Moving ahead from Hydrogen to Methanol Economy: Scope and challenges

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Abstract

Energy is the driver in the economic development of any country. It is expected that the developing countries like India will account for 25% hike in world-wide energy demand by 2040 due to the increase in the per capita income and rapid industrialization. Most of the developing countries do not have sufficient oil reserves and imports nearly all of their crude oil requirement. The perturbations in the crude oil price, sanctions on Iran and adverse environmental impacts from fossil fuel usage are some of the concern. Therefore, developing countries have started investing heavily in solar and wind power and are considering hydrogen as a future energy resource. Hydrogen is possibly the cleanest fuel and produces only water vapour upon combustion. However, to tap the potential of hydrogen as a fuel, an entirely new infrastructure will be needed for transporting, storing and dispensing it safely, which would be expensive. In the transportation sector, a liquid alternate to fossil fuels will be highly desirable as the existing infrastructure can be used with minor modifications. Amongst the possible liquid fuels, methanol is very promising. Methanol is a single carbon atom compound and can be produced from wide variety of sources such as natural gas, coal, and biomass. The properties of methanol are conducive for use in gasoline engines since it has high octane number and flame speed. Other possible uses of methanol are: as a cooking fuel in rural areas, and as a fuel for running the fuel cells. The present study reviews the limitations in the hydrogen economy and why moving towards methanol economy is more beneficial.
Keywords: Hydrogen, methanol, biomass, carbon dioxide, syngas, gasification

1. Introduction

The ever increasing population of the world will require more calorie intake, hence pushing the production of food on arable land to its limit. The energy demands of the increasing population

will also increase. International Energy Agency (IEA) predicts that the energy demand of the world will increase by 25% by the year 2040 (International Energy Agency, 2018). For the year 2017, the total primary energy consumption of the world was 13511.2 Mtoe (million tons of oil equivalent), an increase of 16.6% in the last one decade. A major chunk of the energy consumption (85.18%) comprises of non-renewable sources such as oil, natural gas and coal. Whereas wind, solar, geothermal, biomass and waste resources comprises of 3.6% of the energy consumption. In comparison to 2007, the renewable energy consumption of the world increased by 355% in the year 2017 (British Petroleum, 2018). This shows that the world is warming up to the fact that the renewable energy resources are important for the earth's future.

With the combustion of the fossil fuels, the annual release of the carbon dioxide into the atmosphere is nearly 35 billion metric tons. This has resulted in the rise of carbon dioxide concentration from 270ppm (pre-industrial level) to more than 440ppm at present. The excessive release of CO_2 due to human activity is a major contributor to global warming (*IPCC fourth assessment report: Climate change 2007.*, 2007). The effects of global warming are: melting of ice caps, acidification of the ocean, rise in sea levels, more frequent changes in climatic conditions and change is biodiversity that are unpredictable (*Summary for Policymaker IPCC fifth assessment report: climate change 2014.*, 2014). The most common solution proposed for this excessive carbon dioxide is the capture of CO_2 at the source itself and its sequestration that is concentrating, pressuring and pumping it to various underground locations. However, this relatively newer technology is not commercialized on a large scale i.e., capturing tens of billions of metric tons of CO_2 every year and storing it for centuries without any leaks (A. Goeppert et al., 2012). To counter the problem of fossil fuels, renewable resources will play an important role in providing energy in the form of electrical energy. However, transmitting electrical energy over long distances and large scale storing of electricity for long duration is still a challenge. Another challenge is the intermittent supply of energy from the sun and wind. For example, the power produced from solar energy is less during cloudy conditions and no power is produced in the night time. Similarly, the wind does not blow consistently all the time. Also the power produced from these sources vary season to season. Today the power is produced in the power plants according to the energy demands. The fluctuations in the energy produced from the renewable sources needs to be levelled out for integrating them in to the main electrical grid. The use of smart grids can help resolve the problem along with the need of storing the excess energy which can be used when required. Compounds such as hydrogen, methanol, methane and other higher hydrocarbons has the potential to store surplus energy in the form of chemical bonds. These compounds can be easily stored and transported over any distance and used whenever there is requirement of energy. There are other applications of these compounds such as the transportation sector, cooking and heating. Hydrogen is an excellent energy storage media. It is a clean burning fuel. Besides energy, only water is produced on its combustion. An economy based on hydrogen will be very attractive in theory since only recycling of water takes place (Rifkin, 2002). However, in practical sense it is not possible due to physico-chemical properties of hydrogen (Bossel, 2006). Hydrogen has a low volumetric density, therefore it has to be

compressed to high pressures or liquefied to very low temperatures which makes its storage difficult and high energy is required for either compression or liquefaction. Its flammability is also high and it can diffuse through most of the metals and materials. Therefore to use hydrogen an entirely new infrastructure is required for storing, transporting and dispensing it safely, which would make its use very expensive (Ball & Wietchel, 2009).

For storing energy in chemical bonds other less energy intensive ways are required. Over gaseous medium, a liquid medium is more preferable. Keeping the transportation sector in mind, it is very easy to switch from fossil based liquid fuels to renewable liquid fuel, since the construction of a new storage/transportation/dispensing infrastructure is avoided. With minor modifications, the existing infrastructure can be used for the liquid fuels. Methanol stands out among the possible liquid fuels, since it contains only one carbon and is a liquid at room temperature (Bromberg & Cheng, 2010). It is a volatile, colorless liquid, with a unique smell. Methanol as an energy carrier has many advantages. Its octane number is high, therefore it can be used as a substitute or as an additive to gasoline. The oxides of nitrogen emission and oxides of sulphur emission are very low and the soot formation is minimal with methanol combustion. With slight modifications, they can also be used in diesel engines (Bromberg & Cohn, 2010) and in direct methanol fuel cells (DMFC) which produce electricity at atmospheric conditions by utilizing the methanol's chemical energy (McGrath et al., 2004). Methanol can also be dehydrated to dimethyl ether (DME) using a one-step biomolecular dehydration process. DME is a gas at room temperature which much like liquefied petroleum gas (LPG) can be liquefied at moderate pressures. DME is a good substitute to diesel due to its high cetane rating and nearly no soot forms during its combustion (Arcoumanis et al., 2008). DME can replace LPG for heating and cooking applications. Both DME and methanol can be used in generation of electricity using gas turbines. Methanol is also used for producing solvents and antifreeze agents. Formalin, formaldehyde, methyl formate, acetic acid, and methyl-tert-butyl ether are some of the chemicals which can be synthesized from methanol using direct or indirect routes. Light olefins such as propylene and ethylene can also be produced from methanol, these olefins are the building blocks for polymers such as polyethylene and polypropylene as well as other hydrocarbons which are currently produced using crude oil (Bakhtyari et al., 2016).

Many researchers and governments have been talking for a long time about hydrogen based economy which will alleviate the present problems of the world. It is known that no country has achieved this goal till now. The objectives of the study are (1) understanding the reasons why hydrogen has not become a fuel of choice in terms of its production, storage and usage (2) understand the processes used for methanol production so that CO_2 emission is reduced (3) use of methanol for producing various specialty chemicals (4) use of methanol as a fuel for spark ignition engines, compression ignition engines, fuel cells and as a cooking fuel by converting it into DME (5) importance of methanol economy for India and (6) cost comparison of the infrastructure required for producing, storing, transporting and dispensing hydrogen and methanol.

2. Limitations of hydrogen economy

In a hydrogen-based economy the non-polluting and inexhaustible hydrogen will be produced and used as a fuel for all the needs. Hydrogen is the most plentiful element present on the earth in combined form. It can be used as a fuel to heat the buildings, power the cars, or generate electricity, etc. Its combustion only produces water and no other emissions that are currently harming the environment from the use of carbon-based fossil fuels. The transportation sector in particular relies heavily on fossil fuels, therefore, the automobile manufacturers have started work in development of fuel cell powered vehicles or hydrogen based internal combustion engines. The major energy companies are also working on ways for providing and refueling the vehicles based on hydrogen. Although efforts have been made, the road ahead for hydrogen economy is bumpy. For becoming an everyday fuel like gasoline, diesel or natural gas, the basic problems with hydrogen needs to be resolved.

2.1. Production of hydrogen

Hydrogen is used for the production of a variety of chemicals and refined petroleum products. Electronic, metallurgical and pharmaceutical industries also use hydrogen. As a fuel, hydrogen is only used in rockets and space shuttles. To cater to these needs, nearly 140Mtoe hydrogen is produced yearly which is approximately 2% of the primary energy requirement of the world. So to make hydrogen as the main energy source huge capital is required for increasing the production capacity and establishment of storage and distribution infrastructure. Hydrogen can be produced by reforming fossil resources such as natural gas, coal and oil which represents nearly 96% of the total world production. Almost half of this production is from reforming of methane which is an inexpensive method, but the carbon footprint of the method is high and it relies on exhaustible natural gas (G. Olah et al., 2009). It is also possible to produce hydrogen from renewable sources such as reforming of biomass or splitting of water by electrolysis. The energy for electrolysis can be obtained from fossil fuels or from renewable sources of energy. Different routes through which hydrogen can be produced is shown in Fig.1. Common methods for hydrogen production are discussed in the following section.

Fig. 1 Different routes for hydrogen production (G. Olah et al., 2009)

2.1.1.   Fossil resource reforming

Natural gas is widely available, easy to handle and the hydrogen to carbon ratio is highest. Hydrogen can be produced from natural gas by using steam reforming process or by partially oxidizing it with oxygen or combination of both the processes called as auto-thermal reforming (Holladay et al., 2009). The reforming can also be carried out from other streams containing methane such as land fill gas or biogas (Alves et al., 2013). Since methane contains less carbon, the CO_2 emissions from the reforming process is less. In the steam reforming process, methane and steam are passed over a catalyst in a reactor at high pressure and temperature resulting in the formation of carbon monoxide (CO) and hydrogen. The CO again reacts with steam through water gas shift reaction and more hydrogen and carbon dioxide is formed. Hydrogen is then purified and retrieved whereas, at present, CO_2 is released in the atmosphere (Ball & Wietchel,

2009). In the United States nearly 90% hydrogen in produced using this method. However, the method is approximately 72% efficient on volumetric heating basis (Lipman, 2011). Coal can also be used to supply hydrogen, since it is widely available in all parts of the world and it will be the only available fossil fuel long after other fossil fuels are exhausted. Currently, integrated gasification combined cycle, a clean coal technology, is used for simultaneous conversion of coal into hydrogen and electricity. This technology improves the overall efficiency of the plant in comparison to the commercial thermal plants. Similar to methane reforming, coal is gasified by partial oxidation with oxygen and then steam is passed at high pressure and temperature resulting in the formation of synthesis gas (mixture of CO and H_2). The synthesis gas is then treated with steam and by water gas shift reaction the yield of hydrogen is increased. The hydrogen is recovered by cleaning the gas (Moore & Raman, 1998).

For the reforming process nickel is the most widely used catalyst as it is cheap and highly active. Nieva et al. (Nieva et al., 2014) used Ni/Zn/Al catalyst for steam reforming and found that at temperatures of 500 and 600°C, the conversion efficiency of the catalyst was higher than conventional catalysts. The authors also found that there were lower carbon deposits and sintering of the catalyst due to metal support. Besenbacher et al. (Besenbacher et al., 1998) found that the deactivation of Ni/Al catalyst was reduced from 70% to 30% after 10 hours by adding boron to the catalyst. The conversion efficiency of methane was also increased from 56% to 61% by adding boron. Activated carbon has also been used as catalyst for reforming process because of its porosity, low cost and tunable surface chemistry (Rodríguez-reinoso, 1998). However, it cannot be used in hydrogenation reactions above 427°C or with oxygen above 227°C, since it can be easily gasified thereby producing methane or carbon dioxide (Levalley et al., 2014). Hence, it is more suited as a support due to its higher surface area and porous nature. Carbon supported catalysts are used for steam reforming of methanol as lower reaction temperatures are required for its reforming. However, the catalysts must be selected expeditiously since byproducts such as methyl formate, methane and dimethyl ether can form thereby reducing hydrogen selectivity (Choi & Stenger, 2002). Setthapun et al. (Setthapun et al., 2008) examined many metals supported on Mo/C and found that palladium had the highest activity and 99% conversion of methanol could be achieved and the CO_2 selectivity was never higher than 70%. However, doping of the support with base metals showed higher CO_2 selectivity as compared to noble metals since the noble metals catalyze the methanation reaction. Catalysts used for the processes are summarized in Table 1. With the help of converters, small scale steam reforming of methane can also be performed, which is useful for producing hydrogen at filling stations. This would avoid the dangerous and cumbersome transportation from centralized centers of production. However, the costs of production will be high and the conversion efficiency will be less. Moreover, the capture of emitted CO_2 will be costly. For a sustainable and matured economy steam reforming is not an attractive route for the hydrogen based economy because with the increase in demand of hydrogen the natural gas reserves will be depleted and since the reserves are concentrated in some parts of the world it would again lead to geopolitical tension and instability in supplies. The problem with the use of fossil fuels in hydrogen production is the

emission of CO_2, which needs to be captured and sequestered so that global warming can be reduced. Although the technologies exist for capturing and sequestering CO_2, but they are still immature. Even if they mature in the future, they still possess danger, since the stored carbon dioxide can be released into the atmosphere due to the movements of earth, such as earthquakes or volcano eruption which will lead to a catastrophe. Therefore, other sustainable methods such as reforming of biomass or electrolysis of water as well as other renewable resources such as atomic energy can be used for hydrogen production.

Table 1. Catalysts used for hydrogen production

2.1.2. Hydrogen from biomass

Biomass has the potential to become a source of hydrogen. Wastes from crop residues, wood processing, short rotation woody crops (Chum & Overend, 2001), municipal solid wastes, animal wastes (A Demirbas, 2003), aquatic plants, waste paper, short rotation herbaceous species (switch grass) (Steinberg, 2004) and many more can be used for the production of hydrogen. The current technologies that are used for hydrogen production from biomass include gasification and pyrolysis along with the reforming with steam (Ayhan Demirbas, 2004). The gasification technology used for coals is also applicable for biomass wherein their partial oxidation results in the formation of a mixture of carbon monoxide, carbon dioxide, methane, hydrogen and nitrogen which is also known as producer gas (M. F. Demirbas, 2006). The process has low thermal efficiency, since the moisture present in the biomass has to be vaporized (Yamada, 2006). The process can be performed without or with a catalyst (G. Chen et al., 2004) and in a fluidized bed or fixed bed reactor with fluidized bed reactor having higher conversion efficiency (Asadullah et al., 2002). Some of the catalysts and feedstock used for hydrogen production are given in Table 2. If steam or oxygen is added in the gasification process then syngas is produced which either through water gas shift reaction can be converted into hydrogen or it can be fed to a Fischer-Tropsch reactor for producing higher hydrocarbons (Ayhan Demirbas, 2004). The gasification units are mostly small or mid-sized for biomass since the cost of gathering and transporting the biomass is high. Also, the quantity of available biomass is less and dispersed over a large area. Currently, the plants are operating nearly at 26% efficiency and the cost of hydrogen production is very high (National Research Council, 2004). Another alternative method is to gasify coal and biomass simultaneously which has been commercially demonstrated with mixture containing nearly 25% biomass (Romm, 2004). With this type of gasifier, there won't be any need to design a biomass specific gasifier, since if biomass is unavailable the unit can work with only coal. The net CO_2 emissions from biomass use is nearly zero, since the biomass absorbs the CO_2 from the atmosphere for its growth and releases it back when it is burnt. However, if the crops are cultivated for only energy related use then the debate arises for the use of arable land for food crops or for energy crops. Also the crops require water, fertilizer, and energy for cultivating, harvesting and transporting. One should also think of the impacts that will appear on the soil and biodiversity. Switch grass can be used as a suitable biomass because of its high yield and it can be grown on non-arable lands with minimum energy input. Also, algae is a suitable biomass that

can be grown on marshy lands and in the vast expanses of sea. In any case, all the biomass available can supply only a part of the total hydrogen required.

Table 2. Catalyst and feedstock for hydrogen production

2.1.3. Hydrogen from photobiological cleavage of water

In this method, hydrogen is generated by direct cleavage of water by microorganisms without producing biomass first. The main technologies for bio-hydrogen production are: use of green algae or cyanobacteria for cleavage of water in the presence of sunlight, photo fermentative processes, and dark fermentative process during the acidogenic phase of anaerobic digestion (Nandi & Sengupta, 1998). Manish and Banerjee (Manish & Banerjee, 2008) conducted a life cycle assessment of bio-hydrogen production from sugarcane juice using dark-fermentation, photo-fermentation, two-stage process and bio-catalyzed electrolysis. The authors compared these processes with steam methane reforming process for hydrogen production on the basis of energy efficiency, net energy ratio and greenhouse gas emission. The authors found lower energy efficiency when the by-products formed from the biological process were not considered. Whereas, the efficiency of the biohydrogen production process increases when by-products were considered. The highest increase in efficiency was observed with dark fermentation process. Also, all the biological processes reduced the net greenhouse gas emission and saved the use of non-renewable energy in the form of electricity. Melis (Melis, 2002) produced hydrogen from green alga by using the direct photolysis method. The author concluded that the hydrogen production is limited by (i) the bioreactor's solar conversion efficiency (ii) The hydrogen production process as the gas may be converted to water and (iii) the design and cost of the bioreactor. Benemann (Benemann, 1997) estimated the cost of an indirect biophotolysis microalgae system consisting of 14ha photobioreactor and 140ha open ponds. At an operating capacity of 90%, the authors estimated that the system will yield 1.2 million GJ of energy per year. The author considered the total capital cost to be US$ 43million, and the yearly operating cost to be US$ 12million. The hydrogen production cost was estimated to be around US$ 10/GJ. Tredici and Zittelli (Tredici & Zittelli, 1998) estimated the cost of a single stage tubular photobioreactor to be US$ 50/m^2 considering 10% sunlight conversion efficiency. The authors assumed that the yearly capital cost was 17% and the gas handling charge was not considered. The authors estimated the hydrogen production cost to be US$ 15/GJ which is similar to hydrogen production cost (Euro 19/GJ) from biomass residues using a two stage process. Tao et al. (Tao et al., 2007) found that dark fermentation of sucrose resulted in the formation of 3.67 mol. of H_2 along with acetate, butyrate and small amounts of valerate, propionate, caproate and n-butyl alcohol formation. To increase the hydrogen yield and reduce the waste, the authors carried out another step of photo-fermenting the by-products using *Rhodobacter sphaeroides* SH2C. The authors found that the yield of hydrogen increased to 6.63 mol. using the two-step process. These production processes offer advantage over other processes since the energy requirement is low. However, the rate of hydrogen production by these processes is too low for it

to be efficient. These technologies are still in nascent stage and significant breakthroughs are required if they have to become a potential source of hydrogen.

2.1.4. Electrolysis of water

Cleavage of water into hydrogen and oxygen using electricity is called as water electrolysis. This process requires lot of energy but it is a well proven method. As compared to natural gas reforming, the cost of this method is nearly three to four times, which is why, the share of this method in production of hydrogen on global scale is very low. It is reported that natural gas reforming accounts for 48% of the world hydrogen production, followed by oil with 30%, then coal with 18% and electrolysis contributing only 4% of the total share (G. Olah et al., 2009). However, in terms of greenhouse gas emissions, this method is the cleanest one, only if the electricity required for electrolysis comes from renewable energy sources such as solar power, hydro power, wind power or nuclear power. The commercial production of hydrogen is a mature technology which has been known for over 200 years. The advantage of using this technology is that hydrogen with high purity can be produced. Oxygen produced as a by-product has many industrial applications such as iron-ore smelting, cutting and welding of metals, medical applications and in syngas production. Theoretically, 39.4 kWh energy is required for 1kg production of hydrogen, but practically the energy required is nearly 50-65kWh per kg of hydrogen produced (Simbeck & Chang, 2002). Olivares-Ramirez et al. (Olivares-Ramírez et al., 2007) presented the work on hydrogen reactivity with respect to the different electrodes and electrolyte solutions. The electrodes used were stainless steel with different grades of 304, 316 and 430. The electrolyte solutions used are NaOH and KOH with different molar concentrations of 0.5, 1.0 and 2.0. Based on the design of experiments the study was conducted on different combinations to analyse the H_2 production. For the separation of hydrogen and oxygen a porous plastic membrane was used. It was inferred from the study that the SS 316 electrode is the best when compared to other grades due to the presence of nickel. KOH electrolyte is best for the electrolysis process. Lavorante and Franco (Lavorante & Franco, 2016) experimented the stainless steel 316 grade in the application of hydrogen production with electrolyser. The study was conducted by using two inter-electrode gaps 5.3 and 6.1 mm. Due to presence of bubble resistance it was observed that if the gap between electrodes is more, then performance of the electrolyser was improved. The electrodes with gap 6.1 mm had the optimum production of hydrogen than that of the 5.3 mm gap electrode cell. Nabil et al. (Nabil, 2019) analyzed multiple combinations of stack arrangement using SS316L electrodes to determine an efficient and robust generator design. Electrodes were separated with rubber gaskets (4mm thick) and operated with NaOH electrolyte of 0.125M concentration. Among 5, 7, 9, 13 and 19 plate combinations, with single and multiple stacks, 13 plates-two stack arrangement was most superior in terms of gas produced to power input ratio (0.513LPM at 61.2W). Higher current input caused cell temperature to rise, leading to increased electrolyte concentration due to evaporation of water, thereby lowering the generator efficiency. Limiting the current input can prevent the heating. Also, corrosion of electrodes was observed with the use of tap water instead of distilled water.

Dubent et al. (Dubent & Mazard, 2019) studied the corrosion characteristics of the titanium (Ti) elements used for hydrogen production. Characterization of the morphology of damage, embrittlement and determination of corrosion mechanisms was carried out using Scanning Electron Microscopy (SEM) and Glow Discharge Spectrometry. The protective film of oxide on the surface was damaged due its chemical dissolution, causing the newer un-reacted Ti surface exposure. The electrolyser's efficiency is independent on the cell size, therefore, hydrogen can be produced in both decentralized and centralized manner. It has applications in service stations, rockets, space crafts, marine, medical industry, electronic industry and food industry. Since there are no moving parts, their maintenance is low and they are best suited for use with intermittent energy supply sources, such as solar or wind power. Also, the excess electricity produced from these sources during off-peak time can be used for hydrogen production, which can be stored and later used to produce additional energy when the power requirement is high. A relatively newer device known as photoelectrolysis of water is under development in which the solar energy directly splits water into hydrogen and oxygen. Thus, improving the conversion efficiency as there is no requirement of converting the solar energy first into electricity and then utilizing the generated electricity in an electrolyzer. Another method is also explored wherein the solar energy is used for thermochemical splitting of water. It is thus seen that it is possible to produce hydrogen sustainably in the future at a low cost using the solar energy, but more research is required in this regard (Licht, 2008).

2.1.5. Nuclear energy

Nuclear power reactor for production of electricity, similar to renewable sources of energy do not emit any CO_2 or any other environment polluting gases in the atmosphere. During the periods when the demand for electricity is less than the power from the nuclear reactor can be used for hydrogen production which can extend the utilization of the plant and make it more efficient. The new generation reactors can operate at high temperatures (700-1000°C) in comparison to present reactors that have an operating range of 300–400°C (DOE, 2002). These new generation reactors are perfectly fitted for the steam production which can be used for producing hydrogen, as the thermal decomposition of water requires temperature in excess of 2000°C. Instead water can be split thermo-chemically at 800-1000°C into oxygen and hydrogen using chemical cycles (Shenoy, 1997). Sulphur-iodine cycle is the most studied chemical cycle, wherein sulphur oxide and iodine are added to the water, the reaction is exothermic resulting in the formation of hydrogen iodide and sulfuric acid. At temperatures above 350°C the hydrogen iodide is broken into hydrogen and iodine, which is recycled back. The sulphuric acid decomposes into SO_2 (recycled again), oxygen and water at temperatures above 850°C. Since iodine and SO_2 are recycled continuously, the feed that is used in this cycle is only water and heat, giving out oxygen, hydrogen and some low temperature heat. Although nuclear energy is an attractive prospect since no carbon is utilized in the cycle there are other environmental issues related to mining of the uranium, its processing and lastly the radioactive waste disposal (Acar & Dincer, 2013).

2.2. Hydrogen storage

One of the major challenges with hydrogen is its storage which should be economical, safe and user-friendly. The problem of storage arises as the energy density per unit volume of hydrogen is less than the liquid fuels at the same pressure, since the hydrogen is light in weight. In comparison to gasoline on energy basis, hydrogen requires 3000 times more space at normal conditions. Therefore, to make commercial use of hydrogen, it has to be either liquefied, compressed or absorbed on a material. Depending upon the application of hydrogen, such as stationary or mobile, the space requirement for storage will be different. For example, in air-conditioning of offices and homes, in power generation and other industrial uses, hydrogen can be stored in large spaces. On the other hand, in transportation sector, the storage of hydrogen is limited by volume and weight. Therefore, the key factor in the hydrogen economy is its storage. Table 3 shows the strength and weakness of various hydrogen storing techniques. Some of the storage methods are: storing in an insulated high pressure container in liquefied form or compressed form, chemically storing the hydrogen in materials that absorb and readily release it when required.

Table 3 Strength and weakness of various hydrogen storage techniques (Jiang et al., 2014)

2.2.1.   Hydrogen storage in liquid form

On weight basis, the energy content of hydrogen is highest among the known fuels. However, on volume basis, the energy content is nearly three times less than gasoline (Geo et al., 2008). So hydrogen in liquid form is a strong contender to gasoline in the transportation sector. In fact, liquid hydrogen is used in space vehicles as a propellant. However, the problem with liquid hydrogen is the energy required in converting hydrogen gas to liquid hydrogen since its boiling point is -253°C. So a complex multi-stage cooling system is required for obtaining liquid hydrogen. Nearly 30-40% of hydrogen energy content is required by the system for liquefaction (Bossel et al., 2003). Moreover, liquid hydrogen is evaporated from the storage system over time. The loss rate is dependent upon the insulation of the tank and the amount of hydrogen stored, which is generally lower for large amount of stored hydrogen. Zheng et al. (Zheng et al., 2019) used the gaseous hydrogen discharged from liquid hydrogen tank for insulating the tank. In this method a thermoacoustic refrigerator driven by the burning of hydrogen reduces the temperature of the cold shield placed on the tank. An insulation material is also placed on the cold shield to further lower the temperature of the tank thereby reducing the gaseous hydrogen formation. A similar work was also carried out by Xu et al. wherein leaked gaseous was used to operate a fuel cell which in turn operated a refrigerator for cooling the liquid hydrogen tank (Xu et al., 2020). In both the studies the authors have not used any external energy source for driving the refrigerator. Moreover, such systems can be used for larger applications and are not suitable for mobile applications because of space constraints. Furthermore, automobile tanks contain low amount of hydrogen, therefore nearly 1-5% of hydrogen may be released everyday which may result in low pressure build-up and possible explosion (Rifkin, 2002). Since, large amount of

energy and cost is invested in producing hydrogen, the loss of hydrogen is unacceptable from both environmental and economic viewpoint. Also, the liquid hydrogen has to be handled with utmost care.

2.2.2. Hydrogen storage as a compressed gas

Currently, the most preferred solution for both internal combustion engine and fuel-cell powered cars is storing hydrogen as a compressed gas. Since, in small cylinders at high pressure, the same quantity of hydrogen can be stored. Research was done over the years on cylinders that can withstand pressure up to 700bar, which are made from carbon fiber reinforced composites which are light in weight. Even then, the energy density of hydrogen on volume basis, at 700bar, is nearly 4.6 times less than gasoline. Therefore for the same driving range, a cylinder that can carry more volume of hydrogen is required. Also the liquid fuel tanks can be made in any shape according to the space available in the vehicle, whereas the compressed hydrogen cylinder shape is fixed as a cylinder. So more attention needs to be paid for integrating the hydrogen cylinder in a vehicle (G. Olah et al., 2009). The energy requirement for compressing hydrogen is equivalent to 10-15% of the energy that the hydrogen contains, although this energy is less than that required for liquefaction, it is still high (Bossel et al., 2003). The diffusivity of hydrogen through many materials including metals is high. Also some metals become brittle after prolonged exposure to hydrogen. Since the fuel system parts of a vehicle are made of metal, prolonged exposure to hydrogen can cause material failure resulting in leaks and fire hazard as hydrogen is highly flammable when it comes in contact with air. During accidents, if collision occur, then the on-board hydrogen is a grave concern which may result in instant explosion of the cylinder.

2.2.3. Hydrogen storage in metal hydrides and solid absorbents

A modern car which is optimized for fuel efficiency requires 24kg of gasoline to run 400km whereas 8kg of hydrogen is required for the same range and a fuel cell electric car requires only 4kg of hydrogen (Singh et al., 2015). Hydrogen for such case can also be stored in liquid and solid compounds such as carbon nanostructures, metal hydrides, borohydrides, alanates, methanol, methane, ammonia, and light hydrocarbons (Dalai et al., 2014). Several studies have reported the development of materials that can store hydrogen like Mg-based alloys (J. Chen et al., 1999; Si et al., 2007), metal hydrides (Sakintuna et al., 2007), carbon based materials (Liu et al., 2014), boron compounds (Fakioğlu et al., 2004), chemical hydrides (Biniwale et al., 2008) etc. These materials absorb hydrogen like a sponge, store it and release it when required.
The most important challenge for a storage material is that it can satisfy three requirements that compete with each other: higher storage capacity of hydrogen, high reversibility of the charging/discharging cycle at moderate temperatures and high rate of charging/discharging kinetics with minimum energy requirement for storing and releasing hydrogen. The first requirement needs the chemical bonds to be strong and close packing of the atoms, second requires that bonds are easily breakable at moderate temperatures so they should be weak, and the third requirement is the loose packing of atoms so that the hydrogen can diffuse at a fast rate

between the surface and the bulk. Also the thermal conductivity should be adequate so that the material does not decompose by the heat released during hydriding. Several materials have satisfied one or more requirements but no material has satisfied all the three requirements. Apart from these requirements, the materials has to satisfy weight, lifetime, cost and safety requirement (Crabtree & Dresselhaus, 2008). For automobile applications, it is crucial that hydrogen is charged at a fast rate so that the waiting time at the dispensing station is low.

Hydrogen in molecular form can be released by the solid metal hydrides. Its charging and release are usually regulated by pressure and temperature, which is unique for different hydrides. Some may quickly absorb but release slowly, while other hydrides may require elevated temperatures to release hydrogen. It is also possible that entire stored hydrogen may not be completely released (Schlapbach & Züttel, 2001). The storage capability of metal hydrides has been intensively studied and most of the hydrides are relatively heavy metals such as $ZrMn_2$, TiFe, $LaNi_5$ and so on. Each metal atom can bound only a few hydrogen atoms, which is why the usable hydrogen contained by these hydrides is only 1-3% of their weight. Therefore, to store 5kg of hydrogen, a tank weighing 200kg or more is required. The weight of other parts of a vehicle has to be reduced to carry a hydrogen tank, this would in turn reduce the fuel efficiency which is a major goal for hydrogen powered vehicles. The metal hydride tanks have an advantage over compressed hydrogen tanks as they are compact and require less space for storing equal amount of hydrogen. Moreover, these tanks can be shaped according to the vehicle's body as they are under moderate pressure. Today the research focus is on lighter hydrides which can contain more hydrogen per unit mass. Some of them are Na_3AlH_6, $NaAlH_4$, $LiAlH_4$, $LiBH_4$, $NaBH_4$ and MgH_2 (Kim et al., 2014; H. Yang et al., 2018; Q. Zhang et al., 2017). Other solid absorbing materials have also shown potential for storing hydrogen. Such as carbon nanotubes and fullerenes, but due to their high price and unproven potential they have still not reached the stage of commercial use in fuel tanks. Metal organic frameworks having high surface area and high porosity has also emerged as a candidate for storing large amounts of hydrogen (Ao et al., 2014; Murray et al., 2009; Serrano et al., 2013).

2.3. Safety with hydrogen

Hydrogen being small and lighter is the most prone gas to leaks. Although, it is non-toxic, but is highly flammable and explosive. Moreover, it is tasteless, odorless and colorless which makes it difficult to detect (Veziroğlu & Şahi˙n, 2008). Natural gas also has similar properties so to detect the leaks, volatile sulphur compounds are added. However, in case of hydrogen these compounds are of no use because these compounds may not leak through materials, through which hydrogen can easily leak. Even hydrogen detecting sensors are also found to be relatively ineffective in detecting leaks. Also, the additives can easily poison and contaminate the fuel cells. The flammability limit of hydrogen is very high in air and the energy required for ignition is low. If the right amount of hydrogen is present in air then the heat produced by friction while sliding on a car seat or mobile phones can cause ignition (Romm, 2004). The flame produced during burning of hydrogen may be almost invisible or slightly bluish, hence one may step on the

flames of burning hydrogen and may not know. Since the metals become brittle after being in prolonged contact with hydrogen, it may result in cracks and fractures resulting in catastrophic failure, especially when high pressure systems are used. Therefore, materials and liners are necessary for storage of hydrogen (G. Olah et al., 2009). In industry, very few incidents have happened related to hydrogen because hydrogen is handled by trained professionals who follow numerous codes and standards. Also long distance travel of large quantities of hydrogen is not possible therefore, most of the industries requiring hydrogen produce it on-site. If the general public has to use hydrogen for transportation, then they need to be made aware of the dangers of hydrogen and they should be given proper training along with strict safeguards. These measures will be very expensive and ensuring adherence will be difficult.

2.4. Usage of hydrogen as a fuel

Hydrogen has drawn lot of attention in the recent years for transportation applications. Many researchers have used hydrogen for operating both the spark ignition engines and compression ignition engines (Saravanan et al., 2008). Since, hydrogen does not contain any carbon, its combustion is virtually free of greenhouse gases. Its heating value is 120MJ/kg which is nearly 2.75 times that of hydrocarbon fuels (Ogden et al., 2004). As discussed in the previous sections, the volumetric energy density of hydrogen is very low, therefore separate tanks are required for carrying hydrogen in a vehicle. Apart from this, the automobile manufacturers do not need to make any changes to the engine manufacturing which is done for any other gaseous fuel like liquefied petroleum gas or natural gas. The properties of gaseous fuels is compared in Table 4. The flammability limit of hydrogen is very wide therefore it can run on very lean mixtures. Its ignition energy is low, however, the ignition temperature is high. Its octane number and flame speed is very high (Balat, 2008).

An SI engine was operated on hydrogen wherein it was injected close to the intake port to avoid backfire. Different hydrogen fractions were used at stoichiometric equivalence ratio with varied throttle positions. Hydrogen at cylinder pressure of 160bar is injected into the intake ports at 30bar after two steps of pressure reduction. The results show that brake thermal efficiency (BTE) increased with hydrogen addition at the same throttle position and it also increased, with increasing throttle for a particular hydrogen fraction. NOx emissions increased with increase in hydrogen fraction (Ji & Wang, 2009). To improve the performance of a lean burn SI engine operating at low speed and low load condition, Ji et al. (Ji & Wang, 2011) investigated the use of H_2 enrichment. The authors kept the original gasoline injection system configuration and mounted a hydrogen port injection system on the intake manifolds. The fuel was tested for different excess air ratios and hydrogen fractions with the main throttle closed. Original injection timings were used and both the fuels were injected simultaneously. For a specified excess air ratio, thermal efficiency and torque were found to increase with the increase in hydrogen addition. The flame propagation and development periods were effectively shortened, especially at lean conditions.

A diesel engine was operated with hydrogen way back in 1978 by Homan et al. (Homan et al., 1979). The authors found that the operating range of engine with hydrogen was limited due to its

high auto-ignition temperature, which they could not resolve by increasing the compression to 29. They also tried glow plugs and multiple strike spark plugs. The initiation of combustion became reliable and the engine operation became smooth with both the methods (Homan, 1989). In a diesel engine, the direct use of hydrogen is limited due to low operating range, which could be improved by using a low ignition temperature fuel such as diesel, straight vegetable oil or biodiesel. These fuels are directly injected into the combustion chamber which acts as a source of ignition for the hydrogen which is mixed with the incoming air by the aid of either a carburetor or an injector. The engine is known as dual fuel engine, since two fuels are simultaneously injected into the engine (Boopathi et al., 2017). The induction of hydrogen improves the engine thermal efficiency and reduction in unburned hydrocarbons, carbon monoxide emission and smoke emission is observed. However, oxides of nitrogen emission increases. The problem with dual fuel engine is that they have low efficiency and higher emissions at low loads and at high loads their operation is limited by knocking (Geo et al., 2008).

Some prototype cars with internal combustion engines were built by automobile manufacturers which can operate on hydrogen. BMW has been researching on hydrogen powered vehicles since 1978. Hydrogen7 their sixth-generation car was produced in limited numbers which was leased to some influential people around the world. The car could operate on both hydrogen and gasoline. 8kg of hydrogen could be stored in the 170L tank which allowed the car to travel 200km. With a 60L gasoline tank, the range was extended to 680km. Mazda and Ford are also researching on hydrogen powered vehicles. Ford built shuttle buses powered by IC engines operating on hydrogen for United States and Canada. Mazda has built its RX-8 model powered by hydrogen-gasoline operated rotary engine wherein the hydrogen is stored under pressure. The hydrogen road of Norway (HyNor) is using these cars for operating between Oslo and Stavanger, a distance of 580km. Later HyNor bought Toyota Prius hybrid was modified to run on hydrogen. The coupling of hydrogen power IC engine with an electric hybrid system increases the efficiency of the system but it is lower than cars running with fuel cells. Fuel cell vehicles operating on compressed hydrogen are being produced commercially. Toyota Mirai, Honda Clarity, Hyundai Tucson FCEV and Nexo are available on lease and sale in the United States, Japan and South Korea. The estimated annual fuel cost for these vehicles are in the range of US$1250-1500. The fuel economy in terms of miles/kg for these vehicles is in the range of 57-68 combining both city and highway driving (DOE, 2018). The demand of hydrogen for vehicles running on either hydrogen powered IC engines or fuel cell and other applications will be limited until an adequate infrastructure for hydrogen distribution is not developed. Even if the infrastructure is developed by investing huge money, there is no incentive if there is no solid demand for hydrogen. One may ask, that if the hydrogen is considered as a fuel for the future then how will the production, storage and transportation of huge quantities of hydrogen be stimulated? Due to strong economic and technical challenges, the commercialization of hydrogen as a fuel is far away in the future.

Table 4. Properties of gaseous fuels

3. Methanol Economy

Methanol (CH_3OH) also known as wood alcohol, methyl alcohol or carbinol is the first compound in the alcohol series which are named by adding the syllable –*ol* to the corresponding paraffin. The methanol economy is a relatively new approach using which we can slowly decrease our dependence on oil and coal which is the main reason of global warming caused by their excessive use. Methanol can be used not only for IC engines or as a household fuel, but it is also used as a chemical in many industries. It is used to produce dimethyl ether (DME), formaldehyde, methyl tertiary butyl ether (MTBE), acetic acid, formalin, and methyl formate. It is also used to produce chemical intermediates such as methylamine, chloromethane, methyl mercaptane, and methylmethacrylate. It is increasingly used in the production of plastics such as polypropylene and polyethylene (Park & Lee, 2013). Methanol currently is produced by an efficient natural gas reforming process, it can also be produced from chemical recycling of CO_2 which is available from many sources such as exhaust from power plants, industries or from capturing CO_2 from the atmosphere. Biomass can also be converted into methanol. Fig. 2 summarizes the essential elements used for methanol production and the use of methanol for producing chemicals and as an energy feedstock.
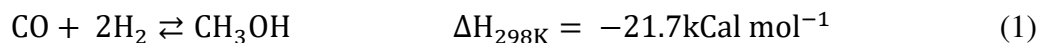
Fig. 2 Raw materials to synthesis gas, methanol, fuels and chemicals. Abbreviations: FT-Fischer Tropsch Process, MTO-methanol to olefins, MTP- methanol to propylene, MTG-methanol to gasoline, DMFC-direct methanol fuel cell (Martin Bertau et al., 2014)
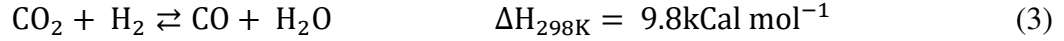
3.1. Methanol Production

Almost any hydrocarbon can be converted to methanol, but mainly natural gas is converted to syngas (CO and H_2) which can then be reformed using catalytic synthesis process into methanol. Natural gas resource is limited therefore other gas resources namely coal bed methane, tight sand gas, methane hydrate resources and any other fossil resource will be used for methanol production. Coal due its widespread availability and vast reserves is being used to methanol production, especially in China. The worldwide demand of methanol was nearly 49 million tons in 2010 which is forecasted to surpass 95 million tons by 2021. China will have 54% of the world capacity and 46% of global production, all dependent upon coal (Protti-Alvarez, 2017). However, using coal has drawbacks like releasing large amount of pollutants apart from carbon dioxide. Also the carbon dioxide produced per unit of energy through coal is higher than petroleum oil and natural gas. Biomass is a better alternative to coal, but the demand for methanol will be huge if all the gasoline cars of the world were to use even 10% blending of methanol, which the biomass won't be able to address. Therefore improved and new methods are required for methanol production.

3.1.1. Syngas production from fossil fuels

Syngas is exclusively used for the production of methanol using a heterogeneous catalyst according to the following equations.

$$CO + 2H_2 \rightleftarrows CH_3OH \qquad \Delta H_{298K} = -21.7 \text{kCal mol}^{-1} \qquad (1)$$

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O \qquad\qquad \Delta H_{298K} = -11.9 \text{kCal mol}^{-1} \qquad (2)$$

$$CO_2 + H_2 \rightleftarrows CO + H_2O \qquad\qquad \Delta H_{298K} = 9.8 \text{kCal mol}^{-1} \qquad (3)$$

The equation 1 & 2 are exothermic reactions, resulting in decrease in volume as the reaction moves. The equation 3 is reverse water gas shift reaction which is endothermic in nature, since this reaction also takes place during methanol synthesis, more amount of methanol is produced as carbon monoxide formed can react with hydrogen to produce methanol (Eq.1). Therefore, according to Le Chatelier's principle, increase in pressure and decrease in temperature favors the formation of methanol. The technology developed by BASF in 1920's used high pressure and temperature over zinc oxide/chromium oxide catalysts to convert syngas to methanol. However, present technologies use pressure in the range of 50-100 bar and temperature in the range of 200-300°C, over a copper based catalyst. Syngas can be obtained from any carbonaceous source, however, methane and shale gas are preferred due to less impurities and relative ease of handling as compared to coal. Since cleaning the syngas produced from coal gasification will increase the cost and more CO_2 will be produced per unit of methanol (Alain Goeppert et al., 2017). The production process of methanol is highly mature but methane and coal are used for their production which are unsustainable and a liability to the environment. To continue using these fuels, one has to reduce their carbon footprint by adopting technologies that are either partially or completely carbon neutral.

3.1.1.1. Methane reformed by steam

As discussed previously, syngas is currently produced by reforming methane with steam in a highly endothermic reaction with nickel based catalyst. The reaction temperature and pressure for the process is typically high (800–1000°C, 20–30bar) (Kochloefl, 1997). Equation 4 shows the reaction:

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \qquad\qquad \Delta H_{298K} = 49.1 \text{kCal mol}^{-1} \qquad (4)$$
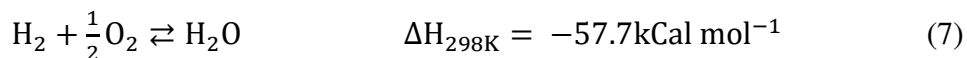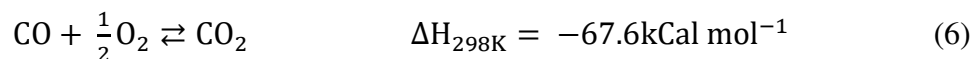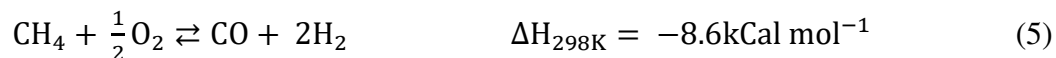
The carbon monoxide formed can also react with steam in water gas shift reaction (Eq. 3) to yield carbon dioxide and more hydrogen. Therefore, the components produced are highly dependent upon reaction conditions such as pressure, temperature and steam to methane ratio. Production of syngas increases with increase in temperature and decrease in pressure. Also the water gas shift reaction becomes less dominant with increase in temperature. Since this process requires large amount of heat, most of the heat can be supplied by burning methane itself. The hydrogen to carbon monoxide ratio of this process is nearly 3 which is higher than required ratio of 2. Therefore, corrections are made to the steam reformers exit gas such as CO_2 addition (Rostrup-Nielsen, J. Christiansen, 2011; Subramani V, Sharma P, Zhang L, 2009).

3.1.1.2. Methane partial oxidation

Methane can be reacted with insufficient oxygen with or without a catalyst producing a mixture of H_2 and CO whose ratio ideally will be 2, which is required for methanol synthesis (Choudhary

& Choudhary, 2008). However, due to side reactions, the carbon monoxide and hydrogen may oxidize to carbon dioxide and water, resulting in loss of product gases required for methanol synthesis. As shown in Eq. 6 & 7, these oxidation processes are highly exothermic in nature as the heat produced is wasted if there is no immediate requirement of the heat and it is also a safety concern.

$$CH_4 + \frac{1}{2}O_2 \rightleftarrows CO + 2H_2 \qquad\qquad \Delta H_{298K} = -8.6 \text{kCal mol}^{-1} \qquad\qquad (5)$$

$$CO + \frac{1}{2}O_2 \rightleftarrows CO_2 \qquad\qquad \Delta H_{298K} = -67.6 \text{kCal mol}^{-1} \qquad\qquad (6)$$

$$H_2 + \frac{1}{2}O_2 \rightleftarrows H_2O \qquad\qquad \Delta H_{298K} = -57.7 \text{kCal mol}^{-1} \qquad\qquad (7)$$

3.1.1.3. Autothermal reforming

It is seen that partial oxidation of methane tends to release a lot amount of heat, whereas steam reforming of methane requires heat. Many modern plants combine both the process so that an overall neutral thermodynamic reaction is obtained. This process of combining the cycle is called as autothermal reforming of steam. In the same reactor, both the processes can be conducted by reacting a mixture of oxygen and steam with methane, which reduces the complexity and cost of manufacturing. However, the optimized conditions for both the reactions are different, therefore, it is suitable to conduct the processes in two steps. After the methane is reformed with steam in the first reactor, the product is fed to the second reactor where partial oxidation is carried out. Since oxygen is required for this step, an oxygen producing plant is required which can be avoided if only air is used. However, the produced syngas will also contain nitrogen which needs to be removed before methanol synthesis. Therefore, modern plants producing methanol prefer pure oxygen instead of air (J.B. Hansen, 1997).

3.1.1.4. Methane dry reforming

Equimolar amount of carbon dioxide can be reacted with methane to give an equal ratio of H_2 and CO (Eq. 8). The process is called as dry reforming since steam is not required for the process (Bradford & Vannice, 1999). However, the process is endothermic in nature and temperatures in the range of 800 to 1000°C is required. Ni/MgO or Ni/MgAl$_2$O$_4$ are used as catalyst for carrying out the reaction. Since one mole of methane requires equal amount of CO_2, the method is an attractive way to reduce global warming, as the heat required for the reaction can come from renewable energy source and CO_2 can be recycled from a stream rich in CO_2.

$$CH_4 + CO_2 \rightleftarrows 2CO + 2H_2 \qquad\qquad \Delta H_{298K} = 59.1 \text{kCal mol}^{-1} \qquad\qquad (8)$$

Due to low H_2/CO ratio this product gas is an advantageous feed for processes such as Fischer-Tropsch process and iron ore reduction. However, for methanol production from this process, hydrogen needs to be added to the produced gas so that the ratio of H_2/CO reaches the required level. Renewable sources can be used to produce hydrogen. Another method is combining the

carbon dioxide and steam reforming process which can provide the required syngas composition (G. Olah et al., 2009).

3.1.1.5. Bi-reforming of methane

Steam reforming and dry reforming of methane can be combined to form a bi-reforming process (Eq. 9) resulting in the formation of metgas, having hydrogen to carbon monoxide ratio of 2, which is required for methanol synthesis (US Patent 7,906,559 B2, 2011). Shale gas (natural gas) is best suited for this process, as it contains high amount of carbon dioxide which needs to be removed and released into the atmosphere if natural gas is to be used for any other purpose. Different regions will have different amount of carbon dioxide which can then be adjusted for producing metgas (US Patent 8,133,926, 2012).

$$3CH_4 + 2H_2O + CO_2 \rightleftarrows 4CO + 8H_2 \qquad (9)$$
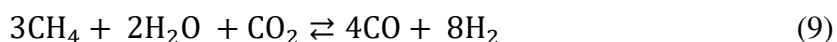
3.1.1.6. Higher hydrocarbons and petroleum oil conversion to syngas

On small scale, different fractions obtained by refining of petroleum oil (such as naptha and liquefied petroleum gas) can be used to produce syngas for the manufacturing of methanol, ammonia and other higher alcohols. Asphalt, tar and heavy oil is also used to produce syngas. The methods for producing syngas from these sources are similar to what is used for reforming methane into syngas. However, the biggest problem of converting these feedstock into syngas is the presence of sulfur compounds which are a poison to the catalysts used in steam reforming and also in methanol synthesis. Therefore, the costs of purifying these feedstock would increase the overall cost of methanol production. Also, more research is required to identify those catalyst which are resistant to poisoning by these impurities. These hydrocarbons also contain aromatics and their hydrogen content is relatively low, therefore, the syngas produced from these sources will have high amount of CO_2 and CO but hydrogen will be less (G. Olah et al., 2009).

3.1.1.7. Syngas from coal

Coal has been the first feedstock for production of syngas in the industries. China and South Africa still uses coal for syngas production, as they have huge reserves of coal. Coal is gasified using a combination of partial oxidation and steam reforming process, according to Eqs. 10-13.

$$C + \frac{1}{2}O_2 \rightleftarrows CO \qquad (10)$$

$$C + H_2O \rightleftarrows CO + H_2 \qquad (11)$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (12)$$

$$CO_2 + C \rightleftarrows 2CO \qquad (13)$$

Over the years, different types of coal gasification processes has been developed, depending upon the characteristics of coal available. The syngas produced from coal has less amount of hydrogen and more CO and CO_2, therefore water gas shift reaction is performed to improve the

hydrogen content. Also hydrogen sulfide needs to removed, as it acts as a poison for the catalyst used in the synthesis of methanol (G. Olah et al., 2009).

All the processes previously discussed require fossil fuels, which are limited and unsustainable in the long run. Utilization of methane, which is considered cleanest of all fossil fuels, will result in significant CO_2 emissions. If the cost of capturing CO_2 emission is also factored in the production of methanol synthesis from fossil fuels, then its production cost will be significantly higher than using non-fossil sources. Therefore, for sustainable development, we need to move away from fossil fuels and increase our use of renewable sources along with carbon dioxide recycling.

3.1.2. Methanol from biomass

Biomass is carbonaceous substance (plant or animal material) that uses the sun's energy to recycle water and carbon dioxide into new plant life. Production of methanol from biomass, therefore, is a way of recycling carbon dioxide. As previously discussed, biomass includes, waste of wood and agricultural crops, animal wastes, algae, aquatic plants and municipal solid wastes. Originally, thermal destructive distillation of wood was used for methanol production which gave methanol the name 'wood alcohol'. However, this method is not used anymore. Today technologies such as liquefaction, gasification, pyrolysis and combination of these are used for methanol production based upon the feedstock (Williams et al., 2011). Fig. 3 shows some of the thermo-chemical conversion technologies. For solids such as wood and other cellulosic materials, gasification is employed for conversion to syngas followed by synthesis of methanol. Same technology is used for converting coal to methanol. For conversion of feedstock such as animal manure to methanol, first the feedstock is converted into biogas, then it is reformed to syngas and finally syngas is reformed to methanol (Budzianowski, 2016; Sheets et al., 2016). An overview of the conversion method of biomass into methanol is shown in Fig. 4. Another attractive method is biomass direct conversion into methanol using enzymatic routes, but it is in early phase of research.

Fig. 3 Products and their uses from the thermochemical conversion of biomass (Chmielniak & Sciazko, 2003)

In the gasification process, the biomass feedstock is first dried and then pulverized so that the moisture content is less than 15-20%. The biomass is then sent to a gasifier wherein it mixes with oxygen and water at high pressures. The heat required for the gasification process is produced by burning some part of the biomass in oxygen. CO_2 and water then reacts with the rest of the biomass in absence of oxygen resulting in the formation of hydrogen and carbon monoxide. Since, biomass acts as a heating fuel, no separate external source of heat is required. The syngas produced by the single-step partial oxidation of biomass is an attractive proposition but it has its own share of technical problems. Therefore, a two-step process is used for the gasification of biomass. In the first step, the dried biomass is pyrolyzed in the temperature range of 400 to 600°C in an oxygen deficient atmosphere resulting in incomplete combustion. The gas obtained

called as pyrolysis gas is a mixture of hydrogen, methane, carbon monoxide, carbon dioxide, volatile tars and water. The residue, charcoal, is about 10-15% of the initial biomass. In the second stage, charcoal reacts with oxygen at 1300-1500°C to form carbon monoxide. The obtained syngas is then purified and sent for methanol production (Milne et al., 1998).

Fig. 4 Schematic of methanol production from biomass (Alain Goeppert et al., 2014)

It is seen that some part of the biomass has to be burnt for providing the heat required for gasification resulting in underutilization of biomass for methanol conversion and carbon dioxide is also generated. Renewable sources of heat such as solar and nuclear can be used. In one study, (Adinberg et al., 2004) in a molten salt medium the biomass is dispersed and concentrated solar energy is used to heat the mix. The syngas is produced from the biomass without interruption by the energy stored in the molten salt. The biomass can also be dried before gasification using solar energy thus reducing the energy requirement. Biomass conversion also faces problems similar to that experienced in converting coal to methanol, i.e., the low hydrogen to carbon ratio in syngas and high CO_2/CO ratio. The optimal ratio for methanol synthesis is close to 2, therefore after gasification some of the CO_2 is removed (Ribeiro et al., 2010). The CO_2 can be sequestered, vented directly or used in some other processes. One method is to react hydrogen (produced from renewable source) with CO_2 (Specht et al., 1999). Another method is to mix syngas produced from natural gas and biogas. Since, the syngas produced from natural gas steam reforming has a H_2/CO ratio close to 3, whereas the syngas produced from biogas has low hydrogen to carbon ratio (H. Li et al., 2010). Hybrid plants using both biomass and natural gas can solve the above problems as the hydrogen to carbon monoxide ratio can be easily adjusted. Also the CO_2 required for the natural gas reforming can be obtained by biomass reforming hence there is no net output of CO_2. The process is known as Hynol process, it was first used on a pilot scale for converting woodchips into methanol (Dong & Borgwardt, 1998). Coke oven gas containing 66% hydrogen was also used with biomass for methanol formation (Lundgren et al., 2013). Although these gases can be used but utilizing renewable sources for hydrogen production is a better alternative as it would decrease the carbon footprint of the methanol production process. Table 5 summarizes the raw materials and the conversion technologies for converting biomass to methanol. Various studies have proposed systems combining both biomass and alternative sources of energy for production of methanol and other hydrocarbons through Fischer-Tropsch process (Agrawal et al., 2007). For example, bio-methanol can be produced from biomass and hydrogen, obtained by water electrolysis. The electricity required for the process was obtained from hydroelectric power plant (Ouellette et al., 1995). In Denmark, hydrogen and biomass were converted into methanol and DME. The hydrogen used in the process was obtained using a solid oxide electrolyzer cell (SOEC) which converted water into hydrogen (Fig. 5). In comparison to a plant undergoing biomass gasification without electrolysis, the study found that the plant using a combination of hydrogen and biomass produced double amount of methanol and the methanol conversion efficiency increased to 71% from 59%. The total efficiency of the plant was 81.6%. The study also found that oxygen produced from the SOEC can be used for gasifying the

biomass, thus eliminating the requirement of an air separation unit (Lebaek et al., 2011). Other potential industries which can produce methanol from the biomass are paper mills and sugar refinery. The biomass used for producing pulp is digested in a highly alkaline solution at a temperature of 150-170°C in the presence of a sulfide (Joelsson & Gustavsson, 2008). The produced pulp is washed and a black liquor is recovered. Other chemical processes are carried out on the pulp before it is converted to paper. Whereas, the black liquor is used for producing steam and meeting the energy demand of the mill. However, this black liquor can be gasified and converted into more valuable energy products such as methanol. Naqvi et al. (Naqvi et al., 2012) compared the Chemrec black liquor gasification (CBLG) process with dry black liquor gasification (DBLG) for producing syngas which could be later converted to methanol. The authors through modeling found that 77 million tons of methanol can be produced in a year using the CBLG process whereas only 30 million tons of methanol can be produced by the DBLG process. The potential CO_2 reduction from the CBLG process was around 0.32 million tons/year whereas for DBLG it is around 0.12 million tons/year. The greatest advantage of the CBLG process was that 44MW of electricity can be produced. As the mill requires only 22MW the rest of the electricity can be given to the grid. Whereas 30MW of electricity needs to be taken from the grid for the DBLG process. Also the methanol conversion efficiency of the CBLG process was better than the DBLG process. The sugar bagasse in a sugarcane industry is used either as a fuel for generating heat and power or it can be used for producing ethanol through enzymatic hydrolysis. Another route is the thermo-chemical conversion of the bagasse into synthetic fuels, ethanol, methanol or synthetic natural gas. Albarelli et al. (Albarelli et al., 2017) studied the potential of converting the sugarcane bagasse into methanol through modelling. The study reveals that the overall energy efficiency of the refinery increases with methanol production in comparison to the use of bagasse for electricity generation. However, the investment needed for setting up a methanol production plant is higher and the system is more complicated as compared to simple burning of bagasse for electricity production. It was also seen that the cost of methanol produced would be higher than the current methanol market price. Moreover, the authors did not carry out any study on the benefits of CO_2 reduction by not burning bagasse. It can be easily seen that the sugarcane unit will earn carbon credits.

Fig. 5 Synthesis of methanol using electrolysis assisted gasification of wood (Lebaek et al., 2011)

Table 5. Summary of biomass feedstock for methanol production

Biogas is commercially produced by anaerobic digestion of feedstock such as animal dung, sewage sludge, municipal organic waste, and wastewater from paper and pulp, food, fiber, milk, meat, pharmaceutical plants, and brewing industry (Weiland, 2010). Biogas can be produced from any biomass can as long as they have hemicellulose, cellulose, proteins, carbohydrates and fat as their main component. However, anaerobic digestion is not suitable for wood which is a strong lignified organic substrate as the process will be slow. Depending upon process effectiveness and feedstock, the gas produced in the digester is 50-70% methane and the rest

contains large amount of CO_2. The gas is mostly used for electricity generation or as a heat source. After removal of impurities such as hydrogen sulphide, the gas can be used for methanol production using processes used for natural gas reforming. Oberon Fuel in California, United States uses biogas for the commercial production of methanol and DME on a small scale. The syngas produced from biogas, similar to the syngas produced from biomass gasification has excess CO_2 which needs to be removed. The carbon dioxide can be either stored, released in to the atmosphere, or reacted with hydrogen produced from renewable source (Clausen et al., 2010). Therefore, in Denmark, electricity produced from wind energy is utilized in an SOEC for electrolysis of water into hydrogen, which combined with biogas is used for methanol and DME production (Lebaek et al., 2011). It is clear that different types of biomass can be used for methanol production. However, the quantity of methanol generated is limited and as the demand for methanol would increase reliable and large sources of biomass will be required. There is also a concern of using food crops for fuel production as is the case of ethanol produced from corn which has resulted in the increase of food prices (FAO, 2008). For significant quantities of methanol production non-food crops have to be cultivated on a very large scale. Tests are carried out for producing methanol from trees and grasses (fast growing ones). However, these crops has to be grown on the same land which is used for food production, thereby limiting their use. Moreover, sufficient amount of water, fertilizers, suitable temperature, agricultural land and time are required for crop production. Therefore, it is necessary that there should not be any competition between energy crops and crops used as food for these resources. Further, incessant use of fertilizer leads to pollution of ground water, or their run-off resulting in "dead zones" in the ocean (Donner & Kucharik, 2008). Another problem that biomass production has is its high carbon footprint (Fargione et al., 2008). Taking the above mentioned and other factors into account, it is estimated that use of biomass for sustainable production of methanol can cover only about 20% of our future energy requirements (Hedegaard et al., 2008).

3.1.3. Methanol from recycling of CO_2

When any carbon containing compound is burned water and carbon dioxide is formed. The biggest challenge today is the reversal of this process i.e. producing chemicals, fuels and different materials using water and CO_2. Trees, plants and crops captures CO_2 from air and use water, sun's energy and a catalyst (chlorophyll) to produce new plant life. After the plane dies, it takes millions of years for it to be converted into fossil fuel. In short cycles, the biomass collected from the plant can also be converted to fuel and other products. However, this resource is not enough to satisfy human needs. Therefore a technology has to be developed that can recycle carbon dioxide efficiently within a short duration of time. One such approach is the electrochemical or catalytic hydrogenation of CO_2 into DME or methanol and their subsequent conversion to other products using hydrogen. Converting hydrogen and carbon monoxide to methanol is known since early 20th century. In 1920s and 1930s some methanol producing plants in the US used CO_2 obtained as a by-product of the fermentation process. Copper and zinc metals and their oxides were used for the conversion process. These catalyst are similar to the

ones used today for converting fossil-based syngas into methanol. The mechanism of methanol formation from syngas shows that it is expected that similar catalyst will work. The CO in syngas is first converted into CO_2 and H_2 by undergoing water gas shift reaction. The CO_2 is then hydrogenated into methanol on the catalyst's surface (Ostrovskii, 2002; Rozovskii & Lin, 2003). Fig. 6 shows the recycling of CO_2 for producing methanol and synthetic hydrocarbons.

Hydrogenation of CO_2 to methanol on the industrial level has a history spanning 26 years, summarized in Table 6. Lurgi AG, has developed a catalyst having high activity for the conversion of carbon dioxide and hydrogen into methanol (Goehna & Koenig, 1994). It operates at around 260°C which is a notch higher than conventional catalyst and gives excellent methanol formation efficiency. The catalyst activity decreased at a similar rate as for conventional catalyst used in synthesis of methanol. In Japan, a laboratory pilot scale plant produced 50kg of methanol per day from H_2 and CO_2 having methanol selectivity of 99.8% (Saito, 1998). The Carbon Recycling International (CRI) company successfully synthesized methanol in a pilot plant in Iceland using CO_2 (US8198338B2, 2007). The plant has a capacity of producing 3500 tons of methanol annually using CO_2, which is readily available with cheap geothermal energy source. The hydrogen required for the process can be produced by electrolysis of water using electricity generated from hydroelectric plant or geothermal energy. Mitsui chemicals has also constructed a demonstration plant having 100 ton per capacity of methanol production (Tremblay, 2008). The CO_2 for the plant will come from industries that produce CO_2 as a by-product. The hydrogen will be generated using solar energy by photochemical splitting of water. More recent plants include $MefCO_2$ plant in Niederaussem, Germany, and PetroChina pilot plant in cooperation with the Dalian Institute of Chemical Physics. Several new plants for methanol synthesis are upcoming as well. These include Mitsubishi Gas Chemical Company in collaboration with Mitsubishi Hitachi Power Systems (MHPS) and Mitsubishi Heavy Industries Engineering (MHIENG). The plant will utilize the CO_2 emitted from the refinery Tomakomai City, Hokkaido, Japan with a 20 ton per day capacity, and will start operation in 2021. Sunfire Germany and Total Oil are constructing a green methanol plant with 160tpa capacity that will utilize a 1-MW electrolyzer powered by wind turbine for hydrogen production(Sarp et al., 2021). It is also found that the investment in methanol synthesis plant from carbon dioxide and hydrogen is similar to the one based on syngas. However, the only problem is the scaling of the plant due to limited availability and price of CO_2 and H_2 and also the source of energy. Various sources such as power plants burning fossil fuels and various industries such as aluminum smelters, cement factories, and fermentation plants produce CO_2 that can be captured and purified. There are natural resources such as geothermal energy and natural gas wherein CO_2 is also found in abundance. Lastly, CO_2 can be separated from air and recycled into methanol and other products. Today fossil fuel based syngas is used for hydrogen production which releases lot of CO_2 into the atmosphere resulting in further increase in global warming. Also, due to diminishing fossil fuels, different sources have to be utilized for hydrogen production. The best way for the future is by splitting of water by electrolysis or any other method.

Fig. 6 Recycling of CO₂ for production of methanol and synthetic hydrocarbon (G. Olah et al., 2009)

Table 6. Summary of plants on industrial scale or demonstration scale for producing methanol from CO₂ (Sarp et al., 2021)

3.2. Storage and distribution of methanol

Similar to the petroleum based fuels, a wide spread distribution network is required for methanol to easily available to the consumers. Dispensing methanol from the refueling stations will be similar to the refueling station dispensing petroleum fuels. The consumers won't feel any change, except that instead of a petroleum fuel they are filling their tanks with a different liquid. In the existing refueling stations or newly designed stations, installing methanol storage tanks and distribution pumps is similar to the installation of gasoline. In California, for fuelling methanol powered vehicles refueling stations are being built since 1980s. Most of the vehicles are flexible fuel vehicles (FFV), i.e. any mixture of methanol and gasoline can be used to run them, whereas some can run only on neat methanol. In parts of the United States and Canada, methanol fuel pumps were also installed. Today, methanol storage and distribution systems are already in place as it is an essential commodity. Nearly 500,000 ton of methanol in the US alone is transported every month by truck, rail and boat (Methanol Institute, 2004). Rail cars that can hold 100 tons each of methanol will be preferred for long distance transportation. Countries having extensive railway networks, such as the United States, Europe, India and other countries can transport methanol to all the major places. For transporting in small volumes to local centers tanker trucks that can hold nearly 30 ton of methanol can be used. Countries with inland waterways can ship methanol through barges that can carry nearly 1250 ton. Another method of transporting methanol is through pipelines which is extensively used for transporting oils and natural gas. For small quantities building a pipeline is not justified given the huge investment in building a pipeline. However, if methanol becomes the prime fuel in the future then transporting methanol through pipelines will be best viable option as it will improve the economics. Also, methanol transportation through pipelines does not poses any problems. Methanol can also be transported from remote locations where it is produced through ocean tankers. By transporting methanol is such big tankers, the cost of methanol shipping will be similar to that of crude oil. It can then be stored in tanks made from stainless steel and carbon steel similar to the way petroleum products are stored (Methanol Institute, 2004).

3.3. Safety with methanol

Methanol is widely used for the synthesis of various chemicals, as an industrial solvent and it is also present in many consumer products. Windshield washer fluid contains large part of methanol. It is also used as a camping cooking fuel and as an antifreeze. This shows that almost every household has used methanol. The public has not faced any significant problems with its use. However, its exposure will increase as its use as an automotive fuel increases. Moreover, the risk for the consumers is similar to that of gasoline or diesel use (G. Olah et al., 2009). Methanol

is toxic to humans and while handling same care should be taken as other fuels require. It can be absorbed by inhalation, ingestion and slowly through exposure of skin. If not timely treated, 25-90ml ingestion of methanol may be fatal (Bromberg & Cheng, 2010). In the human body, liver metabolizes methanol first into formaldehyde and then into formic acid which is either excreted in the urine or metabolized into carbon dioxide (Fig. 7). The severe effects of methanol ingestion take up to 12-18 hours to show because the formic acid produced is metabolized slowly. Increase is blood acidity can be caused by high concentration of formic acid, resulting in dizziness, weakness, headache, and nausea. A person may also find it difficult to breath along with abdominal pain. Its poisoning may lead to coma and death, in severe cases. The formic acid may also affect the optical nerve resulting in blurring of vision to total vision loss (Methanol Institute, 2013). Timely treatment can combat methanol poisoning resulting in complete recovery. Early use of sodium carbonate can reduce the blood acidity and vision impairment can be repaired or reversed. Methanol and formate can also be removed from blood stream by dialysis. 4-methylpyrazole administered orally or intravenously can reduce methanol poisoning along with ethanol and ethylene glycol poisoning (Bromberg & Cheng, 2010; Methanol Institute, 2013). It is seen that methanol overexposure is dangerous for humans but it is essential to know that both methanol and formate are present in our body from the food we eat and it is also produced during metabolism. It is present in vegetables, beverages, fresh foods and fermented foods. Aspartame present in soft drinks and diet foods during digestion is partially converted into methanol. The Food and Drug Administration (FDA) of the United States says that 500mg daily intake of methanol is safe for an adult (Methanol Institute, 2013). Moreover, formate is considered as a building block of many biomolecules and is a component of our DNA (Bromberg & Cheng, 2010). Studies show that methanol itself is neither carcinogenic nor mutagenic hazard whereas gasoline contains several compounds such as benzene, xylene, toluene, n-hexane and ethyl benzene some of which are known mutagens and carcinogens (Cruzan, 2009). It is expected that during refueling of a car with methanol will result in low dose exposure of the public. By inhaling, nearly 2-3mg of methanol will be ingested orally during a refueling (Bromberg & Cheng, 2010). Consider drinking 0.35L diet soda which contains nearly 200mg of aspartame, this will result in 20mg production of methanol by the body. With vapor recovery systems installed, the methanol exposure during refueling will reduce to 3-4ppm. Spill free nozzles are designed to avoid spill during refueling so that the consumer does not comes in contact with methanol. Even if the human skin comes in contact with methanol, water and soap can be used to wash the affected area (G. Olah et al., 2009).

Fig. 7 Human metabolism of methanol (G. Olah et al., 2009)

The major hazard with the transportation fuel is fire and explosion which is also a concern with methanol. However, the physical and chemical properties of methanol as compared to gasoline reduce the fire risk significantly. In combination with lower volatility and heating value, as compared to gasoline, four times more methanol vapor is required for its ignition. Even if it ignites, its flame speed is four times slower and it releases heat at one-eighth the rate of gasoline

fire. Also due to its low radiant heat output, the surrounding ignitable materials are less likely to catch fire (G. Olah et al., 2009). Southwest Research Institute (SWRI) and Environmental Protection Agency (EPA) (Cheng & Kung, 1994) fueled one car with gasoline and the other with methanol. The cars were placed near an open flame and the fuel was allowed to leak on the ground. They found rapid ignition of gasoline and within minutes the entire vehicle was burnt. Whereas, time taken for methanol to catch fire was three times that of gasoline and only the rear end of the vehicle was burnt. By pouring water, methanol fire can be easily extinguished. There is almost negligible smoke when methanol burns resulting in less injuries caused by smoke inhalation and fire-fighting can be easily carried out as loss of visibility is less. It is possible that in fuel tank or reservoir, ignitable air-fuel mixture may be present at ambient conditions. If fire or explosion occurs due to collision, the mixture may not ignite due to property of methanol and modifications in fuel tank or use of a volatile compound which itself vaporizes making the mixture too rich to ignite (Perry & Perry, 1990). Therefore, it can be said that methanol fire is less likely to occur, even it does it's less damaging as compared to gasoline.

3.4. World methanol supply and demand

The world methanol consumption in 2011 was 53 million tons which increased to 91 million tons in 2018 (Methanol Institute, 2019), showing that methanol has become an important commodity for the chemical industry. Acetic acid, formaldehyde, and methyl tertiary butyl ether (MTBE) are the three major chemicals produced from methanol (Fig. 8). Formaldehyde is one of the most important products produced from methanol. It is also used for the production of chemical fibers, plastics, paint, resin, pesticides and pharmaceuticals. Methyl tertiary butyl ether (MTBE) produced from methanol is used to boost the octane rating of gasoline. However, its use as an octane booster has decreased since 2003 when it was found that water resources were contaminated by the spilled fuels containing MTBE (*Motor Gasoline Outlook and State MTBE Bans*, 2004). Now ethanol is used as an antiknock in many stated of the US. Acetic acid produced from methanol is widely converted into vinyl acetate monomer (VAM). The rest of the methanol consumption can be divided into chemical intermediates such methylamine, chloromethane, methylmercaptane and methylmethacrylate, along with methanol and its derivatives such as DME for use as a fuel or a fuel blend. It is seen that nearly one third of methanol globally produced is used as a fuel. Its use as a fuel (MTBE/DME/gasoline) has increased from 26.7 million tons in 2014 to 29.06 million tons in 2018. The methanol to olefins (MTO) process through which methanol is converted into ethylene and propylene is becoming a large scale consumer of methanol. Methanol demand for MTO has increased from 9.1 million ton in 2014 to 20.88 ton in 2018. Both ethylene and propylene are used as feedstock for producing polyethylene and polypropylene. It is also seen that the production of methanol has shifted to countries having reserves of natural gas and coal like the Middle East and Asia. As the amount of shale gas availability in the US increased, the methanol production cost dropped significantly due to the drop in the prices of natural gas. China's annual consumption of methanol is nearly 50% of the global consumption. The methanol's consumption growth rate is

expected to grow in the range of 10-20%, as China wants to reduce its dependence on crude oil (highly fluctuating cost) by blending coal-based methanol with gasoline (C.-J. Yang & Jackson, 2012).

Fig. 8 Global methanol demand sector-wise (2019 data is estimated) (Methanol Institute, 2019)

3.5. Methanol use in chemical industry

The chemical industry holds great interest in methanol since it can be easily interconverted as an energy or a chemical raw material. Most of the methanol produced worldwide is converted into a diverse variety of chemicals and materials such as acetic acid, formaldehyde, methyl-tert-butyl ether (MTBE), construction materials, paints, adhesives and polymers among others.

3.5.1. Methyl-tert-butyl ether (MTBE) and di-methyl ether (DME)

Methyl-tert-butyl ether is formed by reacting methanol and iso-butylene over an acidic catalyst at nearly 100°C. MTBE gained attention when it was known that it can act as an octane booster (octane number 116) and replace the harmful and toxic tetra-ethyl lead (Hamid & Aliin, 2004). Its use in gasoline also reduced the need of benzene and toluene which are also high octane components but are known carcinogens. Therefore, MTBE use in reformulated gasoline helped in the clean burning of fuel which reduced unburnt hydrocarbons, carbon monoxide and ozone emissions. However, in the later years it was found that MTBE had high solubility in water and did not degrade naturally. Therefore, the groundwater was contaminated in those areas where the underground gasoline tanks in the filling station were leaking (Donahue et al., 2002). Even in low concentrations, humans detected the foul odour and taste of MTBE in water. However, its toxicity is much less than other compounds present in gasoline. Nevertheless, it was banned in the USA. In Europe, it was not phased out but with the directives of using biofuels for transportation, the European countries moved towards bio-ethanol and ethyl tert-butyl ether (ETBE). Most of the MTBE plants in Europe were then retrofitted for producing ETBE. Moreover, in Asia, MTBE is still used (G. Olah et al., 2009).

Dimethyl ether is the simplest of all ethers. It is an environment friendly colorless chemical which is neither corrosive, nor toxic and not even carcinogenic. It is used in spray cans as an aerosol propellant instead of the banned chloro-floro-carbon gases. Since the flame of DME is soot-less, it is also used for blowing glass. It is a gas under ambient conditions and its boiling point is -25°C (Park & Lee, 2013). Therefore, like LPG, DME is also stored in pressurized tanks in liquid form. Its use as a compression ignition engine fuel lies in the fact that its cetane number is very high (Park & Lee, 2014). It is a clean burning fuel producing low quantities of NOx, and no SOx and soot emission (Thomas et al., 2014). Methanol is dehydrated to produce DME. Since methanol is produced from various feedstock such as biomass, coal, and natural gas, it can be said that DME is directly produced from these feedstock (Youn et al., 2011). In one study, a method was developed for producing DME from syngas in a single step by combining synthesis

of methanol and its dehydration (Ogawa et al., 2003). By using carbon dioxide and hydrogen, DME production has also been studied (Hirano et al., 2004). The global demand for DME till 2004 was only 150,000 tons per annum. However, after that, the demand for DME has tremendously increased on account of its use as a fuel. The DME production in China in the year 2008 was more than 2 million tons which is continuing to grow (Xia, 2008). In the methanol to olefins and methanol to gasoline production process, DME is also an important intermediate.

3.5.2. Methanol to Olefins

The methanol to olefins process was a two stage process, wherein the coal or natural gas is converted to methanol via syngas production, then the methanol is transformed into light olefins. The process was so developed such that natural gas can be used for sources which are far away from major consumer centers. In this process, DME is first produced by dehydration of methanol which is further reacted to form propylene and ethylene. The catalyst used in the process is the zeolite H-ZSM-5 (Kvisle et al., 2008). Also small amount of other hydrocarbons such as butene, alkanes, some aromatics and higher olefins are also produced. This process was first pioneered by Mobil who could produce 100 barrels per day through a demonstration plant in Wesseling. Germany. An olefins to gasoline and distillate process was also developed by Mobil. They oligomerized the olefins over a ZSM-5 catalyst to form gasoline and distillate having selectivity greater than 95%. By changing the reaction conditions, the gasoline and distillate ratio can be varied considerably. When operated at high pressures and low temperatures, olefins having high molecular weight are formed, which upon hydrogenation can produce diesel and jet fuels. Whereas, at high temperatures and low pressure, low molecular weight olefins with high aromatic content can be produced. Silicoaluminophosphate (SAPO) molecular sieves such as SAPO-34 and SAPO-17, are also known to have high selectivity for the methanol to olefin process. These catalysts have a definite three-dimensional crystalline structure. The catalysts are micro-porous in nature with cages and channels of specific size. The activity of a catalyst is defined by these pores and channels. If the reagent size is small then only it can access these sites and these sites also control the size of the products. SAPO-34, having the size of 3.5Å allows good control of the olefin size that emerges from the catalyst (Chang, 1997). Therefore, olefins having large size diffuse out a lower rate and ethylene and propylene diffuse out a higher rate. UOP and Norsk hydro developed a methanol to olefin plant using SAPO-34 catalyst (Stocker & Weitkamp, 1999). The ethylene and propylene selectivity of the process is nearly 80% and nearly 10% is converted into butylenes, which are also of high value. Based on the conditions of the reaction the ethylene to propylene ratio can be varied which allows flexibility and adaptability in accordance to market conditions. Near the capital city of Nigeria, Lagos, a commercial methanol to olefin plant is producing nearly 2.5 million tons per year of olefins. Lurgi, unlike UOP, developed a methanol to olefin process to produce mostly propylene. The yield of propylene from this method is nearly 70%. One such methanol plant is commercially operating in Norway producing nearly 99.7% pure propylene. Trinidad and Tobago are producing 450,000 tons of propylene per year using the same technique from its vast natural gas resources. Two Chinese

companies are also producing 450,000 tons of propylene per year using coal derived syngas (Tullo & Tremblay, 2008). The methanol to olefin process is an alternative route for producing ethylene and propylene whose demand is ever increasing. Steam cracking of naptha is mainly used for producing these compounds. In this process, naptha or lower paraffins is mixed with steam and thermal cracking is carried out at temperatures above 800°C (Ren et al., 2006). Methanol to olefin process is advantageous to naptha cracking, since different raw materials can be used in comparison to crude oil for naptha formation. The process consumes less energy and releases less CO_2. Also the olefins produced by the process are of polymer grade (Martin Bertau & Wernicke, Hans Jürgen Schmidt, 2014).

3.5.3. Acetic Acid

Acetic acid is one of the most important aliphatic intermediates. It can be generated through oxidative fermentation of ethanol. Also, it can be produced from wood coking or from molasses of sugar cane. Since the beginning of the 20th century, acetic acid is being commercially produced from acetaldehyde. Later on, instead of acetylene, ethylene was used for acetic acid production. In the 1920s, BASF developed the methanol carbonylation process for acetic acid synthesis. This process was replaced by the Monsanto process which utilized rhodium based catalyst. Later on Cativa process, which uses iridium based catalyst for the reaction, replaced the Monsanto process. Since, the methanol carbonylation process was more economical, the acetaldehyde oxidation was eventually phased out (Martin Bertau et al., 2014). Acetic acid is used throughout the world for the production of acetic anhydride and vinyl acetate monomer (VAM). The use of acetic acid as a solvent for purified terephthalic acid (PTA) production is also growing worldwide (El-Zeftawy, 1995).

3.5.4. Formaldehyde

Formaldehyde, due to its high reactivity is an important chemical which is used in textiles, construction, wood processing, and carpeting industry. At ambient conditions, it is a colorless gas that rapidly polymerizes in the presence of small impurities. Therefore, it is commercially used in three forms namely as an aqueous solution containing 35-55% formaldehyde rest is methanol and a polymerization inhibitor, cyclic trioxane, and paraformaldehyde (Martin Bertau et al., 2014). Today formaldehyde is produced by using two methods: (1) oxidation-dehydrogenation of methanol using a silver catalyst and (2) using metal oxide catalyst, direct oxidation of methanol to formaldehyde (Formox process). Nearly 50% of the methanol produced in the world is used in formaldehyde synthesis (Franz et al., 2016). Formaldehyde is produced close to the consumption centers since it is fairly easy to make but shipping over long distance is problematic due to stability issues. Therefore, there is virtually no world trade of formaldehyde. Formaldehyde around the world is mainly used for the production of thermosetting resins. Among them amino resins produced by condensing either melamine or urea with formaldehyde is the largest user (El-Zeftawy, 1995).

3.6. Methanol use as a fuel

Methanol falls in the category of light alcohol and is considered as one of the cleanest alternative fuel for running the I.C engine. It is a clear and colourless liquid, obtained from a wide variety of sources, discussed earlier. The initiative of using methanol as an alternative fuel came into existence in the early 1970s due to higher perturbation in the price of conventional fuels in the world market. Table 7 shows the comparison of different fuel properties of methanol with diesel, gasoline, and ethanol. In comparison to hydrogen (Table 4), methanol has a lower heating value. However, the volumetric energy content of hydrogen gas is several times lower than methanol. Even liquid hydrogen has nearly two times lower volumetric content than methanol. Methanol has a lower flammability limit than hydrogen. Its flame speed is higher than gasoline but lower than hydrogen. Although, the octane number of both methanol and hydrogen is more than 100 but methanol still has slightly lower octane number than hydrogen. Theoretically, on burning hydrogen produces only water vapor whereas on burning of methanol a mixture of carbon dioxide, carbon monoxide and water vapor may be produced. The section below shows the influence of addition of pure and different blends of methanol on gasoline and diesel engines.

Table 7. Comparison of fuel properties diesel, gasoline, biodiesel, ethanol and methanol (Çelebi & Aydın, 2019)

3.6.1. Methanol as a fuel for Spark Ignition (S.I) engines

Methanol has already attracted the attention in the past due to its large-scale usage in high-speed racing cars. The abundant availability options, lower energy density, and higher octane rating and flame speed compared to gasoline make it competent for running in SI engine with minor modifications (Verhelst et al., 2019). Wang et al. (C. Wang et al., 2019) studied the chemical, cooling, and octane sensitive effects of methanol on the operating characteristics of an SI engine. The experimental results showed that the engine running on pure methanol could operate at a higher compression ratio as compared to gasoline. The higher-octane number facilitates the fuel-air mixture entering into the cylinder to compress at a much smaller range of volume. Thus, improving the atomization and combustion characteristics. The previously published literature reveals that ability to operate with leaner mixtures, higher compression ratio (CR) and latent heat of evaporation attached with methanol-fueled engine can provide up to 10-20% increase in thermal efficiency for the same engine running on gasoline fuel. The improvement in the BTE, brake specific fuel consumption (BSFC) and maximum heat release rate and cylinder pressure can be obtained by optimizing the ignition timing of the SI engine using methanol as a fuel (J. Li et al., 2010). The results showed a significant change in the performance, combustion, and emission characteristics of direct injection SI methanol engine running at a speed of 1600 rpm, full load condition, optimal fuel injection, and injection timing. Hence, the exhaustive literature showed some outrageous feature of methanol. The characteristics such as sulphur free fuel, fewer emissions, high octane number, vast availability, etc. make it a best potential substitute for gasoline fuel. However, high NOx emissions, formation of formaldehyde, lower calorific value, etc. associated with the usage of 100% methanol in spark ignition engine precludes its usage as a complete replacement fuel in SI engine and most of the times methanol is used an extender in

gasoline engines (Awad et al., 2018)**.** Table 8 shows problems associated with the use of neat methanol as SI engine fuel.

Another fuel reformulation technique to utilize the assets of methanol in fuel economy is to use it as an extender fuel. The amalgamation of methanol in gasoline and light alcohols in the form of binary/ternary blends is a favorable approach which can minimize the shortcomings associated with the usage of neat methanol in SI engine. Sharma et al. (Sharma et al., 2019) in their experimental research, investigated the noise and vibration characteristics of Gasoline Direct Injection Engine using the blends of gasoline and methanol. 10% and 20% (v/v) of methanol were used for blending with gasoline during the analysis. The study showed that the binary blends of gasoline and methanol significantly improved the in-cylinder pressure, heat release rate (HRR), rate of pressure rise, and CHR as compared to neat gasoline. Similarly, Elfasakhany (Elfasakhany, 2018) studied the performance and emission characteristics of ternary blends of iso-butanol–bio-methanol–gasoline (iBM) and n-butanol–bio-ethanol–gasoline (iBE). The comparative assessment of various engine parameters and exhaust emissions of the ternary blends were carried out. The result showed that the iBM mixture showed lower CO, CO_2, and UBHC as compared to iBE and gasoline. Also, higher performance characteristics were obtained with iBM blends compared to iBE. Yanju et al. (Yanju et al., 2008) performed an investigation on performance and emission characteristic of the SI engine. Three different blend ratios of methanol-gasoline, i.e., M10, M25, and M85, were analyzed. The results showed that the addition of methanol to gasoline fuel improved the brake thermal efficiency and reduced the CO and NOx emissions from the engine. Also, the maximum reduction in CO and NOx emission were observed for M85 concentration blend. Hence, the outcomes above showed that the utilization of methanol in the form of blends with gasoline and alcohols has proven to be a more viable solution in comparison to pure methanol. To reduce the dependency on petroleum fuels and reduce the harmful gases from the atmosphere, the government should enforce some strict amendments to encourage and transit the automotive industries approach towards methanol fuel economy. The British automotive company 'Lotus' known for its light weight architectures, efficient designs has already started promoting the blends (methanol-ethanol-gasoline) in their high speed and luxury cars named as "tri-flex-fuel" car, the Exige 270E (Turner & Pearson, 2012). The Lotus is focusing on the utilization of methanol fuel obtained by hydrogenation of carbon dioxide. However, problems such as corrosion of engine parts, the stability of blends and higher fuel mass flow intensity which are associated with long term usage of methanol blends. These issues can be adequately resolved by using different additives, surfactants and with minor engine modifications.

Table 8. Merits and demerits of using neat methanol in an SI engine

3.6.2. Methanol as a fuel for Compression Ignition (CI) engines

Diesel engines are known for their heavy-duty applications; commonly used for running industrial/ transportation engines and power generators. It plays a crucial role in driving the

economy of the developing nations. Unfortunately, diesel fuel is the largest emitter of harmful pollutants such as smoke, soot, and NOx into the atmosphere. The introduction of stringent emission norms (Euro VI) is forcing the fuel economy to explore a potential alternative fuel which can sustainably replace diesel fuel and also facilitates in preserving the existing C.I engines running on the roads. The distinctive physical and chemical properties of methanol have attracted the attention of the entire research fraternity. Methanol on its combustion does not emit toxic smoke or soot particles, even the amount of NOx reduces drastically in comparison to diesel (Yao et al., 2017). Also, the higher volatility and vapor pressure of methanol promotes its usage as CI engine fuel. Methanol-fueled heavy-duty engines have the leverage to run efficiently in cold weather condition, thereby providing an appropriate solution to the difficulties of cold starting and white smoke attached with neat diesel. The methanol powered C.I engines are already in practice in different parts of the world especially in the USA (Bechtold et al., 2007). Detroit, also known as "motor city," stepped on methanol fuel to run its public transportation system. DDC (Detroit Diesel Corporation) in the early 90's retrofitted '6V-92TA' a heavy-duty diesel engine to run on neat alcohol, methanol (Wuebben et al., 1990). It was also certified as the low emission heavy duty diesel engine by the Environmental Protection Agency (EPA) and the California Air Resource Board (CARB) in the year 1992 (G. Olah et al., 2009). The methanol fueled engine can provide a quantum leap in minimizing the perilous issues of unwanted climate changes and acid rain occurring due to excessive utilization of diesel fuel. However, there are certain barriers in using neat methanol in diesel equipped engines due to which the vehicles running on 100% methanol are now obsolete. The lower cetane number of methanol resulting in longer ignition delay and other abiding issues such as higher maintenance cost due to corrosion of engine parts and issues with fuel system etc. are some of the shortcomings which restricts its usage as neat fuel.

Nevertheless, there are various fuel reformulation techniques which can surmount the above discussed difficulties. Methanol in the form of blends (binary/ternary), fumigation, and derivate DME (Di-methyl Ether) are some of the approaches which can widespread the use of methanol in CI engines (Verhelst et al., 2019). Methanol containing immense quantity of oxygen content and high enthalpy of vaporization can be used as a blend with diesel i.e., 85% methanol and 15% diesel) or other proportions. Canakci et al. (Canakci et al., 2009) conducted the experimental study to investigate the performance, combustion and emission characteristic of CI engine fuelled with methanol-diesel blends. The results showed improvement in peak cylinder pressure, HRR, combustion efficiency as the injection pressure increases. Also, the emissions such as UBHC, and CO were also reduced considerably. However, the BSFC, BTE, NO_x and CO_2 showed negative trend as the value of injection pressure changes, for all fuel blends. Huang et al. (Huang et al., 2004) investigated the combustion behavior of diesel-methanol blends under different fuel injection angles. The results showed that the increase in the concentration of methanol in the blends improves the heat release rate in the premixed burning phase and also trimmed off the combustion duration. As discussed earlier there are lot of starting issues in using pure methanol in CI engine. The unmatched physio-chemical properties of methanol and diesel

makes them difficult to mix with each other. Hence, formation of stable blend with diesel is always an objection. To overcome these stability challenges the mixture is usually blended with an appropriate surfactants or additives. Surfactants are the compounds which helps in reducing the surface tension between methanol and diesel. Methanol and biodiesel in the presence of some cetane number improver can improve the CI engine characteristics (R. Li et al., 2014). The study showed improvement in the ignition delay period and combustion duration on addition of cetane improve 'cyclohexyl nitrate'. Also, NO_x and smoke were also reduced to a greater extent. Some previous published research showed that methanol in the form of ternary blend with diesel and oxygen rich compound has the potential to run-over the gaps associated with binary blends. Chen et al. (H. Chen et al., 2019) analyzed the combustion and emission characteristics of ternary blends of (diesel-n-pentanol-methanol) blends. The higher oxygen content delivered by n-pentanol provide higher intensity of combustion. However, increasing the oxygen content results in prolonged ignition delay and higher combustion temperature peaks. Also, the emission characteristics such as soot emissions decreases to a greater extent and NO_x emission increased due to high combustion temperature.

Dimethyl ether (DME), derivate of methanol is the best suited replacement of diesel fuel. It can be obtained from the dehydrogenation of methanol in the presence of some suitable catalyst. The distinctive non-toxic, non-corrosive, non-explosive and non-carcinogenic nature of DME makes it the most favorable choice to be used as CI engine fuel (Park & Lee, 2014). Interestingly the properties of DME such as cetane index, low boiling point motivates the fuel economy to utilize it as neat fuel in diesel engine. Compared to other alternative fuels especially methanol, it burns clean, emissions are free from soot and smoke and also produces very little NO_x, a major concern in diesel engine. DME fuelled engines are very popular in many parts of the world especially Europe (Evans et al., 2014). Volvo, a Swedish luxury vehicle company is currently focusing on utilizing the applications of DME in their vehicles. Also, other leading automobile industries like 'Isuzu' are working on fuel injection systems to make their engines compatible for DME use. Denmark a leading name in the field of renewable energy, is already running their public transport buses on DME fueled engine (John Bøgild Hansen & Mikkelsen, 2001). The DME powered CI engines not only provide improved performance and emissions but also produces less noise as compared to diesel. The noise of the DME fueled engines are somehow comparable with the noise produced by gasoline engine. Besides many advantages of DME as an environmentally friendly fuel, there are certain issues such as low density, viscosity and poor lubricity which neglects it usage as neat fuel. Therefore, various studies were done in the past to utilize DME as blends with diesel/biodiesel. Raza et al. (Raza et al., 2019) conducted a comparative analysis using blends of three different test fuels pentanol/diesel and DME/diesel and pentanol/DME/diesel. The combustion, performance and emission characteristics were tested. The result showed reduction in the concentration of PM for DME/diesel blends and the lowest PM were noted for pentanol/DME/diesel blends. However, higher BSFC were recorded for the binary and ternary blends as compared to the diesel due to the presence of oxygen rich compounds.

3.6.3. Methanol as a fuel for fuel cells

Methanol can also be used to power the fuel cells. It is a device based on an electrochemical process which converts the chemical energy of the fuel/hydrogen into electricity in the presence of some suitable oxidant. The countless issues arising with the usage of conventional fuels is forcing the fuel economy transition towards electric vehicles. The electric cars unlike internal combustion engines takes advantages of the fuel cells for its working. As already discussed, hydrogen is the cleaner and eco-friendly fuel; however, the stability, higher maintenance, and other undesirable handling issues makes it difficult to be used for fuel applications. Therefore, to utilize the innumerable advantages of hydrogen as a fuel, it can be employed to drive the fuel cells (Tanç et al., 2019). Almost all the fuel cells currently being manufactured for electric vehicles operate primarily on the hydrogen fuel. A fuel cell is the best alternative which can reduce reliance on the millions of existing IC engines in the world (Sudhakar et al., 2018). It can provide higher efficiency and reduced emissions as compared to the diesel/gasoline.

Methanol can be reformed into two ways, to produce hydrogen, used for running the fuel cells. The most popular and economical fuel cell functioning on hydrogen gas is PEMFC (Proton Exchange Membrane Fuel cell). The PEMFC requires pure hydrogen for its operation, hence methanol can be potentially used as feedstock for hydrogen generation. In PEMFC the hydrogen is generated externally and is then fed into the fuel cell, therefore, these fuel cell can be used in large system applications (US 2006/0029853 A1, 2006). However, methanol also has the flexibility to be fed directly for running the fuel cell systems known as DMFC (Direct Methanol Fuel Cell). In DMFC, methanol is internally reformed to generate hydrogen. It is a continuous generation process which uses appropriate catalyst for converting methanol to hydrogen. The temperature range in which the fuel operate is 60ºC to 130ºC (Hsueh et al., 2012). Therefore, the DMFC fuel cells are restricted to light duty systems and can be potentially used for battery charging applications such as electric cars, folk lift trucks etc. The commonly used catalyst in DMFC fuel cell is ruthenium-platinum. It converts liquid methanol into hydrogen, therefore pure methanol can be used as fuel. Zhang et al. (F. Zhang et al., 2017) investigated the performance of DMFC by incorporating a methanol barrier known as methanol-resisting pervaporation film (PVF), a buffer cavity and a water-resisting PVF. The anode controls the flow of methanol coming from the tank. The results showed a significant increase in the efficiency of the fuel cell. Also, the performance of the fuel cell showed no change over 400hrs of continuous working. There is lot of research undergoing on the development of Fuel Cell Vehicles (FCVs) especially in the USA and the European countries. German automotive company "Diamler" is one of the leading organizations working on DMFC FCV's. In the year 1997 and 2000, Diamler demonstrated and tested its first FCVs, the Necar 3 and Necar 5 (updated version). Both the fuel cell and the reforming system were placed in the car, which can run at maximum speed of 150 km/h. The Necar 5 consisted of 85kW fuel cell and had a driving range of 500 km in single run (G. Olah et al., 2009). Later, the rise in depletion of conventional fuels compelled other the automotive companies such as Ford, Nissan, Volvo, General Motors, and Honda etc. to develop FCVs running on hydrogen fuel. The research is in developing stages to improve the

performance of the fuel cells in terms of complexities in design, high investment cost, durability, storage and handling. Babu et al. (Vijay Babu et al., 2018) investigated the performance of PEMFC by fabricating electrode membrane assembly of 40% Pt/C. The results showed that cell temperature plays an important role on the performance of the fuel cell. During the study a fuel cell prototype was also developed and run continuously under different loading conditions to study the performance. González-Espasandin et al. (González-Espasandín et al., 2019) compared the performance of PEMFC and DMFC fuel cell in Unmanned Aerial Vehicle (UAV). The test was conducted at atmospheric flight conditions. The results showed that PEFC/H_2 is more likely effected by the atmospheric flight conditions as compared to DMFC. Low pressure and relative humidity adversely effects the efficiency of the PMFC fuel cell. Hence, DMFC is more compatible to operate under low-medium altitude. Fuel cells can be a viable replacement of internal combustion engine because of their tremendous performance and cleaner operation. However, the commercialization of this technology is yet to be achieved. Reliable technology and durability are some of the major hurdles in the path of fuel cell availability (J. Wang et al., 2018). Many countries especially United States has started the installation of fuel cell system, across many states. More than 7000 fuel cell systems with an overall capacity of 16.3 MW have been installed across many states of the USA (Jenn et al., 2016). The progression in the growth of fuel cell technology and reliability among the end users can only be achieved if all the bodies including scientists, modelers, engineers, government and funding agencies collaborates and supports the technology integration.

3.6.4. Methanol as a fuel for cooking applications

The perturbation in the prices of petroleum product is forcing the fuel economy to search for a clean burning cooking fuel. Due to a massive increase in the population of the developing nations like India, China and Brazil, the demand for LPG (Liquified Petroleum Gas) is sporadically rising. The past energy scenario reports reveled that during the period 1990 to 2001, China has accounted an extensive increase in the LPG production i.e., from 2.4 Mt. to 9.2 Mt followed by India which noted 2.15 Mt to 7.27 Mt increase (Arya et al., 2016). LPG is the by-product of oil and gas industries. Therefore, the excessive increase in the demand of LPG in the domestic sectors is causing direct threat to fossil fuels. Asia-Pacific regions has encountered maximum increase in its consumption since the year 2000 i.e., around 5%. The dependency on LPG can be only be reduced if it can be sustainably replaced with a non-crude oil derived product. Biogas, Producer gas and Natural gas are some of the possibly explored substitute which can replace LPG. However, complexity such as operating/installation cost, low calorific value and harmful emissions etc. restricts their usage in cooking applications. Out of all the possible substitutes Dimethyl ether (DME) can potentially replace LPG from the domestic/household sectors. As discussed, earlier DME is a derivate of methanol, having properties similar to LPG. It can be obtained from wide variety of feedstock such as coal, natural gas, biomass and municipal solid waste and CO_2 (Azizi et al., 2014). Immensely populated countries like China and Brazil have already started installing DME plants at commercial scale.

The Govt. of China has mandated up to 20% blending of DME with LPG for domestic cooking purposes (Fleisch et al., 2012). DME, molecular weight of 46.07 g/mol is the only ether which has lowest carbon to hydrogen ratio. The non-toxic and sustainable nature makes it specifically different from other gases. DME is easily soluble in water and has density 2/3 of water. The similar properties to that of LPG makes it widely acceptable to be used in household applications as it can be easily stored and handled in LPG vessels. The current Indian market scenario shows that LPG alone cannot feed the increasing demand of households. Hence, the recent discoveries in the field of oil and gas estimated that there will be clear shortage of LPG in the forthcoming years. India has ample quantity of biomass resources and low-grade coal reserves. Therefore, biomass and coal can be easily used for the production of thousand and million tons of DME. According to a survey, about 26% of Indian coal is located in eastern region such as Jharkhand and West Bengal (Grové et al., 2017). However, surprisingly more than half of the population in these regions use coal, lignite and charcoal as a fuel for household applications causing serious damage to their health and environment. Hence, construction of coal to DME resources in these regions will help in reducing the dependency on LPG imports and thereby providing availability of energy resources to remote areas. The previous literature survey reveals that mixtures of DME and LPG has proven to be an excellent choice as new alternative fuel for domestic/cooking applications. The DME is easily compatible with the stove designed for methane with minor modifications in Japan. Marchionna et al. (Marchionna et al., 2008) showed that 15-20% DME-LPG blends showed improved performance in terms of fuel consumption and efficiency as compared to neat DME and LPG. Anggarani et al. (Anggarani et al., 2014) studied the performance of LPG-DME blends in modern household stove. Different concentration range of DME i.e., 5%, 10%, 15%, 20%, 25%, 30% and 50% were considered for the investigation. The heat input, efficiency of the blends and flame stability were determined. The analysis reveals that increasing the concentration of DME above 50% results in decrease in thermal efficiency. Similarly, LERC (LPG Equipment Research Centre) investigated the thermal efficiency of DME-LPG mixture by using a blend of 20% DME. An overall reduction of 5.26% in thermal efficiency were noted. CSIR Indian Institute of Petroleum also conducted a research to observe the changes in thermal efficiency of DME-LPG blends by considering different varying the concentration of DME in the mixture. The results showed significant decrease in efficiency as the concentration of DME increases in the blends. Hence, the similar thermo-physical properties to that of LPG, easier availability and cleaner production from numerous feedstocks makes DME a viable substitute of LPG in the world-wide market. Blends containing up to 20% of DME can be easily used for household cooking applications with no or minor changes in the existing setup. However, issues such as corrosive action on rubber material, low boiling point, critical flammability limits, lower combustion enthalpy and modulus of elasticity causing its usage hazardous to be used for the household purposes. Therefore, to commercialize its large-scale usage among the household communities it is necessary to taken into account the different flames behavior of DME-LPG blends, design and development of efficient burners and materials which can withstand for DME and DME-LPG blends applications.

3.7. Importance of methanol in Indian context

The methanol production in India is at a nascent stage. Since 2012, the methanol production capacity has stayed static at 0.474 metric ton. The production of methanol from the plants has decreased by nearly 57%. However, the methanol consumption has increased by about 61%. Therefore, India relies heavily on import of methanol from countries like Iran and Saudi Arabia. These countries have abundant reserves of cheap natural gas thereby reducing the cost of methanol production. The methanol producing plants in India are natural gas based which is also imported, therefore, it is cheaper for India to import methanol rather than producing it domestically. Moreover, there are no coal based methanol production plants in India although coal is abundantly available in India. Also coal to methanol is a proven technology. Also municipal solid waste and biomass can be used for methanol production, but their continuous availability is a challenge. Nevertheless, due to its large coal reserves, India has an opportunity to move towards methanol rather than hydrogen (Saraswat & Bansal, 2017).

Methanol can be either substituted or mixed with gasoline and diesel to reduce the country's dependence on highly volatile imported crude oil. India is targeting a 10% reduction in import of oil and gas by 2022, domestically produced methanol can help in achieving this target. Indian railways can also run their locomotives on methanol. Nearly 3 billion liters of diesel is consumed annually by Indian railways costing the exchequer in excess of INR 15,000 crores. Indian railways is trying to build a methanol powered locomotive, which if successfully implemented can reduce the annual diesel bill by 50% (MORTH, 2017). This conversion program is complementary to electrification goals of the railways. India is also rolling out in-land water transportation system where-in steel and coal will be shipped from coastal areas to cities far away from coastline. These ships run on diesel which causes lot of pollution and may spoil the water eco-system, therefore methanol powered ships is a better alternative as is would cause far less pollution. Methanol can be used to produce chemicals like formaldehyde, acetic acid and oleic acid. These chemicals are high value chemicals and the demand for these chemicals in the world market is very high, which would enable India to earn high foreign exchange. Methanol can also be produced from biomass and municipal solid waste, disposing which is already a huge problem for the country. It is also an opportunity to convert landfills into methanol so that there is no toxin leaching into the soil and greenhouse gas emission. Currently investing in methanol or DME will not look attractive due to low prices of crude oil, however, as the price of crude oil increases and its availability decreases then the significance of methanol will gain importance.

4. Cost comparison of hydrogen and methanol

The capital required for building a hydrogen infrastructure is the biggest impediment in its use in vehicles. Table 9 shows the capital cost in building a refueling infrastructure for hydrogen. The options considered are (1) from a centralized steam reformer liquid hydrogen is delivered (2) from a centralized plant hydrogen is delivered through pipeline (3) onsite production through steam reforming of methane and (4) use of electrolysis for onsite production. For serving 1.41

million fuel cell cars the infrastructure costs varies from US$440-870 million which comes out to be US$310-620 per car. For onsite generation the capital cost is US$516 million or US$370 per car (Ogden et al., 1999). In comparison to hydrogen infrastructure which requires special equipment for handling low temperatures and high pressure, methanol fuel stations require less capital. Another problem is the regulation formed by National Fire Protection Association (NFPA) that does not allow any hydrogen fueling station to be 25m near to the gasoline pump (Dolan, 2002). Thus making it difficult for hydrogen dispensing fuel station to be installed in the existing stations. In cities space is already a constraint, therefore it is very difficult to install new hydrogen-only fuel stations. Whereas, methanol can be dispensed by converting existing gasoline fueling stations. The conversion cost of existing retail outlets for methanol dispensing is quite low. The double-walled underground tank used for diesel or gasoline can be easily cleaned and used for methanol storage. Only new pipes and dispenser pumps that are compatible with methanol will be required. The cost of conversion is nearly US$20,000 and takes nearly a week. By spending nearly US$ 60,000 to 65,000 a new underground methanol storage tank of 40,000L capacity and pipes, pumps, dispensers and valves compatible with methanol can be added to an existing fuel station. In areas where space is available, the storage tank can be placed above the ground thus reducing the overall cost by about US$10,000 (American Methanol Foundation, 1999). That means, by investing US$ 1 billion 10% of the existing service stations can be converted to dispense methanol and for less than US$ 3 billion one-fourth of the existing fuels can additionally supply methanol (Basu & Wainwright, 2001; Dolan, 2002). Methanol, being an essential commodity, its storage and distribution systems is already in place. However its current production capacity is limited and if a million fuel cell vehicles operate on methanol then the production capacity needs to be increased and as seen in Table 10 its costs considering the terminal conversion, tanker shipping capacity and new production capacity would be around US$330-570 per car (Ogden et al., 1999). Therefore, the costs per car would be slightly lower for methanol infrastructure as compared to hydrogen infrastructure. In India, it is estimated that the cost of methanol produced from coal will be around INR 16-17 per liter whereas by using natural gas methanol costs around INR 25-27 which may vary depending upon the cost of natural gas. By steam methane reforming of natural gas the cost of hydrogen production is INR 25.67 per kg whereas from coal gasification hydrogen costs INR 57.5 per kg. The cost of hydrogen at a fueling station would be INR 85.54, when the cost of transportation through pipeline without storage and steam reforming method is considered (Balachandra & Reddy, 2007). In both the processes carbon dioxide is released in hydrogen production which may be used for other purposes. Whereas methanol itself contains carbon, hence the carbon dioxide release is very less as compared to hydrogen production.

Table 9 Cost for developing new hydrogen production, delivery and refueling station infrastructure (Ogden et al., 1999)

Table 10 Capital cost of methanol infrastructure (Ogden et al., 1999)

5. Conclusion

Hydrogen is considered to be best alternative to fossil fuels as it is completely free of carbon. However, there are issues with hydrogen use namely storage, safety and development of new infrastructure for storing and dispensing hydrogen through fuel stations. Methanol is a simple oxygenated liquid hydrocarbon and it is a better energy carrier than hydrogen. It can be produced by biomass and from sources rich in CO_2. The hydrogen required for the process can be derived from water using a renewable energy source. In this way, both hydrogen and CO_2 can be safely stored in the form of methanol. It is not only a safe means of storing energy but it is also an excellent fuel and a building block for many chemicals. Therefore, moving towards 'Methanol Economy' may be the solution to our present problems viz. an alternative to fossil fuels and reduction of global warming by capturing CO_2.

5.1. Future research

On the production front, research can be carried out on the methods of reducing the cost of methanol production using renewable feedstock or wastes. The catalyst plays a major role in the syngas production, a lot of research has already been done but new materials such as grapheme has not been explored much. Research can also be carried out on efficient ways of capturing CO_2 from the atmosphere and converting it into methanol rather than storing which may leak in the future and create major problems. Methanol powered fuel cells can replace the internal combustion engine may become obsolete in the future. However, the current technologies for on-board conversion of methanol to hydrogen is still in nascent stage and a lot of scope is available for improvement.

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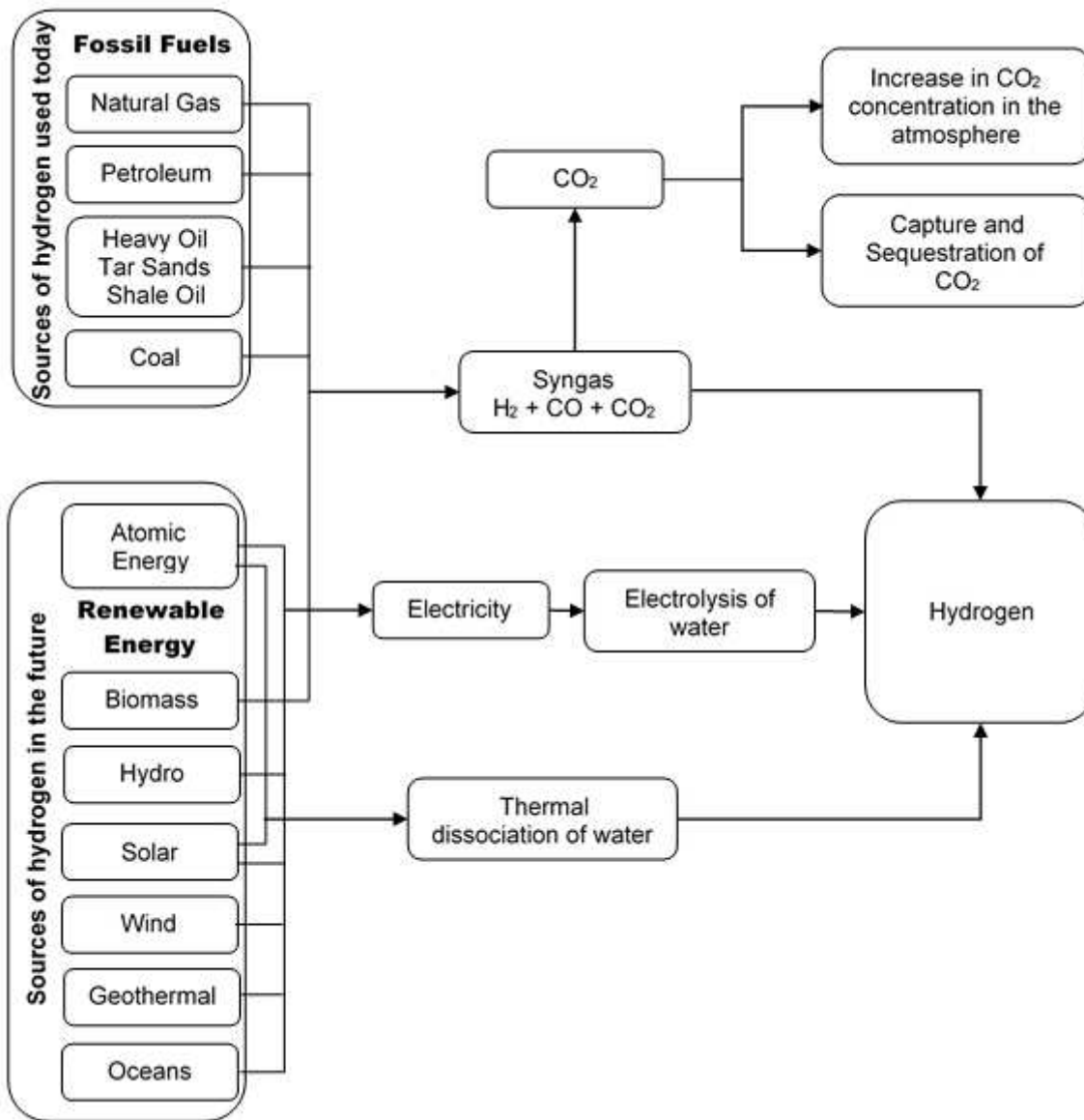
Figures

Figure 1

Different routes for hydrogen production (G. A. Olah et al., 2009)
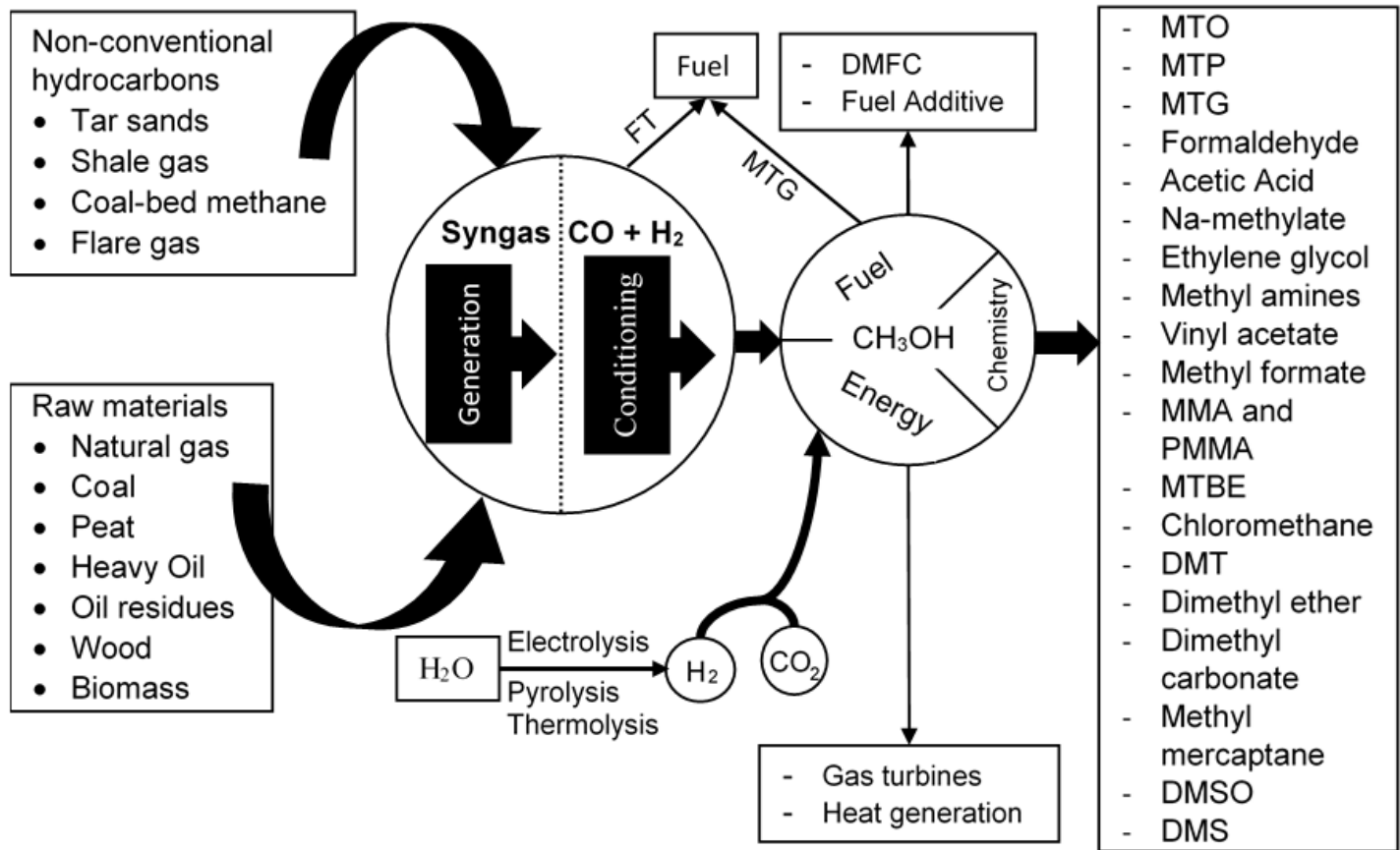
Figure 2

Raw materials to synthesis gas, methanol, fuels and chemicals. Abbreviations: FT-Fischer Tropsch Process, MTO-methanol to olefins, MTP- methanol to propylene, MTG-methanol to gasoline, DMFC-direct methanol fuel cell (Martin Bertau et al., 2014)
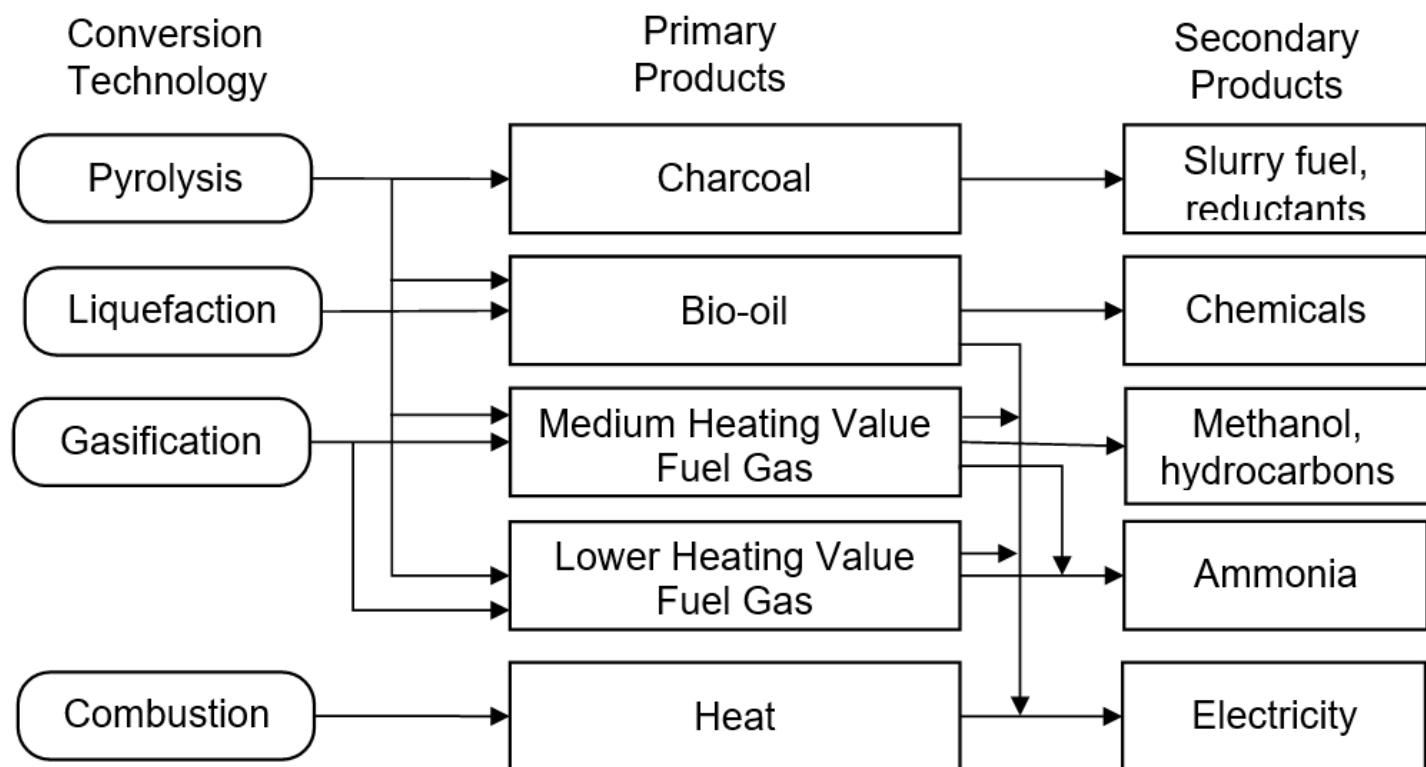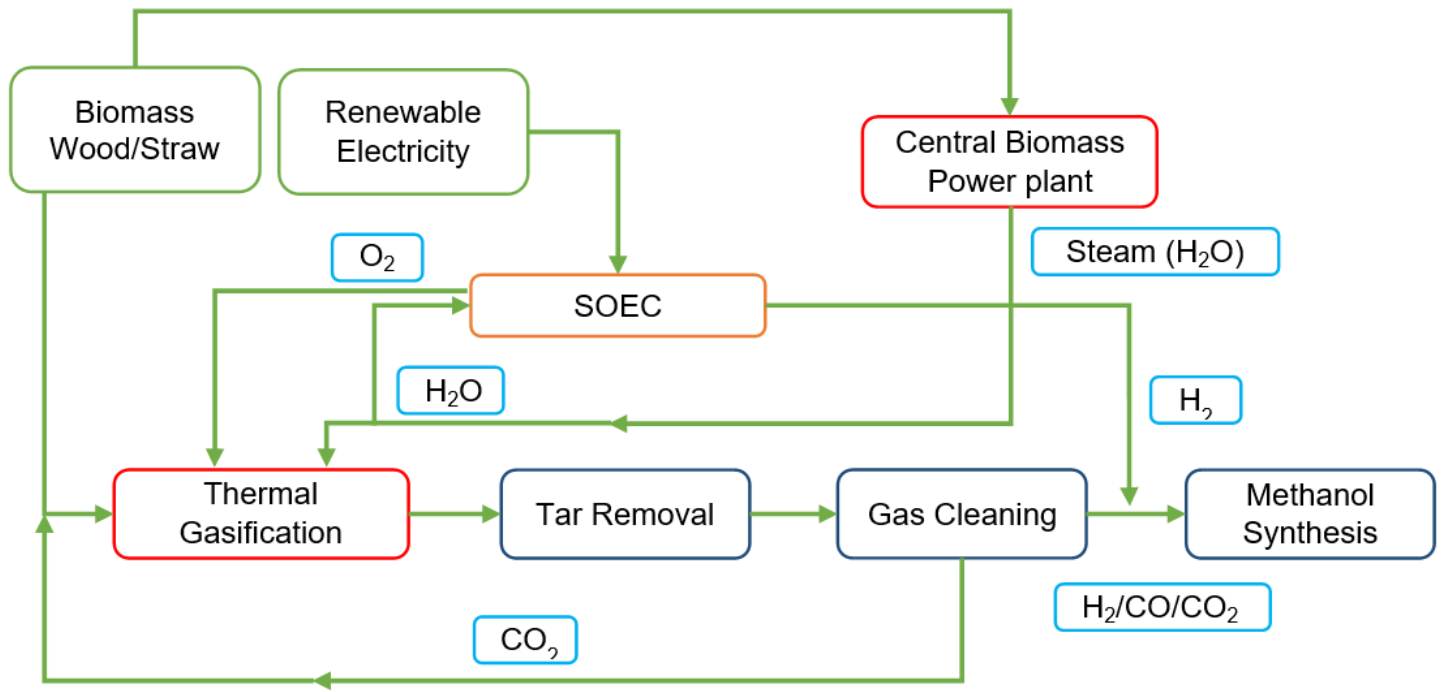
Figure 3

Products and their uses from the thermochemical conversion of biomass (Chmielniak & Sciazko, 2003)
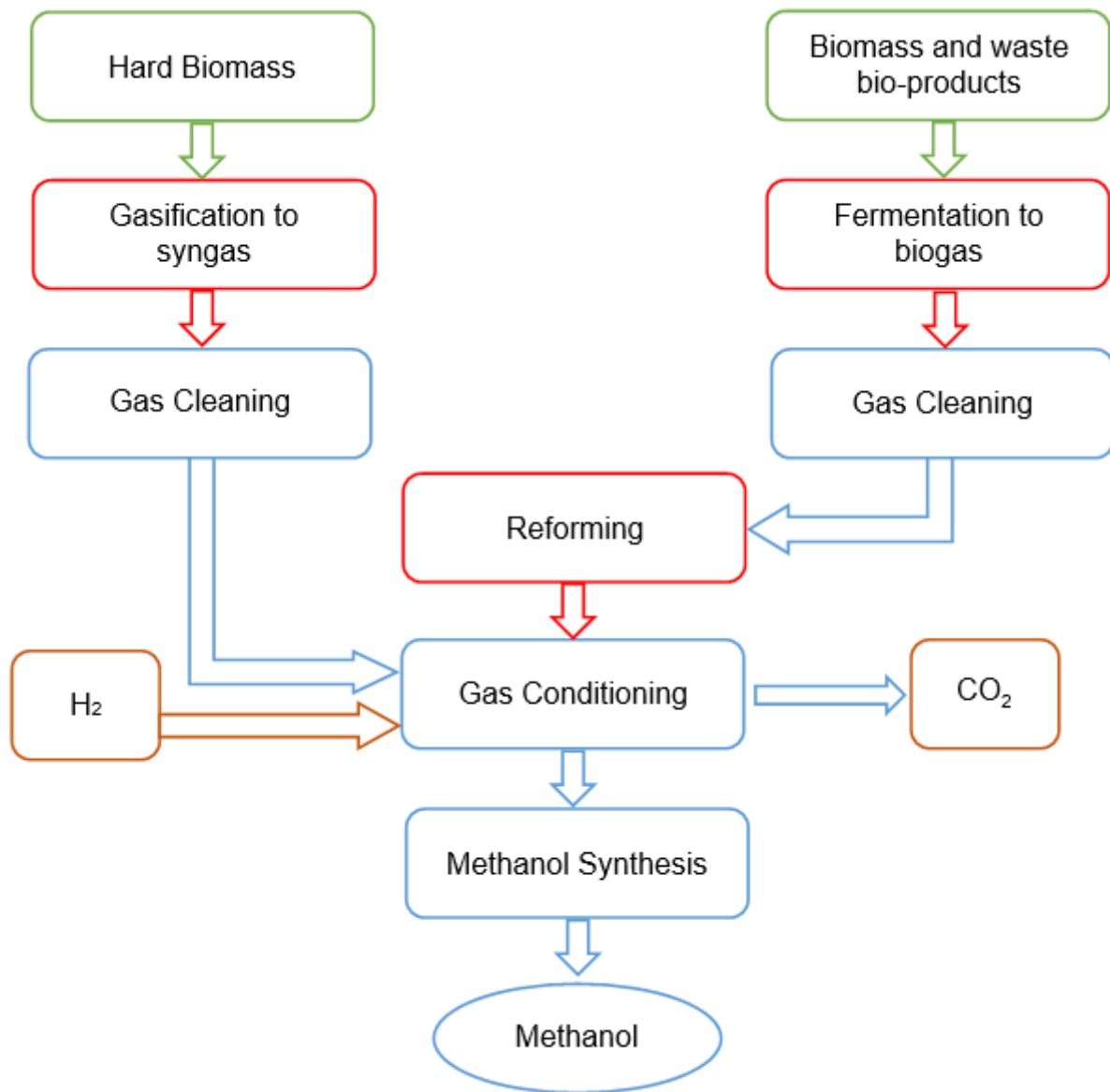
Figure 4

Schematic of methanol production from biomass (Alain Goeppert et al., 2014)

Figure 5

Synthesis of methanol using electrolysis assisted gasification of wood (Lebaek et al., 2011)
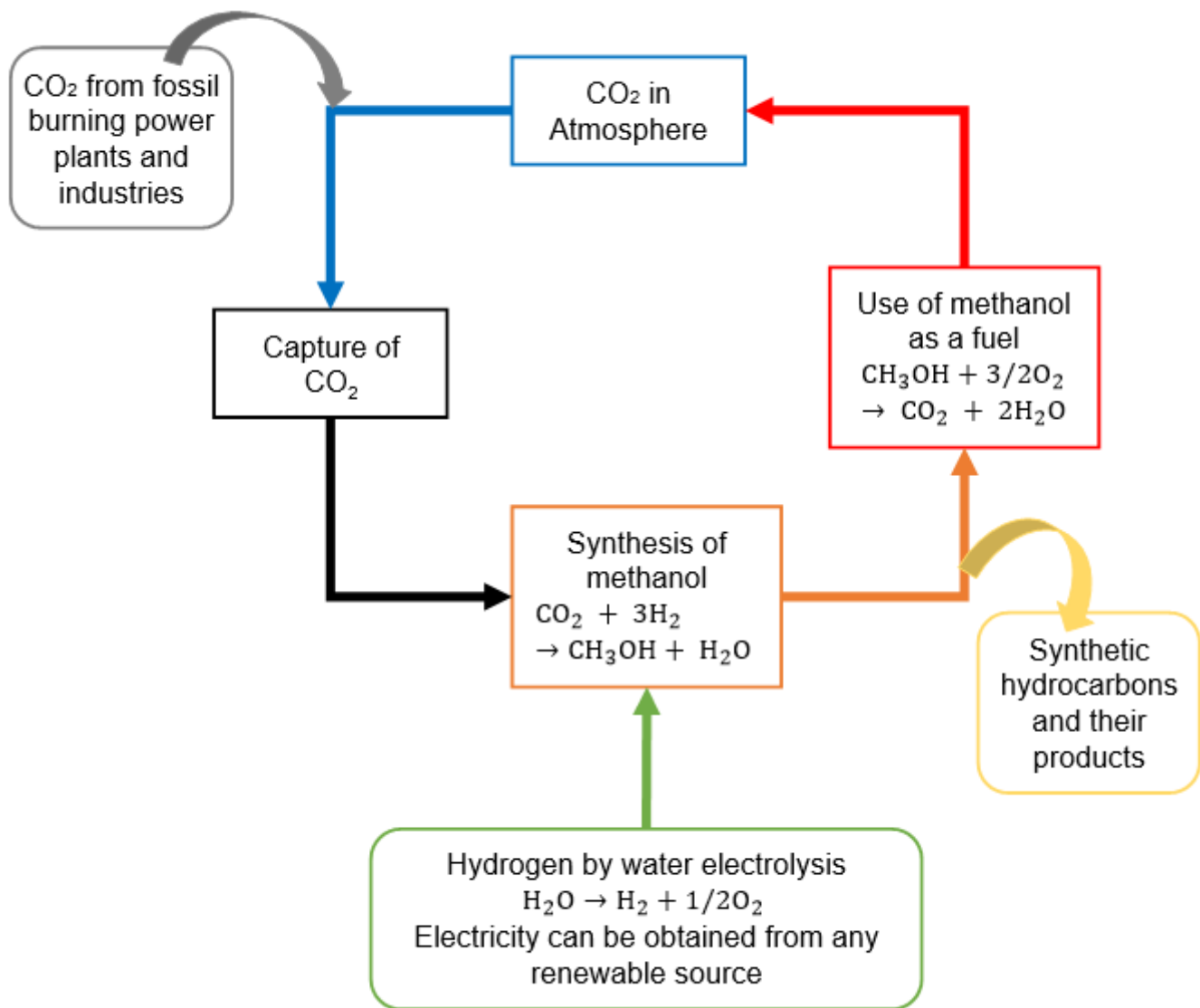
Figure 6

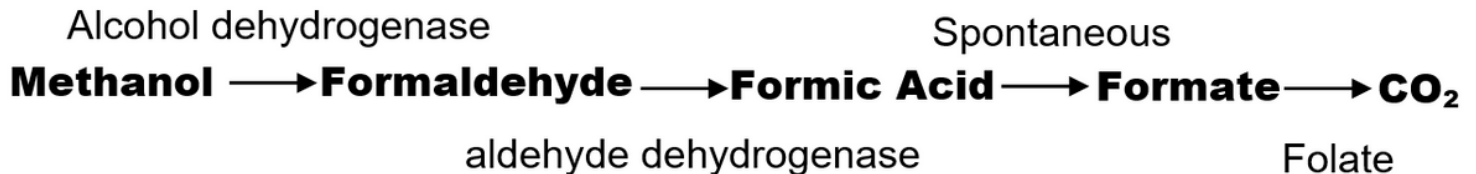Recycling of CO2 for production of methanol and synthetic hydrocarbon (G. A. Olah et al., 2009)

Figure 7

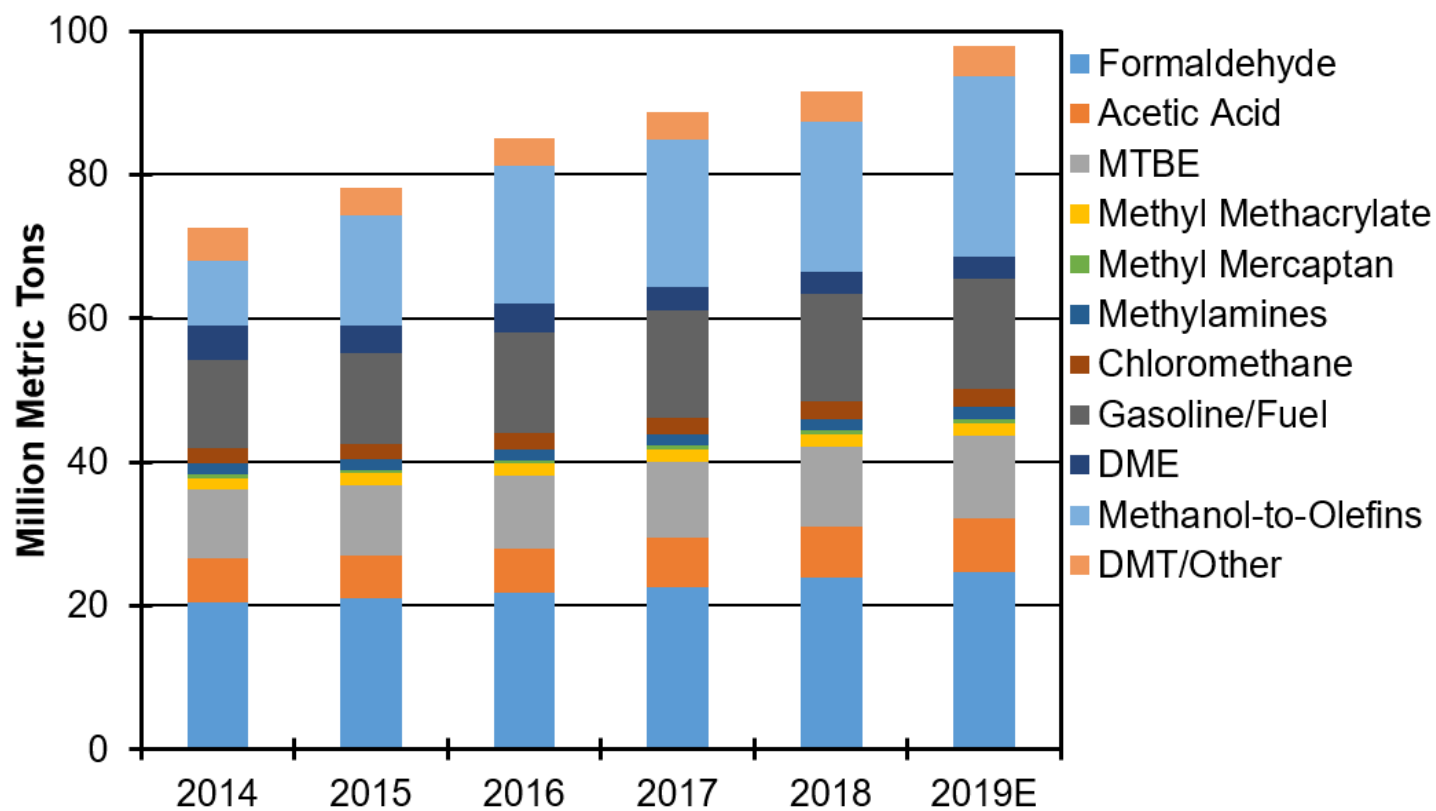Human metabolism of methanol (G. A. Olah et al., 2009)

Figure 8

Global methanol demand sector-wise (2019 data is estimated) (Methanol Institute, 2019)

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