

## **Catalytic pyrolysis of wood biomass in an auger reactor using calcium-based catalysts**

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### **Abstract**

Wood catalytic pyrolysis using calcium-based materials was studied in an auger reactor at 450°C. Two different catalysts, CaO and CaO·MgO were evaluated and upgraded bio-oils were obtained in both cases. Whilst acidity and oxygen content remarkable decrease, both pH and calorific value increase with respect to the non-catalytic test. Upgrading process was linked to the fact that calcium-based materials could not only fix the CO<sub>2</sub>-like compounds but also promoted the dehydration reactions. In addition, process simulation demonstrated that the addition of these catalysts, especially CaO, could favour the energetic integration since a lowest circulation of heat carrier between combustor and auger reactor should be needed. An energy self-sustained system was obtained where thermal energy required for biomass drying and for pyrolysis reaction was supplied by non-condensable gas and char combustion, respectively.

### **Keywords**

Biomass, catalytic pyrolysis, auger reactor, bio-oil, deoxygenation catalysts

## **1. Introduction**

The current world dependency of fossil fuels produces concerns over energy security and global warming. One way to mitigate this is to promote the use of alternative fuels such as biomass. Biomass is known as a renewable, sustainable and environmentally benign fuel (Sirijanusorn et al., 2013). Forestry waste represents a good opportunity in this sense as a by-product from forest management with not a wide spread usage (Puy et al, 2011). To obtain energy out of the forestry waste, pyrolysis is an alternative to direct combustion due to the recovery of solid and liquid materials which can be readily stored and transported (Bridgwater and Peacocke, 2000). The liquid material known as bio-oil is advantageous because its volumetric energy density is 4–5 times higher (or even more) than the solid biomass. However, it presents some disadvantages for its application as fuel such as high water content, high viscosity, poor ignition characteristics and corrosiveness (Oasmaa and Czernik, 1999), as well as high oxygen content, high solid content and chemical instability (Bridgwater, 2012). Bio-oil improvements can be reached through several actions before, during and after pyrolysis, such as torrefaction or demineralizing the feed, use of certain catalysts within the process and catalytic post-treatment processes (Bridgwater, 2012). Hence, an increasing number of methods for bio-oil upgrading are being investigated, including hydroprocessing, catalytic cracking, esterification and reactive distillation. Refining and subsequent purification of the raw bio-oil increase the production costs and greatly reduce the net energy efficiency of the process (Kersten and Garcia-Perez, 2013). One simple solution in pyrolysis is the introduction of catalysts to eliminate and to substitute oxygen and oxygen-containing functionalities, increasing the hydrogen to carbon ratio of the final liquid products. In general, different high cost catalysts have been mainly tested for biomass catalytic pyrolysis such as microporous zeolites,

mesoporous M41S and mesoporous aluminosilicates (Taarning et al., 2011; Perego and Bosetti, 2011). All these catalysts lead to a bio-oil with improved characteristics, which could be a valuable product as bio-refinery feedstock. On the other hand, some other cheap catalysts such as bulk metal oxides (Lin et al., 2010) or supported sulphide/oxide and metal catalysts, mainly on alumina, have been also tested for biomass catalytic pyrolysis (Bulushev and Ross, 2011). Although an improved bio-oil is also obtained, further bio-refinery processing is required for practical application. Summarizing, catalysts should be highly active, selective to particular products, resistant to deactivation, readily recycled and whenever possible, cheap.

CaO has been used in coal pyrolysis to obtain a liquid with low viscosity and low sulphur and oxygen contents (Khan, 1987). In addition, indications of CO<sub>2</sub> sorption from the gas phase and fixation of CO<sub>2</sub>-like substances directly in the liquid product have been previously reported (Tingyu et al., 2000). The feasibility of CaO for *in situ* deoxygenation of bio-oil has been confirmed by Lin et al. (2000). Biomass catalytic pyrolysis with CaO in a fluidized bed reactor produces a liquid with a reduction of 21% in the oxygen content when a CaO to biomass ratio of 5 is used. Similarly, calcined dolomite (MgO·CaO) has been used in coal pyrolysis to decrease tar yield and to increase the H/C ratio in the resulting liquid fraction (Yeboah et al., 1980). Therefore, both CaO·MgO and CaO seem to be promising catalysts for catalytic pyrolysis process in an auger reactor since they are also relatively inexpensive and, their uncalcined precursors, greatly abundant.

Conventionally, several processes have been proposed to implement the pyrolysis within a self-sustainable system from an energetic point of view (Meier et al., 2013; Xu et al., 2011). Proposed layouts vary depending on the desired product. When bio-oil is the desired product, char and gas obtained could be combusted to provide the necessary

heat for the endothermic pyrolysis and also other intermediate processes, such as the drying of biomass. Some systems propose the introduction of a heat carrier, such as sand (Sirijanusorn et al., 2013). These solids could circulate between the pyrolysis and the combustion reactors, providing the necessary heat for the pyrolysis process.

Furthermore, it would be very useful that these solids could also act as catalysts in the pyrolysis reactions.

There are many types of reactor designed and tested for biomass pyrolysis such as free-fall, fluidized-bed, vacuum, ablative, rotating cone and auger (Sirijanusorn et al., 2013; Yildiz et al., 2013). Under this context, the auger reactor has been stated to have high potential in technical and market aspects since its design is relatively simple, applies low carrier gas flow and is suitable for large biomass particle. This type of reactor operates in continuous mode and it has been proved to show an excellent reproducibility and stability (Puy et al., 2011). The auger reactor may also be well suited for small, portable pyrolysis systems in distributed or decentralized processing schemes. However, the catalytic pyrolysis of biomass in an auger reactor has not been widely study. To the best of author's knowledge, there is only one study (Yildiz et al., 2013) showing the *in situ* catalytic pyrolysis of biomass by adding a mixture of commercial ZSM-5 and sand. That work showed that although *ex situ* catalytic upgrading could consume less catalyst, the overall performance of *in situ* catalysis in terms of oil quality is considerably better. Therefore, the objective of this paper is to study the catalytic pyrolysis of biomass in a single screw auger reactor by using a mixture of sand and a low cost calcium-based material as catalyst (either CaO or CaO·MgO). To reach this aim, the effect of these calcium-based materials on yields and properties of the pyrolysis products are studied, being more widely analysed the liquid product. In addition, the storage stability of the pyrolysis liquids produced is studied following an accelerated aging test under the

following conditions: 24 h at 80 °C. Finally, it is proposed a self-sustainable pyrolysis system, from an energetic standpoint, including both char and gas combustion. The simulation of the energetic integration of the whole system is developed to assess the possibility of being an autothermal process.

## **2. Material and methods**

### **2.1 Biomass**

The biomass used in the present study was forest pine woodchips (*Pinus halepensis*) including bark, obtained from the north east area of Spain. The biomass was initially dried up to moisture levels lower than 2 wt. % and subsequently milled and sieved to provide a maximum size of 15 mm. The value obtained for LHV was 18.0 MJ/kg (determined by means of a calorimeter IKA C-2000, standard procedure: UNE 164001 EX). Proximate and ultimate analyses of the received biomass are shown in Table 1.

### **2.2 Materials**

Silica sand, calcined calcite (90% CaO, Calcinor) and calcined dolomite (58% CaO, 36% MgO, Calcinor) were used in this work. CaO and CaO·MgO materials were commercially available and obtained after calcination at 900 °C of calcite and dolomite, respectively. These materials were fed as received after sieving; with a particle size distribution in the range of 300–600 µm. Silica sand particle size was in the range of 200–600 µm.

### **2.3 Auger reactor**

Experiments were carried out in an auger reactor of 100 kW<sub>th</sub> of nominal capacity for woody biomass, operating at atmospheric pressure. A detailed description of the reactor can be found elsewhere (Puy et al., 2011).

Biomass and catalyst diluted with sand were kept in two separated hoppers, and fed to

the auger reactor by two variable speed screw feeders, respectively. The reactor was heated by three electrical furnaces disposed in series to provide the energy required by pyrolysis reactions. Three thermocouples were disposed along the reactor to follow the temperature profiles. The mixture of solids and volatile products were separated at the end of the reactor. The solids fell inside a vessel and were recovered at the end of each experiment. The volatile products were directed to a condensation system, as they left the reactor and were cooled down and separated in condensable and non-condensable fractions. The condensable fraction constituted the raw bio-oil. The non-condensable fraction was sampled at ambient temperature using Tedlar bags, once the process steady state was reached. The non-condensable gas stream was conducted to a burner before leaving the experimental system to the atmosphere.

It should be pointed out that before experimental conditions were chosen, different preliminary tests were carried out at different CaO to biomass ratios (3:1, 1:1, 1:2, 1:3) at 450°C. Catalysts were diluted (if needed) with sand, keeping a (sand + catalyst) to biomass ratio of 3:1. This solid inventory would be required as heat carrier according to process simulation, as shown later. A lack of balance together with very poor bio-oil yields were observed at high CaO to biomass ratio (3:1, 1:1 and 1:2). This fact was linked to the promotion of secondary reactions leading to tar formation, which was stuck in the pipes of the pilot plant and, eventually, produced operational problems. Thus, a low catalyst to biomass ratio of 1:3 was selected as the optimum value. The non-catalytic run was performed with sand to biomass ratio of 3:1. It is worth commenting that the use of 500°C as pyrolysis temperature was ruled out since it significantly promoted the occurrence of secondary reactions, leading to both low bio-oil yield and poor mass balance. Thus, biomass and sand (or sand + catalysts) mass flows of 2 kg/h and 6 kg/h, respectively, were fed to the auger reactor at 450°C. N<sub>2</sub> was

used as carrier gas, with a flow of 5 L<sub>N</sub>/min. Residence time for solids inside the auger reactor was of 7 min. Experiments duration was approximately of 2 h, being the steady state reached after 45 min.

Once the bio-oil and the solid products were recovered, their respective yields were calculated directly by weight. The gas yield was calculated from N<sub>2</sub> percentage in gas stream, which was used as an internal standard to quantify the outside gas production. Mass balance closed at 100 ± 3%.

## **2.4 Product characterization**

**2.4.1 Gas characterization.** Non-condensable gases were analysed by GC/TCD (HP 5890-Series II) using a Molsieve 5 Å and Hayesep Q columns. The analysed compounds were H<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>8</sub>.

**2.4.2 Char characterization and CO<sub>2</sub> catalyst carbonation.** After experiments, used calcium-based materials and char were separated by sieving. Ultimate, moisture, ash and lower heating value (LHV) analyses were performed to the obtained char, following the same procedures as described for biomass in Table 1. CO<sub>2</sub> carrier carbonation of the calcium-based materials was determined by weight difference by calcination at 850°C in static air for 3 hours.

**2.4.3 Bio-oil characterization.** Bio-oil (also named liquid product/fraction) was obtained as a heterogeneous liquid in which two different phases were observed. The sample recovered was homogenized by shaking. The whole sample was treated in aliquots of 50 mL that were centrifuged at 1500 rpm for 1 h. Two liquid phases (aqueous and organic) were subsequently collected by decantation. Then, physicochemical properties were determined for the organic liquid phase. Besides, the chemical composition was determined by GC/MS.

*2.4.3.1 Physicochemical properties.* These properties were measured for the organic

phase according to standard methods: water by Karl Fischer titration according to ASTM E203-96 in a Crison Titromatic KF, pH was measured at room temperature by means of a pH meter Mettler Toledo T50 with an electrode Inlab Micro, total acid number (TAN) was determined by potentiometric titration using also the Mettler Toledo T50 equipment with an electrode DGi118-solvent and following the ASTM D664, density was measured using a syringe of 1 mL by weighting 0.1 mL of sample and viscosity was measured in a rotational viscometer model Brookfield DV-E following the ASTM D445 Standard Test Method. Finally, ultimate analysis and heating value of organic phase were performed.

*2.4.3.2 Liquid composition analysis by GC/MS.* The chemical composition of organic phase was analysed by GC/MS using a Varian CP-3800 gas chromatograph connected to a Saturn 2200 Ion Trap Mass Spectrometer.

A capillary column, CP-Sil 8 CB, low bleed: 5% phenyl, 95% dimethylpolysiloxane, (60 m × 0.25 mm i.d., film thickness 0.25 µm) was used. An initial oven temperature of 40 °C was maintained for 4 min. Then, a ramp rate of 4 °C/min was implemented to reach a final column temperature of 300 °C. This temperature was maintained for 16 min. The carrier gas was He (BIP quality) at a constant column flow of 1 mL/min. The injector, detector and transfer line temperatures were 300 °C, 220 °C and 300 °C, respectively. Samples volumes of 1 µL (1:25, wt.%, in a mixture of 1:1 CH<sub>2</sub>Cl<sub>2</sub>:C<sub>2</sub>H<sub>6</sub>O) were injected applying 1:5 split mode, with a solvent delay of 7.5 min. The MS was operated in electron ionization mode within 35–550 m/z range. Each peak attributed to determined compounds, was integrated according to the corresponding m/z (reported in Table 1SI). The interpretation of the mass spectra given by the GC/MS analyses was based on the automatic library search NIST 2011.

The storage stability of the pyrolysis liquids was studied following an accelerated aging

test under the following conditions: 24 h at 80 °C (Oasmaa and Kuoppala, 2003).

## **2.5 Process simulation**

Finally, a simulation process model for a self-sustainable (from an energetic point of view) biomass pyrolysis system has been developed in Aspen Hysys.

## **3. Results and Discussion**

The results presented in this paper show the influence of adding calcium-based materials on product distribution and composition during catalytic biomass pyrolysis in an auger reactor. Experiments were repeated three times and average values are shown. In addition, the stability of the organic phase produced is analysed with an accelerated aging test, taking into account its physicochemical properties and its chemical composition. And finally, the process simulation is performed to obtain an energetic analysis and evaluate the possibility of reach a self-sustainable system.

### **3.1 Catalyst influence on product distribution**

The distribution of pyrolysis products (gas, char and the whole liquid product before phase separation) is analysed in terms of their yield (wt.%, g of product/g of biomass fed). Fig. 1 shows the different pyrolysis product yields obtained when calcium-based materials are added. Results obtained with only sand are also shown. Pyrolytic water is included within the liquid yield and the percentage of CO<sub>2</sub> absorbed in calcium-based materials is included as gas yield, being 6.9 wt.% and 5.1 wt.% for the CaO and CaO·MgO runs, respectively, which is in agreement with the higher CO<sub>2</sub> sorption capacity of CaO versus CaO·MgO. As can be observed in Fig. 1, char, gas and liquid yields are not significantly affected when either CaO or CaO·MgO catalysts are added (yields were around 48–50 wt.% for liquid, 25–27 wt.% for char, and 26–27 wt.% for gas). A different behaviour was reported by Yildiz et al. (2013) who found that lower

liquid yields were obtained for the catalytic pyrolysis of wood biomass in an auger reactor using a mixture of sand and commercial ZSM-5 (about 50 wt.%), compared to the non-catalytic process with sand (about 59 wt.%). Different biomass properties, much higher catalyst to biomass ratio (5:1) and a different experimental setup could explain this different behaviour. According to our experimental setup, it should be commented that both liquid yield and gas residence time (around 4 s) are within the range of intermediate pyrolysis of wood reported in the literature (Bridgwater, 2012), whilst pyrolysis in an auger reactor using heating carriers was claimed to be a fast pyrolysis process (Brown and Brown, 2012; Yildiz et al., 2013). This difference could explain the lower catalyst to biomass ratio requested, since higher contact times in our reactor could clearly promote the occurrence of secondary reactions, eventually leading to operational problems, as shown before.

Regarding the use of CaO and CaO·MgO as catalysts in biomass pyrolysis, there have not been found published results where these materials have been used in auger reactors. Some works have analysed the effect of adding these solids in a fluidised bed reactors. For instance, Lin et al., (2010) studied the catalytic pyrolysis of white pine using this type of reactor with a CaO/biomass ratio from 0 to 5 at 550 °C. As expected for fast pyrolysis in fluidised bed reactors (Bridgwater, 2012), a liquid production higher than that found in this work was reported. Conversely, in this work an intermediate pyrolysis takes place and the volatiles released in the process (condensable and non-condensable compounds) are exposed to higher residence time than those usually found in fast pyrolysis (about 2-4 times). So, secondary reactions of organic condensable compounds are favoured, resulting also in lower liquid yields. Additionally, Lin et al. (2010) observed that increasing the CaO to biomass ratio led to an increase in the liquid yield and a slight raise in the char yield, while the gas production decreased. However, they

did not found significant variations on the pyrolytic yields at low CaO to biomass ratio, in agreement with the results found in this work.

### 3.2 Catalyst influence on gas composition

Table 2 shows the average gas composition and LHV for each of the experiments performed. Gas composition shows certain variations for catalytic and non-catalytic runs. Specifically, an increment on H<sub>2</sub> concentration, a slight rise in both CH<sub>4</sub> and CO concentrations and a decrement on CO<sub>2</sub> are observed when CaO or CaO·MgO are used. This fact could be due to CO<sub>2</sub> capture by calcium-based materials according to Eq. 4, which simultaneously favours H<sub>2</sub> production from water gas shift reaction and consequently the methane reforming reaction (Eq. 5 and 6). It should be pointed out that only CaO is considered in the carbonation reaction since MgO does not contribute to CO<sub>2</sub> capture at these experimental conditions, which is in agreement with the lower CO<sub>2</sub> concentration found for the CaO experiment.



As mentioned above, the increasing concentration observed for H<sub>2</sub>, CH<sub>4</sub> and CO, could also be related to the promotion of cracking reactions since these calcium-based materials have shown some catalytic effect on biomass pyrolysis (Mohan et al., 2006). Accordingly, a higher LHV for those experiments with calcium-based materials is attained, being this improvement more accused for CaO.

### 3.3 Catalyst influence on char composition

Table 2 also shows the char analysis for the catalytic and non-catalytic runs. The percentages of oxygen in char are higher for those experiments using CaO and CaO·MgO catalysts respect to those for the non-catalytic experiment. It can be assumed

that the promotion of secondary reactions by the addition of calcium-based catalysts can lead to the formation of heavy organic compounds as oxygenated polyaromatic compounds, which form carbonaceous deposits throughout retrogressive reactions. Against this background, it should be commented that significant differences in the char yield after catalyst addition are not found although an increase in the relative amount of heavy polycyclic aromatic hydrocarbons is detected in the bio-oil by GC/MS. On the other hand, it cannot be completely ruled out that some  $\text{CaCO}_3$  particles could be deposited on the char surface.  $\text{CaCO}_3$  has higher oxygen content than char (48% vs 17%). This fact could lead to an increase in the overall oxygen content of the mixture. Unfortunately, an increase in the ash content of the samples is not observed. Thus, a sole explanation to the higher oxygen content of the pyrolytic char after catalysts addition cannot be stated. On the other hand, carbon shows the opposite trend. Carbon content is higher for the non-catalytic experiment than those using the calcium-based materials, while the rest of elements remained practically constant. This caused that the LHV of char is higher for the non-catalytic run.

### **3.4 Catalyst influence on liquid phase**

The raw bio-oil recovered from the tests showed a heterogeneous aspect with different liquid phases. After centrifugation, two phases are clearly differentiated. The top phase is fluid and light brown colour. The bottom phase is thicker and dark brown colour. Regarding water contained in each phase, the bottom phase presented lower moisture percentages (13% in sand tests, 12% in CaO tests and 11% in CaO·MgO tests), being remarkably higher for the top phase (about 50% for the non-catalytic run and about 60% for the catalytic runs). Therefore, taking into account its appearance and water contents, hereinafter the top phase will be named as aqueous phase, and the bottom phase as organic phase.

The results obtained from sand test agree with those observed by Garcia-Pérez et al. (2007) from the pyrolysis of pine chips and pine pellets using an auger reactor at 500 °C. These authors also obtained an aqueous top phase, and an oily phase with a 13.5% of water, similar to that found in the present work when only sand is used (13.4%).

#### **3.4.1 Liquid phase yields**

Although overall liquid yield is hardly affected, the phase distribution exhibits certain variations, being the formation of organic phase favoured for both catalysts. It is observed that catalyst addition increases the organic phase formation versus the non-catalytic process from 27 % to 34% and 31% for CaO and CaO·MgO, respectively. A prevalent abundance of the aqueous phase is in agreement with literature data from pine pyrolysis in auger reactor without heat carriers (Garcia-Perez et al., 2007), which showed more production for the aqueous phase versus the organic phase (around 38 wt.% of the pristine biomass for the aqueous phase compared to about 20 wt.% corresponding to the oily phase). However, it should be highlighted that the use of catalyst lead to an overall increase in the water production, since water percentage in the aqueous phase is greatly increased from about 50 wt.% to 60 wt.% after catalyst addition. Therefore, total water content is increased about 5 nominal points after catalyst addition. It is well-known that calcium-based materials can promote dehydration reactions of the oxygenated species during pyrolysis, leading to an increase in the water yield and a quality enhancement of bio-oils (Lin et al., 2010).

#### **3.4.2 Physicochemical properties of the organic phase**

Among the all phases obtained in bio-oil, it is generally accepted, that the organic phase has the best potential properties as renewable feedstock in a refinery. Thus, relevant characteristics for this aim, such as water content, pH, acidity, density, viscosity and oxygen content are analysed in this section for each calcium-based material. Some

physicochemical properties for this organic phase are shown in Table 3. This table shows that the organic phase obtained in the non-catalytic run exhibits fuel characteristics comparable to those obtained in other works for biomass pyrolysis (Garcia-Perez et al., 2007; Sirijanusorn et al., 2013). In addition, it can be observed that although the organic phase shows properties that are not within the range of the specifications required in a bio-oil to be used either as fuel or as feedstock in a refinery, the presence of both CaO and CaO·MgO improves some of these properties respect to the non-catalytic process.

Although water content for the catalytic tests is comparable to the result obtained with the non-catalytic run, CaO and CaO·MgO addition produce an outstanding decrement on the total acid number (TAN) of the bio-oil. The observed trends agree with the elimination of acid compounds in the pyrolysis vapours as reported by Lin et al. (2010) and Lu et al. (2010). As shown later, acid compounds detected by GC/MS were significantly reduced after catalyst addition. This fact points out that CO<sub>2</sub>-like compounds can react directly with CaO particles in order to form calcium salts, which are then fixed in the catalyst surface. These results are very satisfactory because high acidity makes the bio-oil harder to be used in pipes and engines, catalyses polymerization reactions and decreases its stability over time (Stefani et al., 2011). In accordance with the exposed results, another improvement observed after use of calcium-based catalysts is the reduction on the oxygen content respect to the non-catalytic run. Much higher oxygen content in bio-oil than that found in conventional fuels causes an increment of corrosiveness and viscosity, as well as low energy density and thermal instability. Since oxygen contents about 20 wt.% are required to be used as feedstock in a refinery, further improvement are still needed (Sanna and Andresen, 2012). Finally, it is worth commenting that, although the aforementioned

physicochemical properties for the organic phases are very similar for both CaO and CaO·MgO tests, greater selectivity to the organic phase production is attained for the CaO catalyst. CaO·MgO seems to promote retrogressive reactions, slightly decreasing the content of organic compounds in the organic liquid phase.

### **3.4.3 Chemical composition.**

Tentative identification of the compounds of the organic phase is performed by comparing the mass spectra of unknown components with the ones of the NIST 2011 library. Relative area percentage for each chromatographic peak according to m/z shown in Table S1 is employed as a semi-quantitative approach. Samples are injected by duplicate and results are an average of the two injections. The GC/MS chromatograms of the three bio-oils are quite similar in composition, differing slightly in the component contents. In general, bio-oil is a complex mixture highly oxygenated with a great number of molecules, which nearly involve all species of oxygenated organics. In this way, the compounds of bio-oils are classified in the following classes: furans, phenols, acids, aldehydes (linear and cyclic), ketones (linear and cyclic), cyclic hydrocarbons, polyaromatics, esters and “others”, involving 96 identified compounds according to the NIST 2011 library (Table 5). In addition, levoglucosan and BTX compounds are separately reported. It can be observed in Table 4 that regardless the nature of process, either catalytic or non-catalytic, phenolic compounds originated from the decomposition of lignin (Lin et al., 2010) are the main components in bio-oil. In addition to their influence on instability, it is well-known that the lignin-derived products are mainly responsible for the high molecular weight and viscosity of bio-oils and thus, one of the aims of any upgrading process is to remove these compounds. It can be observed in Table 5 that the addition of calcium-based catalysts does not affect to the overall amount of phenolic compounds. However, a different distribution in the

percentage of these compounds after catalyst addition can be observed, since the relative amount of those phenolic compounds with higher oxygen content (Ethylmethoxyphenol Creosol, and Guaicol) is reduced (see Fig. 2), whilst the relative amount of those compounds with lower oxygen content (Cresol and Phenol) is increased. Therefore, this transformation is beneficial to the decrease of bio-oil oxygen content, regardless either CaO or CaO·MgO is added to the process.

During pyrolysis of holocellulose (hemicellulose and cellulose), two competing pyrolytic pathways are mainly responsible for its primary decomposition: depolymerisation and pyrolytic ring scission. Depolymerisation process through transglycosylation (Mohan et al., 2006; Thangalazhy-Gopakumar et al., 2011) forms various anhydrosugars (mainly levoglucosan), furans and other products; whilst ring-opening reactions of holocellulose forms some volatile molecules, mainly lineal carbonyls, after decomposing and reforming reactions. As shown in Table 4, although the levoglucosan area ratio seems not to be affected by the addition of calcium-based catalysts (either CaO or CaO·MgO), the relative amount of furans is slightly decreased. On the other hand, it can be observed that the relative area of the linear carbonyl groups, especially those with lower molecular weight, is increased (e.g. 2-butenal relative amount is increased from about 0.05% to 0.1%). These results are in agreement with those reported by Lin et al. (2010), which stated that “the active quasi-CO<sub>2</sub> intermediates” can react directly with the CaO, leading to a preferred path of decomposition and reforming reactions during cellulose pyrolysis. Unfortunately, GC/MS specifications do not allow quantifying other light organic compounds such as methanol, acetaldehyde, and acetone, among others, which could confirm this reaction mechanism.

Acetic acid was the predominant carboxylic acid in the bio-oils. Acetic acid is produced

through removal of acetyl groups in 4-methyl-3-acetylglucuronoxylan (hemicellulose containing glucuronic acid and xylose as its main constituents) and also in a minor extend from cellulose during its pyrolysis (Mohan et al., 2006). The relative amount of this compound was remarkable reduced after addition of calcium-based catalysts (from 5.0% to about 2.5%). Accordingly, an overall reduction in the amount of acid compounds is observed. Again, it is observed that acid compounds CO<sub>2</sub>-like substances can react with the CaO (Lin et al., 2002). The presence of acids is detrimental to the use of the organic phase as bio-oil, due to their corrosiveness and because they affect to the stability of the liquid. So, the observed decrement in the overall acids group after CaO or CaO·MgO addition leads to an enhancement of the liquid properties. These results are supported also by the TAN and pH results reported in Section 3.4.2.

From Table 4, it can be also observed that the relative abundance of cyclic-ketones is increased by the addition of calcium-based catalysts. Therefore, it can be stated that CaO can also promote dehydration reactions during pyrolysis, in agreement with the overall increase in the water content of the bio-oil. It is also worth commenting that although the relative amount of BTX compounds is not increased after the introduction of calcium-based catalysts, catalyst addition seems to promote the formation of polyaromatic compounds, especially retene, which is one of the major products for the pyrolysis of conifer trees (Ramdahl, 1983). Percentages of retene about 1.7% and about 3.0% and 2.7% are obtained for non-catalytic and catalytic runs, respectively. The presence of polyaromatic compounds deserves special attention due to their carcinogenic component. In addition, the formation of this type of compounds can also point out the above mentioned promotion of retrogressive reactions after catalyst addition (Mohan et al., 2006). These reactions seem to be marginally favoured for the CaO·MgO catalyst, since slightly higher concentration of these heavy organic

compounds is observed for the bio-oil produced in this experiment. Accordingly, a higher viscosity is attained. Finally, no major differences are found for the other families of compounds after the incorporation of calcium-based catalysts.

Taking into account the obtained results, the addition of low amounts of CaO or CaO·MgO to the pyrolytic process in an auger reactor, produces several benefits since an upgraded bio-oil with lower oxygen content, lower acidity character and higher calorific value is obtained. Unfortunately, it is also worth commenting that calcium-based catalysts slightly favour the formation of heavy polycyclic aromatic hydrocarbons, being this effect more apparent for the CaO·MgO catalyst.

#### **3.4.4 Organic phase stability.**

According to Elliott et al. (2012a) the major changes in aging take place in carbonyl groups (that could be measured by aldehydes and ketones variations), and water insoluble fractions. Besides, water insoluble compounds are related to the increment on molecular weight distribution and viscosity. So, both composition and viscosity has been stated as parameters for the analysis of the pyrolysis liquid stability.

Thus, the viscosity of the three different bio-oils has been measured after an accelerated aging test (80°C for 24 h). This parameter is found to be variable for all the liquids tested, varying from 99 to 255 cP, 123 to 286 cP, and 139 to 280 cP for the non-catalytic runs, CaO and CaO·MgO, respectively. The relative increase of the viscosity for the non-catalytic bio-oil is higher than that observed for the catalytic upgraded bio-oils. Variations higher than 100% are found in all the cases, which is the limit value accepted for stable bio-oils (Chiaramonti et al., 2007). The observed instability for the liquid samples analysed is coherent with the composition of the samples, which favours the increase of the bio-oil viscosity (Elliott et al., 2012b). GC/MS analysis shows few differences either in the identified compounds or their relative abundances with time. In

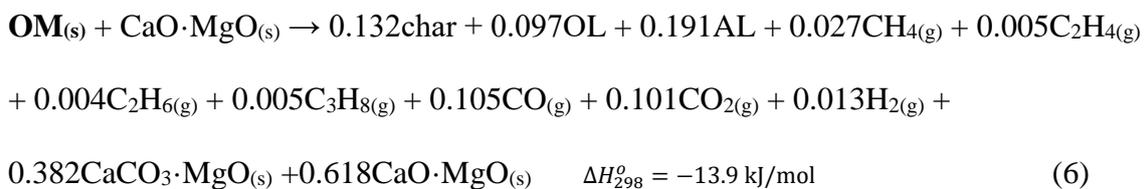
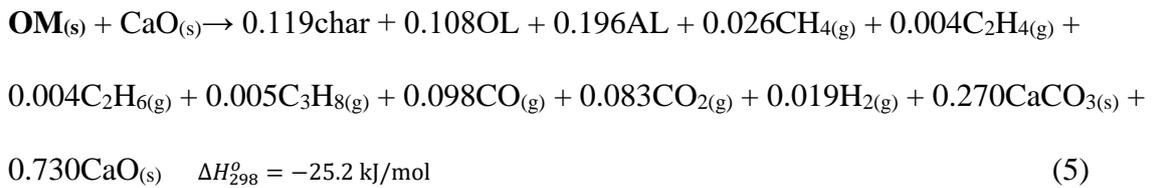
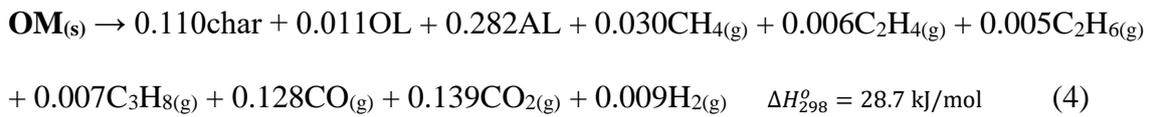
fact, as can be observed in Table 4, the same dominant organic compounds, associated with phenolic compounds derived from lignin, are found for the three bio-oils. These samples generally present an increment in the relative abundance observed for levoglucosan as well as for acids, cyclic-aldehydes and esters, whilst other families of compounds keep comparable relative values. The pyrolytic organic components formed under reducing conditions, are highly susceptible to oxidation. The normal reaction sequence for such components is formation of alcohols followed by ketones or aldehydes, followed by carboxylic acids. The latter molecules dissociate in the aqueous emulsion, becoming proton donors, and thus tend to increase the acidity of the oil. Esterification reactions between acids and alcohols come to equilibrium and water is generated as a by-product (Elliott et al., 2012b). Accordingly, an increment in the relative abundance of acids, cyclic-aldehydes and esters as well as relevant changes in the acidic character is observed for these bio-oils after accelerated aging. Unexpectedly, similar water percentages are found for the three bio-oils after the aging test, which could be related to the experimental error of the measurement. Therefore, it can be concluded that the incorporation of calcareous sorbents (either CaO or CaO·MgO) to the heat carriers does not have any major influence on the stability of the bio-oils and further upgrading processes should be carried out for this purpose.

### **3.5 Catalyst influence on energetic integration**

Finally, a simulation process model for a self-sustainable (from an energetic point of view) biomass pyrolysis system has been developed in Aspen Hysys. Fig. 3 shows the simplified layout of the process model proposed. Bio-oil (stream 4 in Fig. 3) is the desired product in the assessed model, allowing the rest of pyrolysis products (char and gas) to be used separately as fuels in secondary combustors. Energy is required for driving the endothermic reactions involved in pyrolysis as well as in the biomass drying

step. Pyrolysis reactor is considered to operate at around 450°C, whereas drying occurs at around 120°C by putting into contact diluted air at around 250°C (stream 8) with biomass at ambient temperature (stream 1).

In the proposed layout, either sand as heat carrier or a mixture of sand and calcium-based materials (CaO and/or CaO·MgO) as both heat carrier and catalyst, are introduced in the auger pyrolysis reactor to provide the required heat. For the different mixtures, mass balances from the experimental tests and characterization results, aid in the determination of a global chemical reaction for describing the pyrolysis process in each case. Global pyrolysis reactions determined when using sand (Eq. 4), CaO (Eq. 5) and CaO·MgO (Eq. 6) are introduced in the auger reactor step of the process model. In all cases, it was assumed that only the organic matter of the biomass (OM<sub>(s)</sub>) interacts in the pyrolysis reaction for giving way to four different fractions: char, organic liquid (OL), aqueous liquid (AL) and a mixture of non-condensable gases (CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, CO, CO<sub>2</sub> and H<sub>2</sub>). The CaO and CaO·MgO reactions to form CaCO<sub>3</sub>, were also taken into account in the pyrolysis process.



Heat carriers are introduced in the pyrolysis reactor at around 790°C coming from a combustor reactor, where char from pyrolysis is burnt with 20 % of air excess. This

temperature is estimated as the necessary to ensure complete calcination of  $\text{CaCO}_3$  in the combustor, according to equilibrium from Baker (1973) and considering an acceptable margin of around 0.05 atm between equilibrium  $\text{CO}_2$  partial pressure and  $\text{CO}_2$  partial pressure at combustor outlet (Martinez et al., 2012). Based on this temperature, the mass flow rate of the heat carrier flowing from the combustor to the pyrolysis reactor is calculated. In this way, it is ensured the desired temperature (450 °C) in the pyrolysis reactor. Heat carrier at combustor outlet is mainly composed by sand and char ashes, with around 6 wt.% and 11 wt.% of CaO when using CaO·MgO and CaO as catalysts, respectively. Combustion gases are cooled down to around 120°C to produce superheated steam at 60 bar and 425°C that is expanded in a steam turbine to produce power. Additional superheated steam is produced by the energy recovered inside the combustion chamber. Thermal-to-mechanical efficiency considered for this expansion stage was 25 %.

The light gas fraction (mainly CO,  $\text{CO}_2$  and  $\text{CH}_4$ , see Table 2), was separated from the volatiles released in the pyrolysis process at around 35°C, and it is combusted in a burner with 20 % of air excess. Internal heat recovery in this second combustor is not considered. Then, flue gas from this combustion chamber (around 1700-1800°C, stream 7 in Fig.3) is mixed with atmospheric air to produce diluted air (around 250°C, stream 8 in Fig. 3) that is used for biomass drying. Part of the exhaust air from this drying step is recirculated to the char combustor for gas dilution, whereas the non-recycled gas is sent to the stack. On the whole, an energy self-sustained system is obtained where required thermal energies for driving biomass drying and pyrolysis process are supplied by light gas and char combustion, respectively. In addition, an upgraded bio-oil and electricity are produced.

To analyse the effect of catalyst addition on the proposed system performance, a basis

for comparison of 5 ton/h of biomass (with 30 wt.% of moisture content) is assumed. Parameters analysed are: (1) electricity generated, (2) bio-oil production, (3) heat carrier circulating from combustor to pyrolysis reactor (per mass unit of dry biomass introduced to the auger reactor), and (4) energy ratio between organic phase in bio-oil and biomass in case both are used as fuels in a combustion process. Results for the different scenarios (sand, CaO/sand and CaO·MgO/sand) are included in Table 5. This Table shows that the electricity generation process shown in Fig. 3 is hardly affected by the heat carrier used, and net electricity produced is around 1.4 MW in each simulated case. Concerning bio-oil production and its organic phase, differences between non-catalytic and catalytic runs become significant, as expected from pilot plant experiments. As stated above, the addition of CaO allows obtaining a bio-oil with a higher organic phase content than that using CaO·MgO, and even larger than that using only sand (see Table 2SI). This effect is reflected into a larger energy ratio between the organic phase in bio-oil and the biomass introduced in the auger reactor, both measured through LHV. When the pyrolysis process is performed by using only sand, the energy released by the combustion of the organic phase barely represents around 9.6 % of the energy associated to the biomass used. In contrast, this energy ratio increases up to 17.1 % when using CaO and up to 14.7 % when using CaO·MgO. Moreover, the exothermicity of the global pyrolysis reaction using CaO results in a lowest circulation between combustor and auger reactor (Table 5). These advantages associated to the use of CaO together with the production of a higher yield of bio-oil with better properties elucidate its potential as catalyst in pyrolysis processes conducted in auger reactors.

#### **4. Conclusions**

Catalytic pyrolysis of biomass has been performed in an auger reactor pilot plant. It has been observed that the addition of low cost calcium-based material (CaO and

CaO·MgO) improves the bio-oil properties. In comparison with bio-oil found using a non-catalytic solid, both oxygen content and acidity character decrease, while both pH and calorific value increase. In addition, an energy self-sustained system has been proposed for the production of both bio-oil and electricity. The process simulation demonstrated that these catalysts, especially CaO, need a lowest circulation between combustor and pyrolysis reactor and hence the energetic integration is favoured.

### **Acknowledgements**

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### **References**

1. Baker, R., 1973. The reversibility of the reaction  $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$ . J. Appl. Chem. Biotech. 23, 733-742.
2. Bridgwater, A. V., 2012. Review of fast pyrolysis of biomass and product upgrading. Biomass Bioenerg. 38, 68-94.
3. Bridgwater A. V., Peacocke, G. V. C, 2000. Fast pyrolysis processes for biomass. Renew. Sust. Energ. Rev. 4, 1-73.

4. Brown, J. N., Brown, R. C. 2012. Process optimization of an auger pyrolyzer with heat carrier using response surface methodology. *Bioresource Technol.* 103, 405-414.
5. Bulushev, D.A.; Ross, J.R.H., 2011. Catalysis for conversion of biomass to fuels via pyrolysis and gasification: a review. *Catal. Today.* 171, 1-13.
6. Chiaramonti, D., Oasmaa, A., Solantausta Y., 2007. Power generation using fast pyrolysis liquids from biomass *Renew. Sust. Energ. Rev.* 11, 1056–1086.
7. Elliott, D. C., Oasmaa, A., Preto, F., Meier, D., Bridgwater, A. V., 2012a. Results of the IEA round robin on viscosity and aging of fast pyrolysis bio-oils. *Energ. Fuel.* 26, 3769-3776.
8. Elliott, D. C., Oasmaa, A., Meier, D., Preto, F., Bridgwater, A. V., 2012b. Results of the IEA round robin on viscosity and aging of fast pyrolysis bio-oils: long-term tests and repeatability. *Energ. Fuel.* 26, 7362-7366.
9. Garcia-Perez, M.; Adams, T. T., Goodrum, J. W., Geller, D., Das, K. C., 2007. Production and fuel properties of pine chip Bio-oil/Biodiesel blends. *Energ. Fuel.* 21, 2363-2372.
10. Kersten S., Garcia-Perez, M., 2013. Recent developments in fast pyrolysis of ligno-cellulosic materials. *Curr. Opin. Biotech.* 24, 414-420.
11. Khan, M. R., 1987. Production of high quality liquid fuels from coal by mild pyrolysis of coal-lime mixtures. *Fuel Sci. Techn. Int.* 5, 185-231.
12. Lin, Y., Zhang, C., Zhang M., Zhang, J., 2010. Deoxygenation of bio-oil during pyrolysis of biomass in the presence of Cao in a fluidized-bed reactor. *Energ. Fuel.* 24, 5686-5695.

13. Lu, Q., Zhang, Z. F., Dong, C. Q., Zhu, X. F., 2010. Catalytic upgrading of biomass fast pyrolysis vapors with nano metal oxides: An analytical Py-GC/MS study. *Energies*, 3, 1805-1820.
14. Martínez, I., Grasa, G., Murillo, R., Arias, B., Abanades, J.C., 2012. Kinetics of calcination of partially carbonated particles in a Ca-looping system for CO<sub>2</sub> capture. *Energ. Fuel*. 26: 1432-1440.
15. Meier, D., Van De Beld, B., Bridgwater, A. V., Elliott, D. C., Oasmaa, A., Preto, F., 2013. State-of-the-art of fast pyrolysis in IEA Bioenergy member countries. *Renew. Sust. Energ. Rev.* 20, 619-641.
16. Mohan, D., Pittman Jr, C. U., Steele, P. H., 2006. Pyrolysis of wood/biomass for bio- oil: A critical review. *Energ. Fuel*. 20, 848-889.
17. Oasmaa, A., Czernik, S., 1999. Fuel oil quality of biomass pyrolysis oils- state of the art for the end-users. *Energ. Fuel*. 13, 914-921.
18. Oasmaa, A., Kuoppala, E., 2003. Fast pyrolysis of forestry residue. 3. Storage stability of liquid fuel. *Energ. Fuel*. 17, 1075-1084.
19. Perego, .C, Bosetti, A., 2011. Biomass to fuels: The role of zeolite and mesoporous materials. *Micropor. Mesopor. Mat.* 144, 28-39.
20. Puy, N., Murillo, R., Navarro, M. V., López, J. M., Rieradevall, J., Fowler, G., Aranguren, I., García, T., Bartrolí J., Mastral, A. M., 2011. Valorisation of forestry waste by pyrolysis in an auger reactor. *Waste Manage.* 31, 1339-1349.
21. Ramdahl, T., 1983. Retene—a molecular marker of wood combustion in ambient air. *Nature*, 306, 580-582.
22. Sanna, A., Andrésen, J. M., 2012. Bio-oil deoxygenation by catalytic pyrolysis: new catalysts for the conversion of biomass into densified and deoxygenated bio-oil. *Chem. Sus. Chem.* 10, 1944-1957.

23. Sirijanusorn, S., Sriprateep K., Pattiya, A., 2013. Pyrolysis of cassava rhizome in a counter-rotating twin screw reactor unit. *Bioresource Technol.* 139, 343-348.
24. Stefanidis, S. D., Kalogiannis, K. G., Iliopoulou, E. F., Lappas, A. A., Pilavachi, P. A, 2011. In-situ upgrading of biomass pyrolysis vapors: Catalyst screening on a fixed bed reactor. *Bioresource Technol.* 102, 8261-8267.
25. Taarning, E., Osmundsen, C. M., Yang, X., Voss, B., Andersen, S. I., Christensen, C. H, 2011. Zeolite-catalyzed biomass conversion to fuels and chemicals. *Energ. Environ. Sci.*, 4, 793-804.
26. Thangalazhy-Gopakumar, S., Adhikari, S., Gupta, R. B., Fernando, S. D., 2011. influence of pyrolysis operating conditions on bio-oil components: a microscale study in a pyroprobe. *Energ. Fuel.* 25, 1191-1199.
27. Tingyu, Z., Shouyu, Z., Jiejie H., Yang, W., 2000. Effect of calcium oxide on pyrolysis of coal in a fluidized bed. *Fuel Process. Technol.* 64, 271-284.
28. Yeboah, Y. D., Longwell, J. P., Howard J. B., Peters, W. A., 1980. Effect of calcined dolomite on the fluidized bed pyrolysis of coal. *Ind. Eng. Chem. Proc. DD.* 19, 646-653.
29. Yildiz, G., Pronk, M., Djokic, M., van Geem, K. M., Ronsse, F., van Duren, R., Prins, W., 2013. Validation of a new set-up for continuous catalytic fast pyrolysis of biomass coupled with vapour phase upgrading. *J. Anal. Appl. Pyrol.* 103, 343-351.
30. Xu, R., Ferrante, L., Briens, C., Berruti, F., 2011. Bio-oil production by flash pyrolysis of sugarcane residues and post treatments of the aqueous phase. *J. Anal. Appl. Pyrol.* 91, 263-272.

**Table 1.** Proximate and ultimate analyses of forest pine woodchips

<b>Proximate analysis (wt.%) a.r. Analytical standard</b>		
Moisture	ISO-589-1981	4.0
Ash	ISO-1171-1976	1.1
Volatile	ISO-5623-1974	78.6
Fixed carbon	By balance	16.3

<b>Ultimate analysis</b>	<b>Analytical</b>	
<b>(organic fraction) (wt.%) a.r.</b>	<b>instrument</b>	
C	Thermo flash 1112	49.6
H	UNE EN 5104	6.4
N		0.2
S		<0.1
O	By balance	43.8

a.r. as received, wt. weight

**Table 2.** Composition and calorific value of the gas fraction. Char ultimate and proximate analysis.

	<b>Sand</b>	<b>Sand-CaO</b>	<b>Sand-CaO·MgO</b>
<b>Average gas composition (vol.% free of H<sub>2</sub>O and N<sub>2</sub>)</b>			
<b>H<sub>2</sub></b>	2.9	8.0	5.1
<b>CO</b>	39.3	41.0	40.5
<b>CO<sub>2</sub></b>	42.9	34.4	38.7
<b>CH<sub>4</sub></b>	9.3	10.9	10.2
<b>C<sub>2</sub>H<sub>4</sub></b>	1.8	1.9	1.9
<b>C<sub>2</sub>H<sub>6</sub></b>	1.7	1.8	1.7
<b>C<sub>3</sub>H<sub>8</sub></b>	2.1	2.1	1.8
<b>LHV (MJ/Nm<sup>3</sup>)</b>	12.7	14.1	13.2
<b>Pyrolytic Char (wt.%)</b>			
<b>Moisture<sup>a</sup></b>	3.5	5.9	6.3
<b>Ash<sup>a</sup></b>	3.5	3.6	3.6
<b>C<sup>b</sup></b>	79.2	76.7	74.9
<b>H<sup>b</sup></b>	3.6	3.4	3.1
<b>N<sup>b</sup></b>	0.1	0.1	0.1
<b>S<sup>b</sup></b>	<0.1	<0.1	<0.1
<b>O<sup>c</sup></b>	17.1	19.7	21.9
<b>LHV (MJ/kg)</b>	28.9	26.4	26.0

<sup>a</sup> as received, <sup>b</sup> dry base, <sup>c</sup> by difference.

**Table 3.** Physicochemical properties of the organic liquid phase. Results after accelerated aging tests in parenthesis.

	<b>Sand</b>	<b>Sand-CaO</b>	<b>Sand-CaO·MgO</b>
<b>H<sub>2</sub>O (wt.%)</b>	13 (13)	12 (12)	11 (11)
<b>pH</b>	2.9 (2.3)	4.3 (3.6)	4.6 (3.6)
<b>TAN (mg KOH/g)</b>	70 (93)	34 (58)	33 (53)
<b>Density at 15°C (kg/m<sup>3</sup>)</b>	1244	1233	1257
<b>Viscosity at 40°C (cP)</b>	99 (255)	123 (286)	139 (280)
<b>Ultimate analysis (wt.%) a.r.</b>			
<b>C</b>	60.6	67.9	66.8
<b>H</b>	7.7	7.6	7.5
<b>N</b>	0.2	0.3	0.3
<b>S</b>	<0.1	<0.1	<0.1
<b>O<sup>a</sup></b>	31.5	24.2	25.4
<b>O/C<sup>b</sup></b>	0.4	0.3	0.3
<b>H/C<sup>b</sup></b>	1.5	1.3	1.3
<b>LHV (MJ/kg)</b>	22.4	30.2	29.6

<sup>a</sup> By balance. <sup>b</sup> mol/mol

**Table 4.** Chemical composition of fresh and aged liquid organic phase obtained using calcareous solids as catalysts (area %)

	Sand	Sand-CaO	Sand-CaO·MgO	Sand	Sand-CaO	Sand-CaO·MgO
	Initial			Aged		
<b>Levogluconan<sup>a</sup></b>	1.6	1.6	1.6	1.7	1.9	2
<b>BTX</b>	0.76	0.74	0.67	0.42	0.60	0.44
<b>Furans</b>	11	8.6	8.7	10	6.3	6.1
<b>Phenols</b>	50	50	50	50	50	52
<b>Acids</b>	7.8	4.5	3.9	8.0	5.1	4.3
<b>Linear-Aldehydes</b>	0.25	0.29	0.31	0.17	0.22	0.21
<b>Cyclic-Aldehydes</b>	3.0	2.8	2.8	3.2	3.2	3.1
<b>Linear-Ketones</b>	8.3	10	9.8	8.5	10	9.3
<b>Cyclic-Ketones</b>	4.6	5.1	5.1	5	5	5
<b>Cyclic-Hydrocarbons</b>	5.1	5	4.7	4.9	4.9	4.6
<b>Polyaromatics</b>	4.1	7.6	8.9	4.2	8.5	9.0
<b>Esters</b>	3.5	3.2	3.4	3.8	4.1	3.6
<b>Others</b>	0.24	0.21	0.21	0.14	0.22	0.22

<sup>a</sup>Not included in their chemical class

**Table 5.** System performance results obtained for the different calcium-based catalysts  
(8000 working hours per year assumed)

	<b>Sand</b>	<b>Sand-CaO</b>	<b>Sand-CaO·MgO</b>
Electricity (MWe)	1.42	1.57	1.32
Bio-oil production (ton/year)	11093	14085	13648
Organic phase in bio-oil (wt.%)	28	37	32
Aqueous phase in bio-oil (wt.%)	72	63	68
kg heat carrier/kg dry biomass	3.4	2.4	4.2
MW organic phase in bio-oil/MW biomass (%)	9.63	17.08	14.68

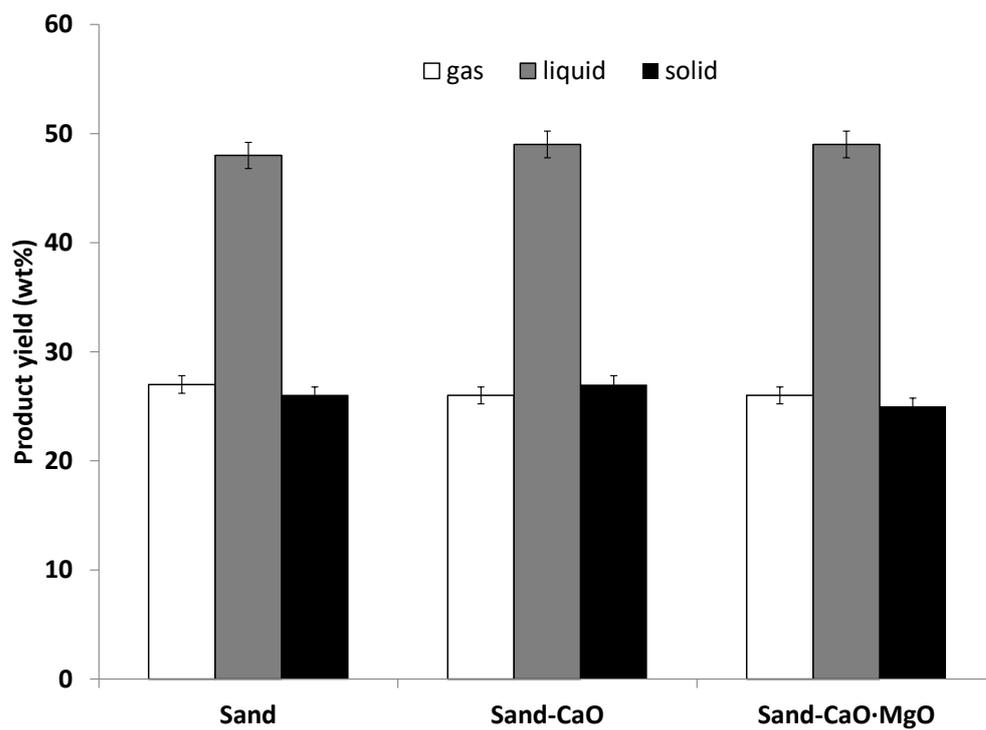
### **Captions for figures**

**Fig. 1.** Effect of catalysts on product yields at 450°C. CO<sub>2</sub> absorbed in calcareous sorbent is included as gas yield.

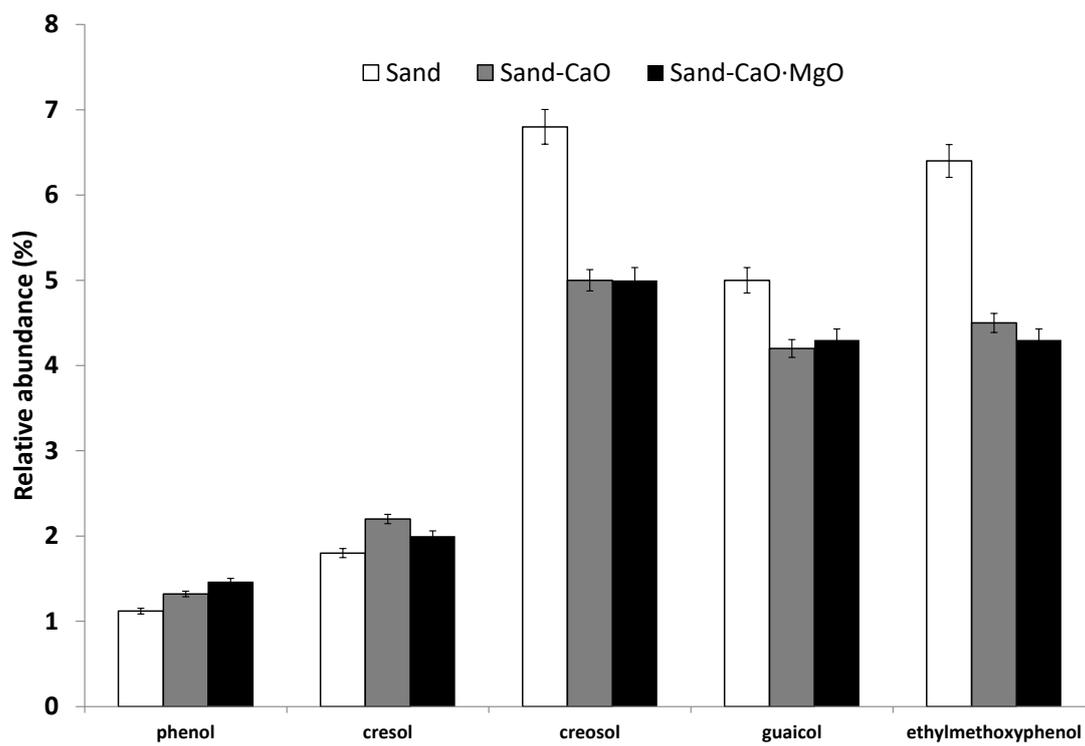
**Fig. 2.** Effect of catalyst addition on the relative abundance of some phenolic compounds.

**Fig. 3** Layout of the proposed process.

**Figure 1.**



**Figure 2**



**Figure 3**

