. "The Influence of Tars on Hot Gas Filter Performance in Air Blown Gasification of Coal and Biomass," in *High Temperature Gas Cleaning*. Edited by P. Schmidt, P. Gäng, T. Pilz, and A. Dittler, Universität Karlsruhe.

Tar material can cause high pressure drop across filters, which cannot be recovered using normal reverse pulse cleaning. Desulfurization and de-halogenation systems operate at 400°–600°C, so this is the target range for filtration. Refers to "heavy" tar components up to coronene. Laboratory tests of pressure increase with real and simulated tars did not show the blinding behavior seen in pilot tests.

Carlsen, H. 1996. "Stirling Engines for Biomass: State-of-the-Art with Focus on Results from Danish Projects," in *Biomass for Energy and Environment: Proceedings of the 9th European Bioenergy Conference, June 1996*. Edited by P. Chartier et al. Pergamon, pp. 278–283.

Biomass combustion was tested in early Stirling engines developed by Phillips, GN, United Stirling, and Ford. "Results were not very encouraging because of fouling of the narrow passages in the hot heat exchangers with slag." Danish projects are under way for direct combustion of biomass, using large diameter heat transfer tubes and fin spacing to avoid fouling.

Gives tables of eight groups looking at biomass in Stirling engines, either adapted to, or designed for, biomass.

Carlsen, H.; Amandsen, N.; Traerup, J. 1996. "Forty kW Stirling Engine for Solid Fuel," IEEE Paper 96461.

Tar not mentioned in this direct, solid fuel-fired system. Fouling and slagging are the chief concerns.

Carty, R.H.; Lau, F.S.; DeLong, M.; Wiant, B.C.; Bachovchin, D.M.; Ruel, R.H. 1994. "Commercialization of the RENUGAS Process for Biomass Gasification," presented at the Thirteenth EPRI Conference on Gasification Power Plants, Oct. 19–20, 1994, Palo Alto, CA.

Typical gas product from whole-tree chips, using the IGT PDU: Total oil yield (lb oil/100 lb feed: O_2; 1.1 and air 2.3; C_6H_6: 0.48, O_2 and 0.53, air (vol %). "Condensation is avoided at gas temperature above 1,000°F. Some of the heavier tar compounds may be subject to coking in the filter if not removed by a tar cracker."

Chen, G.; Brage, C.; Yu, Q.; Rosén, C.; Sjöström, K. 1997. "Co-Gasification of Woody Biomass with Coal in Pressurized Fluidized Bed Reactor," in *Proceedings of the 3rd Biomass Conference of the Americas, Vol. 1*. Edited by R.P. Overend and E. Chornet. Canada: August, p. 663.

"The formation of tar in co-gasification was somehow different from the formation of both biomass tar and coal tar." (Abstract only available.)

Chen, G.; Yu, Q.; Brage, C.; Rosén, C.; Sjöström, K. 1998. "Synergies in Co-Gasification of Biomass with Coal in Pressurized Fluidized Bed Reactor," in *Biomass Energy and Industry*. Edited by H. Kopetz, T. Weber, W. Palz, P. Chartier, and G.L. Ferrero. 10th European Conference and Technology Exhibition, Würzburg, Germany, C.A.R.M.E.N., pp. 1552–1555.

Chowdhury, R.; Chakravarty, M.; Bhattacharay, P. 1992. "Prediction of Venturi Scrubber Efficiency Used in an Updraft Gasifier Cleaning Train," *Int'l. J. Energy Res*. 16, pp. 731–741.

Chrysostome, G.; Lemasle, J.M. 1986. "Fluidized Bed Oxygen Gasification of Wood," *Energy from Biomass and Wastes* 8, pp. 29–71.

Clark, S.H.; Dicks, A.L.; Pointen, K.; Smith, T.A.; Swan, A. 1997. "Catalytic Aspects of the Steam Reforming of Hydrocarbons in Internal Reforming Fuel Cells," *Catalysis Today* 38, pp. 411–423.

Both the MCFC and the SOFC operate at high enough temperatures to take advantage of the benefits of internal fuel reforming (typically 650°C and 800°C, respectively). Carbon may be formed by thermal cracking of hydrocarbons in the absence of air. Thermal or steam cracking of hydrocarbons can occur above 600°–650°C, even in the absence of Ni catalysts. The cracking leads to olefins followed by a carbonaceous polymer, which can dehydrogenate to produce coke. It is common to carry out some pre-forming of hydrocarbon feeds, such as natural gas, to remove

the C_2+ hydrocarbons before the gas is fed to the main reformer. There is a need to establish if fuels such as liquefied petroleum gas, propane, naphtha, or alcohols can be internally reformed. Early work by Westinghouse suggested that carbon deposition was a major concern for SOFC, particularly from the decomposition of higher hydrocarbons in the feed.

Clift, R.   1988. "Hot Gas Cleanup: The State-of-the-Art and Prospects for the Future," in *Proceedings of the VTT Symposium 83: Pressurized Fluidized Bed Combustion and Gasification Power Systems.* Espoo, Finland: Technical Research Centre of Finland.

Mainly reviews particulate problem with coals. Tar mentioned only as a component of char. HCl and NaCl real issues in some coals. See Singh, A. et al. I. Chem. E. Symp. Ser 99, p. 167 (1986).

Corella, J. 1996. "Thermochemical Biomass Conversion: Upgrading of the Crude Gasification Product Gas, Final Synthesis Report," Agro-Industrial Research, EC/AIR, project: AIR2-CT93-1436.

A summary of results for tar cracking using synthetic tar (TPS-AB) and actual gasifier output (KTH). Dolomites and Ni catalysts tested. Engines need tar content less than 20–500 mg/Nm^3. An optimized operation of a fluidized-bed gasifier can produce only as low as about 2 gm/Nm^3. Above this level Ni catalysts cannot be used due to coke laydown. Increasing equivalence ratio from 0.2–0.45 only reduces tar by 50%, while increasing H/C (by steam) from 1.6 to 2.2 decreases tar by 75%. In-bed use of dolomite leads to troublesome elutriation of fines. At pressurized condition, dolomite is deactivated by carbonate formation. At 10 bar it may need to operate at >920°C. Tars produced in air gasification are more refractory than those produced in steam. Under some conditions, dolomite has remained active for 16 hours. See reports by these groups for details.

Corella, J.; Adanez, J.; Gonzalez-Saiz, J.; Herguido, J. 1987. "Steam Gasification of Biomass in a Fluidized Bed Reactor," in *Biomass for Energy and Industry (4th EC Conference).* Edited by G. Grassi, B. Delmon, H.Y. Zibetta, and J.F. Moulle. London: Elsevier Applied Science, pp. 1107–1111.

Small fluid bed gasifier, with bottom feeding, produced about 2.4% of C_2+ in gas at 750°C.

Corella, J.; Aznar, M.P.; Cebrián, N.; Iglesias, J.I.; Martinez, M.P. 1989a. "Steam Gasification of Biomass in Fluidized Bed with a Secondary Catalytic Bed-I. Results with the Secondary Reactor Empty and with Sand," in *Pyrolysis and Gasification*. Edited by G.L. Ferrero, K. Maniatis, A. Buekens, and A.V. Bridgwater. London: Elsevier Applied Science, pp. 624–628.

Gasification studies of tar in a 6-cm i.d. fluidized-bed, top-fed gasifier show no change in tar composition when the raw gas is fed to an empty secondary bed (later to be filled with tar-cracking, methanation, and steam-reforming catalysts. Raw gas yields about 100 g/Nm^3 of tar at 750°C (quotes 76 g/Nm^3 ≡ 0.059 kg/kg dry feed).

Corella, J.; Aznar, M.P.; Delgado, J.; Aldea, E.; Martinez, P. 1992. "Fuel and Useful Gas by Steam Gasification of Biomass in a Fluidized Bed Followed by a Tar Cracking Fluidized Bed of Dolomite/Limestone/Magnesite," in *Biomass for Energy, Industry and Environment* (6th E.C. Conference). Edited by Grassi, Collins, and Zibretha. London: Elsevier, pp. 714–720.

Dolomite, calcite, and magnesite, all from Spain. These "stones" are stated to be very cheap. Several techniques used for analysis, including TOC, were tested. Above 1 mm particle size of dolomites, diffusion controls tar cracking. Calcite has about same activity as dolomite but magnesite is much poorer.

Corella, J.; Aznar, M.P.; Delgado, J.; Aldea, E. 1991a. "Steam Gasification of Cellulosic Wastes in a Fluidized Bed with Downstream Vessels," *Ind. Eng. Chem. Res*. <u>30</u>, pp. 2252–2262.

Metal filter (porous Inconel); calcined silica sand and carbonaceous solids were tested. Tars said to be mainly polynuclear aromatics. Condensibles and gases to C_2 are reported. Many techniques such as weighing, TOC, LC, HPLC to measure organic content. Behavior of filter, second reactor, and sand with temperature and residence time. Temperature to 850°C. Gasifier, filter, second fluid catalytic bed, baseline study to assess non-catalytic thermal effects and deactivation of the sand. "The hot filter chamber, the silica sand in the second bed and the carbonaceous solids formed are not inerts, but they crack the produced tars . . . "

Corella, J.; Aznar, M.P.; Delgado, J.; Martinez, M.P.; Aragües, J.L. 1991b. "The Deactivation of Tar Cracking Stones (Dolomites, Calcites, Magnesites) and of Commercial Methane Steam Reforming Catalysts in the Upgrading of the Exit Gas from Steam Fluidized Bed Gasifiers of Biomass and Organic Wastes," in *Catalyst Deactivation*. Edited by C.H. Bartholomew and J.B. Butt. Amsterdam: Elsevier, pp. 249–253.

Tested following catalysts: Calcined stones such as dolomites, calcites, and magnesites; Commercial methanation catalysts, mainly Topsoe R-67. Typical product distribution from the fluid-bed gasifier (6 cm id) is 80 wt % gas, 10 wt % tar and 10 wt % char. Calcined stones crack tars at 800°–880°C steam-reforming, Ni catalysts run at 680°–760°C methanation catalysts at 300°–400°C. All the catalysts tested so far deactivate seriously in 1–8 hours, due to coke.

Corella, J.; Aznar, M.P.; Gil, J.; Caballero, Francés; E., Martin, J.A. 1998. "Advances in Catalytic Hot Gas Clean Up and Conditioning at Pilot Scale with Nickel Based Catalysts in Fluidized Bed Biomass Gasification," in *Biomass for Energy and Industry*. Edited by H. Kopetz, T. Weber, W. Palz, P. Chartier, and G.L. Ferrero. 10th European Conference and Technology Exhibition, Würzburg, Germany, C.A.R.M.E.N., pp. 1794–1797.

Corella, J.; Aznar, M.P.; Martinez, M.P.; Iglesias, J.I. 1990. "Steam Gasification of Biomass in Fluidized Bed with a Secondary Catalytic Bed-III. Use of Methanation Catalysts," in *Biomass for Energy and Industry (5th E.C. Conference)*, Vol. 2. Edited by G. Grassi. London: Elsevier Applied Science, pp. 2749–2754.

Methanation catalyst Harshaw Ni-3288. Others tested but results not reported. Used separate reactors for methanation and gasification. Tar in real gasifiers deactivates the methanation

catalyst by coke formation that exceeds that from $2CO \rightarrow CO_2 + C$. Need to limit tars before the methanation catalyst.

Corella, J.; Herguido, J.; Alday, F.J. 1988b. "Pyrolysis and Steam Gasification of Biomass in Fluidized Beds. Influence of the Type and Location of the Biomass Feeding Point on the Product Distribution," in *Research in Thermochemical Biomass Conversion*. Edited by A.V. Bridgwater, J.L. Kuester. London: Elsevier Applied Science, pp. 384–398.

In fluidized beds, top feeding gives much more tar and less gas than bottom feeding. At 750°C top feed gave ~15% tar, bottom feed, ~3%.

Corella, J.; Herguido, J.; González-Sáiz, J. 1989b. "Steam Gasification of Biomass in Fluidized Bed. Effect of the Type of Feedstock," in *Pyrolysis and Gasification*. Edited by G.L. Ferrero, K. Maniatis, A. Buekens, and A.V. Bridgwater. London: Elsevier Applied Science, pp. 618–623.

Tar yields from a 15-cm i.d. continuous fluidized-bed gasifier vary from about 8 to about 4 wt % of dry feed from 650°–780°C with only minor differences in yield for the feedstocks straw, pine woodchips, pine sawdust, and thistle.

Corella, J.; Herguido, J.; González-Sáiz, J.; Rodrígez-Trujillo. 1988a. "Fluidized Bed Steam Gasification of Biomass with Dolomite and with a Commercial FCC Catalyst," in *Research in Thermochemical Biomass Conversion*. Edited by A.V. Bridgwater, J.L. Kuester. London: Elsevier Applied Science, pp. 754–765.

An "in equilibrium" spent FCC catalyst and dolomite were tested. Tar in: No analysis. Tar out: No analysis, measure gas and LHV increase. Conditions studied: Fluidized bed, with added catalyst or catalyst/biomass co-feed. FCC catalyst is quickly elutriated from the bed. Dolomite is quickly eroded. Need circulating fluidized bed. Both are very active in cracking. Dolomite in bed reduced tar from 6.5% to 1.29%. C_2S not much affected. (One wt % of feed as tar = about 5,000 mg/Nm^3.) Don't recommend dolomite use in fluid bed unless harder form can be found. Tar cracking increases CH_4 and C_2S.

Corella, J.; Narváez, I.; Orío, A. 1996a. "Advanced Gasification of Biomass with Downstream Commercial Steam Reforming Catalysts for Hot Flue Gas Cleaning: Comparison of Different Catalysts with Their Apparent Kinetic Constants for Tar Conversion," in *9th European Bioenergy Conference and 1st European Energy from Biomass Technology Exhibition*. Edited by P. Chartier et al. Pergamon, p. 368.

Use three-stage facility at Madrid. Continuous, 6-cm fluid-bed reactor with bottom feed, followed by a hot metallic filter (500°–600°C) and a catalytic bed with commercial steam reforming catalyst. Before the catalytic bed there is a guard bed of dolomite to eliminate 90% of the tar and sulfur present. Tested BASF, ICI, Topsoe, Engelhard, and United Catalysts. Achieved a very clean exit gas with only 1 mg tar/Nm^3 (tar not defined) for some catalysts. Abstract only available.

Corella, J.; Narváez, I.; Orío, A. 1996b. "Criteria for Selection of Dolomites and Catalysts for Tar Elimination from Biomass Gasification Gas; Kinetic Constants," in *New Catalysts for a Clean Environment. Second Symposium of the VTT Research Programme on Chemical Reaction Mechanisms*. Espoo, January. Edited by A. Maijanen and A. Hase. VTT Technology Group, pp. 177–183.

Notes the dependence of the apparent catalytic kinetic constant on the analysis method used for tar.

Corella, J.; Narváez, I.; Orío, A. 1996c. "Effectiveness Factors for a Commercial Steam Reforming (Ni) Catalyst and for a Calcined Dolomite Used Downstream Biomass Gasifiers," in *New Catalysts for Clean Environment. Second Symposium of the VTT Research Programme on Chemical Reaction Mechanisms*. Espoo, January. Edited by A. Maijaanen and A. Hase. VTT Technology Group, 7 pp.

The importance of particle size and diffusional effects in comparing catalyst effectiveness is discussed and illustrated.

Corella, J.; Narváez, I.; Orío, A. 1995a. "Fresh Tar (from Biomass Gasification) Destruction with Downstream Catalysts: Comparison of Their Intrinsic Activity with a Realistic Kinetic Model." Espoo, Finland: *Seminar on Power Production from Biomass II,* 6 pp.

"Tars produced in the gasification of biomass with steam are different than those produced in spruce gasification of biomass in air or with steam +O_2." No data or reference given.

Corella, J.; Narváez, I.; Orio, A. 1995b. "Biomass Gasification in Fluidized Bed: Hot and Catalytic Raw Gas Cleaning. New Developments," in *Proceedings of the 8th European Biomass Conference, Biomass for Energy, Environment, Agriculture and Industry*. Edited by P. Chartier, A.A.C.M. Beenackers, and G. Grassi. Pergamon, pp. 1814–1818.

"The tar sampling and analysis methods can significantly modify the number for the tar content. So, precision in such sampling procedures and measurement is basic--.." Using a new bench scale primary fluid bed air gasifier, with 0.5 kg/h throughput and feeding of biomass at the bottom of the bed, unlike the earlier bench scale system. With dolomite or magnesite guard beds, and G1-25-S steam reforming catalyst the tar content was reduced from 82–36 g/Nm^3 to 0.9–1.3 g/Nm^3 after the guard bed, to 10–100 mg/Nm^3 after the catalytic fluid bed.

Corella, J.; Orío, A.; Narváez, I.; Aznar, M.P.; Gil, J.; Martin, J.A. 1996d. "Biomass Gasification in Fluidized Bed with Calcinated Dolomites for Downstream Gas Cleaning: Effect of the Tar Sampling and Analysis Methods and of the Kinetic Analysis on the Final Evaluation," in *9th European Bioenergy Conference and 1st European Energy From Biomass Technology Exhibition*. Edited by P. Chartier et al., Pergamon, p. 373.

Six different dolomites studied. Use simple kinetic model to compare activities based on tar disappearance (reforming, cracking, etc.). We have checked how the overall kinetic constraints can change a lot depending on how the tar sampling and analysis is made.

Coutts, T.J.; Benner, J.A. (eds.) 1994. "The First NREL Conference on Thermophotovoltaic Generation of Electricity," in *AIP Conference Proceedings 321*. New York: AIP Press.

A continuing series, organized by the National Renewable Energy Laboratory, Golden, CO.

Craig, J.D. 1994. "Development of a Small Scale BIGGT Power Plant," in *Sixth National Bioenergy Conference*, Reno/Sparks, NV, October 2–6, pp. 441–448.

For their air-blown system, all gas cleaning processes must be dry and very simple. Particulate filter uses sintered metal. "There was some noticeable tar condensation on the sample filters" (24-h run). Typical product gas: C_2H_4 1.0% mol %; C_2H_6 0.3; particles 3.1 ppmw.

Craig, K.R.; Koch, R.W. 1988. "Gas Cleanup Systems Analysis." Morgantown, WV: Morgantown Energy Technology Center.

Treats coal IGCC. Claims hot-gas cleanup saves in all cases, even for methanol synthesis. No tar discussion.

CRE Group Ltd. 1997. "Identification and Processing of Biomass Gasification Tars," Energy Technology Support Unit (ETSU), Department of Trade and Industry, DTI Contract No. B/T1/00418/00/00.

Presents the results of centralized analysis of collected tars from: UK updraft and downdraft fixed-bed; fluidized-bed (Lund); and entrained-bed (DMT) gasifiers. Tars from the UK updraft gasifier ESP showed signs of considerable post-deposit reaction. "In-situ" sampled tars were "highly polar, consisting essentially of phenol and methoxy-type compounds and to a lesser extent polynuclear aromatic hydrocarbons (PAHs)." The tar from the downdraft gasifier, by in-situ sampling, "was comparable with the species identified in the updraft tars, the main difference being the lower concentration of compounds with molecular weights > 150 and more importantly the absence of high molecular weight PAHs > 200." The tar and condensate from the Lund fluidized-bed gasifier was mainly composed of "essentially parent PAHs containing a small proportion of oxygenated (polar) components." The entrained flow DMT tars were "essentially parent PAHs." Minor concentrations of nitrogen species were seen from this straw-fired gasifier. Tables of identified compounds in the tars are presented from both qualitative and quantitative GC/MS and direct insertion probe MS data. Tar components are expressed as g/Kg of tar but tar as percentage of feed is not given. In-situ sampling of the fixed-bed gasifier was through a heated probe, with condensation of tar vapor in acetone at -55°C DMT condensed tar and water are cooled in water-cooled heat exchanger. Lund captures tar in a vessel cooled in an ice bath and aerosol capture vessels. It is recommended to store tar samples at -50°C to prevent polymerization and loss of volatiles. Thermal and catalytic destruction of model compounds and updraft gasifier tar was studied. Catalysts were a dolomite and a Ni/Mo catalyst. The Ni/Mo was more active but the dolomite produced a more favorable cracking pattern and no coke. Ni/Mo produced no coke at 400°–600°C. Combined thermal and catalytic cracking offers advantages whereas thermal alone needs T > 1000°C. The authors call for the development of a European standard "for the sampling and quantification of condensible compounds found in biomass thermochemical processes."

Cuda, R.; Ziak, R. 1995. "Gas Cleaning and Conditioning, Part 1. Theoretical Background, Construction, Properties, Experiments," *Nordvestuysk Folkecenter for Vedvarfende Energi*, Hurup, Denmark, 32 pp.

Brief review of gas cleaning approaches for gasifiers to be coupled to Stirling and ICEs. No quantitative fuel specifications are given, but advantages of the Stirling are acknowledged. "The cross-draught gasifier operates with the gas flow perpendicular to the bed. It is used only with charcoal feedstocks and operating temperature are usually in excess of 1500°C. . ." Tars not discussed as such.

Das, A. 1985. "Contaminant Testing Method for Biomass Gasifier Engine Systems," *The Tipi Workshop*. Golden, CO: Biomass Energy Foundation Press.

Long engine life and reliable operation requires a gas with less than 30 mg of tar and particulates per cubic meter (30 ppm).

Dasappa, S.; Shrinivasa, U.; Baliga, B.N.; Mukunda, H.S. 1989. "Five-Kilowatt Wood Gasifier Technology: Evolution and Field Experience," *Sadhana* <u>14</u> (3), pp. 187–212.

Compares performance of old, closed-top downdraft gasifier with new, open-top gasifier (after Reed). Typical tar and particulate levels of open top, after cooling and cleaning; Tar, 50–120 ppm; particulates, 80–150 ppm.

Dayton, D.C.; Evans, R.J. 1997. "Laboratory Gasification Studies via Partial Oxidation of Biomass Pyrolysis Vapors," in *Proceedings of the 3rd Biomass Conference of the Americas, Vol. 1*. Edited by R.P. Overend and E. Chornet. Canada: August, pp. 673–82.

Partial oxidation of switchgrass as a function of pyrolysis temperature, steam, and O_2 concentration, was studied by MBMS in a flow reactor simulation of gasification conditions of partial oxidation. To simulate gasification, O_2 was added downstream of the pyrolysis of single switchgrass particles (50 mg). The "tar" species monitored were benzene, toluene, and phenol. More benzene was formed at the higher pyrolysis temperature and the lower O_2 concentrations. The addition of steam tends to enhance the formation of benzene. The formation of toluene tends to track that of benzene. More phenol was produced at the lower pyrolysis temperatures at low O_2 concentration. Steam enhanced the phenol production.

DeCorso, M.; Newby, R.; Anson, D.; Wenglarz, R.; Wright, I. 1996. "Coal/Biomass Fuels and The Gas Turbine: Utilization of Solid Fuels and Their Derivatives," *ASME Paper*, 96-GT-076, 13 pp.

References to hot sulfur removal methods, "The use of dry separation methods is critical to the successful use of pressurized fluidized combustion and pressurized air blown gasification systems, for which the costs and thermal losses incurred in wet scrubbing are unacceptable."

Quotes tar levels after hot filter cleaning: Air-blown gasifier 500 ppm or 150 mg/Mj; O_2-blown gasifier: ~0 (coal). Sulfur in biomass usually about 0.1% or less but still can cause slagging effects.

Deglise, X.; Magne, P.; Donnot, A.; Large, J.F.; Molodtsof, Y.; Lelan. A. 1992. "Catalytic Pyrolysis," in *Biomass for Energy, Industry and Environment, 6th E.C. Conference*. Edited by G. Grassi et al. Elsevier, pp. 650–656.

Describes T.N.E.E's fast pyrolysis-gasification process in a dual fluidized bed system. The temperature level of the heat carrier entering the pyrolysis reactor had to be higher than 900°C for "good detarring action."

Deglise, X.; Magne, P.; Donnot, A.; Reningovolo, J. 1985. "Wood Tars Cracking in Gasifiers: Kinetics Data," paper 13-12 in *Symposium on Forest Products Research International— Achievements and Future*, CSIR Conference Centre, Pretonn, Republic of South Africa, April.

In a two-stage system, pyrolysis tars were reacted in the second stage, with and without catalyst. Conclusion: We have determined tar residence times for almost complete conversion (at a ratio of 10^{-4}) and we found rather high values from 15 s at 800°C to 5 s at 1,000°C. These values confirm that it is not possible to decompose tar in the fluid-bed gasifiers.

Common siliceous sand increases slightly the decomposition rate of tar coming from pine bark pyrolysis. On the other hand, decarbonated dolomite and even carbonated dolomite have significant catalytic efficiencies. However, it seems difficult, if not impossible, to use them as a heat carrier in fluid-bed gasifiers because they are too soft and would be very quickly transformed into dust and carried along with the gases or the smoke.

Delahay, G.; Duprez, D. 1989. "Effects of Dispersion and Partial Reduction on the Catalytic Properties of Rh/Al_2O_3 Catalysts in the Steam Reforming of Mono- and Bicyclic Aromatics," *J. Catalysis* 115, pp. 542–550.

Catalysts: Variations on Rh/Al_2O_3. Tar in: Toluene, cumene, and methy l-1-naphthalene as model compounds. Tar out: Looked at dealkylation, dehydrogenation,and degradation (ring opening, followed by transformation to CO_x and H_2). Conditions studied: steam reforming.

Delgado, J.; Aznar, M.P.; Corella, J. 1997. "Biomass Gasification with Steam in Fluidized Bed: Effectiveness of CaO, MgO, and CaO—MgO for Hot Raw Gas Cleaning," *Ind. Eng. Chem. Res.* 36 (5), pp. 1535–1543.

Refers to the tobacco companies' world-wide standardized methods of tar collection and analysis. But each biomass gasifier uses its own method, with no equivalence between numbers for tar yields or composition. Repeats their method of tar determination. Water and tar condensate is first filtered. Non-soluble fraction remains in coke. Coke is treated with acetone for tar extraction. Acetone solution is distilled at 80°C giving a residue named "nonsoluble tars." The filtered water is analyzed to obtain soluble organic compounds by TOC method.

Vassilatos et al. (1992) demonstrated that naphthalene is the dominant component of tar when the gasifier raw gas is treated over a hot bed of dolomite.

Delgado, J.; Aznar, M.P.; Corella, J. 1996. "Calcined Dolomite, Magnesite, and Calcite for Cleaning Hot Gas from a Fluidized Bed Biomass Gasifier with Steam: Life and Usefulness," *Ind. Eng. Chem. Res.* 35 (10), pp. 3637–3643.

Tar Definition: Condensed fraction with steam. Wash with acetone to extract tar. How Measured: Tar yields and destruction depend on how tar is measured. Destruction Method: Catalytic. Sum of soluble and insoluble tar gives tar content of gas.

Delgado, J.; Aznar, M.P.; Corella, J. 1995. "Fresh Tar (from Biomass Steam Gasification) Cracking over Dolomites: Effect of Their Particle Size and Porosity," in *Proceedings of the 8th European Biomass Conference, Biomass for Energy, Environment, Agriculture and Industry*, Edited by P. Chartier, A.A.C.M. Beenackers, and G. Grassi. Pergamon, pp. 1825–1829.

Tars in biomass gasification range from 10–200 g/Nm^3. "Tar causes fouling and corrosion of equipment, downstream catalyst deactivation, environmental pollution and a serious health damage." Under proper porosity and particle size conditions, dolomite can clean raw gas to 0.5 g/Nm^3 at gasification temperature of 780°C and ratio of steam/biomass of 1. Catalyst deactivation is negligible under these conditions.

Denniss, T. et al. 1996. "Development and Testing of an Entrained Flow Gasifier Power Generating Unit," ERDC 269, ISBN 0 642 19164 6. Australia: Energy Research and Development Corporation.

Description of cyclonic combustor/reducer gasifier. Refined the gas cleaning system to ensure that particle and tar loadings to the engine were less than 200 mg/Nm^3 and 50 mg/Nm^3, respectively. There was no tar buildup on the intake to the engine. Gas cleaning consisted of two hot cyclones, a spray tower, an impingement scrubber, a centrifugal tar separator, a rotary swirl scrubber and a demister.

De Ruyck, J.; Allard, G.; Maniatis, K. 1996. "An Externally Fired Evaporative Gas Turbine Cycle for Small Scale Biomass Gasification," in *Biomass for Energy and Environment: Proceedings of the 9th European Bioenergy Conference, June 1996*. Edited by P. Chartier et al. Pergamon, pp. 260–265.

Describes plans for a system based on producer gas de-dusted to 500 mg/Nm^3. Expected gas temperatures will be 600°C, high enough to avoid tar condensation. Eventually, dedicated gas-cleaning will be considered if deposition or corrosion are too important. Dinamec NV gasifier (Belgium).

Desilets, D.J.; Kissinger, P.T.; Lytle, F.E.; Horne, M.A.; Ludwiczak, M.S.; Jacko, R.B. 1984. "Determination of Polycyclic Aromatic Hydrocarbons in Biomass Gasifier Effluents with Liquid Chromatography/Diode Array Spectroscopy," *Enviro. Sci. Technol.* 18, pp. 386–391.

To downdraft gasifiers at pilot and full scale were sampled and the tars analyzed. Can distinguish unsubstituted PAH and their methylated analogues. Naphthalene through coronene were identified.

De Sousa, L.C.; Hütter, P.; Mayor, J.C.; Quintilii, M. 1994. "Fluidized Bed Reactor for the Gasification of Biomass," *Annual Report 1994, Annex V, PSI General Energy Technology, Newsletter 1994*, Paul Scherrer Institut.

Describes the BIOMETH laboratory gasifier. Tars identified as aromatic and polyaromatic compounds. Tars are collected by a multi-stage condenser/absorber sampling train. Determine light tars (B.P. 80°-400°C benzene-pyrene) by GC. Heavy tars (B.P. > 400°C pyrene-coronene), are quantified gravimetrically only. No tar data.

De Sousa, L.C.; Stucki, S. 1997. "Gasification of Urban Waste Wood in a Fluidized Bed Reactor," in *Proceedings of the 3rd Biomass Conference of the Americas, Vol. 1*. Edited by R.P. Overend and E. Chornet. Canada: August, pp. 447–452.

Results from a laboratory-scale fluidized bed research facility at PSI are presented (The Biometh Project). "Tars are collected by a multi-stage condenser/absorber sampling train. Light tars (boiling point 80°–400°C, benzene-pyrene) are identified and quantified by GC. Heavy tars (boiling point above 400°C, pyrene-coronene) are quantified gravimetrically only." Heavy tars amounted to 2.2 g/Nm^3 out of a total tar content of 12.6 g/Nm^3. For the experiment reported, the following tar compounds were quantified as follows:

Compound	Concentration in mg/Nm^3
Benzene	4,700
Toluene	1,300
Xylene	96
Styrene	600
Phenol	550
Naphthalene	1,800
Indene	0.00
2-methylnaphthalene	160
1-methylnaphthalene	200
Biphenyl	50
Acenaphthene	0.00
Flourene	230
Phenanthrene	320
Anthracene	180

Deutch, S. 1998. "Rapid Screening Process for Gasifier Tar Sampling Methods," poster paper presented at the IEA/EC/USDOE session on Tar Protocol, Workshop WS2 at the 10th European Conference and Technology Exhibition, June 8–11. *Biomass for Energy and Industry*.

The NREL MBMS is applied to the behavior of a synthetic "tar" (benzene, naphthalene, toluene) in various trapping solvents, as a function of time.

Dibella, C.A.W.; Fillo, J.P.; Koraido, S.M. 1987. "Contaminant Control in Four Advanced Coal Conversion Power Generation Systems: Technical Issues and R&D Needs." Final Report. KOH Systems, Inc. Rockville, MD. DOE/MC/22012-2302.

Potential contaminants of concern to environment or equipment: H_2S, COS, SO_2, mercaptans, NH_3, HCN, NOx; Na + K chlorides and fluorides, organics (e.g., tars, oils, light hydrocarbons). Destruction Method: For fixed-bed IGCC, tar cracker not specified. Just keep T high enough to prevent condensation. Some HC destruction in zinc ferrite system. For fluidized bed gasifier, bottom-bed feeding is assumed so tars and oils will not be appreciable. Volatile aromatics (B, T, and X) will carry through and be burned in turbine. Zinc ferrite will not affect tars much, but need study of organics on zinc ferrite bed. Tar/oil production and condensation is not an issue in the fluidized-bed system.

Dicks, A.L 1998. "Advances in Catalysts for Internal Reforming in High Temperature Fuel Cells," *J. Power Sources* <u>71</u>, pp. 11–122.

"Some external pre-reforming may be desirable to remove high molecular weight hydrocarbons from the fuel gas, which would otherwise crack to produce elemental carbon."

For the Wellman updraft gasifier a combination of thermal and catalytic processes is best for tar cracking. Kurkela reported that biomass typically produces 100 times more tars than does coal.

Dinkelbach, L.; Kaltschmitt, M. 1996. *Analysis and Coordination of the Activities Concerning a Gasification of Biomass* (AIR3-CT94-2284), Minutes, Second Workshop. Espoo, Finland.

Dinkelback, L.; Klein Teeselink, K.; van der Meijen, C.M.; Neeft, J.; Schenk, E.P.; Ytsma, S.D. 1998. "Gasification of Wood Waste from Public Gardens for CHP Production," in *Biomass for Energy and Industry*. Edited by H. Kopetz, T. Weber, W. Palz, P. Chartier, and G.B. Ferrero. 10th European Conference and Technology Exhibition, Würzburg, Germany. C.A.R.M.E.N., pp. 1761–1764.

Dittrich, V. 1995. "Fluidised-Bed Gasification of Biomass," in Seminars on Power Production from Biomass II. Espoo, Finland, March. VTT.

Destruction Method: Run gasifier above 850°C. Getting ready to run in ICE. Typical raw-gas tar 0.4–2.0 g/m³. At 850°C, 0.5 g/m³. ATEKO a.s. converted a fluidized-bed air gasifier from lignite to sawdust in 1993. Capacity 30 kg/h. Temperatures above 800°C significantly suppress tar. Tests are under way with a gas combustion engine.

Donnot, A.; Magne, P.; Deglise, X. 1991a. "Experimental Approach to the Catalyzed Cracking Reaction of Tar from Wood Pyrolysis," *J. Analy. Appl. Pyrolysis* 22, pp. 265–280.

Catalysts: (1) Soaked various salts into graphon (carbon black) (Ni, Cu, Fe, Ca, Na, Mg, Zn salts). (2) Ni and Na salts on alumina (inactive) and decarbonated. (3) Some of same catalysts reported earlier. Tar in: (1) Collected condensed tar and re-fed by syringe. (2) Same apparatus as in Donnot 85. Tar out: First breakthrough detected by change in color of cotton filter. (Occurs when fractional conversion is less than 0.975.) How measured: IR and GC after dry-ice-acetone trap. Conditions studied: 600°–700°C for salts on graphon. The TNEE dual fluidized-bed pyrolysis unit produces a pyrolysis gas with ~1% tar and thus is unsuitable for running engines. Ni the best salt catalyst.

Donnot, A.; Magne, P.; Deglise, X. 1991b. "Kinetic Parameters of the Cracking Reaction of Tar from Wood Pyrolysis; Comparison of Dolomite with Industrial Catalysts," *J. Analy. Appl. Pyrolysis* 22, pp. 47–59.

Tar Definition: Condensibles ~ more than 100 compounds. Destruction is defined as % conversion to gas, or to nothing but naphthalene.

Donnot, A.; Magne, P.; Deglise, X. 1991c. "Method of Determining Catalyst Lifetime in the Cracking Reaction of Tar from Wood Pyrolysis," *J. Analy. Appl. Pyrolysis* 22, pp. 39–46.

Catalysts: (1) Mg, Cu, Zn, Ni, Fe, and Na deposited on graphon. (2) Ca salt deposited on graphon and decarbonated dolomite. (3) Commercial anti-soot product called "Vulcain." Examines poisoning effects. Measured g of tar/g of catalyst for salts. Ranged from 3.33 for Ni $(NO_3)_2$ down to 0.07 for Mg $(CH_3 CO_2)_2$. Catalyst deactivation is "mainly due to the deposition of a thin layer of carbon on the catalyst surface."

Donnot, A.; Magne, P.; Deglise, X. 1985. "Flash Pyrolysis of Tar from the Pyrolysis of Pine Bark," *J. Analy. Appl. Pyrolysis* 8, pp. 401–414.

Catalysts: (1) Fontainbleau silicious sand (~100% alpha-quartz) 0.72 m^2/gm; (2) Dolomite (Ni 60 ppm. Cr 50 ppm, V40 ppm). MgO 20%, CaO 32.3% and CO_2 46.5%; BET 0.89 m^2/g (Kr). Decarbonated at 900°C before study; (3) Recarbonated dolomite. Tar in: Pure bark at 650°C dropped on grid. Tar out: Filtered. Gas only analyzed to C_2s. How measured: condensate on a cotton filter at dry ice-acetone temperature. GC of gases up to C_2H_6 after drying. Tar destruction defined as conversion of C_2s. Conditions studied: 600°–1,000°C Various reductions from ~1–15 sec. (See work by Ekström and by Chembukulam.) Fixed-bed pyrolysis of pine bark at laboratory scale. Assume first order pyrolysis. Decarbonated dolomite effective, but too soft to use in a fluidized bed. Converting tar completely to gas requires >1,100°C without catalyst.

Duprez, D. 1992. "Selective Steam Reforming of Aromatic Compounds on Metal Catalysts," *Applied Catalysis A: General* 82, pp. 11–157.

Treats many aromatics of interest to gasifier tars.

Easterling, J.C.; Keenan, D.J.; Brenchley, D.L.; Russell, J.A. 1985. "Identifying the Barriers to Commercialization of Low-Btu Gasifiers: Proceedings of a Workshop," in *Proceedings of the Low-Btu Gasifier Workshop, Southeast Industrial Biomass Conference.* Atlanta, GA, 50 pp.

The panels called for controlled testing of the effects of tar, char, and ash, as well as alkali, on turbines. Almost all panels called for standards development. In particular, ASTM, EPA-5, and other test methods should be modified to create new standards acceptable to the gasification industry. Working Group #1 on cogeneration called for an assessment of tar, char, and ash effects on engines, and the testing of cleanup approaches under controlled conditions. Effects on lubricating oil are especially important. In the ranking of needs, standards were given the greatest attention followed by testing and evaluation.

Ekström, C.; Lindman, N.; Pettersson, R. 1985. "Catalytic Conversion of Tars, Carbon Black and Methane from Pyrolysis/Gasification of Biomass," in *Fundamentals of Thermochemical Biomass Conversion.* Edited by R.P. Overend, T.A. Milne, and L.K. Mudges. London and New York: Elsevier Applied Science, pp. 601–618, Nov. 82.

Catalysts: Dolomite, char, Ni-based catalyst. Tar in: Total slate from fast pyrolysis of salix, hardwoods, and peat at $700°–750°C$ How measured: weight of condensate. Conversion of tars goes through primary tar; secondary tar and residual tar. Operate Ni catalyst at $900°–1000°C$, dolomite at $700°–800°$. For primary tar at 50 gm, get secondary tar of 15 and 3 g at $700°C$ and $900°C$ respectively. Residual tar after carbon black is 3 g at $750°C$ ~0.1 over dolomite; and ~0.1 over Ni.

Electric Power Research Institute. 1985. "Biomass Gasification for Electric Utility Diesel Generating Units," EPRI AP-3865.

A literature search on gasifier-diesel systems, going back into the 1930s, identified 79 references from which 25 were selected for review. References to early experience are given, but contain no information on endurance tests. Gasifiers used included 16 downdrafts, three fluid beds, and four crossdrafts. Few researchers have measured the condensible tars or particulates in the primary gas. "There is no evidence to indicate the degree of gas cleanliness required by a utility-size diesel engine." "Burns and McDonnell believe there is no technical reason why low BTU gas cannot be applied in gen combustor-chamber diesel engines. Indeed, there are good technical reasons why a diesel engine is to be preferred."

Electric Power Research Institute. 1984. *Proceedings: EPRI/TVA Workshop on the Use of Biomass for the Generation of Electric Power.* EPRI AP-3678. Prepared by Battelle Columbus Laboratories.

Should look at Stirling engines and indirect-fired turbines. See EPRI RP-1348-16 (Fuels for Diesels). See AP-2265 (1982) BCL. Biomass Systems for Electricity Generation. AP-25617 (1982) Syn. Fuels Assc. Technical Evaluation of Wood Gasification. AP-3101 (1983) Fred Hart. Survey of State-of-the-Art Wood Gasification Technology.

Electric Power Research Institute Journal. 1997. "Market Potential High for Fuel Cells," May/June, pp. 8–17.

With government support, Arthur D. Little has developed a compact, lightweight reformer that converts gassoline and other fuels into hydrogen-rich gas. Westinghouse has tested a 25-kW SOFC module on jet fuel and diesel fuel (requiring a separate fuel-processing unit) in addition to natural gas.

Ellig, D.L.; Lai, C.K.; Mead, D.W.; Longwell, J.P.; Peters, W.A. 1985. "Pyrolysis of Volatile Aromatic Hydrocarbons and *n*-Heptane over Calcium Oxide and Quartz," *Ind. Eng. Chem. Process Des. Dev.* <u>24</u>, pp. 1080–1087.

Benzene, toluene, 1-methylnaphthalene, and *n*-heptane pyrolysis over packed beds of CaO/quartz and quartz, at 550°–950°C. The CaO significantly increased the rates of pyrolysis. Coke was the major product.

Elliott, D.C. 1988. "Relation of Reaction Time and Temperature to Chemical Composition of Pyrolysis Oils," ACS Symposium Series 376, *Pyrolysis Oils from Biomass*. Edited by E.J. Soltes and T.A. Milne. Denver, CO. April 1987.

Sequence of tar maturation from primary pyrolysis oil is:

$$\frac{\text{Mixed}}{\text{Oxygenates}}_{\ 400°C} \rightarrow \frac{\text{Phenolic}}{\text{Ethers}}_{\ 500°C} \rightarrow \frac{\text{Alkyl}}{\text{Phenolics}}_{\ 600°C} \rightarrow \frac{\text{Heterocylic}}{\text{Ethers}}_{\ 700°C} \rightarrow \frac{\text{PAHA}}{800°C} \rightarrow \frac{\text{Larger}}{\text{PAH}}_{\ 900°C}$$
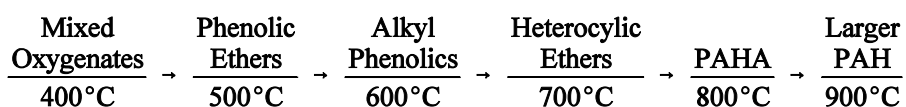
Table I. Chemical Components in Biomass Tars			
Conventional Flash Pyrolysis (450°–500°C)	**High-Temperature Flash Pyrolysis (600°–650°C)**	**Conventional Steam Gasification (700°–800°C)**	**High-Temperature Steam Gasification (900°–1000°C)**
Acids	Benzenes	Naphthalenes	Naphthalene
Aldehydes	Phenols	Acenaphthylenes	Acenaphthylene
Ketones	Catechols	Fluorenes	Phenanthrene
Furans	Naphthalenes	Phenanthrenes	Fluoranthene
Alcohols	Biphenyls	Benzaldehydes	Pyrene
Complex	Phenanthrenes	Phenols	Acephenanthrylene
Oxygenates	Benzofurans	Naphthofurans	Benzanthracenes
Phenols	Benzaldehydes	Benzanthracenes	Benzopyrenes
Guaiacols			226 MW PAHs
Syringols			276 MW PAHs
Complex Phenolics			

Elliott, D.C. 1987. "Analysis of Medium-Btu Gasification Condensates, June 1985–June 1986," Richland, WA: Battelle Memorial Institute, Biofuels and Municipal Waste Technology Division, PNL-5979.

Comprehensive analysis of gasifier tars from Battelle Columbus, IGT, University of Missouri at Rolla, and Syngas, Inc. Sees direct relationship between operating temperature and chemical composition of the condensate. *"There is no typical tar composition for all biomass gasifiers, nor is it reasonable to classify the organic condensates as 'primary oils' and 'secondary tars' as has been attempted by some."* Contains a table of 100+ chemicals found in the four gasifier tars. Some tar results are affected by differences in condensate collection. The BCL *"quench system appears to be ineffective in recovery of the light aromatic hydrocarbons (BTX and naphthalene). The Syngas, Inc., tar composition suggests they are low temperature tars."* Apparently, there is a significant amount of channeling in the bed to bypass the hot gases.

Elliott, D.C. 1986. "Analysis and Comparison of Biomass Pyrolysis/Gasification Condensates—Final Report," Richland, WA: Battelle Memorial Institute, Biofuels and Municipal Waste Technology Division, PNL-5943.

Detailed analyses of 14 submitted gasifier tars from a broad range of gasifier types. Review of older literature reveals little chemical analysis of gasifier tars. Elemental and physical characteristics are reported. Large tables of quantified chemical compounds in the variety of tars. Tar evolutionary scheme proposed as follows: mixed oxygenates-to-phenolic ethers-to-alkyl phenolics-to-heterocyclic ethers-to-PAH-to-larger PAH.

Elliott, D.C. 1985. "Comparative Analysis of Gasification/Pyrolysis Condensates," presented at the Biomass Thermochemical Conversion Contractors' Meeting, Minneapolis, MN, October.

Condensates from a number of gasifier types were analyzed by common procedures. Condensates included tar phases, aqueous phase and, in some cases, both. Postulates general pathway of "tar chemical functional degradation" as:

$$\text{Mixed Oxygenate} \rightarrow \text{Phenolic ethers} \rightarrow \text{Alkyl phenolics} \rightarrow \text{Heterocyclic ethers} \rightarrow \text{PAH} \rightarrow \text{larger PAH}$$

Major condensible organic products of raw and catalytically treated tar are shown for 17 compounds.

Elliott, D.C.; Baker, E.G. 1986. "The Effect of Catalysts on Wood-Gasification Tar Composition," *Biomass* 9, pp. 195–203.

Catalysts: K_2CO_3 and supported Ni. Tar in: From steam pyrolysis in a fluid bed with bottom feeding. Tar out: Lists 17 aromatics in uncatalyzed (pyrolysis output) tar. How measured: Combine three fractions for total tars: Decanted condensate; extracted aqueous phase with methylene chloride; and acetone rinse to remove adhering tars. GC/MS of ambient tars. Conditions studied: Bench-scale, twin fluidized-bed system for pyrolysis and secondary cracking. Produced about 9.3 wt % tar at pyrolysis system outlet (mostly phenols and other aromatic hydrocarbons). After Ni catalysis, largest component is benzene, followed by toluene and naphthalene. Ni has strong tendency to demethylate aromatics.

Espenäs, B-G. 1996. "The Kinetics of Conversion of Naphthalene into H_2 and CO Catalysed by Dolomite," in *9th European Bioenergy Conference & 1st European Energy from Biomass Technology Exhibition*. Edited by P. Chartier et al. Copenhagen, Denmark: Pergamon, p. 270.

Naphthalene has been chosen as a model substance for tar. Behavior over dolomite studied as a function gas composition and temperature.

Esplin, G.J.; Fung, D.P.; Hsu., C.C. 1986. "A Comparison of the Energy and Product Distribution from Biomass Gasifiers," *Can. J. Chem. Eng.* <u>64</u> (4), pp. 651–662.

Lists tars from several types of gasifiers. "Tars are arbitrarily defined to be a complex mixture of organic compounds which are non-soluble in water but soluble in acetone." Lists major PNAs, water-solubles in aqueous condensate.

Esplin, G.J.; Fung, D.P.C.; Hsu, C.C. 1985. "Development of Sampling and Analytical Procedures for Biomass Gasifiers," *Can. J. Chem. Eng.* <u>63</u> (6), pp. 946–953.

Analysis results for the previously described sample train (Esplin and McDonald 1982) are given for an updraft and a fluidized-bed gasifier. Acetone solutions of tar are evaporated at 25°–30°C and tar determined by weight. The determination of the water content in tar is important for measuring calorific value and carbon content.

Esplin, G.; McDonald, E. 1982. "Development of Analytical Methodology for Biomass Gasification Products," in *Proceedings of the 4th Bioenergy R&D Seminar*. Edited by B.A. Summers. Ottawa, Canada: National Research Council, pp. 273–277.

Gives sampling consideration for high-tar gasifiers. Aerosols discussed along with particulates and vapors.

Evans, R.J.; Knight, R.A.; Kosowski, G.M. 1985. "Operating Results from a Pressurized Fluidized Bed Biomass Gasification Process," in *Energy Biomass Wastes*, IX, Chicago: IGT, pp. 573–594.

Pressurized fluidized-bed PRU results. Tables of water-soluble and insoluble tar components. Oils found in product gas were of the order of 1.2%–2.6% of feed.

Evans, R.J.; Knight, R.A.; Onischak, M.; Babu, S.P. 1988. "Development of Biomass Gasification to Produce Substitute Fuels," Richland, WA: Pacific Northwest Laboratory, PNL-6518.

External GC analysis of organics; total tars from 0.5–3.0% of biomass fed. PDU proving tests: C_2H_2, not seen. C_2H_4, 0.1–0.4 mol % (dry). C_2H_6, 0.3–0.8 mol % (dry). C_6 +, 0.2–0.5 mol % (dry). C_3H_4, 0.01–2 mol % (dry). TOC in condensate; lb/100 lb feed carbon ~0.1 at 300 psi; Phenols ~0.01 at 300 psi; TOC ~0.6 at 100 psi; Phenols ~0.5 at 100 psi. Pages 104,5 contain large tables of compounds found in oils from product gas; Phenol yield drops rapidly from

1,390°F-1,510°F; Steam reduces concentration of oxygenates; p. D-3 gives description of gas sampling system.

Evans, R.J.; Milne, T.A. 1997. "Chemistry of Tar Formation and Maturation in the Thermochemical Conversion of Biomass," in *Developments in Thermochemical Biomass Conversion, Vol. 2*. Edited by A.V. Bridgwater and D.G.B. Boocock. London: Blackie Academic & Professional, pp. 803–816.

This paper describes the effects of time, temperature, and oxygen on product composition and the maturation of tars through four distinct classes of products. The effect of oxygen at temperatures of 600°C to 700°C is shown to accelerate the destruction of primary pyrolysis products but has no significant effect on benzene. The four classes of tar are:

1. Primary products characterized by cellulose-derived species at m/z 126, 98, 85, 73, 60, and 43. Hemicellulose-derived products at m/z 114, etc. and lignin-derived products at 180, 164, 150, 137, and 124.

2. Secondary products characterized by the phenolic peaks at m/z 136,120,110, and 108 and olefins at m/z 56,42.

3. Alkyl tertiary products that include methyl derivatives of aromatics at m/z 166 (methyl acenaphthylene), m/z 142 (methyl naphthalene), m/z 92 (toluene), m/z 116, (indene), as well as m/z 94 (phenol) and benzene, m/z 78.

4. Condensed Tertiary Products, that show the polynuclear series without substitutents: benzene (m/z 78), naphthalene (m/z 128, acenaphthylene (m/z 152), anthracene/ phenanthrene (m/z 178), and pyrene (m/z 202).

Results from the reaction severity study showed a temperature where secondary tars are maximum and primary and tertiary tars are minimum, which may be a balance between decreasing the amount of material and controlling the composition so that catalytic materials can function effectively. The effect of oxygen level on hydrogen is more complicated and hydrogen appears to be more reactive to oxidation than CO.

Evans, R.J.; Milne, T.A. 1987a. "Molecular Characterization of the Pyrolysis of Biomass. 1. Fundamentals," *Energy & Fuels* 1 (2), pp.123–138

By use of direct MBMS of pyrolysis vapors at increasing levels of severity, three classes of tars: primary, secondary, and tertiary are described. The primary oil ("tar") is typical of a fast pyrolysis oil containing mostly fragments and monomers of the polymeric constituents in lignocellulosics. The secondary tars are intermediate cracked species that rise and ultimately fall, to be replaced by tertiary "tars" that comprise a simple slate of polynuclear aromatics plus benzene, indene, and naphthalene. These tertiary tars are practically indistinguishable from coal tars.

Evans, R.J.; Milne, T.A. 1987c. "An Atlas of Pyrolysis-Mass Spectrograms for Selected Pyrolysis Oils," Internal report. Golden, CO: Solar Energy Research Institute.

MBMS fingerprints of the whole oils and fractions that were part of the B.C. Research, Biomass Liquefaction Centralized Analysis Program. Shows a variety of primary products in pyrolysis.

Evans, R.J.; Milne, T.A. 1987b. "Molecular Characterization of the Pyrolysis of Biomass. 2. Applications," *Energy & Fuels* 1 (4), pp. 311–319.

MBMS of oils and tars from updraft and downdraft gasifiers show the largely primary nature of the former and the tertiary nature of the latter.

Evans, R.L.; Zaridic, A.M. 1996. "Optimization of a Wood-Waste-Fueled, Indirectly Fired Gas Turbine Cogeneration Plant," *Biores. Technol.* 57, pp. 117–126.

No discussion of contaminant limits for the heat exchanger.

Fenske, J.; Schulz, K. 1994. Hot Gas Filters for Biomass Gasification, Schumacher Umwelt-und Trenntechnik. Minutes prepared by Suresh Babu from paper presented at the International Energy Agency Biomass Thermal Gasification Meeting, Copenhagen, May 9–12.

Fercher, E.; Hofbauer, H.; Fleck, T.; Rauch, R.; Veronik, G. 1998. "Two Years Experience with the FICFB-Gasification Process," in *Biomass for Energy and Industry.* Edited by H. Kopetz, T. Weber, W. Palz, P. Chartier, and G.L. Ferrero. 10th European Conference and Technology Exposition, Wurzburg. April. C.A.R.M.E.N., pp. 280–283.

Fernandez, A.J.; Iyer, P.V.R.; Grover, P.D. 1993. "Thermal Cracking of Tar for Purification of Pyro-Gases," in *Proceedings of III National Meet/PICCOP*, November 1991. India: Ministry of Non-Conventional Energy Sources, pp. 385–394.

Defines "tar cracking" as conversion to gas. Thermal cracking reported to 1,000°C.

Fernandez, J.-C. 1997. "Revalorizacion de Residuos Solidos Mediante la Gasificacion en Lecho Fluidizado: Estudio de los Sistemas de Acondicionamiento de Gases y Valoaracion Ambiental del Proceso," Ph.D. Thesis, UPC, Barcelona, Catalinga, Spain.

Flanigan, V.J.; Sitton, O.C.; Huang, W.E. 1988. "The Development of a 20-Inch Indirect Fired Fluidized Bed Gasifier," Richland, WA: Pacific Northwest Laboratory, PNL-6520, 126 pp.

Tar definition: Condensibles. How collected: Condense tar in scrubber water, then tar drop out drum and demister. Tar estimated from total carbon in the scrub water in a series of five H_2O-filled glass cylinders. Gas contains C_2H_4, C_2H_6, and C_3+, at about 5–6% of gas. Tar from .1 lb/lb wood at 1150°F to 0.075 at 1400°F. Heating value of gas greater in top feed, but tar not reported. No tar analysis, no C_3+ analysis. No mention of BTX.

Foley, G.; Barnard, G.; Timberlake, L. 1983. "Gasifiers: Fuel for Siege Economies," *Earthscan*. London: International Institute for Environment and Development.

Reviews early history of gasifiers, e.g., producer gas was first used to drive an ICE in 1791.

Furman, A.H.; Kimura, S.G.; Ayala, R.E.; Joyce, J.F. 1993. "Biomass Gasification Pilot Plant Study, Final Report," Washington, DC: U.S. Environmental Protection Agency, AEERL-748, 3R, 98 pp.

Gasified wood chips and bagasse in the GE pressurized, air-blown, fixed-bed coal gasifier (updraft). Water, tars and oils collected in condensate traps. Fuel gas composition: Bagasse: 0.28 mol % tars and oils. Wood chips: 0.23 mol % at 290 psig, and 0.09 mol % at 200 psig. Particulates at single cyclone exit were: 30–100 ppm for bagasse and 150–300 for wood chips. Sampling and analysis procedures are discussed.

Gale, K. 1997. "Going Back to Gas with Modern Plant Ends Fuel Hangups," UK: Wellman Incandescent Ltd.

Describes a "hot, detarred gas" from a Wellman producer, using a hot electrostatic detarrer. Can distribute gas over long distance without danger of oil or tar dropout. Cold, clean gas uses above, plus washing and passage through a second electrostatic percipitator to remove light oils.

Garcia, L.; Salvador, M.L.; Arauzo, J.; Bilbao, R. 1997a. "Steam Gasification of Biomass in Fluidized Bed Using a Ni-Al Coprecipitated Catalyst," in *Proceedings of the 3rd Biomass Conference of the Americas, Vol. 1*. Edited by R.P. Overend and E. Chornet. Canada: August 24–29, pp. 373–382.

Catalytic steam gasification of pine sawdust is carried out in a bench-scale fluidized bed modeled after the Waterloo Fast Pyrolysis Process technology. The NiAl (1:2) catalyst was mixed with fuel at ratios of sawdust/catalyst from about 11 to 0.2. Increase of steam/biomass ratio lowered the rate of catalyst deactivation at 700°C. No tar measurements are given but total gas doubles as catalyst ratio increases.

Garcia, L.; Salvador, M.L.; Arauzo, J.; Bilbao, R. 1997b. "Coprecipitated Ni-Al Catalysts in the Pyrolysis and Steam Gasification of Biomass," in *Biomass Gasification and Pyrolysis*. Edited by M. Kaltschmitt and A.V. Bridgwater. Newbury, UK: CPL Press, pp. 249–258.

Waterloo fast pyrolysis system was used to test catalyst behavior in the bed as a function of steam. In an experiment at 700°C, and with no added steam, liquid was reduced from 41% of feed to 3.1%. Steam prevents catalyst deactivation under some circumstances.

Garcia, L.; Sanchez, J.L.; Salvador, M.L.; Bilbao, R; Arauzo, J. 1997b. "Assessment of Coprecipitated Nickel-Alumina Catalysts for Pyrolysis of Biomass," in *Developments in Thermochemical Biomass Conversion*, Vol. 2. Edited by A.V. Bridgwater and D.B.G. Boocock. London: Blackie Academic & Professional, pp. 1158–1169.

The effect of Ni-Al$_2$O$_3$ catalysts on pyrolysis gasification in a Waterloo Fast Pyrolysis Process type fluidized bed is shown. Catalyst variables are calcining temperature and activation conditions. Tar is condensed in traps and measured by weight. With a silica bed only, at 650°C "liquid (tar)" yield is 46%. For various Ni-Al$_2$O$_3$ calcination and activation treatments tar was reduced to from 3.4% to 27%. Total sawdust fed-to-catalyst in the bed ratios of about 0.05 to 1.6 were studied with noticeable deactivation at 1.6.

Garcia, L.; Sanchez, J.L.; Salvadore, M.L.; Bilbao, R.; and Arauzo, J. 1996a. "Hydrogen-Rich Gas from Steam Gasification of Biomass Using Coprecipitated Nickel-Alumina Catalysts," *Bioenergy 96*, The Seventh National Bioenergy Conference, p. 859.

No tar or lifetime data reported.

Garcia, L.; Sanchez, J.L.; Salvador, M.L.; Bilbao, R; Arauzo, J. 1996b. "Development of Coprecipitated Nickel-Alumina Catalyst for Pyrocatalytic Gasification of Biomass," in *Proceedings of the 9th European Bioenergy Conference*. Edited by P. Chartier et al. Copenhagen, Denmark: Pergammon, pp. 1359–1364.

The effect of a Ni-Al$_2$O$_3$ catalyst mixed with sawdust in a waterloo type pyrolyses is studied at 650° and 700°C in a pyrolysis mode. Such catalysts have been found effective by Baker et al. (1987), Chornet et al. (1994), and Tanaka et al. (1984). Tar is condensed and measured by weight. With no catalyst, liquid tars are reported at 46 and 39 wt % at 650° and 700°C respectively. In experiments with catalysts, liquid tars are reduced to 11% and 8% under similar conditions.

Garcia, X.A.; Hüttinger, K.J. 1989. "Steam Gasification of Naphthalene as a Model Reaction of Homogeneous Gas/Gas Reactions during Coal Gasification," *Fuel 68*, pp. 1300–1310.

Detailed study of steam gasification of naphthalene, as a model compound for coal gasification. Pyrolysis also studied, large list of mainly PNA is given, from benzene to binaphthyl at M.W. 254 at temperatures from 800°–950°C and residence times of 6–60 s and variable naphthalene to steam ratios: "The gas yields at temperatures up to 950°C and residence times up to 60 s are low because polymerization and condensation reactions are favored, whereby tar and a carbonaceous residue are formed." H$_2$ is an inhibitor of the naphthalene-steam reaction. "Water was separated from the tar with the aid of potassium carbonate."

Gay, R.L.; Barclay, K.M.; Grantham, L.F.; Yosim, S.J.; 1980. "Fuel Production from Waste Using Molten Salts," in *Thermal Conversion of Solid Wastes and Biomass*. Edited by J.L. Jones and J.M. Radding. ACS Symposium Series, 130, pp. 227–236.

Destruction Method: Molten Carbonate Gasification (air). Inject waste below melt surface, at 900°–1000°C. Only HCs found were CH$_4$ and small amount of C$_2$H$_6$. Halogens went to chloride, S to Na Sulfide. Wood: CH$_4$, 3.0%; C$_2$, 0.9%. HHV of 6.7 Mj/m^3 or 181 Btu/SCF.

Gebhard, S. 1995a. "Evaluation of Battelle Columbus Laboratory Modified Method #5 Tar Sampling Procedure and Performance of Catalysts Tested with the 9 Tonne/Day Indirectly Heated Biomass Gasifier," *Thermochemical Conversion: Process Research Branch C-Milestone Completion Report*.

Slipstream, fluidized-bed reactors were used by Battelle to test the effect of DN-35, DN-60, DN-38, DN-40, DN-36, and DN-50 catalysts on tar from 9 ton/d PRU. Identical samples of toluene solutions from the sampling train were analyzed for tar by BCL (gravimetric) and by NREL (GC/MS). All the catalysts showed some activity, but variability was too great to permit ranking. "The absence of toluene, benzene and other more volatile compounds is an operational characteristic of the BCL tar collection technique." Raw tar concentrations in the hot gas, measured gravimetrically, were between 0.3 and 1.5 g/ft^3, in essential agreement with the NREL GC/MS values. Tar content in the raw syngas ranged from 0.2 to 0.5 mol %, not counting volatile hydrocarbons such as benzene or constituents not soluble in toluene. NREL MBMS work suggests the tar content with volatile components added could be as high as 1–2 mol %.

Gebhard, S.C. 1995b. "Annual Report," Biosyngas Conditioning Research (BF524122) and Biosyngas Synthesis Research (BF524123). National Renewable Energy Laboratory.

A dual bed of alumina upstream of United Catalyst G90B Ni-steam reforming catalyst is effective in tar cracking but does not significantly increase the Ni catalysts lifetime. Catalyst lifetime and water-gas shift activity are improved by going from steam mole fraction of 0.3 to 0.4. DN-34 has excellent high-temperature water-gas shift activity but low activity for destroying benzene, naphthalene, and other simple unsubstituted polycyclic aromatic hydrocarbons. Contains tables of major compounds in the Battelle-Columbus gasifier collected tar, before and after processing with DN-36. (Benzene and toluene were not captured in BCL sampling train.) Tests with DN-39, DN-60, DN-40, DN-38, DN-36, DN-50, and DN-34 showed that all these BCL catalysts had some tar destruction activity but it was not possible to rank them.

Gebhard, S.C. 1992. "Evaluation and Modeling of Catalysts for Methanol Syngas Conditioning," *Chemical Technologies Research Branch Milestone Completion Report*, Methanol Syngas Conditioning, BF153434.

Toluene in a synthetic syngas studied over five Ni catalysts, using direct MBMS sampling. The catalysts were UCI G90C; UCI C150-1-3; ICI 46-1, ICI 506, and BASF G1-2GS. Toluene conversion determined by the toluene parent ion (92+) intensity before and after catalyst. Best performers were the ICI 46-1, a potassium promoted, supported, Ni: catalyst, UCI G90C, and 15% Ni supported on ceramic. No products of partial "conversion" were reported except to note a slight increase in benzene.

Gebhard, S.C.; Gratson, D.A.; French, R.J.; Ratcliff, M.A. 1994a. "Molecular Beam Mass Spectrometry Applied to Biomass Gasification Monitoring," in *Proceedings: Applications of Free-Jet, Molecular Beam, Mass Spectrometric Sampling*. Estes Park, CO, hosted by the National Renewable Energy Laboratory and Extrel Mass Spectrometry. Edited by T. A. Milne. NREL-CP-433-7748, p. 227.

Direct MBMS sampling of the Battelle-Columbus gasifier, with and without DN-34, is reported for tar components. Raw syngas contains about 0.2 mol % tar (avg. MW 100 assumed). Major compounds identified were: benzene, toluene, phenol, styrene, cresols, indene, naphthalene, methylnaphthalene, and phenanthrene/anthracene. With DN-34 the phenols and substituted aromatics were greatly reduced but the more stable aromatics were only slightly reduced. Benzene, naphthalene, phenathrene/anthracene and pyrene remained at a few hundred ppmv range.

Gebhard, S.C.; Gratson, D.A.; French, R.J.; Ratcliff, M.A.; Patrick, J.A.; Paisley, M.A.; Zhao, X.; and Cowley, S.W. 1994b. "Characterization and Catalytic Conditioning of Synthesis Gas Produced by Biomass Gasification," *ACS Fuel Division* <u>39</u> (4), pp. 1048–1052.

The effectiveness of DN-34, a proprietary BCL catalyst, was studied at bench scale using 10% naphthalene in toluene as a tar surrogate, and by direct mass spectrometric sampling of a slipstream from the Battelle Columbus gasifier. DN-34 was found to be active for tar destruction. Destruction in this case refers mainly to dealkylated aromatics such as toluene. Phenols were also converted. DN-34 was less active for benzene, naphthalene, and higher simple PNA.

Gebhard, S.C.; Scahill, J.W.; Gregoire, C.E. 1993. "Characterization of Biomass Gasifier Tar and Ash," *Process Research Branch Milestone Completion Report*.

MBMS and GC-MS were used to analyze tars collected from the Battelle 9-ton/day PRU firing switchgrass. Two complete sampling trains were shipped to NREL. A slip-stream was transported 35 ft, in a 1-in. stainless steel pipe (heated at 650°C to prevent condensation of tar and steam), to a modified method #5 (EPA) glass sample collection train. Tar vapors in the raw syngas were typically 0.2–1 vol %. At Battelle, tar was removed from the trap by washing with toluene, the solution was dried and the remaining "solid (tar)" was weighed. BCL reported tars do not reflect the loss of volatile organics during the evaporation step. For MBMS analysis of shipped traps, tar was scraped from end traps and the traps were washed with toluene. Toluene and ethyl acetate extractions were performed on the aqueous fractions to identify water soluble species (e.g., phenols). "Tar evaporation for MBMS analysis is at least as susceptible to thermal reaction effects as is GC/MS analysis. No one analytical technique is sufficient. Major tar components identified by MBMS and GC/MS were: phenol, cresols, naphthalene, methylnaph-thalene, anthracene, phenanthrene, acenaphthalene, fluorene, styrene, and 1H-indene, pyrene, pyridine, and methylpyridines."

Gebhard, S.C.; Wang, D.; Overend, R.; Paisley, M.A. 1994c. "Catalytic Conditioning of Synthesis Gas Produced by Biomass Gasification, *Biomass and Energy*, <u>7</u> (1-4), pp. 307–313.

Tar Definition: Complex synthetic tar with phenols, cresols, and PNA measured by MBMS. Destruction Method: Bed of DN-34, followed by ICI-46-1. Only partial destruction with DN-34.

GENGAS. 1979. A translation by the Solar Energy Research Institute of "Generator Gas-The Swedish Experience from 1939–1945." Edited by T.B. Reed and D. Jantzen, SERI/SP-33-140. Golden, CO: National Renewable Energy Laboratory.

Contains major discussion of cooling and cleaning of generator gas, especially particulates. Tests on a Volvo passenger car with an Imbert generator showed tar contents of 0.34–0.64 g/m^3.

Gil, J.; Aznar, M.P.; Caballero, M.A.; Francés, E.; Corella, J. 1997. "Biomass Gasification in Fluidized Bed at Pilot Scale with Steam—Oxygen Mixtures. Product Distribution for Very Different Operating Conditions," *Energy & Fuels* <u>11</u>, 1109.

Fluidized bed, pilot-scale gasifier tested on pine wood chips as function of steam/O_2 ratio, steam-oxygen/biomass ratio, and temperature. Wood fed near bottom of the bed. Tar sampling device as described in Narvaez et al. *Ind. Eng. Chem. Res,* <u>35</u> 2110 (1996). Tar analyses by NREL and KTH (RIT) showed mainly phenolics and aromatics, but many components not identified. KTH reports wt % of tar as follows: phenol-37%, cresol-13%; xylenol-5%; unknown phenolics-25%; unknown phenolics-25%; unknown aromatics-12%; naphthalene-3%; toluene-2%; benzene-1%. Tar content from 2–50 g/Nm^3 reported. With bed temperature of 800°–900°C, (H_2O + O_2)/biomass of 0.8–1.2 kg/kg (DAF), and H_2O/O_2 around 30 mol ratio and a gas residence time of around 2 s, "a quite clean gas (tar contents of around 5g (Nm^3) is obtained."

Gil, J.; Aznar, M.P.; Caballero, M.A.; Francés, E.; Martin, J.A.; Corella, J. 1998. "In-Bed Use of Dolomite in Fluidized Bed Biomass Gasification with Air. Product Distribution and Gas Quality Improvement," in *Biomass for Energy and Industry*. Edited by H. Kopetz, T. Weber, W. Palz, P. Chartier, and G.B. Ferrero. 10th European Conference and Technology Exhibition, Würzburg, Germany. C.A.R.M.E.N., pp. 1785–1788.

Gornall, L. 1997. Practically Green, Londonderry, Northern Ireland. Private communication.

Engine withstands 10,000 ppm H_2S and 50% methane in biogas.

Graboski, M.S.; Brogan, T.R.; Darland, M.G.; Graham, G.A. 1985. "Oxygen Blown Downdraft Gasification of Wood," SynGas, Inc., Golden, CO. Interim Report, Solar Energy Research Institute, Contract ZK-5-05058-1.

Scaled-up SERI/REED gasifier tests. Observed more tar formation with O_2 than air. More condensation of tar in uninsulated piping due to lower mass flow with O_2.

	Tar (ppm)	C$_2$ - C$_3$ (vol % gas)*	Dust
Rm #1 on Air		~2 –2.5	
Rm #2 on O$_2$		~2–2.5	
Rm #3 on O$_2$	~20,000 ppm**	~2–2.5	~4,000 ppm
Rm #4 on O$_2$		~2–2.5	
*NO C$_4$s observed. **Approx. 4% of carbon.			

Graham, R.G. 1991. "Task VII. Biomass Conversion Activity 4: Thermal Gasification," IEA Bioenergy Agreement, compiled by ENSYN Technologies, Inc., Gloucester, Ontario, Canada.

Extensive, un-annotated, biomass gasification bibliography. Categories are: economics/system analysis; feedstock preparation/handling; gas cleaning; municipal solid waste, refuse derived fuel, sludge gasification; sampling/analysis/characterization; environmental assessment.

Graham, R.G.; Bain, R. 1993. "Biomass Gasification: Hot-Gas Clean-Up," *International Energy Agency, Biomass Gasification Working Group*. December 21, p. 44.

Review considers fluidized-bed and circulating fluidized-bed gasifiers (particulates, tar, gas and aerosols, alkali, HC, NH_3). Good table of typical tar and dust loadings from referenced gasifiers. Need gas cleaning strategies unique for biomass. Cold-gas cleanup largely abandoned due to costs. "Tars are oxygenated aromatic compounds." "Tars" contain low molecular wt oxygenates ("oils") and PNA. Tar has been defined as oxygenated organics that boil at >150°C. All but close-coupled heat applications are affected by tars. Fouling of: valves, mixers, turbocharger, fuel line, turbine blade, catalysts and lubricants. Energy content loss in tars can be great. HC are only a problem in synthesis gas application: loss of efficiency and catalyst poisoning (olefins). NH_3 a problem as NO_x precursor. Good discussion of types of gasifiers and consequences. End use tolerances. Very little published on turbine tar limits.

Guanxing, C.; Qizhuang, Y.; Sjöström; Björnbom, E. 1994a. "Pyrolysis/Gasification of Biomass in Presence of Dolomite in a Pressurized Fluidized Bed," in *Advances Thermochemical Biomass Conversion*, Vol. 2. Edited by A.V. Bridgwater. London: Blackie Academic, p. 1197.

Dolomite. Fed mixture of wood and catalyst to fluid-bed reactor. Conditions studied: Dolomite and steam varied in a pressurized fluidized bed. "The yields of H_2, as well as the yields of naphthalene and polycyclic hydrocarbons (PAH) in tar seem to increase in the presence of dolomite and/or steam."

Guanxing, C.; Sjöström, K.; Björnbom, E.; Brage, C.; Rosén, C.; Quizhuang, Y. 1994b. "Co-Gasification of Biomass and Coal in a Pressurized Fluidized Bed Reactor," in *Biomass for Energy, Environment, Agriculture and Industry, Proceedings of the 8th European Biomass Conference*. Edited by P. Chartier et al. pp. 1830–1835.

For various conditions and mixtures of biomass and coal the % of fuel-C in tar ranged from 0.08–0.24. Percentage of tar as phenols: 18-62; neutrals 33–82; bases 0.4–4.4.

Guigon, P.; Large, J.F. 1990. "Environmental Aspects of Gasification," *Comm. Eur. Communities [Rep.]*, Eur 12736, pp. 115–131.

Reviews reported "tar" composition from a variety of sources.

Gulyurthu, I.; Franco, C.; Mascarenhas, F.; Cabrita, I. 1994. "Steam Gasification Versus Fast Pyrolysis to Produce Medium Calorific Value Gaseous Fuel," in *Adv. Thermochem. Biomass Conversion*, Vol 2. Edited by A.V. Bridgwater. London: Blackie, pp. 1187–1196.

Gas, char, and tar production compared in a top-fed fluidized-bed laboratory gasifier as a function of steam versus inert gas. For pine in inert gas, tar varied from 10.7 to 9.2 wt % of feed from 790°–990°C. For pine, from 18.2–9.2 from 600°–990°C. In steam, liquids varied from 24–6 wt % from 700°–900°C. Collected tar/liquids at 0°C.

Hacker, V.; Faleschini, G.; Fuchs, H.; Fankhauser, R.; Simader, G.; Ghaemi, M.; Spreitz, B.; Friedrich, K. 1998. "Usage of Biomass Gas for Fuel Cells by the SIR Process," *J. Power Sources* 71, pp. 226–230.

Biomass gas produced in the gasifier is prepurified in a tar extractor and the gas is oxidized in the Sponge Iron Reactor (SIR). *"The resulting lean gas will be further used in the process after combustion or it can be supplied to a second electricity generation system. The heat from burning the lean gas is used in the SIR, the gasifier and for wood dehydration."*

Hallgren, A.; Andersson, L.A.; Bjerle, I. 1994. "High Temperature Gasification of Biomass in an Atmospheric Entrained Flow Reactor," in *Advanced Thermochemical Biomass Conversion*. Edited by A.V. Bridgwater. London: Blackie Academic, pp. 338–349.

Laboratory entrained-flow gasifier showed 3–20-fold reduction in tar (not defined) from 1,000°C to 1,400°C. Steam enhanced tar cracking.

Ham, D.O.; Simons, G.A.; Moniz, G.A. 1985. "Catalytic Cracking of Aromatic Hydrocarbons," Physical Sciences Inc., 5th Annual Contaminate Control Meeting. Morgantown, WV: METC. pp. 395–403.

Catalysts: Siderite, ankerite, pyrite, magnetite, hematite, and jarosite. Tar in: In coal gasification, product gases contain heavy hydrocarbons that are mainly aromatic hydrocarbons (AHCs). Can reach concentrations as high as 8000 ppm from a variety of fixed-bed gasifiers. AHCs include benzene, toluene, and xylenes, polycyclic hydrocarbons, phenolic compounds, and organic sulfur hetero-cyclics. Combined, these are referred to as tars. Low temperature cleanup would be costly for application such as molten carbonate fuel cells, where reheating is necessary. State of knowledge of cracking of AHCs is well reviewed by Tamhambar in "Review of in-Bed Hydrocarbon, Alkali, and Trace Metals in Coal Conversion Processes." DOE/MC/14731-1297 (August 1981). Iron in a reduced state is thought to be the most effective catalyst for AHC destruction.

Hanson, R.L.; Royer, R.E.; Carpenter, R.L.; Newton, G.J. 1979. "Characterization of Potential Organic Emissions from a Low-Btu Gasifier for Coal Conversion," in *Polynuclear Aromatic Hydrocarbons*. Edited by P. Jones and P. Leber. Ann Arbor, MI: Ann Arbor Science Publishers, pp. 3–19.

Tables of largely PNA tars from a low-Btu coal gasifier. Mainly aromatics and alkyl-substituted aromatics.

Hart, F.C. 1983. "State-of-the-Art Survey of Wood Gasification Technology," EPRI AP-3101.

Gas from a downdraft gasifier has low tar content and can be fed directly into the manifold of a modified (compression ratio) spark-ignition engine. Tars present in gas will condense at below 700°F. Rome, GA (APCO) updraft had 25 wt % tars and oils, phenols and lignin-related material. C_1 and C_2 hydrocarbons are at 2–3 vol %, Levesque had C_2H_x at 2.0 vol %. Used to retrofit a boiler (Omnifuel-Updraft).

Harvey, R.G. 1997. *Polycyclic Aromatic Hydrocarbons*. New York: Wiley-VCH.

Comprehensive review of PNA (PAH), including structure, nomenclature, and thermolysis.

Hasler, P. 1997. Communication on CREST Network, 8/8/97.

"We are not very happy with all the tar values presented in the literature. We think that almost all these values are noncomparable if they do not come from the same group. Moreover, only very few people give precise definitions of their tars. Furthermore, we think that not only sampling and evaporation temperature are important, but also the laboratory treatment procedure. According to our guideline, we use several tar values. Generally, we only determine the heavy tars which represent the distillation residue from an organic absorption solution at a temperature of 150°C. The organic solution is free of particles. The uncertainty in the different tar definitions is one of the major reasons why we also determine 16 PAH compounds according to the US EPA list. These PAH values are analytical values and the sampling and analysis procedures are well defined. For the heavy tars and the PAH, we use the same sampling train and the same stock solution. Quite often, we are able to find a certain correlation between the heavy tar content and the PAH content (as the sum of all 16 US EPA PAH). Normally, the PAH level is 5 to 10 times lower than the heavy tar level. Hence the major quantity of the heavy tars are other components than the US EPA PAH. We have not yet determined the PAH content in the heavy tars, but we think that only minor amounts of the US EPA PAH will be found in the heavy tar residue. The vapor pressure of some of the lower boiling point PAH e.g., naphthalene is so high that no naphthalene will remain in the heavy tars during solvent evaporation."

Hasler, P.; Bühler, R. 1994. "Gasification of Urban Waste Wood (Altholz)," *International Energy Agency, Biomass Gasification Working Group*. September.

How Measured: Lurgi-Gas continuously monitored with a process mass spectrometer. Tar collected from condenser. Reports results from three gasifiers: 2.5 MW Lurgi pilot CFB; 300 kW Wamsler fixed bed gasifier (cocurrent downdraft); 500 kW Juch fixed-bed gasifier, cocurrent downdraft. Table of heavy metals for Altholz vs. wood given. Tar content after cooling condenser: (Lurgi) 0.2-1.1 g/Nm³ (dry). Gasification leads to higher transfer of Pb and Zn into the gas than does combustion with CFB. Particle transfer to gas is greater than in combustion. Gasification of Urban Waste Wood. Lurgi CFB, after cyclones, before cooling condenser: (Raw Gas), C_2H_4 ~ 0.77 vol %. Tar 160–1050 mg/Nm³. Particulate 9,900–21,900 mg/Nm³. HCl 84–180 mg/Nm³; HF 1.6–5.7; H_2S 150–342; NH_3 ~ 3000. Metals transfer data emphasized.

Hasler, P.; Bühler, R.; Nussbaumer, T. 1998. "Evaluation of Gas Cleaning Technologies for Biomass Gasifiers," in *Biomass for Energy and Industry*. Edited by H. Kopetz, T. Weber, W. Palz, P. Chartier, and G.B. Ferrero. 10th European Conference and Technology Exhibition, Würzburg, Germany. C.A.R.M.E.N., pp. 272–275.

Hasler, P.; Bühler, R.; Nussbaumer, T. 1997. "Evaluation of Gas Cleaning Technologies for Small Scale Biomass Gasifiers." Zurich: Swiss Federal Office of Energy and Swiss Federal Office for Education and Science.

This review covers *"appropriate gas cleaning systems for fixed bed cocurrent biomass gasifiers in; the capacity range of several 100kWt, both wet and dry gas cleaning systems...." "The quench/sand bed filter system has already been successfully tested in small scale biomass gasifiers. The investment costs are distinctively lower than for other systems..."* only gasifiers which produce a similar gas quality as a cocurrent type gasifier are considered as promising candidates *"f*or engine use...*"there are some doubts that the postulated gas quality given in the literature is of general applicability."* These authors classify the various components of "tar" as follows":

Heavy tars: Polyaromatics (PNA or PAH) with boiling points typically above 200°C. Generally determined gravimetrically.

PAH: Recommends the 16 environmentally relevant compounds from EPA.

Light tars: Aromatic hydrocarbons boiling from 80°C–200°C. (e.g., benzene, toluene, xylene).

Light HCs: Non-aromatic hydrocarbons up to about C5 (e.g., methane, ethylene, propane).

Phenols: Aromatic hydrocarbons with at least one-OH group (e.g., phenols, cresols).

Oxygenates: Organic, non-aromatic compounds such as acetic acid, methanol, and acetone.

Heavy tars, PAH, phenols, and oxygenates are of major concern in gas cleaning and engines.

This report quotes other sources for the tar limit for ICEs of less than 100 mg/Nm^3. No limit is quoted for gas turbines. It is noted that: "High performance power generators may display a higher sensitivity to impurities than 'old fashioned' engines," "High speed IC engines are more delicate than low speed engines." Typical tars from a good cocurrent gasifier must be reduced by 90%. For turbo-charging or compression, downdraft levels of tar may lead to corrosion or wear. For atmospheric gasifiers, compression will be necessary for turbines, and compressor tolerances may be as severe as are IC engine tolerances. Critical discussion are given for the following gas conditioning systems: Wet-gas cleaning systems, such as scrubbers, sand-bed and sawdust filters, wet electrostatic precipitators and waste-water treatment. Dry gas cleaning systems include cyclones, rotational particle separators, fabric filters, and ceramic filters. Tar removal and tar cracking systems reviewed include adsorption on activated carbon filters, thermal tar cracking and catalytic 'tar' reformation. Investment costs for the various wet and dry systems are discussed but not quantified. "For state of the art cocurrent gasifiers generating

less then 1000 mg/Nm^3 *of 'tars,' thermal and catalytic tar cracking is considered as an option of minor priority."*

Hasler, Ph.; Salzmann, R.; Kaufmann, H.P.; Nussbaumer, T. 1998. "Method for the Sampling and Analysis of Particles and Tars from Biomass Gasifiers," in *Biomass for Energy and Industry.* Edited by H. Kopetz, T. Weber, W. Palz, P. Chartier, and G.L. Ferrero. 10th European Conference and Technology Exhibition, Würzburg, Germany. C.A.R.M.E.N., pp. 1600–1603.

Hatherill, D.W. 1996. "Tarry Liquor Production in a Downdraft Gasifier," ETSU B/M5/00533/07/REP, Power Gasifiers International Ltd.

"Gas condensate" and "fuel compartment" liquors were collected (condition not stated) from a downdraft gasifier (type and condition of operation not stated). Samples were sent for GC analysis. Fuel was Shimada briquettes (no composition or references given). Samples were solvent extracted with dichloromethane and concentrated (details not given). Many phenols were seen in the liquors. Even primary organics such as syringol, vanillin, and coniferyl alcohol were seen, which is unusual for downdraft gasification. Also seen in both samples were many polynuclear aromatics such as naphthalene, fluorene, pyrene, and benzo (a) pyrene. (Benzene and toluene were presumably lost in handling.)

Hedden, K.; Heike, T.; Ramananda Rao, B. 1986. "Testing and Optimization of Commercial Biomass Gasifiers." Karlsuhe Univ. (T.H.) (Germany, F.R.). DVGW-Forschungsstelle, p. 150.

Heinzel, A.; Formanski, V.; Ledjeff-Hey, K.; Schaumberg, G. 1996. "Fuel Cells for Electrical Energy from Gasified Biomass," in *Biomass for Energy and Environment: Proceedings of the 9th European Bioenergy Conference, June 1996.* Edited by P. Chartier et al. Pergamon, pp. 1462–1467.

Development of a small and efficient gas cleanup system is the key to realize systems for electricity generation from biomass by fuel cell. Tars, metal vapors, and sulfur oxides are typical catalyst poisons for SOFC and MCFC.

Henriksen, U.; Christensen, O. 1995. "Gasification of Straw in a Two-Stage 50 kW Gasifier," in *Biomass for Energy, Environment, Agriculture and Industry, Vol. 2, Proceedings of the 8th European Biomass Conference.* Edited by P. Chartier et al. Vienna, Austria: Pergamon, pp. 1568–1578.

A two-stage, pyrolysis, partial oxidation, char gasifier was tested with an internal combustion engine. The raw gas had very low tar—30–35 mg/kg straw (text value) and 38 mg/Nm^3 (table value).

Hepola, J. 1993. "Usability of Catalytic Gas Cleaning in a Simplified IGCC Power System," Deactivation of Ni/Al$_2$O$_3$ catalysts. Literature review, Finland. VTT Publication 1445.

Introduction contains a good review of past work on Ni-based catalysts for tar reforming. "Nickel-based catalysts have proved to be efficient for tar and ammonia decomposition in

laboratory-scale gas purification experiments, in which biomass, peat and coal gasification was applied. A potential location for a separate catalyst reactor for an IGCC process using biomass gas derived from a fluidized-bed gasifier is downstream of cyclones before the ceramic filter unit. Complex nature of biomass and peat gas cannot be simulated completely in the laboratory. Long-term tests using a gas stream from an operating gasifier are likely the best way to test catalyst deactivation. Catalyst deactivation may be chemical, mechanical or thermal. Poisoning, fouling, thermal degradation and vaporization are the four intrinsic mechanisms. Poisoning and thermal degradation are generally slow and irreversible; fouling with coke and carbon is rapid but easily reversed by gasification. Loss of metals by vaporization is completely irreversible. Deactivation is more easily prevented than cured. Poisoning by impurities may be prevented by purifying the reactants. Carbon deposition and coking may be prevented by minimizing formation of precursors and by manipulating mass-transfer regimes to minimize the effect of carbon or coke on activity. Sintering is avoided by operating at a low temperature. The catalyst should also have a sufficient mechanical strength so that it does not dust or crack while in operation. Thermodynamic calculations showed that in the process conditions likely to be used in the catalytic cleaning unit, nickel oxide is reduced to metallic nickel. Carbon (graphite) and nickel sulphide are formed depending on the temperature, pressure and the gas composition of the process. The higher the pressure the more probable is the formation of carbon and nickel sulphide. The probability for carbon formation decreases when the moisture content of the gas increases. Some 40 references are discussed."

Hepola, J.; Simell, P. 1997. "Sulphur Poisoning of Nickel-Based Hot Gas Cleaning Catalysts in Synthetic Gasification Gas. I> Effect of Different Process Parameters," *Applied Catalysis B.*: 14 pp. 287–303. II> "Chemisorption of Hydrogen Sulphide," pp. 305–321.

"Long-term tests (50–190 h) made at about $900°-1,000°C$ in a real product gas stream under atmospheric pressure and in dust-free conditions with commercial nickel catalysts did not indicate any decline in tar or ammonia decomposing activity." Tests with benzene, naphthalene, or toluene were substantially the same, indicating toluene is a suitable surrogate for tar.

Hepola, J.; Simell, P.; Kurkela, E.; Ståhlberg, P. 1994. "Sulphur Poisoning of Nickel Catalysts in Catalytic Hot Gas Cleaning Conditions of Biomass Gasification," in *Catalyst Deactivation 1994*. Edited by B. Delmon and G.F. Froment, pp. 499–506.

"Biomass-derived gasification gas contains tar that can plug the particulate filters . . ." Gas conditioning is promising with Ni catalyst to decompose both tar and ammonia. Sulfur poisoning was studied from $800°-950°C$ under 1–20 bar pressure, with real and simulated gasification gas mixtures containing various amounts of H_2S. For simulation, toluene is used as "tar" surrogate. In long term tests tar was reduced from 1.6–23 g/Nm^3 before to 0–0.2 g/Nm^3 in the presence of 90–750 ppm of H_2S, for 2 Ni catalysts (VTT fluid-bed gasifier). "Tar sampling was facilitated by absorbing tar into dichloromethane, followed by capillary gas chromatography." Toluene decomposed mainly to H_2, CO, CO_2, CH_4, benzene, and carbon. When H_2S was removed from the gas, the activity of the catalyst regained rapidly.

Herguido, J.; Corella, J.; Antal, G.; Garcia-Bordeje, J.E. 1992a. "Results with a Multisolid Circulating Fluid Bed Pilot Plant for the Improved Steam Gasification of Biomass," in *Biomass for Energy, Industry and Environment*, 6th E.C. Conference. London and New York, pp. 792–796.

"In equilibrium" FCC catalyst (spent). Tar in: Condensibles. Tar out: Condensibles-no gases above C_2 reported. Results from a 15 cm i.d. riser-gasifier with a stable fluidized bed of sand at its bottom. Operation similar to FCC in petroleum refining. Without catalyst tar = 78 g/Nm^3 but deactivates in 40 min. With catalyst and recirculation and continuous regeneration of catalyst, tar = 9 g/Nm^3, but lifetime not stated.

Herguido, J.; Corella, J.; Gonzalez-Saiz, J. 1992b. "Steam Gasification of Lignocellulosic Residues in a Fluidized Bed at a Small Pilot Scale. Effect of the Type of Feedstock," *Ind. Eng. Chem. Res.* <u>31</u> (5), pp. 1274–1282.

Same technique for tar analysis as in Sjöström et al. (1988) and Corella et al. (1991, p. 2252). 15-cm i.d. pilot scale fluid-bed. Tar yields from pine sawdust, straw, wood chips, and thistle very similar. Yields decrease with increasing gasification temperature and with steam/biomass ratio. At 750°–800°C tar yields are between 2.8 and 5.0 wt %.

Herguido, J.; Rodríguez-Trujillo, J.L.; Corella, J. 1990. "Gasification of Biomass with Tar Cracking Catalysts in a Circulating Multisolid Fluidized Bed Pilot Plant," in *Biomass for Energy and Industry (5th E.C. Conference)*, Vol. 2. Edited by G. Grassi et al. London: Elsevier Applied Science, pp. 2.793–2.797.

Discussion of the system used later for tar studies. No tar data.

Hofbauer, H.; Veronik T.F.; Rauch, R.; Mackinger, H.; Fercher, E. 1997. "The FICFB-Gasification Process," in *Developments in Thermochemical Biomass Conversion,* Vol. 2. Edited by A.V. Bridgwater and D.G.B. Boocock. London: Blackie Academic & Professional, pp. 1016–1193.

Tar Definition: Condensibles at 10°C, measured by GC. Destruction Method: Steam gasification in internal recirculation version of BMI process. The FICFB-Gasification Process studied at 100 kW thermal pilot scale. "Tar" did not exceed 1 g/Nm^3 dry product gas. Quotes air-blown gasification as 10-15 g/Nm^3. Product gas: ethene 3.5 vol %; ethane 0.6; propene 0.3. See Rei et al. (1986) *App. Cat*. <u>26</u>, pp. 27–37. Baker et al. (1987) *Ind. & Eng. Chem.* <u>26</u>, pp. 1335–1339.

Hörnell, C.; Myrén, C.; Brage, C.; Qizhuang, Y.; Björnbom, E.; Sjöström, K. 1998. "Biomass Gasification for Electricity Production: Upgrading of Tars," in *Biomass for Energy and Industry*. Edited by H. Kopetz, T. Weber, W. Palz, P. Chartier, and G.B. Ferrero. 10th European Conference and Technology Exhibition, Würzburg, Germany. C.A.R.M.E.N., pp. 1662–1664.

Houmoller, S.; Hansen, M.W.; and Henricksen, U. 1996. "Two-Stage Fluid-Bed Pyrolysis and Gasification Unit." NEI-DK-2672, pp. 1347–1353.

Describes the expected advantages of this system in terms of lower tar and lower alkali in final gas for engine or boiler use.

Huijsmans, J.P.P.; van Berkel, F.P.F.; Christie, G.M. 1998. "Intermediate Temperature SOFC-a Promise for the 21st Century," *J. Power Sources* 71, pp.107–110.

Hulkkonen, S. 1996. "Performance and Cost of an Ivosdig Biomass GCC Plant," *Analysis and Coordination of the Activities Concerning a Gasification of Biomass* (AIR3-CT94-2284), Second Workshop, Espoo, Finland, pp. 1–10.

IVOSDIG process for New Bern expects tar levels of 0.3 gas vol % after gasifier and 0.22% at gas turbine.

Hummelshøj. 1995. "Decentral Gasification of Pelletized Char Produced from Biomass," in *Proceedings of the 8th European Biomass Conference, Biomass for Energy, Environment, Agriculture and Industry*. Vienna, Austria: Pergamon, pp. 1842–1847.

A pyrolyzer for straw or other biomass produces about 2/3 pyrolysis gas and 1/3 "bio coal" (char) when operated at 600°C Gasification of this char produces a gas with less than 50 mg/Nm^3 of tar, avoiding the costly tar removal step.

IEA 1995-7. International Energy Agency. Bioenergy, Biomass Utilization Task XIII, "Thermal Gasification of Biomass" Activity.

IEA 1990. Thermal Conversion Activity 4. Lake Buena Vista, FL, January.

Data gaps: Gasification of condensate oils/tars; staged condensation to separate oils and tars; catalytic cracking; steam reforming of oils/tars; high-temperature desulfurization and ammonia removal. Contains big lists of gasifiers throughout the world. Mentions tests of wet ESP for combined solids and tars.

Jacoby, W.A.; Gebhard, S.C.; Vojdani, R.L. 1995. "Lifetime Testing of Catalysts for Biosyngas Conditioning—Single versus Dual Catalyst Comparison," *Thermochemical Conversion: Process Research Branch C-Milestone Completion Report*.

Tar definition: Synthetic mix of benzene, toluene, and naphthalene. UCI G90B was active longer than 585 hours. γ Al$_2$O$_3$ co-catalyst before UCI was also tested. How measured: GC No intermediates reported.

Jarafors, K.; Marks, J.; Wanless, M. 1996. "Electricity from Wood Powder Report on a TPV Generator in Progress," in *AIP Conference Proceedings* 358(1), American Institute of Physics, pp. 177–180.

Progress on a wood powder-fired thermo-photovoltaic generator is presented.

Jansen, D.; Mozaffarian, M. 1997. "Advanced Fuel Cell Energy Conversion Systems," *Energy Convers. Mgmt.* <u>38</u>, (10–13), pp. 957–967.

For an integrated gasifier, molten carbonate fuel cell, hot gas cleaning will increase efficiency 2%–3%. Coal-fueled, fuel-cell power plants will have to face severe competition from advanced pulverized coal and IGCC power plants, despite their higher electrical efficiency.

Järås, S.; Johansson, M. 1996. "Catalytic Combustion of Gasified Biomass for Electricity and Heat Production," Final Report. Stockholm: NUTEK P5439-1.

Tested several high-temperature oxidation catalysts with simulated gasified biomass composition. Only hydrocarbon was CH_4. In future work will look at effects of H_2S, HCl, alkali, and heavier hydrocarbons such as ethene, propene, toluene, and benzene tars. Emphasis of work is on NH_3 conversion and burning stability of low Btu gases.

Jayamurthy, M.; Dasappa, S.; Paul, P.J.; Sridhar, G.; Sridhar, H.V.; Mukunda, H.S.; Rajan, N.K.S.; Brage, C.; Liliedahl, T.; Sjöström, K. 1997. "Tar Characterization in New Generation Agro-Residue Gasifiers–Cyclone and Downdraft Open Top Twin Air Entry Systems," in *Biomass Gasification and Pyrolysis*. Edited by M. Kaltschmitt and A.V. Bridgwater. UK: CPL Press, pp. 235–248.

In a pulverized fuel cyclone reactor, tar levels were about 700–800 ppmw. In an open top, twin air entry system, tar was 70–100 ppmw. A char bed lowered tar by about 40%.

Jensen, P.A.; Larsen, E.; Jørgensen, K.H. 1996. "Tar Reduction by Partial Oxidation," in *Biomass for Energy and Environment: Proceedings of the 9th European Bioenergy Conference, June 1996*. Edited by P. Chartier et al. Copenhagen, Denmark: Pergamon, pp. 1371–1375.

Catalysts: None. O_2 added to second stage of pyrolysis/cracker system. Tar in: From batch pyrolysis of 5.1 g wheat straw heated at a rate of $100°$/min to $500°C$. Tar out: Condensate at $-78°C$ into acetone. How measured: Gravimetric. Lighter tars (to $180°C$ measured by GC-MS. Conditions studied: Gas residence time in second reactor about 0.17 seconds. An O_2/N_2 mixture was added to the secondary reactor. Tar reduced from 12% of straw to 11% by adding 2% O_2 in N_2 at $900°C$. The tar is preferentially oxidized vis-a-vis CO. (H_2 not mentioned.) Lighter components of tar actually increase when temperature is raised or oxygen is added.

Jess, A. 1996. "Mechanisms and Kinetics of Thermal Reactions of Aromatic Hydrocarbons from Pyrolysis of Solid Fuels," *Fuel* <u>75</u>, (12), pp. 1441–1448.

Results for the kinetics of thermal conversion of naphthalene, toluene, and benzene in the presence of hydrogen and steam are given. Order of reactivity is: toluene > naphthalene > benzene. Besides gaseous organic products such as methane and ethene, condensed products and soot are formed, principally from naphthalene. Steam has only a small influence on the conversion of the aromatics. For toluene, naphthalene, and benzene, at 0.5 s residence time, 80% conversion occurs at about $960°$, $1,200°$ and $1,270°$, respectively.

Johansson, L.; Ziph, B.; McKeough, W.; Houtman, W. 1996. "Biostirling™: A Small Biomass Power Conversion System Using an Advanced Stirling Engine," in *Proceedings of the Seventh National Bioenergy Conference*, Nashville, TN, pp. 312–316.

The Chiptec gasifier is a two-stage combustor in which the second combustor stage reaches 1600°C. The combusted gas provides direct heat transfer into the compact heater of the Stirling engine. Since the producer gas burns continuously against hot walls, it requires little or no treatment before its combustion. The capability of burning "raw" producer gas is a major advantage of the Bio-Stirling™ concept.

Jönsson, O. 1985. "Thermal Cracking of Tars and Hydrocarbons by Addition of Steam and Oxygen in the Cracking Zone," in *Fundamentals of Thermochemical Biomass Conversion*. Edited by R. Overend, T. Milne, and L. Mudge. London and New York: Elsevier Applied Science, pp. 733–746.

Catalysts: None. Steam/thermal cracking with and without addition of O_2 to the cracking reactor. Tar in: Pyrolysis vapors at 750°C. Tar out: Tar condenser runs at 120°C to separate water. How measured: Condensibles by weighing the tar condenser before and after. Gases by GC. Conditions studied: Cracking temperatures varied from 950°–1,250°C. Added steam and O_2 in some cases. At 4 s reactor residence time, tar + soot decreased from 0.07 kg/kg fed with steam only, to about 0.025 kg/kg with 0.1 kg O_2/kg feed. Effect on H_2 and CO was not reported. The "tar" produced under these conditions was mainly soot.

Joseph, S.; Denniss, R.; Lipscombe, R.; Errey, S.; Fletcher, D.F.; Haynes, B.S. 1996. "The Development and Testing of an Air/Steam Blown Entrained Flow Gasifier Fueled with Cotton Waste and Sawdust," *Bioenergy '96—The Seventh National Bioenergy Conference*, pp. 304–311.

An entrained-flow vortex gasifier, with reinjection of char, "ensures a larger proportion of the tar and higher molecule hydrocarbons are cracked and undergo reduction."

Kaba, T.; Godo, M.; 0tsuki, S.; Ishihara, A.; Qian, W.; Miwa, S.; Katahira, H.; Mukai, K. 1997. "Reactivity of Naphthalene in Pyrolysis of Coal Tar Using the 14C Tracer Method," *Energy & Fuels* 11, pp. 1299–1232.

Studied naphthalene at 800°–950° C and 40–50-s residence time.

Kaltschmitt, M.; Bridgwater, A.V. (eds.). 1997. *Biomasss Gasification; and Pyrolysis, State of the Art and Future Prospects*," Newbury, UK: CPL Press, CPL Scientific Ltd.

Many papers from the Stuttgart meeting.

Kamat, P.P.; Shashikantha; Parikh, P.P. 1993. "On Wear and Maintenance of Producer Gas Dual Fuel Engines-Effect of Tar and Particulates," in *Proceedings of III National Meet/PICCOP*, November 1991. India: Ministry of Non-Conventional Energy Sources, pp. 33–49.

Engine wear measured for downdraft gasifier with gas cooler, feeding single cylinder C.I. engine 400 h. Major concern was phenolic nature of tar and particulates. (Phenol and acetic acid main objectionable constituents.) Deposits form in critical locations. Tests made at tar levels of 40–170 mg/Nm^3 and particulates at 20–109 mg/Nm^3. Conclusion: engine wear increases significantly at these levels.

Karlsson, G.; Ekstrom, C.; Liinanki, L. 1995. "The Development of a Biomass IGCC Process for Power and Heat Production," in *Biomass for Energy, Environment, Agriculture and Industry. Vol. 2, Proceedings of the 8th European Biomass Conference*. October 1994. Pergamon, pp. 1538–1549.

The VEGA program uses bubbling fluidized-bed technology originally developed by IGT and licensed to Enviropower Inc., a joint venture of Tampella Power Oy, Finland and Vattenfall AB, Sweden. Tests on smaller scale (up to 400 kW at VTT in Esbo and pilot scale (up to 15 MW at Gaspi). Cool gas to 500°C before dust removal in ceramic candle filters (achieve dust at ~5 mg/Nm^3). Alkali at 0.05 ppmw. No clogging of filter with tars. Light tars were 1-2 g/Nm^3, excluding benzene and ~ 100–300 mg/Nm^3 heavy tars (used dolomite catalytic bed).

Katofsky, R.E. 1993. "The Production of Fluid Fuels from Biomass," Princeton University, Center for Energy and Environmental Studies. PUICEES, Report No. 279.

Kaufman, H.P. 1994. "Vergasung von Holz und Gras in Festbettvergasern," Neue Erkentnisse zur Thermischen Nutzung von Holz, Tagungsband Zum 3. Holtzenergie- Symposium, 21. Okt. ET, Zurich, pp. 225–250.

Kaupp, A. 1984. "Gasification of Rice Hulls," ISBN 3-528-02002-4. Federal Republic of Germany: Friedr. Vieweg & Sohn Verlagsgesellschaft mbH, Braunschweig.

"Tar is a high energy component of the products of (producer) gasification having a HHV of 20-34 MJ/kg. Tar vapor and liquids have been known to be a health hazard for decades." Proposed definitions: Volatiles: all gaseous and liquid products evolved up to temperature T. Tar: The anhydrous fraction of the liquid products. Tarry Liquids: The entire liquid phase. In downdraft gas producer, "tarry vapours" have a wide range of boiling points from 100°–400°C Particulates range from 700–1,000 mg/Nm^3. Gives total contaminate tolerance of engines as <10 mg/Nm^3. Thermal tar conversion requires T > 900°C.

Kaupp, A.; Creamer, K.; Goss, J.R. 1983. "The Characteristics of Rice Hulls for the Generation of Electricity and Shaft Power on a Small (5-30 Hp) Scale," Energy Res. 3 (Altern. Energy Sources 5, Pt. D), pp. 103–117.

Tar Definition: Condensible hydrocarbons. Discusses thermal tar cracking in downdraft gasifier, in context of ICE use. Need temperatures > 900°C. Carbon catalysis of tars decreases as temperatures approach 1,000°C. Partial oxidation of tars could be effective, but contact of O$_2$ and tar is limited in gas producers.

Kaupp, A.; Goss, J.R. 1984. "Small Scale Gas Producer-Engine Systems," Federal Republic of Germany: Deutsches Zentrum für Entwicklungstechnologien—GATE. Friedr. Viewegt & Sohn, Brauschweig/Wiesbaden. Golden, CO: Biomass Energy Foundation Press.

Gasification generates a gas that is actually a mixture of three gas streams obtained from the partial combustion zone, reduction zone, and distillation zone. Distillation products are the least understood and consist mainly of tar, light and heavy oils, noncondensible gases and water vapor. Tar laden gas in engines will gum the valves. Tolerance of modern engines to tars not well known. World War II experience not transferable quantitatively.

Kennedy, I.A. 1997. "Models of Soot Formation and Oxidation," *Prog. Energy Combust. Sci.* <u>23</u>, pp. 95–132.

Kiel, J.H.A.; Bos, A.; Uil, H. D.; Plaum, J.M. 1995. "Coal/Biomass Cogasification and High Temperature Gas Cleaning," in *Proceedings Third International Conference on Combustion Technologies for a Clean Environment.* ECN-RX-95-029. Lisbon, Portugal.

Study of dry halide removal by absorbents, at 350°–400°C, upstream of the desulfurization process. Molten carbonates have been shown to reduce HCl to <1 ppm in fuel cell work. At 400°C, NaCl, and NaF vapor pressures are sufficiently low to avoid gas-turbine problems. Na_2CO_3 found to be a promising sorbent. Tars not discussed.

Kinoshita, C.M.; Turn, S.Q.; Overend, R.P.; Bain, R.L. 1997. "Power Generation Potential of Biomass Gasification Systems," *J. Energy Engin.*, December, pp. 88–99.

In the biomass gasifier facility at Paia, Hawaii (a 10/1 scaleup of the IGT Renugas™ system) bagasse from a sugar mill (dried to 25% moisture) was gasified over essentially 58 hours of steady-state operation in October 1995. At 841°C, P=2.9 bar and air only, condensible hydrocarbons (C_6 and higher) in the output stream averaged 2.3% of dry fuel feed, with benzene and naphthalene being the principal components. In December, further air tests at 835°C and 4.2 bar, improved the quality of the gas. Condensible hydrocarbons were reduced to 0.8% of dry fuel.

Kinoshita, C.M.; Wang, Y.; Zhou, J. 1995. "Effect of Reformer Conditions on Catalytic Reforming of Biomass-Gasification Tars," *Ind. Eng. Chem. Res.* <u>34</u>**,** pp. 2949–2954.

Tar Definition: Gaseous organic compounds formed in thermochemical reactions. How Collected: Condensation temperature of most tar species is ≤250°C. How Measured: Offline GC. Definition of "tar" is given in *J. Analyt. Appl. Pyrolysis 1994*, <u>29</u>, 169–181. Refers to tertiary tars as defined by Milne and Evans.

Kinoshita, C.M.; Wang, Y.; Zhou, J. 1994. "Tar Formation under Different Biomass Gasification Conditions," *J. Analyt. Appl. Pyrolysis* <u>29</u>, pp. 169–181.

Parametric tests of tar formation, as a function of temperature, equivalence ratio, and residence time, in a bench-scale, indirectly heated, fluidized-bed gasifier. Continuous feeding up to

3.4 kg/h of biomass. GC analysis revealed 20–60 tar species. About 75%–80% of tar species were identified. The following species were present at >5% concentration: benzene, naphthalene, toluene, xylene, styrene and phenol. Indene ranged from 0.4%–6%. Tar yields vary from 43 g/kg at 700°C to 54 g/kg at 750°C to 25 g/kg at 900°C (all at equivalence ratio (ER) of 0.22 and t of 3.75 s. Overall tar yields are nearly constant at 43–40 g/kg from 0.22 + 0.32 equivalence ratio at 700°C. But benzene increased from 25% to 45% of tar. Two-, three-, and four-ring PNA increased in tar percentage from 0.22–0.32 ER. At 800°C and ER=0.22, total tar and char are almost independent of residence time from 2.0–5.0 seconds. Oxygen containing compounds exist in significant quantities only at temperatures lower than 800°C.

Kivisari, J. 1994. "Effects of Sulfur and Other Impurities in the Anode Gas on Fuel Cell Performance." KTH report KTR 94–11.

Kjellstrom, B. 1990. " Producer Gas," in *Bioenergy and the Environment*. Edited by J. Pasztor and L.A. Kristoferson. UNEP. Boulder, CO: Westview Press.

Klett, M.G.; Rutkowski, M.D.; Zaharchuk, R. 1996. "Assessment of Hot Particulate Removal Systems for IGCC and PFBC Advanced Power Systems," *13th Pittsburgh Coal Conference*, 6 pp.

First phase of an NRC Committee on strategic assessment of the DOE coal program—Parsons Power Group assessing hot-gas cleanup systems for IGCC and PFBC (a key recommendation).

Klinger, J.; Kennedy, H. 1987. "Study of the Effects of Soot, Particulate and Other Contaminants on Molten Carbonate Fuel Cells Fueled by Coal Gas," Danbury, CT: Energy Research Corporation, Contract number DE-AC21-84MC21154. Gas stream cleanup papers, METC.

This ERC study lists the following tolerance levels for a non-internal reforming molten carbonate fuel cell: C_2H_6, tolerant; C_2H_4, <0.25 vol %; C_2H_2, <0.2; benzene, <0.5; aromatics, <0.5 (e.g., C10H8); crude phenols to be determined.

Knoef, H.A.M.; Stassen, H.E.M. 1996. "Development of an Integrated Small Scale Combined Heat/Power Fixed Bed Gasification System Fueled by Standard Gasifier Fuel," in *Biomass for Energy and Environment: Proceedings of the 9th European Bioenergy Conference, June 1996*. Edited by P. Chartier et al. Pergamon, pp. 266–271.

Gives outline, objectives, and deliverables for the BTG coordinated JOULE project: "Development of an integrated, small-scale CHP fixed-bed gasification system fueled by a standardized gasifier fuel." Includes a gas cleaning work package.

Knoef, H.A.M.; Stassen, H.E.M.; Hovestad, A.; Visser, R. 1988. "Environmental Aspects of Condensates from Downdraft Biomass Gasifiers," in *Biomass for Energy and Industry,* Applied Science, pp. 1152–1159.

Aqueous and pyrolytic tars from five commercial downdraft gasifiers were collected and analyzed using standard analysis methods being developed at BTG. Some 80 compounds were

identified, with no interpretable trends in composition or amount among the five gasifiers. Categories observed were: aldehydes and ketones, carboxylic acids and esters, phenols, polyhydrics, heterocyclic oxygen compounds, heterocyclic nitrogen compounds, polycyclic aromatics, and BTX. In situ catalysts were tested in a small laboratory pyrolysis reactor. Eight weight percent K_2CO_3 added to the fuel reduced the tars by 75%. 17% Ni/La did likewise, while the combination of the two reduced tar by 95%. The Ni/La catalyst was reported to be cheap and have a long lifetime.

Koljonen, J.; Kurkela, E.; Wilen, C. 1993. "Peat-Based HTW-Plant at Oulu," *Biores. Technol.* 46, pp. 95–101.

Concentrations of naphthalene, benzene, ammonia, and HCN were measured in the product gas. For several conditions of T and P in the Winkler, naphthalene varied from about 0.03–0.20 g/Nm^3.

Koningen, J; Sjöström, K. 1998. "Sulfur-Deactivated Steam Reforming of Gasified Biomass," *Ind. Eng. Chem. Res.* 37, 341–346.

Effect of H_2S steam reforming of methane studied for United Catalyst's C11-9-061 and Haldor Topsoe's HTSR121.

Kornosky, R.M.; Rao, S.N. 1988. *Gas Purity Considerations in Coal Liquefaction Processes, Proceedings of the Eighth Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting*, Morgantown, WV.

There are more than 25 gas-cleaning technologies. See Hydrocarbon Processing 1988 and Vervalin 1988. For methanol feed: H_2S + carbonyl sulfide < 0.06 ppmv. HCl, 0.01; NH_3, 10.0; HCN, 0.01

Kosstrin, H.M.; Ziminsky, P.V. 1988. "The Combustion of MSW Derived LoBtu Gas in an Internal Combustion Engine," in *Energy from Biomass and Wastes XI*. Edited by D.L. Klass. Chicago: Institute of Gas Technology, pp. 217–236.

Tars not reported but design criterion for engine was condensibles ≤0.03 grains/SCF at 3 microns maximum size.

Kristensen, O. 1996. "Combined Heat and Power Production Based on Gasification of Straw and Woodchips," in *Proceedings of the 9th European Bioenergy Conference*. Edited by P. Chartier et al. Pergamon, pp. 272–277.

In the Harboore gasifier, an updraft type, the tar has been minimized from 70 g/Nm^3 to 7 g/Nm^3. An advanced pilot plant has been built for catalytic tar cracking.

Kubiak, H.; Mühlen, H.-J. 1998. "Gas and Electricity Production from Waste Material and Biomass via Allothermal Gasification," in *Biomass for Energy and Industry*. Edited by

H. Kopetz, T. Weber, W. Palz, P. Chartier, and G.B. Ferrero. 10th European Conference and Technology Exhibition, Würzburg, Germany. C.A.R.M.E.N., pp. 1693–1695.

Kuehn, S.H. 1995. "The Latest Twist: the Externally-Fired Combined Cycle," *Power Engineering,* September.

A news article touting the advantages of externally fired, combined-cycle systems. Context is for an atmospheric coal combustor and a ceramic air heater, but applies to gasifiers as well. The hot flue gas flows through a slag screen that removes particulates >12 microns. Only clean air passes through turbine. Pennsylvania Electric system to start up in 1997.

Kurkela, E. 1996a. "Biomass Gasification and Hot Gas Cleaning R&D at VTT Energy," Espoo, Finland: *Analysis and Coordination of the Activities Concerning a Gasification of Biomass* (AIR3-CT94-2284), Second Workshop.

Review with 48 references.

Kurkela, E. 1996b. "Formation and Removal of Biomass-Derived Contaminants in Fluidized-Bed Gasification Processes," VII-PUBS-287, ISBN-951-38-4945-7. Finland: VTT Information Service. Thesis.

An extensive review of VTT work (47 pages + 87 page appendix) from 1988–1994, with 59 references. "Heavy tars" include pyrene to coronene (M.W. 202-301). Heavy tars are total amount condensing at $150°C$ at atmospheric pressure. Covers tars, nitrogen compounds, particulates, and alkali.

Kurkela, E.; Laatikainen-Luntama, J.; Stählberg, J.; Moilanen, A. 1996. "Pressurised Fluidised-Bed Gasification Experiments with Biomass, Peat and Coal at VTT in 1991-1994. Part 3. Gasification of Danish Wheat Straw and Coal," VTT-PUBS-291, ISBN-951-38-4949-X. Finland: VTT Information Service.

High temperature tars are mainly benzene, naphthalene, and heavier PNAs. Define three groups of tars: Light components-pyridine to indene; naphthalene; and PNA heavier than naphthalene. Summary of 1991–1994 tests on wheat, straw, and coal. Part 3, three Danish straws at $800°–900°C$ and 5 bar. Straw sintering was serious above $850°C$. Co-gasification of straw with coal minimized high molecular weight tars, bed additives to decrease sintering were studied. Straw had 0.6–1.3 wt % K, and 0.2–0.3 wt. % Cl. Average tar levels from 100% straw experiments: Benzene ~ 8000 mg/Nm^3; M.W. 79–202 ~ 7,000–11,000 mg/Nm^3; Pyridine-indene ~ 2,000–5,000 mg/Nm^3; Naphthalene ~ 2,400 mg/Nm^3.

Kurkela, E.; Lappi, M.; Pitkänen, P.; Ståhlberg, P.; Leppämäki, E. 1995a. Strategies for Sampling and Analyses of Contaminants from Biomass Gasifiers. VTT Energy, Gasification Research Group, Espoo, Finland. Task Study Report prepared for the IEA Biomass Thermal Gasification Activity (1992-94).

Kurkela, E.; Ståhlberg, P. 1997. "Cleaning of Biomass Derived Product Gas for Engine Applications and for Co-Firing in PC-Boilers," LIEKKI 2 Annual Reports, Project Reports, pp. 562–576.

Summarizes, with references, work on catalytic gas cleaning for engine applications and cofiring in PC boilers. Studies include tests of monolithic Ni catalysts for cleaning the product gas of an updraft, fixed-bed gasifier and a circulating fluidized-bed gasifier. Reactors for testing calcium-based catalysts are also discussed. At 20 bar pressure, temperatures of $970°$–$1,000°C$ are required to keep catalysts in the calcined state at high CO_2 values. CFB tests with Danish wheat straw and demolition wood.

Kurkela, E.; Ståhlberg, P. 1992. "Air Gasification of Peat, Wood and Brown Coal in a Pressurized Fluidized-Bed Reactor. I. Carbon Conversion, Gas Yields and Tar Formation, *Fuel Proc. Technol.* <u>31</u>, pp. 1–21.

The total yield of benzene and tars from a small, pressurized, air-blown fluid-bed pilot plant was 3–4 wt % of dry, ash-free wood at $900°C$. For peat, yield was 0.7–1.2 wt % and for brown coal, the yield was below 0.5 wt %. The most stable tar components were benzene and naphthalene. Toluene and phenol were almost completely decomposed at temperatures higher than $850°C$. Tars were determined from a slip stream into gas washing bottles filled with dichloromethane, followed by GC analysis. Pyridine was seen in wood, peat, and coal at values of 1 (at $800°C$) to 0.02 (at $950°C$) g/kg dry, ash-free feed. Benzene values as high as 25 g/kg feed were observed for wood, while other tar components were less at all temperatures.

Kurkela, E.; Ståhlberg, J.; Laatikainen, J. 1993a. "Pressurized Fluidized-Bed Gasification Experiments with Wood, Peat and Coal at VTT in 1991-1994. Part 1. Test Facilities and Gasification Experiments with Sawdust," Finland: VTT Publications 161.

See also other publications for aspects covered in this 55-page report.

Kurkela, E.; Ståhlberg, J.; Laatikainen, J.; Luntama, J. 1995b. "Pressurised Fluidised-Bed Gasification Experiments with Wood, Peat and Coal at VTT in 1991-1994. Part 2. Experiences from Peat and Coal Gasification and Hot Gas Filtration," VTT-PUBS-249, ISBN-951-38-4787-X. Finland: Valtion Teknillinen Tutkimuskeskus, available from NTIS, Springfield, VA.

Summary of results of peat and coal gasification Part 2. (See Part 1, VTT 161 for sawdust.) PDU-scale pressurized FB. Feed rate to 80 kg/h. Heavy tars defined as those condensing above $150°C$ at 0.1 MPA. Large table of light tar cpds. from coal, peat, and sawdust (pine). (Up to pyrene.)

Kurkela, E.; Ståhlberg, P.; Laatikainen, J.; Nieminen, M. 1991. "Removal of Particles and Alkali Metals from Pressurized Fluid-Bed Gasification of Peat and Biomass Gas Cleanup for Gas Turbine Applications," in *Energy from Biomass and Wastes XIV*. Edited by B.L. Klass. Chicago: Institute of Gas Technology.

Typical range of tar content in filter tests was 6–18 g/Nm^3, "Filtration of wood-derived product gases seems to be much more problematic than filtration of peat or coal derived gases. Heavy molecular tars are formed in wood gasification and some of these tars penetrate through the filter creating a potential emission source. These tars also seem to form a sticky cake on the filter surface, which is not easily removed by pulse cleaning."

Kurkela, E.; Ståhlberg, J.; Laatikainen, J.; Simell, P. 1993b. "Development of Simplified IGCC-Processes for Biofuels: Supporting Gasification Research at VTT," *Biores. Technol.* 46, pp. 37–47.

In fluidized bed gasifiers, most of unstable "pyrolysates" are decomposed, leaving only more stable aromatic components. Typical sawdust tar levels are 8,500 mg/Nm^3 total tar and 5,000 mg/Nm^3 benzene. PNA compounds cited are pyrene, chrysene, perylene, benzo(a)pyrene, benzo(ghi)perylene, and coronene. Dolomite was not particularly effective in catalytic tar reduction when used in the primary fluidized bed. Much better results with secondary bed of dolomite.

Kurkela, E.; Ståhlberg, P.; Simell, P.; Leppälahti, J. 1989a. "Updraft Gasification of Peat and Biomass," *Biomass* 19, pp. 37–46.

Tar contents from the Bioneer updraft gasifier, tar condensed in dichloromethane:

	Tar Distillation Residues at 75°C with No Solvent (g/Nm^3)	Tar Evaporation Residue 105°C 1 h (g/Nm^3)
Hardwood chips	80–160	30–45
Chipped straw	100–140	7–20

Typical raw gas from updraft: 30–150 (g/Nm^3). Typical raw gas from downdraft: 0.5–5 (g/Nm^3). Gas from updraft is used mainly for direct combustion. Partly cleaned gas, with tar from 50–500 (g/Nm^3) can be used for local distribution, combustion, engines, and gas turbines. Clean, dry gas with tar <5 (mg/Nm^3) is needed for long-range distribution. Raw gas was subjected to partial oxidation and the resulting elevated temperature, to reduce tars. (In a secondary chamber.) Tars were quantified by GLC. For tar cracking temperatures from 700°C to 910°C the following tar fractions were observed (mg/Nm^3):

Temp °C	Light Fraction B.P. <150°C	Medium B.P. 150°-250°C	Heavy B.P. >250°C
690	5900	1800	200
800	2000	1000	300
910	1600	500	200
*Raw gas roughly 100,000 mg/Nm^3			

Kurkela, E.; Stählberg, J.; Mojtahedi, W.; Nieminen, M. 1989b. "Pressurized Fluidized Bed Gasification of Peat," in *Pyrolysis and Gasification*. Edited by G.L. Ferrero et al. London: Elsevier Applied Science, pp. 304–311.

Tars and oils are measured in the pressurized fluidized-bed gasifications of peat. Typical dust concentrations after the second cyclone were 4–8 g/Nm^3 (0–20 microns). Tar content generally ranged from 4–8 g/Nm^3 and was dominated by benzene, toluene and naphthalene. "Freeboard temperatures at 830°–870°C seem to be high enough to crack the heavy tars to benzene, naphthalene and other light components, which should not be detrimental to high-temperature gas filtration."

Kwant, K.W. 1996. "State of Small-Scale Biomass Gasification Technology," NOVEM.BTG Biomass Technology Group.

Review of status of some 30 European and World Gasifiers. The VET concept with the reduction of hot combustion gases in the coal-dust cloud is interesting, since the concept appears to solve the tar problem without applying a catalyst or a thermal cracking reactor.

La Fontaine, H. 1986. "Simple Inexpensive Gasifiers for Emergency Use Applications," in *Proceedings of 3rd South. Biomass Energy Res. Conference, 1986*, pp. 397–413.

Reviews history and 1985 status of small, downdraft gasifier for spark-ignition engines. No tar or cleanup discussion.

Lai, C-K S.; Chen, P.; Longwell, J.P.; Peters, W.A. 1986. "Thermal Reaction of *m*-Cresol over Calcium Oxide between 350° and 600°C" *Fuel* <u>66</u>, pp. 525–531.

m-Cresol passed over CaO at 350°–600°C. See 60%–80 % destruction (to toluene). Reaction goes through a calcium *m*-cresolate salt.

Lammers, G.; Beenackers, A.A.C.M.; Corella, J. 1997. "Catalytic Tar Removal from Biomass Producer Gas with Secondary Air," in *Developments in Thermochemical Biomass Conversion,* Vol. 2. Edited by A.V. Bridgwater and D.G.B. Boocock. London: Blackie Academic & Professional, pp. 1179–1193.

For microreactors: Swedish "Glanshammer" dolomite, silica, BASF G-22. For fluid bed: Spanish (Malago) dolomite and BASF G1-25S. How measured: With naphthalene, tar cracker outlet was analyzed for naphthalene, toluene, and CH$_4$ using mass spectroscopy. Conditions studied: Micro-cracking reactor at TPS used with synthetic raw gas containing naphthalene as model tar. Bench-scale, bottom-fed fluidized-bed gasifier at University of Madrid. With and without air addition to bed. Data on effect of air addition to catalytic cracking beds. Conclusions: Air introduces an extra parallel naphthalene decomposition reaction. Air significantly reduces the rate of dolomite deactivation.

Lammers, G.; Orio, A.; Beenackers, A.A.C.M. 1996. "Catalytic Tar Removal from Biomass Producer Gas with In Situ Catalyst Regeneration," in *Biomass for Energy and Environment:*

Proceedings of the 9th European Bioenergy Conference, June 1996. Edited by P. Chartier et al. Pergamon, pp. 1416–1422.

Catalysts: Dolomite. "The combination of catalyst lifetime and catalyst costs is still unfavorable for use of nickel catalysts in large scale tar cracking." Tar in: Naphthalene as model compound for tar. Secondary air is effective in reducing naphthalene and other tar components with dolomite. Also keeps dolomite active. Many of the results are reported elsewhere.

Lehtovaara, A.; Mohtahedi, W. 1993. "Ceramic-Filter Behavior in Gasification," *Biores. Technol*. 46 (1–2), pp. 113–118.

"In the case of biomass gasification, tar formation and destruction are the main issues to be investigated. Cool gas a little for post-gasification gas cleaning." "In gas cooler development the main issue is to keep heat-exchanger surfaces clean by cracking the residual tars." Cooling in two steps: to 400°-650°C then 200°-350°C. Enviropower's system achieves 5 mg/Nm^3 of particulates, which is lower than turbine's required 5 ppm max.

Leppälahti, J.; Kurkela, S. 1991. "Behaviour of Nitrogen Compounds and Tars in Fluidized Bed Air Gasification of Peat," *Fuel* 70, pp. 491–497.

Tar and N-compound formation from peat was measured in laboratory scale, atmospheric pressure, fluidized bed. Effects of secondary air in the freeboard and of dolomite in the bed were measured. A stainless-steel sample probe, maintained at 250°C to prevent tar condensation, extracted gas to condense tars, in wash bottles at +5°C and -70°C in dichloromethane. GC analysis. Both secondary air and dolomite are effective ways to reduce tar content. Total tars varied from ~30 g/kg daf peat to ~12 g/kg over freeboard temperatures from 800–910°C. Dolomite bed cut these levels in half at around 820°C. Benzene, toluene and naphthalene were major tars under most conditions. Main N tar compounds were pyridine, isoqinoline, or methylene-benzeneacetonitrile (C_9H_7N). Pyridine varied from 120–35 mg/Nm^3. Total tar from 5300–12,500 mg/Nm^3.

Leppälahti, J.; Kurkela, S.; Simell, P.; Ståhlberg, P. 1992. *Formation and Removal of Nitrogen Compounds in Gasification Processes*, Vol. 1. Edited by A.V. Bridgwater. United Kingdom, pp. 160–174.

Laboratory updraft gasifier gave typical tar levels of 41–43 g/Nm^3; fluidized-bed gave 4.7–5.4 g/Nm^3. Tar definition and measurement not given.

Leppälahti, J.; Simell, P.; Kurkela, S. 1991. "Catalytic Conversion of Nitrogen Compounds in Gasification Processes," *Fuel Proc. Technol*. 29, pp. 43–56, Elsevier Science Publishers B.V., Amsterdam.

Several catalysts were tested for tar destruction in product gas from a commercial 5 MW updraft peat gasifier. For tar sampling, dichloromethane was used as a solvent in ice and dry-ice acetone wash bottle condensers. Solvent was distilled away at 75°C. Catalysts tested were SiC, iron

sinter, limestone, Fe-dolomite, and Ni-0301. The latter two were the most efficient over the range 800°–900°C.

Levelton, B.H. 1983. "A Comparative Assessment of Forest Biomass Conversion to Energy Forms," Vol. VII of *Unit Processes for Pollution Control*. Simons Resource Consultant. Energy, Mines and Resources, Canada.

Liinanki, L.; Svenningsson, P.; Thessen, G. 1985. "Gasification of Agricultural Residues in a Downdraft Gasifier," in *Energy from Biomass*. Edited by W. Palz, J. Coombs, and D.O. Hall. London: Elsevier Applied Science, pp. 832–836.

A modified Gotland Gengas downdraft gasifier, with a rotating grate, was tested on several fuels. Tar levels varied from 0.61 g/Nm^3 for wood to 0.16 g/Nm^3 for coir dust. "The measured tar content was in all tests below 1g/Nm^3 which is the highest value that can be accepted for a producer gas for internal combustion engines."

Liinanki, L.; Horwath, A.; Lehtovara, A.; Lindgren, G. 1994. "The Development of a Biomass Based Simplified IGCC Process." Thirteenth EPRI Conference on Gasification Power Plants. Oct. 19–21. Palo Alto, CA: Electric Power Research Institute.

Measured total amount of heavy tars (which condense at 150°C at atmospheric pressure) in the air-blown, pressurized, Enviropower fluidized-bed gasifiier was "typically below 100 mg/Nm^3 (90 ppmw), which is a very low level." The measured total light tar concentrations, including benzene, were in the range 4–12 g/Nm^3 (3500–11000 ppmw).

Longwell, J.P.; Peters, W.A. 1987. "Applications of Organo-Calcium Chemistry to Control of Contaminant Aromatic Hydrocarbons in Advanced Coal Gasification Processes," in *Gas Stream Cleanup Papers from DOE/METC-Sponsored Contractors, Review Meetings in 1987*, pp. 260–272.

CaO can produce conversions of pure aromatic compounds, including benzene, of 75%–100% at 600°–800°C for contact times in the range 0.1 to 2 s with coke as the major product. Benzene, toluene, 1-methylnaphthalene, 1-methylanthracene, 9-methyanthracene, and n-heptane were studied. Thermal treatment with CaO continues to show promise as a means of removing newly formed coal pyrolysis tars and pure aromatic compounds including benzene and multi-ring polycyclic aromatic hydrocarbons from coal gasification product streams. High extents of tar and pure compound conversion (75%–100%) have been achieved, with temperature and CaO-to-feed ratio being the most important operating variables. Preliminary estimates suggest that CaO replacement charges would not be expected to render process economics untenable if intermediate (~65%) extents of tar conversion in a single pass reactor can be tolerated. Series staging of three such reactors would appear to offer promise for achieving more severe (>95%) levels of high temperature tar conversion.

Longwell, J.P.; Peters, W.A. 1985. "Applications of Organo-Calcium Chemistry to Control Contaminant Aromatic Hydrocarbons in Advanced Coal Gasification Processes," Fifth Annual Contractors Meeting on Contaminant Control in Coal-Derived Gas Streams. METC,

Morgantown. Cambridge, MA: Massachusetts Institute of Technology, Energy Laboratory and Department of Chemical Engineering, pp. 352–374.

Catalysts: CaO from calcining $CaCO_3$ and $Ca(OH)_2$. Benzene conversion at 860°C, 2 mol %, and 1 second contact time is 75-85% over CaO from $Ca(OH)_2$ and $CaCO_3$, respectively. Tar in: Fresh coal pyrolysis tars or pure aromatic compounds such as benzene.

Lundqvist, R.G. 1993. "The IGCC Demonstration Plant at Värnamo," *Biores. Technol.* 46, pp. 49–53.

No tars reported. Particulate <20mg/Nm^3. Gasifier is CFB at 950°–1000°C, 20 atm, air-blown. Only cyclone and candle-filter for cleanup at 350°C.

Magne, P.; Donnot, A.; Deglise, X. 1990. "Dolomite as a Catalyst for Tar Cracking: Comparison with Industrial Catalysts," in *Biomass for Energy and Industry, 5th E.C. Conference*, Vol. 2, pp. 2,590–2,594.

Catalysts: (1) Charcoal from CEMAGREF gasifier; (2) Charcoal from pine bark; (3) Bentonite (best silica-alumina tested). Used to crack heavy petroleum molecules; (4) Natural sand; (5) Silicagel, Zeosil 125; (6) Dolomite; (7) Recarbonated dolomite. Tar out: see Donnot 85. Same apparatus as in Donnot 85. CEMAGREF charcoal the best—attributed to its high surface area. Then decarbonated dolomite. With cycling, decarbonated dolomite loses activity irreversibly.

Magne, P.; Donnot, A.; Deglise, X. 1985. "Kinetics of Wood Tar Pyrolysis," in *Energy from Biomass*, 3rd E.C. Conference. Edited by W. Palz et al., pp. 822–826.

Common siliceous sand slightly increases the decomposition rate of tar fom pine bark pyrolysis. On the other hand, decarbonated dolomite and even carbonated dolomite have significant catalytic efficiencies. However, it seems difficult, if not impossible, to use them as heat carriers in a pyrolysis process such as that at present under investigation, because they are too soft and would be quickly transformed into dust.

Mäkinen, T.; Leppälahti, J.; Kurkela, E.; Solantausta, Y. 1995. "Electricity Production from Biomass by Gasification and a Solid Oxide Fuel Cell," in *Proceedings of the 8th European Biomass Conference, Biomass for Energy, Environment, Agriculture and Industry*. Pergamon, pp. 1784–1790.

High-temperature fuel cells can use gasifier fuel gas directly. Solid oxide fuel cells (SOFC) are the most interesting. Construction is relatively simple and its development has been rapid. Impurity tolerance not well known, but recent studies indicate tolerance to 5,000 ppm NH_3, 1 ppm HCl and 0.1 ppm H_2S. See Hirschenhofer, J.H. et al. *Fuel Cells. A Handbook* (Revision 3), Morgantown, 1994. DOE/METC-94-1006, 158 pp.

Mårtensson, R.; Lindblom, M. 1995. "Gasification of Sawdust in Pressurized Internally Circulating Fluidized Bed," Espoo, Finland: *Seminar on Power Production from Biomass II.* VTT. March.

First tests of CFB at Lund (18 kg/h) 20 bar and 1,050°C max (100 kw). Typical gasifier output (raw): Condensate tar - 21 g/Nm^3. Refers to "high-temperature condensible hydrocarbons" as "Biotars."

McDonald, E.C.; Aiken, M.; Esplin, G. 1983. "Development of Analytical Methodology for Biomass Gasification Products," ENFOR Project No. C-172. Bioenergy Development Program. Alternative Energy Technology Branch. Canmet. Ottawa: Energy, Mines and Resources Canada.

McLellan, R. 1996. "Updraft Gasification," presented at *Analysis and Coordination of the Activities Concerning a Gasification of Biomass,* Second Workshop, Espoo, Finland.

Describes Wellman's years of experience with updraft, air-blown gasifiers. Raw gas - 58 g/Nm^3 (at -50°C). ESP and cyclic thermal cracker 0.9 g/Nm^3. Thermal oxidation cracking cat. 0.1 g/Nm^3 (at -50°C).

Mehrling, P.; Reimert, R. 1985. "Fuel- and Synthesis Gas from Biomass via Gasification in the Circulating Fluid Bed," *Comm. Eur. Communities,* [Rep.] EUR 10024, Energy Biomass, pp. 905–909.

Describes Lurgi's air blown CFB gasifiers. Tests produced "tar-free gas." C_nH_m ~0.8–1.8 volume %. Wood-char, sand, and Al_2O_3 used as bed material. Made methanol from the wood gas. For running a gas engine, only a "dedusting" unit is used.

METC 1986. "Hot Gas Cleanup for Electric Power Generating Systems," Pacific Northwest Laboratories.

PNL is developing catalysts for fixed-bed tars containing sulfur. Y-zeolite and CoMo-impregnated zeolites. Molten carbonate fuel cell needs sulfur levels < 10 ppm.

Meusinger, J.; Riensche, E.; Stimming, U. 1998. "Reforming of Natural Gas in Solid Oxide Fuel Cell Systems," *J. Power Sources* 71, pp. 315–320.

Complete internal reforming can lead to several problems, including carbon formation in the anode chamber. *"With partial pre-reforming of natural gas these problems can be avoided."*

Miller, B. 1983. "State-of-the-Art Survey of Wood Gasification Technology, Final Report," EPRI. AP-3101.

Gas from a downdraft gasifier has low tar content and can be fed directly into the manifold of a modified (compression ratio) spark-ignition engine. Tars present in gas will condense <371°C. Rome, GA. (APCO) Updraft 25 wt % tars and oil, phenols and lignin-related materials: C1 & C_2 2-3 % vol. Levesque: C_2H_x 2.0 vol %, used to retrofit boiler. Omnifuel-Updraft.

Milne, T.; Agblevor, F.; Davis, M.; Deutch, S.; Johnson, D. 1997a. "A Review of the Chemical Composition of Fast-Pyrolysis Oils from Biomass," in *Developments in Thermochemical Biomass Conversion*. Edited by A.V. Bridgwater and D.G.B. Boocock. London: Blackie Academic, pp. 409–424.

Lists chemical species that have been quantified in fast-pyrolysis oils (primary "tars").

Milne, T.A.; Evans, R.J.; Abatzoglou, N. 1997b. "Biomass Gasifier 'Tars': Their Nature, Formation, Destruction, and Tolerance Limits in Energy Conversion Devices," in *Proceedings of the 3rd Biomass Conference of the Americas, Vol. 1*. Edited by R.P. Overend and E. Chornet. Canada: August 24–29, pp. 729–738.

This paper outlines the report on gasifier "tars" that is being prepared for the IEA gasification activity. One goal of our continuing IEA review is to prepare a set of definitions for organic residuals in gasifier raw gas and to propose definitions for "destruction" for various contemplated end-users. From an evolutionary standpoint, one can define four major product classes:

1. Primary products characterized by cellulose-derived products, such as levoglucosan, hydroxyacetaldehyde, and furfurals; analogous hemicellulose-derived products, and lignin-derived methoxyphenols.
2. Secondary products characterized by phenolics and olefins.
3. Alkyl tertiary products that include methyl derivatives of aromatics, such as methyl acenaphthylene, methyl naphthalene, toluene, and indene.
4. Condensed tertiary products that show the polynuclear series without substituents: benzene, naphthalene, acenaphthalene, anthracene/phenanthrene, and pyrene.

Milne, T.A.; Evans, R J.; Gratson, D.; Nimlos, M.R. 1990. "Catalytic, Hot-Gas Clean Up of Biomass-Produced Synthesis Gas," *Symposium on Energy from Biomass and Wastes XIV*. Chicago: Institute of Gas Technology.

Tars can cause troubles in most end uses, especially during startup or upsets. Transport of medium energy gas can require tar cleanup. For synthesis gas to methanol, etc., unsaturated hydrocarbons such as C_2H_2 and C_2H_4 may even require hydrogenation to avoid catalyst poisoning. In a batch pyrolysis system designed to create primary, secondary, or tertiary tars, the effect of process variables on the entire slate of tar species (methane to pyrene) was examined by MBMS for Pt, Pd, Rh, and Ni catalysts. Except for updraft gasifiers, gasification for synthesis gas production will tend toward tertiary tar production. The real-time tar spectra by MBMS agree, in major features, with the flash re-pyrolysis of collected, actual gasification tars.

Milne, T.A.; Evans, Robert; Soltys, Michael N. 1984. "Characterization of Biomass Pyrolysis Oils by Flash Evaporation and Direct, Molecular-Beam Mass Spectrometry," in *Energy from Biomass and Wastes VIII*. Chicago: Institute of Gas Technology, pp. 1371–1393.

Early mass spectral "fingerprints" of collected oils and tars from pyrolysis, gasification and liquefaction processes. Clearly shows the PNA nature of downdraft "tar."

Moersch, O. 1997a. Communication on CREST. 11/3/97.

The University of Stuttgart BFB-type gasifier produced of the order of 0.5 g/Nm^3 tar. Measured with a quasi-continuous "tar meter" based on FID. They have been working for some time on tar sampling and measurement.

Moersch, O. 1997b. Communication on CREST Network regarding their "tar meter," 11/11/97.

This tar measurement uses two FIDs and compares response of tar-laden gas and gas with tars condensed out at as low as -10°C. About 10 mg/Nm^3 of naphthalene will stay in the gas phase even at this temperature. Benzene and toluene completely pass the condenser/filter. A typical "low-tar" gas has only 100 mg of tar against 50,000 mg of gaseous hydrocarbons, so the tar FIDs must have very similar responses.

Moersch, O.; Spliethoff, H.; Hein, K.R.G. 1998. "Quasi Continuous Tar Quantification with a New Online Analyzing Method," in *Biomass for Energy and Industry*. Edited by H. Kopetz, T. Weber, W. Palz, P. Chartier, and G.B. Ferrero. 10th European Conference and Technology Exhibition, Würzburg, Germany. C.A.R.M.E.N. pp. 1638–1640.

Moersch, O.; Spliethoff, H.; Hein, K.R.G. 1997. "A New System for Tar Sampling and Analysis," in *Biomass Gasification and Pyrolysis.* Edited by M. Kaltschmitt and A.V. Bridgwater. Newbury, UK: CPL Press, pp. 228–234.

A "dry" sampling system developed at the University of Stuttgart is described. "It employs a sampling system consisting of three main components: hot gas filtration, tar probe for the retention of components with high boilng point, and on-line analysis of components passing this filter. Tar is quantified by registering the weight increase of the tar probe. Components with a higher boiling point than naphthalene are retained completely on the probe; BTX components, phenols, and indene pass it completely. The gases are led directly into an online GC-FID system where the major components from benzene up to naphthalene are identified and quantified. Measurements on a bubbling fluidized bed with spruce wood are as follows:

	600°C	700°C	800°C	900°C
BTX, g/m3	2.8	6.6	12.6	3.6
Tar with GC	1.4	1.8	2.4	0.6
Tar on filter	40.5	9.9	5.8	1.0
Total tar	42.0	11.7	8.2	1.6

Moersch, O.; Spliethoff, H.; Hein, K.R.G. 1996. "Influence of Temperature and Stoichiometry on Gas Quality and Conversion Rate in Fluidised Bed Gasification Biomass," in *9th European Bioenergy Conference & 1st European Energy from Biomass Technology Exhibition*. Edited by P. Chartier et al. Pergamon/Elsevier, pp. 1398–1403.

Describes fluidized-bed test facility at University of Stuttgart. 1.5–6 kg/h feed. 600°–900°C esults shown. Lowest tar levels are ~2 g/Nm^3. Shows progression of heavy tars to light, ending with benzene.

Morris, M. 1996. "Atmospheric Pressure Gasification Process for Power Generation," in *Bioenergy '96—The Seventh National Bioenergy Conference*, pp. 275–283.

This paper describes various atmospheric pressure, circulatory fluidized-bed gasifier systems for biomass, including the two 15 Mwth CFB systems at Grève-in-Chianti, Italy. (TPS Termiska Processer AB was formerly a part of Studsvik AB.) Using patented dolomite CFB to crack tars to simpler compounds, thus avoiding clogging of heat exchangers or filters and avoiding soot problems. TPS pilot plant has operated 1,300 hours, 750 with ICE. For IGCC, TPS now favors atmosphere gasifier for sizes as large as 60–80 MW. Can use wet scrubbing, which avoids hot-gas filtration.

Moses, C.B.; Bernstein, H. 1993. "Impact Study on the Use of Biomass-Derived Fuels in Gas Turbines for Power Generation, Final Report," Southwest Research Institute, Contract AV-12148-1 (NREL).

Tar Definition: "Tars are high-boiling hydrocarbons that, if not burned out, can form deposits on the combustor walls and distort the flow patterns." Must preheat valves, manifolds, and injectors to prevent condensation. Cyclones and ceramic filters could be sufficient for industrial gas turbine, but less suitable for aeroderivatives. For industrial turbines, refurbish every 12,000 to 64,000 h. Plan a shortened maintenance interval for biofuels.

MTCI. 1994. "Indirect Gasification of Biomass for Production of Syngas for Both Combined Cycle Power Generation and Methanol," Final Report, *Task 1: Biomass Gasification Tests*. Manufacturing and Technology Conversion International, Inc., Subcontract No. AW-2-12263-1.

From five tests of the MTCI gasifier using wood chips, tar plus oil varied from 1.9–3.7 x 10^{-4} fraction of dry feed rate (from venturi scrubber condensate).

MTC1. 1990. "Testing of an Advanced Thermochemical Conversion Reactor System," January. PNL-7245. Battelle Pacific Northwest Laboratory.

Only looked at carbon content of "tar/oil" collected in quench ice bath. See Johnson, V.J. (1961), Ph.D. Thesis, Purdue University. "The Chemical Composition of Hardwood Smoke." Tar/oil as percent carbon; pistachio shells 1.3–2.1; secondary fiber waste 4.7; wood chips 3.0; urban wood waste 2.4; orchard prunings/bagasse 2.1

Mudge, L.K.; Baker, E.G.; Brown, M.D.; Wilcox, W.A. 1988a. "Catalytic Destruction of Tars in Biomass-Derived Gases," in *Research in Thermochemical Biomass Conversion, an International Conference*. Edited by A.V. Bridgwater and J.C. Kuester. London: Elsevier, pp. 1141–1155.

In two-stage gasification/cleanup, lines must be above 350°C to minimize deposition of tars before entering the second reactor. When methylene chloride-dissolved tars are evaporated at 105°C for 1.5 h, none of the C_6–C_{20} hydrocarbons remained, and the residue was considered to be organics more refractory than C_{20}. "These heavy organics are probably the condensible fraction that leaves gummy deposits in downstream piping and equipment."

Mudge, L.K.; Baker, E.G.; Mitchell, D.H.; Brown, M.D. 1985. "Catalytic Steam Gasification of Biomass for Methanol and Methane Production," *J. Solar Energy Engin.* 107, pp. 88–92.

Laboratory and PDU tests reported earlier are summarized, with new data at 10 atm and determination that the best secondary catalyst is a Ni-Co-Mo on silica-alumina doped with 2 wt % Na. This catalyst appears to retain its activity indefinitely at 750°C and 1 atm. Contact of catalyst with biomass leads to rapid deactivation in hours.

Mudge, L.K.; Brown, M.D.; Wilcox, W.A. 1987. "Bench-Scale Studies on Fluid-Bed Pyrolysis of Wood Using Different Contact Gases," in *Proceedings of the 1987 Biomass Thermochemical Conversion Contractors' Review Meeting*, Atlanta, GA, pp. 141–150.

Tar in: Condensible hydrocarbons measured with CO_2, CH_4, and H_2 contact gases and 650°–800°C. How measured: Two scrubbers in series, filled with methylene chloride and at 0°C and -20°C. Solution analyzed by GC. At 650°C the oils identifiable by GC were about 25 wt % of the condenser oils.

Mudge, L.K.; Gerber, M.A.; Wilcox, W.A. 1988b. "Improved Gasification by Catalytic Destruction of Tars in Biomass-Derived Gases," in *Thermochemical Conversion Program Annual Meeting*. SERI/CP-231–3355. Golden, CO: NREL, pp. 87–100.

Best catalysts for tars from pyrolysis gasification are G90C, G98B, and ICI-46-1. Added air selectively oxidized the coke on catalyst. These catalysts and a special NiCoMo catalyst from Grace remained active indefinitely at 600°C and above. Tar in: Gases containing tars were generated from wood by pyrolysis, steam gasification and air/steam gasification. Tars create plugging problems in downstream equipment and with wastewater treatment. Partial oxidation of the gas stream in a secondary fluidized-bed of catalyst destroys the tars. Reactor is designed to enhance carbon burnoff of catalyst with minimal oxidation of CO or H_2. Gas temperatures in lines etc., kept above 350°C to prevent tar deposition. Catalytic destruction of tars from air-steam gasification was easier than from pyrolysis gasification at the same temperature.

Mudge, L.K.; Sealock, Jr., L.J.; Weber, S.L. 1979. "Catalyzed Steam Gasification of Biomass," *J. Analyt. Appl. Pyrolysis* 1, pp. 165–175.

Batch gasification in a steam/N_2, externally heated downdraft system, was studied for wood mixed with dry catalysts and for wood impregnated with catalysts. Potassium carbonate, sodium carbonate, trona, and borax were studied. Only gas data to C_2H_6 are presented. Gases always increased with catalyst and temperature. Catalyst concentration of 3×10^{-3} and 3×10^{-4} moles of alkali per gram of wood, were tested.

Mukherjee, D.K. 1995. "Experience with Unconventional Gas Turbine Fuels," Espoo, Finland: Seminar on Power Production from Biomass II, VTT. March.

Blast furnace gas containing CO is stable only at temperature <300°C or >600°C due to 2 CO plus catalyst = CO_2 + C. Iron dust on oxidized surfaces can be a catalyst. Turbine tolerance for dust:

Dust Loading	Size
120 ppm	$0.1 \mu m$
110 ppm	$1.0 \mu m$
40 ppm	$4.0 \mu m$
0.1 ppm	$10 \mu m$
0.01 ppm	$15 \mu m$

Mukunda, H.S.; Dasappa, S.; Paul, P.J.; Rajan, N.K.S.; Shrinivasa, U. 1994a. "Gasifiers and Combustors for Biomass—Technology and Field Studies," *Energy for Sustainable Development* 1 (3), pp. 27–38.

Tar Definition: Condensibles. Open core (open top) gasifier is modification of Reed and Markson. For engines the acceptable upper limits are ~ 50 mg/m^3 for particulates. No clear statement of tar tolerance. Must avoid tar deposits in fuel passages. Assume < 50 mg/m^3. Updraft gasifiers produce "smelly" tar implying the presence of components of a wide range of M.W. See some part of the tar deposited in the filter circuit. Check Kaupp (1984) and Stassen (1993) for engine test experience.

Mukunda, H.S.; Dasappa, S.; Shrinivasa, U. 1993. "Open-Top Woods Gasifiers," in *Renewable Energy, Sources for Fuels and Electricity.* Edited by T.B. Johansson, H. Kelly, A.K.N. Reddy, and R.H. Williams. Washington, DC: Island Press, pp. 699–728.

Mukunda, H.S.; Paul, P.J.; Dasappa, S.; Shrinivasa, U.; Sharan, H.; Buehler, R, Hasler, P.; Kaufmann, H. 1994b. "Results of an Indo-Swiss Programme for Qualification and Testing of a 300-kW IISc-Dasag Gasifier," *Energy for Sustainable Development* 1 (4), pp. 46–49.

Tar Definition: Heavies, collected in a series of wash bottles. Open Core Gasifier: Gases contain ~ 0.25% C$_2$ + HC's; average particulate content is 60 ± 100 mg/m^3 hot; 60 ± 15 cold; tar is 70 ± 30 mg/m^3 hot, and 20 ± 10 mg/m^3 cold. Effluent 2.3 g/kg dry feed (dissolved organic content).

Myrén, C.; Hörnell, C.; Sjöström, K.; Yu, Q.; Brage, C; Björnbom. 1997. "Catalytic Upgrading of the Crude Gasification Product Gas," in *Developments in Thermochemical Biomass Conversion,* Vol. 2. Edited by A.V. Bridgwater and D.G.B. Boocock. London: Blackie Academic & Professional, pp. 1170–1178.

Tar is collected by condensation in several steps, and measured by GC and gravimetrically. Destruction Method: Thermal and catalytic cracking of a 700°C pyrolysis gas, at 700°–900°C. Use dolomite and Ni catalysts. Big table of tar compounds. Naphthalene is the most stable. Illustrates destruction by decrease in "tar" compounds.

Myrén, C.; Hörnell, C.; Sjöström, K.; Yu, Q.; Brage, C.; Björnbom. 1996. "Catalytic Tar Cracking of Gas from Agricultural Residues and Biomass," in *Biomass for Energy and Environment: Proceedings of the 9th European Bioenergy Conference, June 1996.* Edited by P. Chartier. Pergamon, pp. 1283–1288.

Catalysts: Dolomite (Sala). Tar in: Pyrolysis of straw, miscanthus, and mixed-hardwoods at 700°C. How measured: Condensed tar in several steps. Multi-step fractionation and analysis of condensates gives detailed compositions. Conditions studied: catalytic reactor at 800°–900°C. "The tar conversions reported here are rather large since benzene has been calculated as belonging to the gas which is not done by all researchers." Tar yields for miscanthus, straw, and mixed hardwoods, after dolomite cracking at 900°C are: 107 mg/100 g feed, 138 and 1825, respectively, C_1–C_3, benzene, and naphthalene dominate in all cases. Phenols are <1% of aromatics.

Narváez, I.; Corella, J.; Orío, A. 1997. "Fresh Tar (from a Biomass Gasifier) Elimination over a Commercial Steam-Reforming Catalyst. Kinetics and Effect of Different Variables of Operation," *Ind. Eng. Chem. Res.* <u>36</u>, pp. 317–327.

Many of the data previously reported in conferences. Guard bed of calcined dolomite at 800°–850°C decreases tar to below 2 g/Nm^3, a value that greatly extends the life of downstream catalysts such as BASF G1-25 S Ni based.

Narváez, I.; Orío, A.; Aznar, M.P.; Corella, J. 1996. "Biomass Gasification with Air in an Atmospheric Bubbling Fluidized Bed. Effect of Six Operational Variables on the Quality of the Produced Raw Gas," *Ind. Eng. Chem. Res.* <u>35</u> (7), pp. 2110–2120.

Reports on gasification output from new bench-scale system. A new tar and gas sampling system, similar to the one used at VTT (Simell and Bredenberg 1990). Five stage condenser to -5°C or -80°C is used. Overall sample of condensates is diluted with water until a homogeneous phase is obtained, then do a total organic carbon determination. Tar levels at the gasifier exit ranged from 2 g/Nm^3 to 10 mg/Nm^3. To get tar contents in the raw gas below 1–2 g/Nm^3 may not be possible.

National Academy of Sciences. 1983. *Producer Gas: Another Fuel for Motor Transport*, National Academy Press, Washington, D.C. Contract No. AID ta-C-1433. Edited by N.A Vietmeyer. Golden, CO: Bioenergy Foundation Press.

Typical producer gas in WWII downdraft gasifiers was methane 3%–5%, heavy hydrocarbons 0.2%–0.4%, 5,200 kJ/m^3 (140 Btu/ft^3). Refers to dry, low-tar fuels.

Nelson, E.T. 1987. "Assessment of Instrumentation Needs for Advanced Coal Conversion Power Plants," in *Gas Stream Cleanup Papers from DOE/METC-Sponsored Contractors Review Meetings in 1987*. Edited by K.E. Markel, Jr., METC. Reading, PA: Gilbert/Commonwealth, Inc.

Tar Definition: Oils and tars are condensed mixture of aromatics, PNA, phenols, organic sulfur. Measured by total hydrocarbon analyzer. Turbines: H_2S ~20,000 ppm; 0.5 ppm Na, K. Sulfur and particulate limits less stringent than environmental limits; MCFC requires purest gas; H_2S, COS, CS_2, and SO_2 > 1 ppm deactivates anode. Cl_2, HCl, alkali halides deactivate cathode. HC > 1 mole percent lead to carbon formation. Particulates (50% < 2 micrometers) at 0.005 gr/ft^3 block flow; Fixed-bed coal gasifiers give 300–700 ppm tar and oil; 700–4000 ppm

HCl; 13 ppb-1000 ppm KCl; "Sampling systems tend to resemble miniature, high-maintenance chemical plants which are difficult to operate."

Nieminen, M. 1995. "Removal of Particulates and Alkali Metals in Gasification," Espoo, Finland: Seminar on Power Production from Biomass II, VTT. March.

Biomass produces much more tar than coal. Has advantages and disadvantages. For filtration, light tars behave like gas. Heavier tars are problematical. Heavy tars can cause filter blocking by soot formation, adsorption or condensation on filter matrix or dust cake. Fed light tars as synthetic tar solution. Also real biomass tar (up to coronene). No references to work of the VTT gasification group.

Nieminen, M. 1997. "The Development of Solid Fuel Gasification Systems for Cost-Effective Generation with Low Environmental Impacts," Liekke 2-L97-1-Pt. 2. Annual Review, Project Reports, pp. 685–696.

In co-gasification of coal and wood, the "pressurized fluidized gasifier showed that .. even with only 15% coal addition the heavy tar concentration was decreased significantly." "The formation of tars and their behavior in gas cooling filtration have been the main questions in earlier wood (and other biomass) gasification tests at VTT. When gasifiying biomass alone the formation of high-molecular-mass tars (molecular mass greater the 202 amu) may have a serious impact on filtration through blinding of ceramic barrier filters." "...coal char particles present in the bed and in the freeboard have catalytic effects on the secondary reactions of the pyrolysis products of wood.". Dolomite and limestone were also tested in the fluidized bed of the gasifier, to reduce heavy tars. "Heavy tar" concentrations in coal/biomass co-gasification are reported as follows: 100% forest residue, 2.3 g/Nm³; 15% Polish coal, about 2 g/Nm³; 36 % Polish coal, essentially the same. For pine sawdust: 100% gave about 1.5g/Nm³, 24% Polish coal, 0.6 g/Nm³; and 48% Polish coal, less than 0.1g/Nm³.

Nieminen, M.; Simell, P.; Leppälahti, J.; Ståhlberg, P.; Kurkela, E. 1996. "High-Temperature Cleaning of Biomass Derived Fuel Gas," in *Biomass for Energy and Environment: Proceedings of the 9th European Bioenergy Conference, June 1996.* Edited by P. Chartier et al. Pergamon, pp. 1080–1085.

Monolith catalysts the most promising to avoid plugging. A 500-h test has shown no deactivation, but catalyst in this test not identified. In fluidized bed gasification it is not possible to remove halides by Ca-based in-bed sorbents (thermodynamics). "Control of trace elements in the gasification process is not well known."

Niessen, W.R.; Marks, C.H.; Sommerlad, R.E. 1996. "Evaluation of Gasification and Novel Thermal Processes for the Treatment of Municipal Solid Waste," Camp, Dresser & McKee. NREL/TR-430-21612. National Renewable Energy Laboratory, Golden, Colorado. Biomass Energy Foundation Press, Boulder, Colorado.

Energy Products of Idaho—Fluidized bed: vol % (dry basis)

C₂H₂	C₂H₄	C₂H₆	C₃H₈	Other	Unknown
0.18	1.5	0.23	0.01	0.15	1.50

TPS Termiska Processor, FBG. C_xH_y = 4.9 vol %, 2% typical (30% of heating value). Distinguishes: low-to-med M.W. HCs. B.P. < 100°C. High-M.W. HCs, sometimes called "tar." Tars are odorous and may be carcinogenic. Proler (Rotary Kiln); C_2H_2 - 0.5; C_2H_4–1.7; C_2H_6–0.1; Benzene– 0.5 vol %. Thermoselect: slow devolatilization <2 h to 800°C then 4:0 s at 1200°C. Even CH_4 is < 0.1%. Thermochem. (MTCI): Only small amounts of light HC. C_2H_2-0.0; C_2H_4-0.6; C_2H_6-0; Other 9.9 vol %.

Nordin, A.; Kallner, P.; Johansson, E. 1997. "Gas Quality from Biomass Gasification; an Extensive Parametric Equilibrium Study," in *Developments in Thermochemical Biomass Conversion, Vol. 2*. Edited by A.V. Bridgwater and D.G.B. Boocock. London: Blackie Academic & Professional, pp. 838–850.

Reports values for CO, H_2, CH_4, CO_2, H_2O, NH_3 and HCN.

Oesch, P.; Leppämäki, E.; Ståhlberg, P. 1996. "Sampling and Characterization of High-Molecular-Weight Polyaromatic Tar Compounds Formed in the Pressurized Fluidized-Bed Gasification of Biomass," *Fuel* 75 (12), pp. 1406–1412.

Sampled tar directly from a PDU gasifier at VTT. Controlled condensation at 150°C. Dissolution in dichloromethane. GC, high-temperature GC, GPC, pyrolysis GC, atomic emission detector, and gravimetric analysis for components above M.W.302. Heavy tars seen from pyrene ($C_{16}H_{10}$) to dibenzo (a,e) pyrene ($C_{24}H_{14}$). If product gas contains particulates, the sample should not be taken at temperatures >700°C, since the tar components can be catalytically decomposed by the particles.

Oja, V.; Suuberg, E.M. 1998. "Vapor Pressures and Enthalpies of Sublimation of Polycyclic Aromatic Hydrocarbons and Their Derivatives," *J. Chem. Eng. Data.* 43, pp. 486–492.

Contains data for several tertiary tar species of interest to wood gasification.

Oja, V.; Suuberg, E.M. 1997. "Development of a Nonisothermal Knudsen Effusion Method and Application to PAH and Cellulose Tar Vapor Pressure Measurement," *Anal. Chem.* 69, pp. 4619–4626.

A new vapor-pressure method, based on the traditional Knudsen method, is validated with anthracene and naphthalene and used to measure the vapor pressure of levoglucosan and a cellulose pyrolysis tar. Cellulose is pyrolyzed within the folds of a resistively heated wire mesh such that the vapors are quickly grounded by rapid mixing with the surrounding cold gas. Tars are collected by washing with methanol or methanol-tetrahydrofuran. "Tars are operationally defined as room temperature condensable materials." Tar samples were prepared by evaporating the methanol in a vacuum oven at a temperature not exceeding 55°C. The tars behave similarly to levoglucosan. The tars were measured to have a number average molecular weight of between 172 and 184 Da. "cellulose tar does not show a large variation in vapor pressure with mass loss

because it contains species that, for the most part, have quite comparable molecular weights and compositions.

Olivares, A.; Aznar, M.P.; Caballero, M.A.; Francés, E; Corella, J. 1997. "Improving the Product Distribution and Gas Quality in Biomass Gasification by In-Bed Use of Dolomite," in *Proceedings of the 3rd Biomass Conference of the Americas, Vol. 1*. Edited by R.P. Overend and E. Chornet. Canada: August 24–29, 1997, p. 745.

In-bed calcined dolomite changes the product distribution at the gasifier exit. "Gasifying with steam-O_2 mixtures, the tar content in the exit gas decreases from 12 to 2–3 g tars/Nm^3. (Fluid bed). The dolomite is continuously fed to the gasifier, mixed with biomass at 2–3 wt %.

Olivares, A.; Aznar, M.P.; Caballero, M.A.; Gil, J.;Francés, E; Corella, J. 1997. "Biomass Gasification: Produced Gas Upgrading by In-Bed Use of Dolomite," in *Ind. Eng. Chem. Res.*, 36, pp. 5220-5226.

Olsen, G. 1989. "Research on Tar Cracking and Application of Tar," in *Pyrolysis and Gasification*. Edited by G.L. Ferrero et al. Elsevier, pp. 479–485.

Catalysts: None. Thermal cracking from 600°–1100°C. Tar out: Distilled tar to obtain a fraction with boiling point between 100° and 200°C. Interested in using this as a substitute for diesel fuel. Acetone is very difficult to separate completely from tar by distillation.

Olsen, G.; Pedersen, P.H.; Henriksen, U.; Kofoed, E. 1989. "Gasification and Pyrolysis of Straw—Research in Denmark," in *Pyrolysis and Gasification*. Edited by G.L. Ferrero et al. Elsevier, pp. 290–295.

Catalysts: Dolomite. Tar in: Steam gasification in batch and continuous modes. Tar is known to cause valves and piston rings to stick when the engine is shut down.

Orío, A.; Corella, J.; Narvaez, I. 1997a. "Characterization and Activity of Different Dolomites for Hot Gas Cleaning in Biomass Gasification," in *Developments in Thermochemical Biomass Conversion,* Vol. 2. Edited by A.V. Bridgwater and D.G.B. Boocock. London: Blackie Academic & Professional, pp. 1144–1157.

Four samples of dolomite from different quarries in Spain. Fe_2O_3 content varied from 0.01 to 0.75 wt %, K_2O from 0.01–0.24. Dolomites were used in a fixed bed of 6.0 cm i.d. following the bubbling fluidized bed of 6 cm i.d. The dolomite was placed in the fixed bed to avoid its erosion if fluidized. Within experimental error the four were about equal in tar reduction. The Fe_2O_3 content may have a second-order effect.

Orío, A.; Corella, J.; Narvaez, I. 1997b. "Performance of Different Dolomites on Hot Raw Gas Cleaning from Biomass Gasification with Air," *Ind. Eng. Chem. Res.* 36, pp. 3800–3808.

Different dolomites studied in a 6.0-cm i.d fixed bed, downstream from an air-blown fluidized-bed gasifier (biomass fed near bottom). Hot gas filter at 500°–600°C between gasifiers and

dolomite bed. Tar analysis methods given in Narvaez et al. (1996). No deactivation of the four tested dolomites in 5–10 h at steady state. Tar content decrease in dolomite depends on equivalence ratio and moisture content of feed. Less moisture or lower the equivalence ratio the greater the tar. Effectiveness of dolomites increases with Fe_2O_3 content. Comparing air gasification results with steam gasification (Narvaéz et al. 1996), shows that tars from steam gasifications are easier to destroy. Postulate that steam gasification tars have more phenolics and C-O-C bonds, which are easier to steam reform. As equivalence ratio increased, "harder" tars are produced in air, but at lower levels. (No mention is made of possible effect of top feeding [steam] vs. bottom feeding [air].) Tar yields after dolomite in the range of 160–6,100 mg/Nm^3 are reported over the range of variables studied. Tar conversions (not defined in this paper) from 60%–99+% are reported.

Overend, R. 1994. "Foreign Travel Report Summary," Graz, Essen, London.

Allothermal Gasification System-DMT to be used in Electrofarming project. Biomass Steam Reforming. Patented BGFC process. Initial Electro-Farming Facility in Union Springs, Alabama. Gas analysis by continuous process M.S.; C_2-C_6 analysis by GC; Tar content by GC; ISO-647 (seems to be a slow pyrolysis method). "Primary Tar" measured by Fischer-Schrader analysis (ISO-647); In gasifier tests at 720°–920°C: C_2H_4 5.9-2.1 vol %, C_2H_6 0.3-0.4 vol %, Tar 11.2-1.0 g/kg.

Overend, R. 1982. "Wood Gasification - Review of Recent Canadian Experience," *Energy from Forest Biomass*. Edited by W.R. Smith. New York-Toronto: Academic Press, pp. 171–207.

"*Engine manufacturers advise that acceptable particle loadings are 50–200 mg/m^3 in piston engines and about 3 mg/m^3 in turbines based on natural gas experience. Since entrained water counts as particulate, the requirements for LJV gas are those of dust and water removal down to a dewpoint at least 5 ℃ below the fuel gas supply temperature.*"

Paisley, M.A. 1997. "Catalytic Hot Gas Conditioning of Biomass Derived Product Gas," in *Developments in Thermochemical Biomass Conversion,* Vol. 2. Edited by A.V. Bridgwater and D.G.B. Boocock. London: Blackie Academic & Professional, pp. 1209–1223.

Tar Definition: Refers to "secondary oils" and "tertiary oils or tars." Straight-chain aliphatics and aromatics. Claims CH_4 must be reduced for power generation(?) Even wet scrubbing can leave "mist" of tars of order of 0.1% of original tars. Could bother compressors or turbines. Summarizes tar destruction from 1993 and other earlier reports. Refers to TMBMS results showing DN-34 destruction of secondary tar (phenols, cresols, etc.), leaving the tertiaries behind.

Paisley, M.A. 1996. "Method for Hot Gas Conditioning," Columbus, OH: Battelle Memorial Institute, U.S. Patent 5,494,653.

Summary of previously reported DN-34 results. DN-34 is "essentially alumina."

Paisley, M.A. 1995a. "Development and Commercialization of a Biomass Gasification/Power Generation System," in *Proceedings: Second Biomass Conference of the Americas: Energy, Environment, Agriculture, and Industry*. Portland, OR, pp. 553–564. NREL/CP-200-8098.

Sixty h test with small gas turbine. Refers to possible fouling of the turbine system by heavy hydrocarbons in the gas. "Condensible materials (tars)." BCL gasifier gives ~0.5–1 wt % of dry wood as tar.

Paisley, M.A. 1995b. "Operation and Evaluation of an Indirectly Heated Biomass Gasifier. Phase II-Task1-Catalyst Screening Tests," February. Battelle.

Tar definition: Toluene wash material. Collected by MM5 sampling train. Destruction method: DN-34 and several alumina-based catalysts. Hybrid poplar showed tar production of 1 x 10^{-3} lb/ft^3; wet hog fuel, 1 x 10^{-2} lb/ft^3; sawdust 2.4-6.5 x 10^{-3}. Severe DN-34 attrition noted. Only DN-40 showed coke deposition, DN-36, 37 lost activity with time. DN-50 and fused alumina may have promise at 871°C DN-34 destroys C_2H_2 more than C_2H_4. C_2H_4 drops a factor of 2–3. DN-38 seemed much better than DN-34 for C_2H_4 destruction.

Paisley, M.A. 1993. "Operation and Evaluation of an Indirectly Heated Biomass Gasifier," January. Phase Completion Report by Battelle Columbus.

Tar Definition: Condensibles in system (probe et al) soluble in toluene. After drying to 200°F. How collected: MM5. Rinsed with toluene, dried at 150°F, then 200°F overnight. How measured: Weighing. Destruction method: ICI-Katalco and DN-34, slipstream. PRU uses commercial scrubber. Removed ~75% of condensed tar. Hybrid poplar T ~ 1600. C_2H_4~ 0.05 vol % (N$_2$ free). Feed 2.7% ash; 0.6 % N; 0.02% S; 0.01 % Cl (dry basis). Switchgrass 0.0004 lb/ft^3; hybrid poplar 0.001 lb/ft^3 (~1% of dry feed wt). Catalysts did not change NH$_3$, HCN much. Switchgrass: 1.2% N; 0.10 % S; 10% ash; 0.14% Cl; 0.0005 lb/ft^3 tar; ~0.05 vol % C_2H_4 at ~1800°F, .006% C_2H_4; most of Cl stays in bed as KCl, NaCl; hot gas cleanup: Ambiguous results. Empty cracker as good as other catalyst for tar but not for C_2H_4; DN-34 better than ICI; Claims BCL gasifer produces less tar than other gasifiers, with lower M.W.

Paisley, M.A.; Anson, A. 1998. "Biomass Gasification for Gas Turbine-Based Power Generation," *J. Eng. Gas Turbines Power* 120, pp. 284–288.

The Battelle process *"depends on very rapid heating of the raw biomass to minimize tar formation." ". . .Tar concentrations measured in the product gas from the Battelle gasifier are typically 16g/m3. These tars are highly aromatic in character and are relatively insoluble in water."*

Paisley, M.A.; Farris, G.; Slack, W.; Irving, J. 1997. "Commercial Development of the Battelle/Ferco Biomass Gasification Process—Initial Operation of the McNeil Gasifier," in *Proceedings of the 3rd Biomass Conference of the Americas, Vol. 1*. Edited by R.P. Overend and E. Chornet. Canada: August 24-29, 1997, pp. 579–588.

The condensible tar fraction of the gas in the BMI gasifier is very low, of the order of 0.5 wt % of the gas and the condensates are predominantly of high boiling point and immiscible in water. ". . . a novel hot-gas conditioning catalyst (DN-34) converts these condensible products to noncondensible forms." DN-34 is a proprietary catalyst described in U.S. Patent 5,494,653. "Tar concentration measured in the product gas from the Battelle gasifier is typically 16 g/Nm^3. These tars are highly aromatic in character and are relatively insoluble in water."

Paisley, M.A.; Feldmann, H.F.; Appelbaum, H.R. 1984. "Scale-Up of a High-Throughput Gasifier to Produce Medium-Btu Gas (500 Btu/SCF) from Wood," in *Energy from Biomass and Wastes VIII Symposium*. Chicago: Institute of Gas Technology.

C_2H_4 typically 6.0 vol % (dry); C_2H_6 1.0 %; C_2H_2 not mentioned.

Paisley, M.A.; Gebhard, S.C. 1995. "Gas Cleanup for Combined Cycle Power Generation Using a Hot Gas Conditioning Catalyst," in *Proceedings, Second Biomass Conference of the Americas: Energy, Environment, Agriculture, and Industry*. Portland, OR, pp. 617–629.

Previously reported BCL-PRU data plus microscale DN-34 tests.

Paisley, M.A.; Litt, R.D.; Creamer, K.S. 1990. "Gasification of Refuse Derived Fuel in a High Throughput Gasification System," *Energy from Biomass and Wastes XIV*. Chicago: Institute of Gas Technology.

In wastewater, phenol was 89 mg/L; TOC 2 mg/L. Condensibles from wood are relatively insoluble in H_2O. C_2H_2 11.2 vol %; C_2H_6 11.3 vol %. Lower "condensed" materials than with wood. No collectible tar materials were found.

Paisley, M.A.; Overend, R. P. 1994. "Biomass Gasification for Power Generation," Thirteenth EPRI Conference on Gasification Power Plants. Palo Alto, CA: Electric Power Research Institute, October 19–21, 1994.

"High heat-up rates possible through indirect heating with a circulating sand phase along with the short residence times in the gasification reactor effectively reduce the tendency to form condensible tar-like materials which results in an environmentally simpler process." Tar concentrations from the Battelle gasifier average 0.5%–1% of the dry wood, by weight. This corresponds to a gaseous tar concentration of approximately 0.5% of the dry product gas.

Palonen, J.; Nieminen, J. 1996. "Pressurized CFB Gasification, Värnamo IGCC Demonstration Plant," Espoo, Finland: *Analysis and Coordination of the Activities Concerning a Gasification of Biomass* (AIR#-CT94-2284), Second Workshop, September 26–28.

Description of Värnamo IGCC plant, owned by Sydkraft and using the Foster-Wheeler (formerly Ahlström) pyroflow circulatory, pressurized fluid-bed gasifier. The Bioflow system has operated 150 h, with the gasifier logging 4500 h. (No tar data given.)

Palonen, J.; Lundqvist, R.G.; Stahl, K. 1995. "IGCC Technology and Demonstration," Espoo, Finland: *Seminar on Power Production from Biomass II*, Hanasaari Swedish-Finnish Cultural Centre, 14 pp. VTT. March.

Describes the Bioflow IGCC-system and the Värnamo demonstration plant. Chemistry of process changes to some extent with pressure. Fluidized solids are ash, char, sand, and dolomite or limestone. Operation at 950°C–1000°C minimizes tar. No other tar removal used. Just cool gas to ~350°C before ceramic filter vessel.

Parikh, P.P.; Bhave, A.G.; Kapse, D.V.; Ketkar, A.; Bhagivat, A.P. 1988. "Design and Development of a Wood Gasifier for I.C. Engine Applications - New Approach for Minimization of Tar," in *Research in Thermochemical Biomass Conversion*. Edited by A.V. Bridgwater and J.L. Kuester. London: Elsevier Applied Science, pp. 1071–1087.

Presence of tar and particulates in producer-gas causes rapid deterioration of lubricating oil in diesel engines. "Minimisation of tar content of producer-gas therefore emerges as an immediate research need in the area of biomass gasification." "Temperatures lower than 1000°–1100°C prove inadequate for tar-cracking." "The downdraft gasifier design is the undebated obvious choice for I.C. engine applications." Design improvement in the oxidation zone are described in the paper. Tars measured using a set-up similar to the THT method, are in the range of 70–85 mg/Nm^3. (Tars are condensed in a solvent at 0°C and are estimated by a solvent method.) The swirl method used to minimize tar, increases the particulate load.

Parikh, P.P.; Paul, A.; Bhave, A.G.; Uma, R. 1987. "Tar in Producer Gas. Why and How Much?," in *Energy Biomass Wastes*. X. Edited by D.H. Klass. Chicago: Institute of Gas Technology, pp. 1633–1637.

Tar and particulate content of producer gas affects: lubricating oil, deposits on combustion chamber wall, inlet passages, nozzle top, valves, piston ring and grooves. Temperatures lower than 1000°–1100°C are inadequate for thermal tar cracking and elimination. Many past works define tar as all the condensible material collected either at room temperatures or 0°C. From the point of view of an ICE application, "the condensates which can be consumed by engines need not be named as tars."

Pedersen, K. 1994. "Catalytic Tar Cracking," Danish Technological Institute, DK–8000, Aarkas C., 13 pp.

Catalysts: Co/Mo, Ni/Mo, Ni/W, Mo, Pt, Ru and Pd. Tar in: In laboratory, synthetic gas with 0.3% phenol (at 16 g synthetic tar/Nm^3) and 10–300 ppm H_2S. Also tests on Kyndby updraft gasifier plant. Tar out: Defined as remaining phenol or tar not converted to gaseous hydrocarbons (include benzene and toluene as gases). How measured: GC. Compounds heavier than toluene are not addressed in this paper. Conditions studied: The gas must not be carburizing, i.e., O/C > 1.6 and H/C > 4.6. Content of H_2 should be adjusted to: molar H_2/tar(C_6) > 10. Describes the process as catalytic hydrocracking. Best catalysts were Ni/Mo and Pt-catalytic system "which obtained nearly total conversion (99%) at 500°C" Phenol tests run for 100 h.

	Updraft	**Downdraft**	**Fluidized**
Exit temperature [°C]	80–250 (400)	800–1000	700–1000
Tar content [g/Nm^3]	10–100	0.1–5	1–3
Dust content [g/Nm^3]	0.1–1	1–10	10
Related purification process	Particles + Hydro-cracking	Particles + (Steam reforming)	Particles + (Steam reforming)
Operation temperature purification [°C]	400–500	900–1000	900–1000
Tar content exit purification [g/Nm^3]	0.1–1 Hydrogenated product	0.1	0.1

Pedersen, K.; Maimgren-Hansen, B.; Petersen, F. 1996a. "Catalytic Cleaning and Hot Gas Filtration," in *Biomass for Energy and Environment: Proceedings of the 9th European Bioenergy Conference, June 1996*. Edited P. Chartier. Pergamon, pp. 1312–1317.

Tar Definition: Used phenol as model "tar." Gaseous tar is converted into noncondensible hydrocarbons. Destruction method: Catalytic conversion of tar into light hydrocarbons. Updraft wood gasifier: Aerosols of tar buildup coke on the catalysts. At 400°C tar sticks to filter. At 500°C most of tar is in gas phase. Tar defined as water insolubles with B.P. <360°C and >360°C Water solubles defined as VOCs and phenols.

Pedersen, K.; Maimgren-Hansen, B.; Petersen, F. 1996b. "Catalytic Hydrotreating and Hot Filtration of Gas from Gasification of Wood," in *9th European Bioenergy Conference & 1st European Energy from Biomass Technology Exhibition*. Edited by P. Chartier. Pergamon, p. 345.

Catalysts: Co/MoO, Ni/MoO, Fe/MoO and Cr/MoO. Tar in: Synthetic mixture containing phenol. Raw gas from Volund updraft gasification plant containing 50g/m^3 tar. Tar out: Gaseous components not converted to light hydrocarbons. How measured: See Brandt-96. Conditions studied: Hot gas filtration with Schumalith candles before the tar cracker. Candles showed stable operation at 535°–550°C with a gas containing 50 g/m^3 tar. Filters operated at above 400°C at least. Aerosols of tar have shown a tendency to build up coke residue on the catalysts.

Peña, M.A.; Gomez, J.P.; Fierro, J.L.G. 1996. "New Catalytic Routes for Syngas and Hydrogen Production," *Applied Catalysis A*: *General* 144, pp. 7–57.

This review summarizes catalytic options for the production of syngas and hydrogen starting from simple hydrogen containing molecules.

Pérez, P.; Aznar, P.M.; Caballero, M.A.; Gil, J.; Martin, J.A.; Corella, J. 1997. "Hot Gas Cleaning and Upgrading with a Calcined Dolomite Located Downstream from a Biomass Fluidized Bed Gasifier Operating with Steam—Oxygen Mixtures," *Energy & Fuels* 11.

The effect of a secondary fluid bed of dolomite on gasifier gas composition is presented for gases and tars. Pine wood is fed near the bottom of the bed. Operation at $800°-850°C$ with variable steam/O_2 and steam-O_2/biomass. Main variable is the space-time of a slip stream through the catalyst bed. Raw gas from the fluid bed contained $2.2-42$ g/Nm^3. "Calcined dolomite is quite soft and it might erode very much if the bed were fully fluidized. No deactivation was observed for the dolomite over 4–10 hour runs." Tar analyzed by total organic carbon by the method in Narvaez et al. *Ind. & Eng. Chem Res.* 35 2110 (1996). Tar conversion increases with space-time and decreases as ($H_2O + O_2$)/biomass increases. Pure steam produces a more phenolic tar that is easier to catalytically convert than tar from steam +O_2 gasification. Dolomite is 8–9 times more effective for tar conversion than for CH_4 conversion. Tar conversions have always been less than 96%. Dolomite activity is diffusion controlled so particle diameter is a variable.

Philp, R.J. 1986. "Methanol Production from Biomass," *NRCC Report No. 27143*, Canada, Ottawa, Canada: National Research Council, August 1986, 177 pp.

Potential methanol synthesis catalyst poisons are listed as sulphur (H_2S, (COS, CS_2), Cu-Zn-Cr, 0.03-0.2 ppm, ZnO, 3-over 30 ppm. Chloride, (Cu-Zn-Cr), 0.2 ppm C_2H_4 and higher olefins are possible poisons. Oil mist a possible poison at modest amount. Updraft gasifier: tars range from 2–30% of feed. Downdraft gasifiers: 200–2000 ppm reported for tars and oils. Reforming catalysts have poison tolerances comparable to methanol synthesis catalysts, e.g., S less than 0.1 ppm and olefins less than 0.5%.

Pindoria, R.V.; Megaritis, A.; Chatzakis, I.N.; Vasanthakumar, L.S.; Zhang, S.; Lazaro, M.; Herod, A.; Garcia, X.A.; Gordon, A.L.; Kandiyoti, R. 1997. "Structural Characterization of Tar from a Coal Gasification Plant," *Fuel* 76 (2), pp. 101–113.

Analysis of tar from gasifier using many technologies. A long list of highly aromatic cpds. in coal gasification.

Pitcher, K. 1996. "The Development of a Gasification Plant Utilising Short Rotation Coppice; Project ARBRE," in *Proceedings of the 9th European Bioenergy Conference*. Edited by P. Chartier, G.L. Ferrero, U.M. Henius, S. Hultberg, J. Sachau, and M. Wiinblad. Pergamon, pp. 1096–1101.

Plans for Project ARBRE are described. TPS gasification technology will be used with a circulating fluid bed of dolomite for tar cracking, followed by a wet scrubber "dolomite at $900°C$ decomposes tars down to levels below 65 (g/Nm^3) (i.e., 99% conversion)." (TPS designed CFB.)

Podesser, E.; Dermouz, H.; Lauer, M.; Wenzel, T. 1996. "Small Scale Cogeneration in Biomass Furnaces with a Stirling Engine," in *Proceedings of the 9th European Bioenergy Conference*. Edited by P. Chartier et al. Pergamon, pp. 1457–1459.

A 3 kW, biomass-fired Stirling engine was designed and constructed for lab tests, "Tubes without fins have been used because of easy cleaning by water or steam jets."

Poutsma, M.L. 1987. "A Review of Thermolysis Studies of Model Compounds Relevant to Processing of Coal," Oak Ridge National Laboratory, ORNL/TM-10637.

Treats the bond breaking, bond making, rearrangement, and hydrogen transfer reactions that occur in thermolysis at 350-1000°C. Many species, such as benzene, toluene, phenols, cresols, and polycyclic aromatics are directly relevant to tertiary tars from biomass gasification.

Rambush, N.W. 1923. "Modern Gas Producers." Ben Brothers Ltd., London, UK.

An oft-cited classic work.

Rapagnà, S.; Jand, N.; Foscolo, P.U. 1998a. "Utilisation of Suitable Catalysts for the Gasification of Biomasses," in *Biomass for Energy and Industry*. Edited by H. Kopetz, T. Weber, W. Palz, P. Chartier, and G.B. Ferrero. 10th European Conference and Technology Exhibition, Würzburg, Germany. C.A.R.M.E.N., pp. 1720–1723.

A tri-metallic La-Ni-Fe catalyst with perovskite structure is tested in a fixed-bed reactor downstream of a fluidized-bed steam gasifier. With olivene in the gasifier bed, the secondary catalyst reduced tar to less than 0.3 g/Nm^3, with negligible carbon deposition.

Rapagna, S.; Jand, N.; Foscolo, P.U. (1998b) "Catalytic Gasification of Biomass to Produce Hydrogen Rich Gas," *Int. J. Hydrogen Energy* <u>23</u>, pp. 551–557.

Ratcliff, M.; Deutch, S.; Feik, C.; French, R.; Graham, J.; Meglen, R. Overly, C.; Patrick, J.; Phillips, S.; Prentice, B. 1998. "Biosyngas Characterization Test Results." Biomass Power Program Milestone Completion Report. NREL.

Gas from a two-stage vortex-pyrolysis/secondary thermal cracking system, simulating the Battelle Columbas indirect gasifier, was passed through a direct contact gas scrubbing system, which removed most other "condensable tars." Volume percents of tars measured by the TMBMS, downstream of the filter, ranged from: Benzene, 1.0–1.4; toluene, 0.2–0.3; and ethylene, 4.4-5.9 for hybrid poplar, switchgrass, and a mix of forest management woods from Vermont.

Ratcliff, M.A.; Czernik, S. 1997. "Specification of Balance of Plant Equipment to Integrate the Thermochemical Process Development Unit with a Molten Carbonate Fuel Cell," *Center for Renewable Chemicals Technology and Materials Milestone Completion Report.* Biomass Power Fuel Cell Testing BP712130.

Tolerances of molten carbonate fuel cells are H_2S, 0.5 ppm; chloride, 0.1 ppm; benzene, 1 vol %; naphthalene, 0.5 vol %. The NREL Thermochemical PDU, an entrained flow gasifier, yields 100 ppm H_2S, and benzene at 1 vol %. Naphthalene was in the low ppm range (hybrid poplar).

Ratcliff, M.A.; Gratson, D.A.; Patrick, J.A.; French, R.J.   1995.   "Monitoring the IGT RENUGAS® Gasifier and Westinghouse Hot Gas Clean-Up System with a Molecular Beam Mass Spectrometer," *Process Research Branch Milestone Completion Report*, Biomass Power Hot-Gas Cleanup Process Monitoring, BP513434.

The NREL transportable, molecular-beam, mass spectrometer (TMBMS) was used to sample directly the IGT RENUGAS® Gasifier. The full spectrum of organics above mass 50 showed a predominance of: benzene; naphthalene; acenaphthalene; phenanthrene/anthracene; fluoranthene/ pyrene, benzo(a), anthacene/chrysene/triphenylene/naphthacene; benzo fluoranthene/ benzo(e) pyrene/benzo(a) pyrene/phenols and toluenes were very small compared to the above. GC analysis of a collected tar was in good agreement except masses at 168, 190, 216, 240, 276, 302, 326 and 350, seen in the TMBMS spectra, were not detected by GC.

Reed, T.B. 1998. Personal communication.

Reed, T.B. 1997a. Communication on CREST. 11/10/97.

In the ICE context "it is also useful to know the tar only, defined as condensible above about 80°C."

Reed, T.B. 1997b. "World State of Gasification," in *Proceedings of the 3rd Biomass Conference of the Americas, Vol. 1.* Edited by R.P. Overend and E. Chornet. Canada: August 24–29, pp. 589–595.

"*The Achilles heel of small gasifiers is the 'tar' and particulate that must be reduced to <100 ppm for operation of engines and much lower for gas turbines.*" The stratified downdraft gasifier yields tar levels of 100–1000 ppm. The more charcoal removed at the grate, the higher the tar levels.

Reed, T.B. 1996a. Personal Communication on CREST.

Mukunda's gasifier in Bangalore, a downdraft type, gives tar at 80–120 ppm in raw gas.

Reed, T.B. 1996b. "The Charcoal-Tar Relationship in Downdraft Gasifiers," Golden, CO: The Biomass Energy Foundation, Private Communication, 3 pp.

The following tar and char production levels are listed:

Gasifier	Char (%)	Tar (ppm)
Indian Institute of Science	0.01	20
Syngas-Graboski	0.05	200
Ayres-Buck Rogers	0.1	4000
Reed-Inverted Downdraft	0.25	200,000

Reed, T.B. 1996c. Private communication.

Tar definition: Reed: Condensate < 100°C Stassen: Condensate < -40°C. Das has a simple tar measurement method (based on EPA method 5). Reed thinks 100 ppm tars is low enough for engines. Stassen (Banff) thinks engines can run indefinitely on 200 ppm tar. Reed says 40 ppm. Reed assumes total tar condensate at -40°C is 5 times the 100°C value.

Reed, T.B. 1985. "Principles and Technology of Biomass Gasification," in *Advances in Solar Energy, Volume 2*, Edited by K.W. Böer and J.A. Duffie. American Solar Energy Society, Inc., New York: Plenum Press, pp. 125–175.

"Australian tests on vehicle gasifiers during WWII showed that the gas should have less than 10 mg/m^3 (approximately 10 ppm) of tar and particulates if the engine wear was to be less than that measured with gasoline."

Reed, T.B.; Das, A. 1988. *Handbook of Biomass Downdraft Gasifier Engine Systems*, Golden, CO: Solar Energy Research Institute, SERI/SP-271-3022, 140 pp.

"A gasifier that produces more than 500 mg/Nm^3 of tar cannot be suitably cleaned for engine applications due to the large amounts of tar that must be captured and disposed of." For a worst-case scenario, a gasifier producing 2 g/Nm^3 (0.2%) tar equates to about 2 g of tar per hp-h.

Reed, T.B.; Gaur, S. 1998. "Survey of Biomass Gasification—1998," Volume 1 *Gasifier Projects and Manufacturers around the World*, Golden, CO: The National Renewable Energy Laboratory and The Biomass Energy Foundation, Inc. (in preparation).

In the review of gasifiers the following observation are made: updraft gasifier gas contains "10-20% tar resulting from the pyrolysis reaction." "The advantage of the downdraft gasifier is that it consumes between 99.9 and 99.999% of the tar." "The (IGT) PDU system produces approximately 0.03 kg/kg dry feed of tars and oils." "The product gas from the JWP Energy Products gasifier . . . with a tar content of approximately 15% of the wood energy," "the Lurgi gasification system produces very few tars (< 1g/Nm^3) due to the high gasification temperature," "the Skygas electric arc gasification process produces a C$_6$→volume percent of 0.1 in the gas." The Volund updraft gasifier produces tar at 30-50 g/Nm^3 at part load, equivalent to 20%–30% of gas lower heating value; the Buck Rogers stratified, open-top, downdraft gasifier produced a tar yield of 800 ppm.

Reed, T.B.; Levie, B.; Graboski, M.S. 1987. *Fundamentals, Development and Scaleup of the Air-Oxygen Stratified Downdraft Gasifier,* Solar Energy Research Institute, SERI/PR-234-2571, Chapter 6 - Tar Conversion, 26 pp.

"The word 'tar' is loosely used to cover a wide variety of materials having a range of chemical compositions." "Tar is a pejorative term to indicate a viscous material that lines pipes and coats valves of gasifiers and downstream equipment."

Gas from a downdraft gasifier has low tar content and can be fed directly into the manifold of a modified (compression ratio) spark-ignition engine. Tars present in gas will condense <371°C Rome, GA (APCO), updraft produces 25 wt % tars and oils, phenols and lignin related materials with C_1 and C_2 2–3% vol. Levesque: C_2H_x 2.0 vol. %. Used to retrofit boiler. Omnifuel, an updraft gasifier, produces up to 20% oil or tar. If this gas is to be compressed, piped any distance or used in an engine, oils and tars must be removed to a level below 50–500 ppm to avoid fouling of compressors, pipes or engines. Downdraft gasifiers produce typically less than 5,000 ppm tar and as low as 500 ppm. Direct mass spec sampling of downdraft tars shows large amounts of benzene, toluene, cyclopentadiene, and styrene, components that are not usually seen in condensed tars due to their volatility.

Reed, T.B.; Levie, B.; Scahill, J.; Evans, R.; Milne, T. 1986. "Moving-Bed Air and Oxygen Biomass Gasification." In *Proceedings of the 1985 Biomass Thermochemical Contractors' Meeting,* PNL-SA-13571. CONF-8510167, Springfield, VA: NTIS.

Gives tar makeup from laboratory simulation of up- and downdraft gasifiers. Qualitative analysis by MBMS.

Rensfelt, E. 1996. "Atmospheric Pressure Gasification Process for Power Generation." Espoo, Finland: *Analysis and Coordination of the Activities Concerning a Gasification of Biomass* (AIR3-CT94-2284), Second Workshop.

Describes various atmospheric pressure, circulating fluidized-bed gasifier systems for biomass, including the two 15 MWth CFB systems at Greve-in-Chianti, Italy. (TPS Termiska Processor AB was formerly a part of Studsvik AB.) Using patented dolomite CFB to crack tar to simpler compounds, thus avoiding clogging of heat exchangers or filters and avoiding soot problems. TPS pilot plant has operated 1,300 hours, 750 with ICE. For IGCC, TPS now favors atmospheric gasifier for sizes as large as 60–80 MWe. Can use wet scrubbing, thus avoiding hot-gas filtration. Recent pilot tests give very low tar, essentially at the vapor pressure level of compounds such as naphthalene.

Rensfelt, E.; Ekström C. 1988. "Fuel Gas from Municipal Waste in an Integrated Circulating Fluid-Bed Gasification/Gas-Cleaning Process." In *Energy from Biomass and Wastes XII.* Edited by D.L. Klass. Chicago: Institute of Gas Technology.

Review of past work at Studsvik on gasification and catalytic tar cracking at pilot and bench scale, using dolomite. Dolomite is used as an active bed material and in secondary reactor. Quotes following tolerances for gas distribution or engines:

<500 mg/Nm^3 and <50 mg/Nm^3 for self priming- and turbo-charged engines respectively. Thermal tar cracking to acceptable levels requires >1100°C and also produces soot. At 800°C with dolomite: "only lower quantities (100–400 mg/Nm^3) of stable compounds like phenanthrene, biphenyl, and naphthalene are present. At 900°C the only remaining heavy hydrocarbons are minor quantities of naphthalene."

From literature, quotes following ranges of tar:

Updraft–fixed bed	10,000–100,000 mg/Nm^3
Downdraft–fixed bed	80–150 mg/Nm^3
Circulating fluid bed	7,000–10,000 mg/Nm^3
Studsvik with dolomite	20–150 mg/Nm^3

Rensfelt, E. 1985. "Practical Achievements in Biomass Gasification," in *Bioenergy 84, Volume 1*, Elsevier Applied Science. Edited by H. Egnéus and A. Ellegård. University of Göteborg, Sweden. London: p. 174.

Lists following applications for clean gaseous fuel from biomass; engines, ovens, lime kilns, brick kilns, metallurgical furnaces, dryers, fuel cells, town gas (local distribution), synthetic natural gas, synthesis of methanol, gasoline, ammonia, hydrogen, ethylene. Cited problems in sampling and definition of tar (organics) and in lack of reliable and comparative tests with tar. Quotes Kjellstrom that engines need tar content less than 500 mg/Nm^3. Normal tar level of a downdraft gasifier, running well, is 300-1,000 mg/Nm^3. Thermal cracking (of tar) might yield non-wettable and extremely fine soot, which could thus cause problems in condensate handling.

Robertus, R.J.; Mudge, L.K.; Sealock, Jr., L.J.; Mitchell, D.H.; Weber, S.L. 1981. "Catalytic Gasification of Biomass," in *1981 Spring Meeting of the Western States Section—The Combustion Institute*. PNL-SA-9173. Pullman, WA.

Catalysts: Many catalysts tested for use in a fluidized-bed gasifier to produce clean synthetic gas for CH_3OH. Reports results on laboratory and PDU scale from work since 1978. Tried K_2CO_3, Na_2CO_3, borax, and trona with the feed. Many catalyst combinations, including several exotic metals (e.g., Ni-Cu-Mo/alumina), and Ni deposited on silica/alumina were placed in the bed. Catalysts increase gas at expense of tar and oil formation.

Rosén, C.; Björnbom, E.; Brage, C.; Chen, G.; Yu, Q.; Sjöström, K. 1996. ""Fundamentals of Pressurized Gasification of Biomass," in *Proceedings of the 9th European Bioenergy Conference*. Edited by P. Chartier et. al. Pergamon, pp. 1295–1300.

Many of the same results as reported in Rosen (1997). The device for tar sampling consists of water-cooled condensers and cyclone-shaped dry-ice traps. Tar analyzed by chromatography. Tar yields are relatively insensitive to test temperature and pressure and for birch or pine. Benzene and toluene are calculated as belonging to the gas-phase. Tar yields vary from 1.2–7.3 g/kg mf fuel for the runs cited. (Two kinds of sand, but no reforming catalyst.)

Rosén, C.; Björnbom, E.; Qizhuang, Y.; Sjöström, K. 1997. "Fundamentals of Pressurized Gasification of Biomass," in *Developments in Thermochemical Biomass Conversion,* Vol. 2. Edited by A.V. Bridgwater and D.G.B. Boocock. London: Blackie Academic & Professional, pp. 817–827.

Tar yield and nitrogen speciation in a top-fed, bubbling fluidized bed to 3 MPa and 900°C (laboratory development unit). Tar yields of about 1–5 g/kg moisture-free fuel are reported. Tar reported to be largely phenols and neutrals. Fuel nitrogen ends up mainly in NH_3 and NO.

Salo, K. 1990. "Applications of Bioneer Updraft Gasification Technology," in *VTT Symp.*, 108 (Low-Grade Fuels, Vol. 2) pp. 365–378.

Description of the Bioneer updraft gasifier and its performance. Main applications are closed-coupled to burner. Tolerates numerous types of fuels. Tar levels are 50–100 g/Nm³ for biomass. Dust content in raw gas is lowest of any gasifier. About 25–150 mg/Nm³.

Salo, K.; Keränen, H. 1995. "Biomass IGCC," *Seminar on Power Production from Biomass II*. Espoo, Finland: VTT, pp. 1–17.

Enviropower is a joint venture of Tampella Power and Vattenfall AB. For biomass, tar formation, destruction, and removal are the main issues. In their concept, tar cracking occurs in the gasifier at high temperature and pressure (using dolomite as long residence time catalyst. See 13th EPRI Conference (1994).

Salo, K.; Patel, J.G. 1997. "Integrated Gasification Combined Cycle Based on Pressurized Fluidized Bed Gasification," in *Developments in Thermochemical Biomass Conversion,* Vol. 2. Edited by A.V. Bridgwater and D.G.B. Boocock. London: Blackie Academic & Professional, pp. 994–1005.

Enviropower/Carbona, Inc. PFB tests. Gas leaving the primary cyclone is cooled in two steps. First to 400°–600°C then after candle filter to 200°–350°C. Use dolomite as absorbent in FB. Results from 360-h run: Heavy tars (condensible) 25–160 mg/Nm³; Light tar (incl. benzene) 5–10 g/Nm³ (Benzene and naphthalene are 55% of light tar); Sum of light tar (pyridine to pyrene) = 1.2-2.5 g/Nm³; Benzene was 4.1–7.9 g/Nm³; NH_3 in range 1,400–2,000 ppm vol dry; HCN 10–30 ppmv; HCl < 30 ppmw %.

Salzmann, R; Kaufmann, H.P.; Hasler, P. 1996. "Guideline for Sampling and Analysis of Tars, Condensates and Particulate from Biomass Gasifiers." ETH/Verenum Zurich, Switzerland: Institute for Energietechnik.

No common or widely accepted composition of tar. Tar is most widely measured gravimetrically. Can't intercompare results. In this guide the following definitions for tar components are used: <u>Heavy tars:</u> Sum of high molecular weight polynuclear aromatics determined gravimetrically by evaporating a solvent (e.g., methoxy benzene, BP=155C, evaporated under vacuum). <u>PAH:</u> Use the EPA list of 16 compounds. <u>Light Tars:</u> Aromatic hydrocarbons with medium volatility, 80°–200°C (e.g., BTX). Does not include phenols. <u>Light Hydrocarbons:</u> Non-aromatic hydrocarbons up to about C_5, gaseous at room temperature (e.g., methane, ethylene). <u>Phenols:</u> Aromatic hydrocarbons with at least one OH group (e.g., phenol, cresols). <u>Oxygenates:</u> Organic, non-aromatic compounds with oxygen (e.g., acetic acid, methanol). Notes: (1) Non-chomatographable hydrocarbons are considered an important fraction of heavy tars. (2) Some tar components may adsorb on carbonaceous particulate. Tar

sampling should be done under quasi-isokinetic sampling conditions. (3) "at the gasifier outlet, most of the organic compounds such as phenols or the PAHs will be present as aerosols." (4) Report contains schematics and discussions of their preferred sampling train for particulates and tar. (5) List of 16 EPA compounds ranges from naphthalene through pyrene, to benzofluoranthene. (N.W. most of these are seen in highly cracked, or tertiary tars.)

Procedures for tar analysis and definitions of tar have been proposed as standards, jointly worked out and verified with the Swiss Federal Laboratories for Materials Testing and Research (EMPA) in Dubendorf. Its sampling system retains naphthalene with >99.5% efficiency and toluene and benzene with 90% and 30%, respectively. Quotes Kurkela et al. (1995) that the best and most often used method for tar sampling from biomass gasifiers is based on the use of impingement trains with an organic solvent.

Schenk, E.P.; van Doorn, J.; Bodegom, M.; van der Drift, A. 1998. "Circulating Fluidized Bed Gasification Experiments at ECN," in *Biomass for Energy and Industry*. Edited by H. Kopetz, T. Weber, W. Palz, P. Chartier, and G.B. Ferrero. 10th European Conference and Technology Exhibition, Würzburg, Germany. C.A.R.M.E.N., pp. 1757–1560.

Schiffer, H.P.; Adlhoch, W. 1995. "Gasification Experience with Biomass and Wastes," Espoo, Finland: Seminar on Power Production from Biomass II, VTT95-3. March.

Rheinbraun high-temperature Winkler. No discussion of tar. Operates at 900°–1000°C claims this is below slagging temperatures. "The HTW process is particularly favorable for the conversion of biomass." Have gasified wood and grasses (no data given). Use water scrub after dust removal and cooling.

Schroeder, R.J.; Ege, H.D.; Hunt, F.E. 1985. "Biomass Gasification for Electric Utility Diesel Generating Units. Final Report," EPRI-AP-3865, 106 pp.

Review of biomass gasifier/diesel. "Literature is notably deficient concerning life and wear data for engines operated on low BTU gas." Only four listings for commercial gasifier/diesel systems. Visited four sites; Coon-Rapids-corn cob gasifier; Fritz-Werner; K. State; KHD facility. Low Btu gas must be cooled and cleaned. Few studies of tars in gas. There is no evidence to indicate the degree of gas cleanliness required by a utility-size diesel engine, nor have there been any sustained, long-term engine tests on biomass-derived low Btu gas. No details found in the literature on contaminates in gasifier gas. List of engine test facilities not visited.

SERBEP Update. 1997. "National Ethanol Conference Report," Southeastern Regional Biomass Energy Program, Muscle Shoals, AL: Tennessee Valley Authority,

MCFCs operate at 650°C and have the ability to operate on natural gas without upstream reforming to produce hydrogen. For these "direct" fuel cells, "an external reformer is still needed for more complex organic materials." "A 1995 SERBEP project that assessed a MCFC in conjunction with an ethanol plant needed an external reformer (P.S. Patel, Ethanol Fuel Cells for Efficient Power Generation from Biomass)."

Seville, J.P.K. 1997. *Gas Cleaning in Demanding Applications*, Blackie Academic.

Has chapters on sampling and measurement and condensible components, but little information on tars.

Sharan, H.N.; Mukunda, H.S.; Shrinivasa, U.; Dasappa, S.; Paul, P.J.; Rajan, N.K.S. 1997. "IISc-DASAG Biomass Gasifiers: Development, Technology, Experience and Economics," in *Developments in Thermochemical Biomass Conversion,* Vol. 2. Edited by A.V. Bridgwater and D.G.B. Boocock. London: Blackie Academic & Professional, pp. 1058–1072.

Reed's "open top gasifier" concept adapted for running small diesel engines (3.7 kWe). Tar varied from 50–120 ppm and particulates from 50–300 ppm.

Sharan, H.; Buhler, R.; Giordano, P.; Hasler, P.; Salzmann, R.; Dasappa, S.; Sridhan, B.; Girish, B. 1996. "Adaptation of the IISc/DASAG Gasifier for Application in Switzerland." Final Report Phase 1. Bundesamt für Energiewirtschaft (BEN). Bern.

Simbec, O. 1997. "Clarify Gasification Issues." Letter in *Power Magazine*, Jan/Feb.

HGCU only significantly affects air-blown gasification (of coal). Refers to "warm gas cleanup."

Simell, P. 1996. "Catalytic Hot Gas Cleaning." VTT Energy, Espoo. VTT-SYMP-163, pp. 123–129.

A review of past results at VTT. "Tars, however, can condense on the filter surfaces or in other downstream units causing plugging problems." "Gas purification experiments with gas containing high-particulate loads showed that complete tar decomposition and about 80% ammonia conversion can be achieved with the monolith catalyst (Ni/Al_2O_4) at 900°C temperature, 1 s residence time (SV 2000 1/h) and 5 bar pressure. "However, deactivation tests in the range of thousands of operating hours are required to demonstrate the suitability of this type of process for gasification process applications."

Simell, P.; Bredenberg, J.B.-son. 1990. "Catalytic Purification of Tarry Fuel Gas," *Fuel* 69 (10). pp. 1219–1225.

Catalysts: Commercial Ni catalyst>dolomite > activated alumina > silica-alumina> silicon carbide (inert). Tar in: Large list of compounds from tar passed through an inert bed at 900°C. How measured: portable catalysts testing unit. *"Tar sampling was facilitated by absorbing a sample into dichloromethane--condensed to ~80°C in 4-bottle sampling train and volatile organics GC with mass spectrometer identification."* Conditions studied: sampled gas from an industrial updraft peat gasifier. Passed over a variety of catalysts. Carbon deposition only observed for silica-alumina with bed at 900°C and residence time of 0.3 seconds. No catalyst lifetimes are reported.

Simell, P.; Hakala, N.A.K.; Haario, H.E. 1997a. "Catalytic Decomposition of Gasification Gas Tar with Benzene as the Model Compound." *Ind. Eng. Chem. Res.* 36, pp. 42–51.

Catalysts: dolomite. Tar in: "Benzene was chosen for the tar model compound because it is the main constituent of high temperature tar . . ." Conditions studied: various temperatures, flow rates, and benzene concentrations at atmospheric pressure.

Simell, P.A.; Hepola, J.O.; Krause, A.O.I. 1997b. "Effects of Gasification Gas Components on Tar and Ammonia Decomposition over Hot Gas Cleanup Catalysts," *Fuel* <u>76</u> (12), pp. 1117–1127.

The tar and ammonia decomposition activities of dolomite, Ni catalyst, alumina, and SiC were compared in various gas atmospheres. Tests were carried out in a fixed-bed tube reactor at $900°C$ under 2.0 and 5 MPa pressure. Toluene was used as a tar model compound. The gas atmospheres studied were mixtures of nitrogen carrier, toluene, and ammonia with H_2, H_2O, CO, CO_2, $CO_2 + H_2O$, $H_2 + H_2O$ or $CO + CO_2$. A gasification gas mixture containing all the components was also used. The predominant reaction of toluene in the empty tube and over SiC and alumina was hydrocracking. With dolomite and Ni catalyst, steam and CO_2 reforming types of reaction took place at high rates, CO_2 reforming being the faster. However, in gasification gas the rates of steam and CO_2 reforming reactions were lowered due to the inhibiting effect of CO, CO_2, and H_2. Tar was sampled by absorption in dichloromethane and the solution was analyzed by capillary GC. The following conclusions can be drawn from the results obtained:

(1) Tar can decompose on dolomite and Ni catalyst by both CO_2 (dry) and steam reforming reactions. Of these, the dry reforming reaction is faster at $900°C$.
(2) The dry reforming reaction on dolomite is inhibited by steam. Thus, tar decomposition on dolomite takes place by steam-reforming types of reaction in steam-containing gas mixture.
(3) Tar decomposition on dolomite is strongly inhibited by the presence of CO.
(4) The most abundant thermal reaction of toluene in gasification gas at $900°C$ and 2.0 MPa is hydrocracking. The main reaction products of toluene are benzene and methane.

Simell, P.; Kurkela, E. 1997. "Tar Removal from Gasification Gas," in *Biomass Gasification and Pyrolysis*. Edited by M. Kaltschmitt and A.V. Bridgwater. Stuttgart: CPL Press. pp. 207–217.

Presents a summary of studies carried out at VTT on minimization of tar formation in gasifiers, tar removal by water scrubbing, and catalytic tar removal. "Downdraft gas scrubbing by water removed the water-soluble tar components, but was ineffective in removing aromatic compounds." No deactivation of the Ni monolith catalyst was observed in a 500-h long-term test at $900°C$ and 5 bar.

Simell, P.; Kurkela, E.; Ståhlberg, P. 1993. "Formation and Catalytic Decomposition of Tars from Fluidized-Bed Gasification," Copenhagen, Denmark: in *Advances in Thermochemical Biomass Conversion*, Vol. 1. Edited by A.V. Bridgwater. London: Blackie, pp. 265–279.

Tar Definition: Absorb tar into Cl_2CH_2. Condensibles in $0°C$ cold trap. How Collected: Condensed and extracted. How Measured: Analyzed VOC by GC. Destruction Method: Catalytic. Big list of major cpds in "outlet gas tar."

Simell, P.; Kurkela, E.; Ståhlberg, P.; Hepola, J. 1996. "Catalytic Hot Gas Cleaning of Gasification Gas," *Catalysis Today*, pp. 55–62.

Reviews studies showing the efficacy of Ni monolith catalysts for tar and NH_3 destruction in dusty gas from updraft and fluidized-bed gasifiers. See notes in Simell et al (1995). Temperatures of 900°C and space velocities of 2,500 L/h were needed for "complete" tar destruction at five bars without coke formation or sulfur poisoning. Studied dolomites, limestones, iron sinter as bulk catalysts, nickel catalysts, alumina, and alumina silicate. Forest waste, bark, wood chips and peat used as feeds, producing 1–7 g/Nm^3 tar. Tar from the updraft gasifier was thermally quite unstable containing phenolic and aliphatic compounds, allowing even SiC to be effective. Fluidized-bed tars were thermally quite stable, requiring Ni catalysts for high destruction (90%–100%).

Simell, P.; Kurkela, E.; Ståhlberg, P.; Hepola, J. 1995a. "Development of Catalytic Gas Cleaning in Biomass Gasification," in *Seminar on Power Production from Biomass II*, Espoo, Finland: 6 pp.

Catalysts: Ceramic monoliths of Ni/Al_2O_3 having square channels. Details are proprietary. SiC and alpha alumina were used as reference. Tar in: "Tar from the updraft gasifier was thermally quite unstable, unlike the tar from the fluidized-bed gasifier, and thus decomposed easily, even with the inert reference material SiC. Tar out: for gasifier with Ni/Al_2O_3 at 900°C and 0.2–0.3 seconds, 1 bar:

	Updraft Inlet	Outlet	Fluidbed Inlet	Fluidbed Outlet
LHC wt %	0.4	0	0.5	0
NH₃ (ppmv)	1,700	<50	4,100	12
Tar ppmv (wood)	9,800	<10	1,500	<10
Tar ppmv (bark)			1,000	<10

"Tars are harmful because they can easily block up the particulate filters or other downstream units like engine suction inlets by condensing or by polymerizing to soot-like deposits." Catalytic unit should be at about the same temperature as that of the gasifier, 900°C for fluid beds. Biomass-derived gasification gas contains ~100 ppm H_2S, a known poison for Ni catalysts. Compensate for this deactivation by going to 900°–950°C.

Simell, P.A.; Leppälahti, J.K.; Bredenberg, J.B.-son. 1992. "Catalytic Purification of Tarry Fuel Gas with Carbonate Rocks and Ferrous Materials," *Fuel* 71, pp. 211–218.

Catalysts: High activity: ankerite and dolomite; Intermediate: limestone, calcitic dolomite, and dolomitic limestone; Low activity: sintered iron ore and pelletized iron ore. Tar in: from updraft gasification of sod peat. With inert bed, tar in = 41-43 g/m^3. Tar out at 900°C and 0.2-0.3 s residence time = 8.9-11 g/m^3. Tar components aggregated as benzene, benzene derivatives, phenolics, heterocyclics, PAH, substituted PAH, heterocyclic PAH, acyclic, and unknown

(<10%). Varied temperature and residence time. How measured: detailed chemical speciation from C_2s to PNA. Continuation of catalyst tests reported in Simell 1990. Under most catalysts, benzene and PAH were the major products. With dolomite, total tar drops from 3% to near zero as temperature increases from 800°–900°C at 0.2–0.3 s residence time. "It's likely that the primary tar decomposed mainly thermally with the tested catalysts as well as with the inert material and that the catalysts affected the secondary tar formation step."

Simell, P.A.; Leppälahti, J.K.; Kurkela, E.A. 1995b. "Tar-Decomposing Activity of Carbonate Rocks under High CO_2 Partial Pressure," *Fuel* <u>74</u>, (6), pp. 938–945.

Tested calcined and carbonated dolomites and Swedish and Finnish dolomites and limestones plus SiC as inert reference. Tar in: Used toluene as model for tar, recognizing that it is easier to crack than benzene, naphthalene etc. Typical tar from fluidized-bed gasification of wood at 850°–950°C contains 50%–60% benzene; 10%–20% naphthalene; and 10–20 wt % of other polynuclear aromatic compounds. Carbonated rocks decomposed PNA more easily than benzene. At 900°C exposure of calcined dolomite to 300 kPa of CO_2, deactivation is quite rapid.

Simell, P.; Ståhlberg, P.; Solantausta, Y.; Hepola, J.; Kurkela, E. 1997c. "Gasification Gas Cleaning with Nickel Monolith Catalyst," in *Developments in Thermochemical Biomass Conversion,* Vol. 2. Edited by A.V. Bridgwater and D.G.B. Boocock. London: Blackie Academic & Professional, pp. 1103–1116.

Ceramic Ni monolith catalysts (Ni/Al_2O_3), manufactured by BASF AG, with square channels. "If the lifetime of the catalyst exceeds 3-5 years in an IGCC process, the monolith catalyst is economically competitive, when compared to NO_x removal by SCR." Review of VTT work, with 27 references. Typical results at 900°–920C°C, SV=2,000–2,500 L/h and pressure 5 bar (up to 6 g/Nm^3 of particulates):

	Benzene (ppm) In	Benzene (ppm) Out	Tar (ppm) In	Tar (ppm) Out
Wood Chips	910	1	590	<1
Bark	780	6	220	<1
Forest Waste Wood	960	24	450	<1
Eucalyptus Chips	2020	2	380	<1
Fuel Peat	720	<1	160	<1

*No effect on H_2S. Severalfold reduction in NH_3.

Simons Resource Consultants; B.H. Levelton & Associates Ltd. 1983. "A Comparative Assessment of Forest Biomass Conversion to Energy Forms: Phase I - Proven and Near-Proven Technology," Volume V - Data Book of Unit Processes for Primary Conversion by Thermal, Chemical, and Biological Methods. ENFOR Project No. C258. Bioenergy Development Program. Alternative Energy Technology Branch. CANMET. Energy, Mines and Resources Canada, Ottawa.

Extensive review and discussion of gasifiers—updraft, downdraft, stirred-bed and fluidized bed. Limited data on "tars and oils" provided as follows:

Type of Gasifier	Name	C_2^+ (vol %)	Tars & Oils Kg/Kg dry feed (after cleaning)	Particulates g/m^3
Updraft	Representative	0.3	0.05–0.1	1–3
"	Applied Eng.		0.15	0.11
"	BPNW Labs	<0.5	0.05	
"	D.M. International	0.2	0.09	
"	EZ	1.39		
"	Westwood Poly Gas	negligible	0.07	2.6
Downdraft	Representative	1.1	Very low	
"	Biomass Corp.	1.8	0.02	
"	Duvant		<10mg/m^3	<15 mg/m^3
"	Imbert	~650 ppm	Benzene 118 ppm Toluene 9 Xylene 2	
"	KHD	0.2		
"	Pillard		20-200 ppm	
Stirred Bed	National Synfuels	1–2	Very low	2-6
Fluid Bed	Representative	2.0	Low	1.8–2.3
"	Alb. Ind. Dev.	0.25		
"	Battelle Columbus		.002–0.02	
"	Energy Resources Data	1.7–4	.02–.1 (at 900°C)	
"	Omnifuel	1.9–2.3	0.1% of gas	
"	Sur-lite	0.5	0.002	

Site, A.D. 1997. "The Vapor Pressure of Environmentally Significant Organic Chemicals: A Review of Methods and Data at Ambient Temperature," *J. Phys. Chem.*, *Ref. Data* 16 (1), pp. 157–193.

Vapor pressure equations and the enthalpy values in the temperature range of measurement are given for the "tertiary tar" species: naphthalene; 1-methyl napthalene; acenaphthene; fluorene; anthracene; phenanthrene; fluoranthene; pyrene; benz(a) anthracene; and benz(a) pyrene.

Sjöström, K.; Brage, C.; Hörnell; M. 1995. "Equipment for Cracking of Pyrolysis Gas from Biomass," in *Proceedings of the 8th European Biomass Conference, Biomass for Energy, Environment, Agriculture and Industry.* Pergamon, pp. 1916–1921.

Permanent gases and hydrocarbons up to toluene are monitored by on-line GC. Higher hydrocarbons are found in the condensates. "The hopper and the tubing connecting different parts of the equipment are heated to 500°C to avoid condensation of tar." Studied pellets made from Danish straw and elephant grass (miscanthus).

Sjöström, K.; Taralas, G.; Liinanki, L. 1988. "Sala Dolomite-Catalysed Conversion of Tar from Biomass Pyrolysis," in *Research in Thermochemical Biomass Conversion.* Edited by A.V. Bridgwater and J.L. Kuester. London: Elsevier, pp. 974–986.

Catalysts: Swedish Sala quarry dolomite. Tar in: From continuous pyrolysis. Tar out: Weighed and TOC. Easy to bring tar content down to 6000 mg/m^3.

Ståhlberg, P.; Lappi, M.; Kurkela, E.; Simell, P.; Oesch, P.; Nieminen, M. 1998. "Sampling of Contaminants from Biomass Gasifiers." VTT Technical Research Centre of Finland. Espoo**,** Finland

Ståhlberg, P.; Kurkela, E. 1990. "Sampling and Analytical Methods for Product Gases from Solid Fuel Gasifiers." Technical Research Centre of Finland. Laboratory of Fuel and Process Technology. Espoo, Finland.

Various sampling and analytical methods have been developed for analyzing the products of gasification. This paper reviews the methods developed at the Laboratory of Fuel and Process Technology of the Technical Research Centre of Finland (VTT), Finland, in the 1980s, and the method developed within the ENFOR Project C-172 at the Energy Research Laboratory CANMET, Canada, in the early 1980s. Both the Finnish and Canadian sampling and analyzing methods have proved to be fairly reliable in studies of the operation of solid fuel gasifiers and of their mass and energy balances.

Ståhlberg, P.; Kurkela, E.; Filèn, H.; Salo, K. 1989. "Updraft Gasification of Waste Fuels," in *Pyrolysis and Gasification.* London: Elsevier Applied Science, pp. 603–607.

Tar levels in Bioneer updraft gasifier were: wood chips, forest residues, and sod peat, 50–100 g/Nm^3; MSW, 10–20 g/Nm^3; and straw, 10–40 g/Nm^3.

Staniforth, J.; Kendall, K. 1998. "Biogas Powering a Small Tubular Solid Oxide Fuel Cell," *J. Power Sources* <u>71,</u> pp. 275–277.

A simulated biogas caused the hot anode to coke up immediately. Steam helped, but air had to be added to the biogas to allow steady operation for several hours. Cell was run at 850°C.

Stassen, H.; Koele, H.J. 1997. "The Use of LCV-gas from Biomass Gasifiers in Internal Combustion Engines," in *Proceedings International Conference, Gasification and Pyrolysis of Biomass—State of the Art and Future Prospects*. Edited by M. Kaltschmitt and A.V. Bridgwater. Stuttgart: CPL Scientific Ltd. UK, pp. 269–281.

Preferable tar concentrations quoted by engine manufacturers: less than 50 mg/Nm^3, with less than 100 acceptable. Six gasifiers reported the following ranges of tar at the engine inlet manifold: 120-150; 100-400; less than 10; 500-700; 3,000-4,000; and 1,000-2,000 mg/Nm^3.

Stassen, H.E.; Knoef, H.A.M. 1995. "UNDP/WB Small-Scale Gasifier Monitoring Programme—Final Findings," *Energy for Sustainable Development* <u>11</u>, pp. 41–48.

System performance (see World Bank Energy Dept., 1983 guidelines for field monitoring project). Dust and tar by THT dust and tar sampler. Tar by Soxhlet apparatus and THT. PAH and phenols by BOD. Gas analysis by ORSAT. Operational performance and tar/particulates for both heat and power (ICE) small, third world gasifiers. See final report: Stassen, H.E.H. 1993. "UNDP/WB Small-Scale Biomass Gasifier Monitoring Report, Volume I - Findings." Dust contents vary from <5 mg/Nm^3 to 300 (<50 acceptable for engines; <5 preferable). Tar varied from <10 to 4000 mg/Nm^3. (<100 ok for engines, <50 preferable).

Stassen, H.E. 1995. "UNDP/WB Small-Scale Biomass Gasifiers for Heat and Power, A Global Review," Energy Sector Management Assistance Programme, WBTP 296-Washington, DC.

Notes: Typical Gas Compositions:

	Tar	LHV
Updraft	2–10 g/Nm^3	5.3–6 Mj/Nm^3
Downdraft	0.1–3	4.5–5.5
Downdraft-Chemical	< 0.3	4.0–5.2

For spark engines, must filter soot, ash, and tar. (Inlet manifolds-four valve stem.) (Diesel must have both diesel fuel and producer gas.) Dust and tar measured at six sites. Dust varied from <5 to 300 mg/Nm^3. Acceptable dust <50; <5 preferable mg/Nm^3. Acceptable tar <100; <50 preferable mg/Nm^3. Rice husk gasifier had 10–40 times the allowable tar.

Stassen, H.E. 1993a. *UNDP/WB Small-Scale Biomass Gasifier Monitoring Report, Volume I - Findings,* BTG Biomass Technology Group. University of Twente, The Netherlands, 59 pp.

Typical tar levels in small gasifiers: updraft, 2–10 g/Nm^3; downdraft, 0.1–3 g/Nm^3; Cross-draft, less than 0.3 g/Nm^3. Gives table of parameters measured in UNDP/WB program. For dust and tar use THT dust and tar sampler Soxhlett apparatus. Condensates analyzed for pH, phenols, PAH, and BOD. Metals in engine oil lead to "the clear conclusion that the tar amount in the gas is the decisive factor governing wear and life-time of producer gas engine."

Stassen, H.E. 1993b. "Strategies for Upgrading Producer Gas from Fixed-Bed Gasifier Systems to Internal Combustion Energy Quality." Report to the IEA Gasification Activity.

Stobbe, S.; Oatley, J.; Brown, R.C. 1996. "Indirectly-Heated Biomass Gasification Using Latent-Heat Ballasting of a Fluidized Reactor," IECEC 96, in *Proceedings of the 31st Intersociety Energy Conversion Engineering Conferenc*e, Vol. 3, August 11–16, Washington, DC.

Hydrocarbon tars are removed through a fiberglass filter submerged in ice water. No tar results are shown.

Studsvik, 1992. "Task VII. Biomass Conversion. Activity 4: Thermal Gasification— Research Needs for Thermal Gasification of Biomass," in *Studsvik AB Thermal Processes Nykôping, Sweden*, Chicago: Institute of Gas Technology, 6 pp.

Contains: "R&D recommendations for the various subdivisions of the overall biomass gasification system, collectively identified by experts in the field who sit as participants in the IEA biomass gasification project." Some tar and cleaning recommendations include: Research on soot formation from tar and soot reactions leading to soot destruction. Effect of gasifier additives, including catalysts, for minimizing tar production. Ash-melting behavior for agricultural feedstocks. Gasification or reforming of condensible hydrocarbons (secondary processing of raw gas). Gas cleaning and tar removal for ICE applications. High-pressure sampling systems for tars and other gaseous impurities. Fuel gas specifications for ICEs and gas turbines.

Stwalley, R.M.; Stwalley, C.S.; Richey, C.B. 1996. "Operation of a Piston Engine with a Downdraft Channel Gasifier," in *Bioenergy '96—The Seventh National Bioenergy Conference*, pp. 612–619.

Describes benefits of the channel downdraft gasifier. Claims low tar but no figures given. See Das (1985) for tar measurements and tar limitations for ICEs.

Susanto, H.; Beenackers, A.A.C.M. 1996. "A Moving-Bed Gasifier with Internal Recycle of Pyrolysis Gas," *Fuel* <u>75</u> (11), pp. 1339–1347.

Tar Definition: condensibles measured gravimetrically. Fixed-bed downdraft gasifier with internal recycle of pyrolysis gas. Lists typical tars from seven gasifiers. Downdrafts range from 500–200 mg/m^3; Updraft 50,000; Fluid beds 320–6,000.

	Conventional downdraft	Recycle & separate combustion of pyrolysis gas
CH_4	~2.3 vol %	0.4–2.0
	C_4^+~1.2 vol % dry	~0.1
	tar 0.4–1.4 g/m^3	0.05–0.10

Taralas, G. 1997. "Cyclohexane-Steam Cracking Catalysed by Calcined Dolomite [CaMg(O)$_2$]," in *Developments in Thermochemical Biomass Conversion,* Vol. 2. Edited by A.V. Bridgwater and D.G.B. Boocock. London. Blackie Academic & Professional, pp. 1086–1100.

Catalysts: dolomite, quicklime, dolomitic magnesium oxide, commercial NiMo/gamma alumina. Tar in: chose cyclohexane as a tar model compound. Tar out: tar reduction seems to be defined as conversion to light gases (up to C_6H_{12} and benzene). Order of effectiveness of catalysts is MgO<CaO<CaCO$_3$,CaMg(CO$_3$)$_2$. "Calcined dolomite and limestone have also been found to decompose tar nearly as effectively as commercial nickel—containing catalysts which are more costly and intolerant to oxygen breakthrough." See Simell (1990) and references therein.

Taralas, G. 1996. "Catalytic Steam Cracking of n-Heptane with Special Reference to the Effect of Calcined Dolomite," *Ind. Eng. Chem. Res.* <u>35</u>, pp. 2121–2126.

Catalysts: limhamm limestone, sala, larsbo and glanshammer dolomites and katjenfine 153S-1.5E Ni Mo/gamma alumina. Tar in: chose n-Heptane as tar model compound. Tar out: studied effects of H$_2$O and H$_2$ level on catalytic cracking at 973 and 1,073°C.

Taralas, G. 1990. "Effects of MgO, CaO and Calcined Dolomites on Model Substance Cracking and Conversion of Tar from Biomass Gasification/Pyrolysis Gas," ISBN 91-7170-043-9. Stockholm, Sweden: Royal Institute of Technology.

Catalysts: dolomites, MgO, CaO. Thesis containing details of work later published.

Taralas, G.; Arvelakis, S.; Koullas, D.P.; Koukios, E.G. 1996. "The Feasibility of Biomass Gasification for Electricity Production from Agricultural Biomass: The Vision of a Southern European Utility," in *Biomass for Energy and Environment: Proceedings of the 9th European Bioenergy Conference, June 1996.* Edited by P. Chartier et al. Pergamon, pp. 1376–1381.

Taralas, G.; Sjöström, K.; Bjornbom, E. 1994. "Dolomite Catalyzed Cracking of n-Heptane in Presence of Steam," in *Advanced Thermochemical Biomass Conversi*on, Vol. 3. Edited by A.V. Bridgwater. Blackie, pp. 233–45.

Catalysts: dolomite. Tar in: used n-heptane "as a model compound in this study to avoid the difficulties in using a complex raw material as tar." Conditions studied: catalytic reactor at 800°C. In absence of steam, the surface of the catalyst is covered by carbonaceous material. Ratio of water to heptane must be above one to remove the carbonaceous material from the surface of the catalyst.

Taralas, G.; Vassilatos, V.; Sjoestroem, K.; Delgado, J. 1991. "Thermal and Catalytic Cracking of n-Heptane in Presence of Calcium Oxide, Magnesium Oxide and Calcined Dolomites," *Can. J. Chem. Eng.* <u>69</u> (6), pp. 1413–1419.

Catalysts: CaO, MgO, and dolomite (glanshammer and sala). Tar in: n-heptane. Tar out: various gaseous products up to benzene and toluene. n-Heptane apparently chosen as a model compound for alkanes in pyrolysis oil.

Techwest Enterprises Ltd. 1983. "A Workbook for Biomass Gasifier Sampling and Analysis." ENFOR Project No. C-172. Bioenergy Development Program. Alternative Energy Technology Branch. Canmet. Energy, Mines and Resources Canada, Ottawa.

Workbook based on the two Aiken reports from Techwest.

Teislev, B. 1996. "Indirectly Fired Gas Turbines for Biomass Fuels," in *Ninth European Bioenergy Conference and 1st European Energy from Biomass Technology Exhibition*, P.C. 37. Edited by P. Chartier et al. Pergamon.

Avoid contaminate problem with an indirectly fired gas turbine (compressed air). Expect an IFGT system to be tested on biomass in Denmark 1997–1998.

Tesner, P.A.; Shurupov, S.V. 1997. "Soot Formation during Pyrolysis of Naphthalene, Anthracene and Pyrene," *Combust. Sci. and Tech*. 126, pp. 139–151.

Soot formation during isothermal pyrolysis of naphthalene, anthracene, and pyrene was investigated. The particle number density of soot aerosol formed was demonstrated to depend linearly on hydrocarbon concentration. The equations to calculate the particle number density and the soot surface area were obtained. Particle number densities of the soot formed during pyrolysis of PAHs were demonstrated to be an order of magnitude higher and the apparent activation energy of soot aerosol formation is two times less than the parameters obtained during pyrolysis of benzene or acetylene. Sooting tendency of the hydrocarbons investigated as relative to methane can be arranged at 1350°C as follows: methane; ethylene; acetylene; diacetylene; benzene; toluene; p-xylene; naphthalene; anthracene; pyrene; 1; 4; 7.6; 50; 7.4; 5.5; 4; 112; 91; 74.

Thermie, 1996. Newsletter—*Biomass Gasification Targeted Projects*, published twice yearly by the Directorate-General for Energy (Thermie).

Project "Energy Farm." Wet-scrubbed tar in multistage system. Acid scrub, alkaline scrub, water. (Pisa) Lurgi gasifier. Project "Arbre" (Yorkshire). Circulating TPS gasifier tars are cracked catalytically to simpler compounds in second FB like the first. Dolomite bed at ~900°C. Add gas-air mixture at bottom.

Trenka, A.R. 1996. "Preliminary Operational Experience from the Biomass Gasification Facility (BGF) in Paia, Hawaii," in *Bioenergy '96—The Seventh National Bioenergy Conference*, pp. 37-43.

"Tar" yields not reported as such. CxHy ranged from 0.2–1.6 vol % of dry gas.

Turn, S.Q.; Kinoshita, C. M.; Ishimura, D. M.; Zhou, J. 1998. "The Fate of Inorganic Constituents of Biomass in Fluidized Bed Gasification," *Fuel* 77 (3), pp.135–146.

Tar yields from a bench-scale, fluidized-bed gasifier are reported as follows: For bagasse and banagrass," "oil and tar" ranged from 12.8–19.5 g/Nm^3 (28.1–35.4 g/kg of dry biomass).

Condensible light "oils" and "tar" species were analyzed by GC/FID after collection in a water-cooled heat exchanger, a twin-chamber dry-ice condenser trap and two ice-bath-cooled methanol inpingers followed by a coalescing filter. The sampling train was washed with acetone.

Turn, S.Q.; Kinoshita, C.M.; Ishimura, D.M. 1997. "The Fate of Inorganic Constituents of Biomass in Fluidized Bed Gasification." Presented at the Engineering Foundation Conference: Impact of Mineral Impurities in Solid Fuel Combustion, November 2–7, 1997, Kona, Hawaii.

Bagasse and four samples of banagrass were gasified at 800°C, and atmospheric pressure in a bench-scale fluidized bed at anominal equisvalence ratio of 0.3. "Oil and tar" in the dry gas ranged from 12.8 to 19.5 g/Nm^3 (28.1–35.4 g/kg dry biomass).

Turn, S.; Ishimura, D.; Zhang, Z.; Masutani, S.; Kinoshita, C. 1996. "Task 2A. Catalytic Gasification," in *Hawaii Integrated Biofuels Research Program Phase 7, Final Report* Vol. 1. Manoa, Hawaii: Hawaii Natural Energy Institute, pp. 8–9.

Continued study of catalytic conversion of condensible species to permanent gases in hot gas from an oxygen-blown gasifier.

Turnbull, J.H.; Hulkkonen, S.; Dracker, R. 1996. "Development of Small, Modular Biomass Power Systems," in *Bioenergy '96—The Seventh National Bioenergy Conference*, pp. 605–611.

"The allure of the indirectly fired gas turbine option also remains: As this paper is being written, EPRI staff are convening a broad mix of experts to look at a U.S. technology that gives promise if a gas-to air heat exchanger that can withstand the corrosion and temperature constraint, can be fabricated at a reasonable cost."

U.S. Department of Energy. 1986. "Hot Gas Cleanup for Electric Power Generating Systems," Morgantown, WV: Office of Fossil Energy, DOE/METC-86/6038.

Coal gasification NH3 and tar. Battelle Pacific NW Labs is developing catalysts for fixed-bed tar containing sulfur. Y-zeolite and CoMo-impregnated zeolite. For MCFC need S < 10 ppm.

Van Swaaij, W.P.M.; Beenackers, A.A.C.M. 1981. "Thermochemical Biomass Gasification," in *Energy from Biomass, Volume 7*. Proceedings of the EC Contractors' Meeting. Edited by P. Chartier and W. Palz, D. Reidel. Copenhagen, Publ. Co, pp. 181–187.

Homogeneous and heterogenous tar cracking from a fluidized- and fixed-bed pyrolysis reactor. Tar in: Phenol used as model compound.

Van de Beld, L.; Wagenaar, B.M; Prins, W. 1997. "Cleaning of Hot Producer Gas in a Catalytic Adiabatic Packed Bed Reactor with Periodic Flow Reversal," in *Developments in Thermochemical Biomass Conversion,* Vol. 2. Edited by A.V. Bridgwater and D.G.B. Boocock. London: Blackie Academic & Professional, pp. 907–920.

Tar Definition: "Tar is a substance without a generally accepted exact definition: it is complex mixture of more or less easily condensible substances." In the context of fouling, tar can be indentified as condensibles on surfaces at 20°C. Dolomite tested achieved 98% tar conversions. (From 20,000 mg/Nm^3 to as low as 100 mg/Nm^3.)

Vassilatos, V.; Brage, C.; Taralas, G.; Sjöström, K. 1992a. "The Effects of Temperature and Additives on Product Composition in Thermal Cracking of Biomass," in *Biomass for Energy, Industry and Environment*, 6th E.C. Conference. Edited by G. Grassi, A. Collina, and H. Zibetta. London: Elsevier, pp. 762–765.

In post-cracking studies of pyrolytic gasification tars, at 700°–900°C the following notes on tar analysis and tar chemistry were presented: "Inconel shavings, and a ceramic material on the composition of gaseous and liquid products in post-cracking of wood pyrolysis tar has been undertaken. Post-cracking performed in the temperature range 700–900°C The tar analysis was performed by CGC-MS, following pre-separation by liquid extraction (LE) or solid phase extraction (SPE) on aminopropylsilane modified silica, and in some cases by preparative HPLC (high performance liquid chromatography) using a C_{18} reversed phase column and UV-detection at 254 and 280 nm. Quantification of target compounds was performed by CGC-FID on a DB-1 column (30 m x 0.25 mm i.ed., 0.25 μm film thickness). Two internal standards were employed: 2-bromo-naphthtalene for aromatics and p-ethoxyphenol for phenols. Heavy tar components, i.e., asphaltenes and carbonaceous particles (constituting together ≈ 30% of the tar weight), which are not amenable to GC analysis, were determined by a gravimetric method based on solvent precipitation and SPE on silica phase. The asphaltenes were further investigated by ^{1}H- and ^{13}C-NMR. The main observed components of the tar were phenol, cresols, benzene, toluene, xylenes, indene, naphthalene, methylnaphthalenes, biphenyl, acenaphthylene, fluorene, phenanthrene, anthracene, and pyrene. At 900°C naphthalene is the major single component. Phenols are relatively stable at 700°C but at 900°C they are significantly decomposed. The yields of the two major aromatics, indene and naphthalene, increase considerably between 800 and 900°C although the total tar yield decreases. The ratio of naphthalene to indene is 0.53 at 700°C, 0.79 at 800°C, and 1.21 at 900°C and thus linearly increasing. On the basis of the results, we propose that the latter compounds are formed by competing reactions starting from the cracking of phenols and proceeding via intermediate cyclopentadiene radicals. The effects of additives on the cracking reactions were examined at 900°C. It was found that their abilities to facilitate the tar cracking decreases in the following order: steam > no additive > ceramic material > Inconel shavings."

Vassilatos, V.; Taralas, G.; Sjöström, K.; Björnbom, E. 1992b. "Catalytic Cracking of Tar in Biomass Pyrolysis Gas in the Presence of Calcined Dolomite," *Can. J. Chem. Engin.* 70, pp. 1008-1013.

Catalysts: Glanshammer dolomite. Tar in: From mixed hardwood pyrolysis at 700°C. Tar out: condensates recovered in dichloromethane. How measured: liquid chromatography. Catalyst at 700°–900°C. Varied steam to biomass ratio and WHSV over catalyst. Under optimum catalyst and steam conditions, reduced tar to 164 mg/Kg dry biomass. Naphthalene to 13 mg/Kg.

Vassilatos, V. 1990. "Thermal and Catalytic Cracking of Tar in Biomass Pyrolysis Gas," CODEN: TRITA/KTR-90/26. Stockholm, Sweden: Royal Institute of Technology.

Catalysts: Dolomite. This thesis contains details of experiments published in later papers.

von Wedel, G. 1994. "Biomass Gasification/Gas Cleanup." LLBL (Lurgi Lentjes); Babcock Energietechnik (MBH) Hot Gas Filter Technology. IEA Thermal Gasification Meeting Minutes, Copenhagen, May.

Wallin, M.; Padban, N. 1996. "Pressurized Fluidized Bed Gasification of Biomass," in *Biomass for Energy and Environment: Proceedings of the 9th European Bioenergy Conference,Vol. 2. June 1996*. Edited by P. Chartier et al. Pergamon, pp. 1392–1397.

Tar Definition: Condensibles in ice bath plus aerosols. Describes the LUND pressurized, fluidized-bed gasifier, 18–20 kg/h feed, 10 cm diam. bed. Has catalytic reactor fixed bed following a SiC ceramic filter. Use Balzers QMG 420-G mass spec. for gas analysis. Six percent of biomass goes to tar at 20–40 g/m^3, PNA with 3–4 rings are dominant components.

Wang, D.; Czernik, S.; Chornet, E. 1998. "Production of Hydrogen from Biomass by Catalytic Steam Reforming of Fast Pyrolysis Oils," *Energy & Fuels* <u>12</u>, pp. 19–24.

Fast pyrolysis of biomass followed by catalytic steam reforming and shift conversion of specific fractions. Bench scale using model compounds. Commercial Ni-based steam-reforming catalysts. The Ude S catalyst was formulated for steam reforming of high molecular weight aromatics and it contains NiO, Cr_2O_3, MgO, La_2O_3, and Al_2O_3. The University of Zaragosa catalyst was stoichiometric Ni aluminate of a spinel lattice structure, with 20% NiO replaced by MgO. Biomass can be converted to bio-oil using fast pyrolysis technology. The yield of bio-oil for a fluidized bed process is on the order of 75 wt % (on dry biomass basis). Bio-oil or its aqueous fraction can be efficiently reformed to generate hydrogen by a thermocatalytic process using commercial, nickel-based catalysts. The hydrogen yield is as high as 85% of the stoichiometric value. Catalysts can be easily regenerated by steam or CO_2 gasification of carbonaceous deposits. Model compounds studied included acetic acid, syringol/MeOH and a 3-component mixture plus a poplar-oil aqueous fraction.

Wang, D.; Czernik, S.; Montané, D.; Mann, M.; Chornet, E. 1997. "Biomass to Hydrogen via Fast Pyrolysis and Catalytic Steam Reforming of the Pyrolysis Oil or Its Fractions," *Ind. Eng. Chem. Res.* <u>36</u>, pp. 1507–1518.

Catalytic steam reforming of the pyroligneous oils left after valuable oxygenates have been extracted. Catalysts screened include: S_1-U_1; Ni/Al/Cr/La/Mg; UCIG-9DC; Ni/Al/Ca; ICI25-4M; Ni/Al/Cu/K; ICI 46-1; Ni/refractory carrier/K; UCI 6-90B; Ni/ceramic carrier/Al/Ca; UCI C18HC; Cu/Zn/Al; BASF G1-255; Ni/ceramic carrier; ICI 46-4; Ni/Cu/Al,Zr; UCI G-91; Ni/ceramic carrier/Al/Ca/K; University of Zaragosa; Ni/Mg/Al. Used only model compounds.

Wang, D; Milne, T. 1991. "A Molecular Beam Mass Spectrometric Study of Rapid Screening of Catalysts for Hot-Gas Cleanup of Gasifier Organic Tars," Golden, CO: Solar Energy Research Institute, Chemical Conversion Research Branch, February 5. Unpublished.

In a laboratory plug-flow simulation of steam gasification under conditions to produce a largely tertiary tar slate, the following yields of tars were observed (in the absence of O_2). CH_4, 7 wt % of wood fed; C_2H_4, 1.7; C_3H_6, 0.5; C_4H_8, 0.3; C_5H_{10}, 0.6; C_6H_6, 0.9; C_7H_8, 0.2; C_8H_{10}, 0.05; Other, ~2.5 (acetylene, naphthalene, etc.).

Wang, D.; Montane, D.; Chornet, E. 1996. "Catalytic Steam Reforming of Biomass-Derived Oxygenates: Acetic Acid and Hydroxyacetaldehyde," *Applied Catalysis A: General* <u>143</u>, pp. 245–270.

Bench-scale tests of the steam reforming of model compounds, using UCI's G-90C commercial catalyst, are presented. Products were measured on line using the NREL MBMS. The results were favorable providing there was enough steam to remove coke on the catalyst.

Wang, Y.; Kinoshita, C.M. 1992. "Experimental Analysis of Biomass Gasification with Steam and Oxygen," *Solar Energy* <u>49</u> (3), pp. 153–158.

Behavior of light hydrocarbons (C_mH_n) with residence time, equivalence ratio, temperature, and steam biomass ratio is measured in a laboratory, indirectly heated, fluidized-bed biomass gasifier with sawdust feed. C_mH_n varies in the range of 0–2.5 vol % of gas.

Wang, Y.; Kinoshita, C.M.; Zhou, J. 1994a. "Catalytic Gasification Phase 6, Task 3B," in *Hawaii Integrated Biofuels Research Program Phase 6, Final Report* Vol. 1. Manoa, Hawaii: Hawaii Natural Energy Institute, pp. 13–16.

Task includes the design of a slip-stream test system for incorporation in the pre-commercial biomass gasifier facility on Maui. (IGT-based fluidized bed.)

Wang, Y.; Zhou, J.; Kinoshita, C.M. 1994b. "Parametric Tests on Catalytic Tar Reforming of Gasified Biomass," in *Bioenergy '94*. Reno/Sparks, Nevada: pp. 267–274.

"Tars are loosely defined as organic condensable (at room temperature) compounds formed in thermochemical reactions. An O_2/N_2-blown, bench-scale fluidized bed is used to gasify sawdust, followed by a sintered metal filter held at 450°C followed by a second fluid-bed with G-90B nickel catalyst. (The condensation temperature of most tar species is ≥250°C. The tar yield from the gasifier at 800°C and an O_2/N_2 ratio of 15.7/7.9, with no steam, is 53.9 g/Kg biomass." "The yield and concentration of each identified tar species decrease as temperatures increase." Benzene and naphthalene are the most persistent tar species. At a reforming temperature of 800°C 86% of benzene and 97% of naphthalenes are decomposed.

Weisgerber, G.A.; Van Der Heijden, S.P. 1979. "Cleaning Wood Gas for Combustion." SPC 4400-1979-1-Alternate Energy. ENFOR Project No. C-166 Bioenergy Development Program. Alternative Energy Technology Branch. Canmet. Energy, Mines and Resources Canada, Ottawa.

A review, based on gas cleanup literature (mainly coal) from 1920–1970 (910 annotated references included). "Since very few references can be found which directly relate to the

cleaning of wood gas, the search has been extended to include the cleaning of coal, coke, and blast-furnace gases." "The state-of-the-art of cleaning gases produced in wood gasifiers and pyrolysis units has not advanced much since the late 1930's." Thirty-seven manufacturers of gas turbines and diesel and gas engines were queried as to particulate and tar tolerances in wood gas. Only 12 companies replied, nearly all turbine manufacturers, and no diesel engine manufacturers. Visits to 11 gasifiers are detailed but few tar data. The Hudson Bay moving-bed, updraft gasifiers produced "condensible hydrocarbons" in the range of 23–64 g/Nm^3.

Wellman Process Engineering. 1997. "Development of an Improved Gas Clean-Up System for Biomass Gasification Plant," *Renewable Energy*, September.

Updraft gasifier, with thermal oxidation reactor followed by catalytic cracker ("inexpensive" catalyst not specified), has been tested for over 1,200 h in 100–250 h runs. Converted 99.8% of condensed organics into permanent fuel gases suitable for an ICE. Condensible organics (at ~50°C) reduced from 58 g/Nm^3 to 0.1 g/Nm^3.

Wenglarz, R.A.; Nirmalan, N.V.; Daehler, T.G. 1995. "Rugged ATS Turbines for Alternate Fuels." ASME International Gas Turbine Institute Turbo Expo '95, Houston, Texas.

ATS advanced turbines place new demands on HGC vis-a-vis first generation coal-fired turbines. Inlet ATS goals are up to 1327°C (2,600°F), 556°C (1,000°F) above current coal experience. Cold gas cleanup can do the job but "economics, complexity and system efficiency" are issues for gasification systems that utilize cold gas cleanup which also usually require oxygen plants. For air-blown plants, HGC could beat O$_2$-blown cold gas.

Westinghouse. 1995. Biomass HGCU Progress Meeting. Westinghouse Presentation. April.

Destruction Method: Fluidized bed, catalytic (BCL). Dust tolerance of turbine: 10–1 ppm for 1-10 micrometers. Remove particulates to <10 ppm; alkali to < 20–50 ppb; tar removal to protect candle filter. Only 33%–50% of oil and tar destroyed at 964°C. Carried out thermodynamic equilibrium calculations. Tar definition: list of MBMS-identified HC (from NREL). Measured by simulated distillation. DN-34 is friable. In coal gasification severe conditions obviate need for tar cracking. Finland says 650°C should prevent PNA condensation. May need tar cracker to convert NH$_3$ to N$_2$. Oil and tar in RENUGAS ~2% of feed carbon with thermal cracking to 982°C Same alumina beads as in gasifier. DN34 at ~816°C. About 82% oil and tar destruction by thermal cracking, but compositions not much altered. (Tertiary tar), DN-34 too friable to get catalytic data. Alfalfa gives 35% more oil and tar than bagasse, but fewer high boiling components, less three-ring + PNA so less likely to deposit carbon on the filter.

Wiant, B.C.; Bachovchin, D.M.; Onischak, M. 1994. "Biomass Gasification Hot Gas Cleanup Demonstration Program Status," in *Bioenergy '94—Sixth National Bioenergy Conference,* October 2-6. Reno/Sparks, Nevada: pp. 471–478.

Ni-based, various alumina and alumina-silicate media and DN-34 catalysts were tested in a secondary reactor. Fluidized bed up to 982°Cand gas residence time of 2 s. IGT gasifier

projected to contain oils and tars at ~2 g/acf. Must keep gas temperature above 538°C to avoid condensation on the ceramic filter. Of total tar ~40% consists of heavier PNA of three or more rings. These may coke on filter. Tar cracker used to convert high M.W. tars and oils to low M.W. species that will burn in the turbine. For turbine no cleaning is needed for HCl and SO_2.

Williams, R.H.; Larson, E.D. 1996. "Biomass Gasifier Gas Turbine Power Generating Technology," *Biomass and Bioenergy* <u>10</u>, pp. 149–166.

Systems study. Need 100–200 ppb or less of alkalies at gasifier exit. A high level of tar may not be of concern for BIG/GT system. Keep tars in vapor-phase. "Tars are desirable, in fact, to boost the heating value of the gas." Fluidized-bed gasifiers are operated at 800°–1,000°C.

Wornat, M.J.; Sarofim, A.F.; Lafleur, A.L. 1992. "The Pyrolysis of Anthracene as a Model Coal-Derived Aromatic Compound," Twenty-Fourth Symposium (International) on Combustion, Pittsburgh: The Combustion Institute, pp. 955–963.

Products and mechanisms are discussed, including the formation of soot.

Yasue, H.; Kato, H.; Takasu, K. 1998. "Development of a 1000 kW-class MCFC Pilot Plant in Japan," *J. Power Sources* <u>71</u> 89–94.

A catalytic burner is applied to the reformer to keep the steam/carbon ratio at 3.5 to avoid carbon formation and deposition inside the cell.

Yu, Q.; Brage, C.; Chen, G.; Sjöström, K. 1997. "Temperature Impact on the Formation of Tar from Biomass Pyrolysis in a Free-Fall Reactor," *J. Analy. Appl. Pyrolysis* <u>40–41</u>, pp. 481–489.

Detailed analysis of tars, collected by a new solid-phase absorption method, is presented for free falling birchwood particles at a gas residence time of ~1.5 s and at temperatures of 700°, 800°, and 900°C. Conclusions: Temperature has a significant effect on both yield and composition of tars resulting from pyrolysis of biomass. Increasing temperature reduces total tar yield and favor formation of carbon monoxide, benzene, naphthalene, and PAH. The proportion of three- and four-ring PAH is slightly increasing above 800°C. There are considerable amounts of phenol and toluene in tar at 700°C which is further cracked to thermally stable components, such as benzene and naphthalene, when increasing the temperature. High-temperature tars (>700°C) "do not contain acids, alcohols, aldehydes, or aliphatic compounds but exclusively contain phenols and aromatic hydrocarbons together with small amounts of basic compounds."

Zanzi, R.; Krister, S.; Björnbom, E. 1993. "Rapid Pyrolysis of Wood with Application to Gasification," in *Advances in Thermochemical Biomass Conversion*, Vol. 2. Edited by A.V. Bridgwater, pp. 977–985.

Secondary pyrolysis of primary oil is studied in a pressurized free-fall reactor at 750°C and 900°C. The volatiles are passed through a metallic filter to remove char particulates, dust and soot and then collected in a water-cooled condenser. Remaining aerosol is removed in cyclone-shaped dry-ice traps and a cotton filter. Tar yield determined after the water is evaporated from

total condensate. Tar yields from wood, at 270 k Pa and residence time of 1.4 s, were 1.3 and 1.1 wt % maf wood at 750° and 900°C, respectively. Benzene and toluene in the gas were in the range of 0.3–0.5 and 0.06–0.15 wt % maf wood, respectively.

Zhou, J. 1994. "Catalytic Tar Reforming for Gasified Biomass," Thesis, University of Hawaii.

From literature, tars may consist of more than 70 compounds, but only about 20 tar species are present in significant quantities. Uses a standard sample containing 23 chemical compounds, representing known tar species for GC calibration.

Zielke, U. 1997. "Tar and Solid Particles in LCV-Gas from Fixed-Bed Gasifiers: Danish Measurement Results." Paper presented at the IEA Seminar, IC Engines for LCV-gas from Biomass Gasifiers, Zurich, October.

Zschetzsche, A.; Hofbauer, H.; Schmidt, A. 1995. "Biomass Gasification in an Internal Circulating Fluidized Bed," in *Proceedings of the 8th European Biomass Conference, Biomass for Energy, Environment, Agriculture and Industry*. Vienna, Austria: Pergamon, pp. 1771–1776.

A gasifier concept with an internal circulating fluidized-bed system is described. Cold flow tests have been made but no operation on biomass yet reported.

Zwinkels, M.F.M.; Heginuz, G.M.E.; Gregertsen, B.H.; Sjöström, K.; Järås, S.G. 1997. "Catalytic Combustion of Gasified Biomass over Pt/Al_2O_3," *Applied Catalysis A: General* 148, pp. 325–340.

Combustion tests at 200°C and above of synthetic gas with NH_3 added and with benzene as model tar aromatic. Gas from a biomass gasifier contains up to a few thousand ppm of NH_3. Reaction products were analyzed by an on-line Balzers QM6 421 quadrupole MS. Benzene was readily combusted but NH_3 went to NO. A study in press shows that naphthalene is also readily oxidized on Pt/Al_2O_3. Need combination of catalysts to convert NH_3 to N_2.

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