

## PROCESSES FOR LIQUID BIOFUEL PRODUCTION FROM BIOMASS

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**ABSTRACT** – With the current declining petroleum resources, combined with increased demand for petroleum by emerging economies, and political and environmental concerns about fossil fuels, it is imperative to develop economical and energy efficient processes for the sustainable production of fuels. Plant biomass is the only current sustainable source of organic carbon, and biofuels derived from biomass, are the only current sustainable source of liquid fuels. The biomass resources are the organic matters in which the solar energy is stored in chemical bounds, and it represents the fourth largest primary energy resource in the world after coal, crude oil and gas. The purpose of this article is to discuss current methods and future possibilities for obtaining transportation fuels from biomass.

Biofuels generate significantly less greenhouse gas emissions than do fossil fuels and can even be greenhouse gas neutral if efficient methods for biofuels production are developed. This paper focuses on biomass conversion into fuel by reviewing the production, characteristics and current statuses of first and second generation fuels. The first generation biofuels seems to create some skepticism among scientists. The main disadvantage of first generation biofuels is the food-versus-fuel debate, one of the reasons for rising food prices is due to the increase in the production of these fuels. Therefore, lignocellulosic feedstock can offer the potential to provide novel biofuel. Second generation biofuels produced from plant biomass refers largely to lignocellulosic materials, as this makes up the majority of the cheap and abundant non food materials available from plants. However, for the time being, the production of such biofuels is not cost effective because there are a number of technical barriers that need to be overcome before their potential can be exploited. Biochemical and thermo chemical processes and their major steps involved during first and second generation biofuels production from biomass have been discussed in detail.

### INTRODUCTION

Today, transportation sector represents a major energy consumer and it is based primarily on a non-renewable fuel source: oil. The rapid worldwide increase in the consumption of fossil fuels in the twentieth century to meet energy demand, mostly by industrialized nations, suggests that the time is not too distant before depletion begins to adversely affect petroleum and natural gas reserves. This is expected to result in increased usage of alternative biomass energy resources [1]. Environmentally speaking, fuel combustion plays a major role in greenhouse gas (GHG) — and especially CO<sub>2</sub> — emissions. Against this backdrop of climate change and reliance on oil, there is a pressing need for the diversification of fuels in the transport sector in general, and for road transport, specifically [2].

The terminology "renewable carbon resource" for biomass is actually wrong because the earth's carbon is in a perpetual state of flux. Carbon is not consumed in the sense that it is no longer available in any form. Many reversible and irreversible chemical reactions occur in such a manner that the carbon cycle makes all forms of carbon, including fossil carbon resources, renewable. It is just a matter of time (even millions of years) that makes one form of carbon more renewable than another [1]. As time is a pressing issue, in order to supplement

energy reserves, we need fixed carbon-containing materials that renew themselves over a period of time short enough to make them continuously available in large quantities. Biomass is a major source of carbon that meets these requirements. If it comes from agriculture, forestry or from organic wastes, biomass can provide heat, electricity and transport fuels. It may also reduce green house gas emissions and contribute to European projects regarding renewable energy. The term biomass (Greek, bio, life+ maza or mass) refers to wood, short-rotation woody crops, agricultural wastes, short-rotation herbaceous species, wood wastes, bagasse, industrial residues, waste paper, municipal solid waste, sawdust, biosolids, grass, waste from food processing, aquatic plants and algae, animal wastes, and a host of other materials.

The most promising biofuels from biomass are biodiesel, bio-ethanol, pure vegetable oil and bio-methane and also second generation biofuels such as bio-hydrogen and Biomass-to-Liquid fuels. As biofuels are produced from biomass, the combustion of these biofuels principally is considered to be CO<sub>2</sub> neutral (this applies only for direct emissions from biofuel combustion). During the combustion process about the same amount of CO<sub>2</sub> is being set free, that has been bound from the atmosphere during photosynthesis and growth of the plants. Therefore the carbon cycle is closed. The emissions during the full life cycle of biofuels, from changes in land use to combustion of fuels, determine their impact on the climate. In modeling this complex calculation, estimates vary widely [3].

For first generation biofuels, feedstock type is still the main factor in the overall process cost. As feedstock prices varies in large limits, the same way varies the price of biofuels. Production of biofuels from crops such as corn and wheat (for ethanol), and soy and rape (for biodiesel) provides an additional product market for farmers and brings economic benefits to rural communities. But production of biofuels can also draw crops away from other uses (such as food production) and can increase their price. This may translate into higher prices for consumers [4]. On the other hand, second generation biofuels are still not produced on a commercial scale. Due to increased production costs, they are not yet competitive, however the technology evolves so they will play an important role in the future of biofuels. The main advantage of second-generation biofuels is the vast range of feedstock that can be used for biofuel production, as well as the reduced feedstock (e.g. cellulose crops) costs. All transport fuels may be classified in fossil fuels and biofuels or renewable fuels. In order to obtain these fuels, different types of feedstock are used. Different methods for producing fuels from biomass are shown in Figure 1.

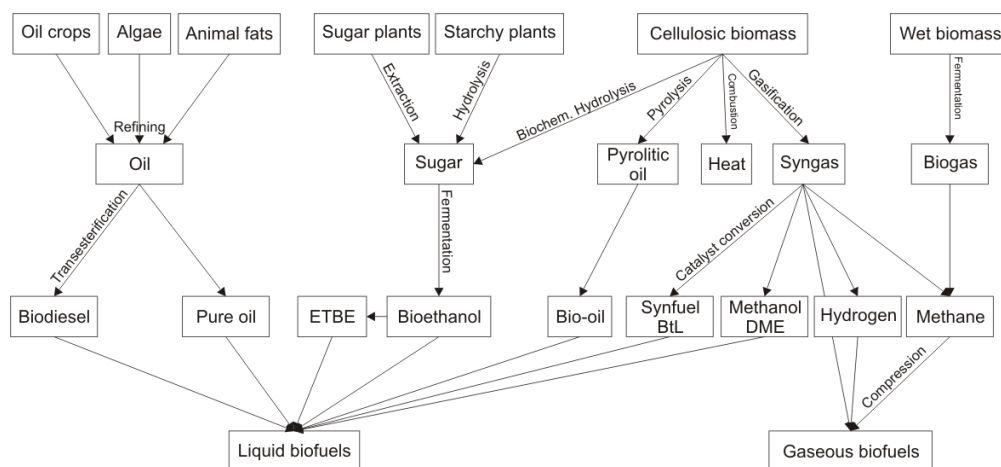


Figure.1 Biomass to biofuel processes

There is a wide variety of feedstock sources, biofuels, equipment and processes. Thus, crude oils and biodiesel can be obtained directly from oil crops, algae or animal fats. Bio-ethanol can be processed from sugar, starch or cellulose. Furthermore, biomass can be liquefied or gasified for obtaining syngas from which other liquid or gaseous fuels can be processed. This paper focuses on biomass conversion into liquid biofuels like biodiesel, bio-ethanol and derived syngas fuels by reviewing the production processes and fuel characteristics. Biochemical and thermo chemical processes and their main steps involved during first and second generation biofuels from biomass are discussed in detail.

## TRIGLYCERIDE CONVERSION

The major components of vegetable oils and animal fats are triacylglycerols (TAG; often called triglycerides). Chemically, triacylglycerols are esters of fatty acids with glycerol (1,2,3-propanetriol; glycerol is often called glycerin) [5]. Triglycerides, or fats and oils, are found in the plant and animal kingdom and consist of water insoluble, hydrophobic substances that are made up of one mole of glycerol and three moles of fatty acids [6]. Fatty acids are aliphatic, usually straight chain, mono carboxylic acids. The broadest definition includes all chain lengths, but most natural fatty acids have even chain lengths between C4 and C22, with C18 the most common. Around 20 fatty acids occur widely in nature; of these, palmitic, oleic, and linoleic acids make up ~80% of commodity oils and fats [7]. Figure 2 shows the basic structure of fatty acids. Fatty acids have a common basic structure: a long alkyl chain and a carboxylic acid group at one end.

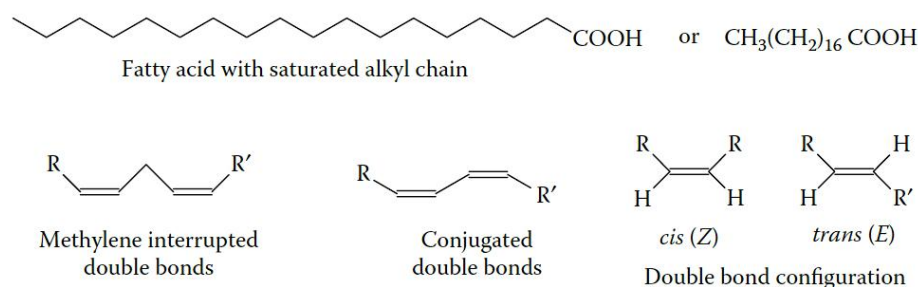


Figure 2 Fatty acids structure

The major reason that vegetable oils and animal fats are transesterified to alkylesters (biodiesel) is that the kinematic viscosity of the biodiesel is much closer to that of petrodiesel. The high viscosity of untransesterified oils and fats leads to operational problems in the diesel engine such as deposits on various engine parts [5]. Four methods to reduce high viscosity of vegetable oils have been investigated: transesterification, blending with petrodiesel, pyrolysis, and microemulsification.

### Transesterification

Transesterification is by far the most common method used to reduce vegetable oils viscosity and to produce biodiesel. Biodiesel is an alternative to diesel, made from renewable biological sources such as vegetable oils, animal fats, waste cooking oils or algae [8]. The fatty acid profile is the most important parameter influencing the corresponding properties of a vegetable oil. In order to obtain biodiesel, the vegetable oil must be subject of a chemical reaction called transesterification. In the transesterification reaction, the oil is reacted with an alcohol (ester), most common are ethanol or methanol, in the presence of a homogenous and heterogeneous catalyst (generally acid or base). The reaction is shown in Figure . After the

transesterification of triglycerides, the products are a mixture of esters, glycerol, alcohol, catalyst and tri-, di- and monoglycerides. To complete a transesterification stoichiometrically, a 3:1 molar ratio of alcohol to triglycerides is needed [9]. Di- and monoacylglycerols are formed as intermediates in this reaction. In homogenous catalysis, alkali catalysis (sodium or potassium hydroxide, or the corresponding alkoxides) is a much more rapid process than acid catalysis [5]. Glycerol, as a co-product, is separated by gravitational settling or centrifugation.

Transesterification can occur at different temperatures, depending on the oil used. The temperatures mentioned in the literature ranges between 20 and 120 °C and it clearly influence the reaction rate and yields of esters [9].

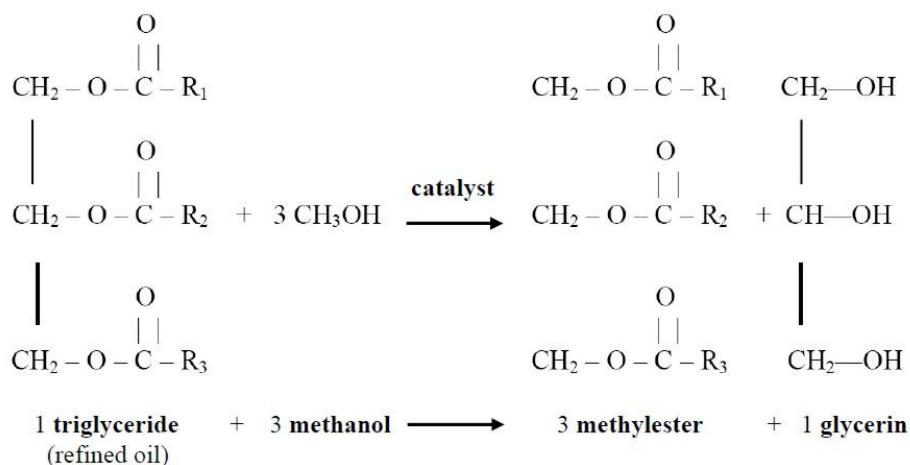


Figure 3. Transesterification of triglycerides with alcohol.

Important properties of biodiesel that are directly influenced by fatty ester composition and the presence of contaminants and minor components include low-temperature operability, oxidative and storage stability, kinematic viscosity, exhaust emissions, cetane number, and energy content [10]. Table 1 lists some selected properties of biodiesel compared to those of no. 2 Diesel Fuel.

Table 1 Biodiesel properties (Adapted from [11])

Fuel property	Biodiesel	No. 2 Diesel Fuel
Chemical formula	Vegetable oil C <sub>18</sub> to C <sub>19</sub> FAME C <sub>12</sub> to C <sub>22</sub>	C <sub>8</sub> to C <sub>25</sub>
Composition, [Weight %]		
Carbon	78-81	84-87
Hydrogen	11-12	13-16
Oxygen	11-7	0
Density [kg/dm <sup>3</sup> ]	0,864-0,900	0,81-0,89
Lower heating value [MJ/m <sup>3</sup> ]	32-37	35-37
Energy content [MJ/dm <sup>3</sup> ]	32,8	35,7
Viscosity [mPa·s, 20°C]	3,5-5,0	2-4,5
Stoichiometric Air-Fuel ratio [Nm <sup>3</sup> /Nm <sup>3</sup> ]	13,8	14,7
Cetane number [CC]	52-63	45-55
Autoignition point [°C]	93-130	38-52

The fatty ester composition, along with the presence of contaminants and minor components, dictates the fuel properties of biodiesel fuel. Because each feedstock has a unique chemical composition; biodiesel produced from different feedstocks will in turn have different fuel properties.

### Blending with petrodiesel

This method consist in using pure vegetable oils or mixed with petrodiesel, in different proportion. Direct using of vegetable oils in diesel engines has generally been considered to be not satisfactory and impractical for both direct and indirect diesel engines [12]. The energy consumption by using pure vegetable oils was similar to that of petrodiesel. The high viscosity, free fatty acid content, gum formation due to oxidation, carbon deposits and lubricating oil thickening are obvious problems [9].

### Pyrolysis

Pyrolysis is defined as conversion of one substance to another by thermal treatment like heating in absence of air or oxygen in the temperature range of 450-850 °C. In some situations, the process goes on in the presence of a catalyst to easily break down molecular chains into smaller molecules. Catalysts involved in pyrolysis processes are: SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. The easy compound/heavy compound ratio is dependent of time and temperature. It is also to be mentioned that pyrolysis equipment is expensive [12]. Table 2 shows main fuel properties of pyrolysed soybean oil.

Table 2 Fuel properties of pyrolysed soybean oil. [9]

Fuel properties	Soybean oil		Cracked soybean oil		Diesel fuel	
	1	2	1	2	1	2
Cetane number [CC]	38.0	37.9	43.0	43.0	51.0	40.0
Higher heating value [MJ/Kg]	39.3	39.6	40.6	40.3	45.6	45.5
Pour point [°C]	-12.2	-12.2	4.4	7.2	-6.7	-6.7
Viscosity [cSt, 37.8 °C]	32.6	32.6	7.74	10.2	2.82	1.9-4.1

### Microemulsions

Microemulsions are defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions mainly in the range of 1-150 nm, formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles [13]. Microemulsions are used to solve problems regarding pure oil viscosity using solvents like simple alcohols. Performances of both ionic and non-ionic microemulsions are similar to those of classic diesel fuel, at a shorttesting time. Good spray characteristics were observed, with explosive vaporization which increased combustion characteristics. After a longer testing time there was no significant characteristics decrease, but some problems are mentioned: significant deposits on the injector, carbon deposits, incomplete combustions, and an increase of lubricating oil viscosity [12].

## BIO-ETHANOL PRODUCTION

Ethanol is a versatile transportation fuel and fuel additive. It can be used directly as a fuel or blended with gasoline in proportion of 10% US and 5.75% in Europe. Because ethanol has a higher octane than gasoline, it also boosts the octane of the blend, reducing the need to use

toxic additives such as benzene. Moreover, ethanol provides oxygen to the fuel, reducing tailpipe emissions of CO and unburned hydrocarbons [14].

A wide variety of feedstocks containing carbohydrates are used for production of bioethanol by fermentation process. These raw materials are classified in three major categories:

- sugar containing plants: sugar cane, sugar beet, wheat, fruits, palm juice, etc.;
- starch containing plants: grain crops like wheat, barley, rice, corn, sweet sorgum, etc.;
- cellulosic biomass: agricultural residues, forestry residues, fibers, energy crops.

Ethanol production is usually obtained via fermentation of sugar, enzymatic hydrolysis for starch containing crops and hydrolysis and fermentation for lignocellulosic biomass.

### Starch and Sugar-Based Ethanol

There are three basic steps that need to occur in the production of ethanol from starch and sugar products:

- the formation of a solution of fermentable sugars;
- the fermentation of sugars to ethanol; and
- the separation of ethanol by distillation.

Sugar derived from biomass is a mixture of hexoses (primarily glucose) and pentoses (primarily xylose) and most wild-type strains of *S. cerevisiae* do not metabolize xylose [15]. Starch or amyllum is a carbohydrate (storage compound) consisting of a large number of glucose units linked via  $\alpha$ -1,4 and  $\alpha$ -1,6 glycosidic linkages (amylose and amylopectin). This polysaccharides produced by all green plants as an energy store. Pure starch is a white, tasteless and odorless powder that is insoluble in cold water or alcohol. It consists of two types of molecules: the linear and helical amylose and the branched amylopectin. Depending on the plant, starch generally contains 20 to 25% amylose and 75 to 80% amylopectin [16].

The starch grain is prepared for ethanol fermentation by either wet milling or dry grinding. The term *fermentation* can generally be defined as the metabolic process in which an organic substrate goes under chemical changes due to activities of enzymes secreted by micro-organisms. There are two types of fermentation: aerobic and anaerobic depending upon oxygen needed in the process or not. The organisms used for sugar fermentation into bioethanol are classified in: yeast, bacteria and mold. These organisms differs in their fermentation characteristics. The general reaction of glucose fermentation is presented in the following equation:  $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$ .

Under anaerobic conditions, yeast convert glucose to ethanol. The maximum theoretical conversion efficiency of this reaction is 51% on the weight basis, and this comes from a stoichiometric calculation of:  $2 \times (\text{molecular wt. of ethanol}) / (\text{molecular wt. of glucose}) \times 100 = 51$ . In practice, the ethanol fermentation efficiency is about 46%, i.e. 1000kg of fermentable sugar produce about 583 lit. of pure ethanol [8].

### Dry Mill Process

In the dry-milling process for ethanol production, the feedstock is first ground into flour and water is added to create a mash. The mash is then cooked and made to undergo a chemical reaction to create fermentable sugars. After the grain products have been processed through wet or dry milling to create six-carbon sugars, fermentation occurs. In this step, yeast cells are

added to the sugar solution to form ethanol and carbon dioxide. As the yeast cells convert the sugars into ethanol, CO<sub>2</sub> is produced and must be vented off continuously. Fermentation is complete when CO<sub>2</sub> is no longer produced. The resulting mixture is called “beer.” Distillation is the process by which ethanol is separated from the beer mixture. Ethanol vaporizes at a lower temperature than water. Therefore, when the mixture is heated, the ethanol vapors are released from the mixture. The collected ethanol is about 95 percent pure. However, in order for ethanol to be sold as fuel, it must be anhydrous, or 100 percent pure ethanol. A dehydration process further isolates the ethanol in order to create pure ethanol.

#### Cellulosic Ethanol

Cellulosic biomass ethanol technology converts agricultural waste, wood waste, and even some types of municipal solid waste into ethanol. Plants use solar energy to combine carbon dioxide and water forming a sugar building block (CH<sub>2</sub>O)<sub>n</sub> and oxygen. The sugar is stored in a polymer form as cellulose, starch, or hemicellulose [6].

In general, cellulosic feedstock is converted to ethanol through processes that are very similar to those used in traditional ethanol production. Sugars must be formed from the cellulosic material as a first step, then, these sugars can be fermented and distilled into ethanol. Biomass feedstock must be prepared before it can be converted into fermentable sugars. After the material is pretreated using physical, chemical, or biological methods, it is converted to fermentable sugars using a hydrolysis procedure. The most promising of these is enzymatic hydrolysis. The process uses the enzyme cellulase, instead of sulfuric acid, to convert the feedstock to sugars. By combining cellulase and yeast, the sugars are produced and fermented in the same step. After the hydrolysis process is complete, like in the starch-based ethanol production process, the sugars are fermented into ethanol. Table 3 shows most important properties for fuel ethanol comparative with those of gasoline.

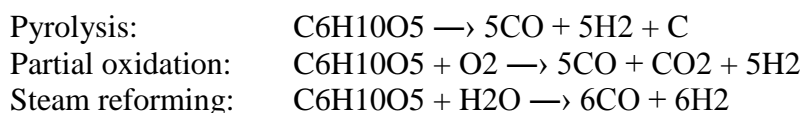
Table 3 Fuel ethanol properties (Adapted from [11])

<b>Fuel property</b>	<b>Ethanol</b>	<b>Gasoline</b>
Chemical formula	C <sub>2</sub> H <sub>5</sub> OH	C <sub>4</sub> to C <sub>12</sub>
Composition %		
- Carbon	52,2	85-88
- Hydrogen	13,1	12-15
- Oxygen	34,7	0-4
Density [kg/dm <sup>3</sup> , 15/15 °C]	0,79	0,69-0,79
Boiling point, [°C]	78	27-225
Vapor pressure, [kPa at 38 °C]	15,9	48-103
Specific heat, [kJ/kg – K]	2,4	2,0
Latent heat of vaporisation, [kJ/kg]	923	349
Lower heating value, [MJ/dm <sup>3</sup> ]	21,1	30-33
Flash point, [°C]	13	-43
Autoignition temperature, [°C]	423	257
Stoichiometric Air-Fuel ratio	9,00	14,7
Octane number - Research	108,6	88-100
- Motor	89,7	80-90

## SYNGAS AND SYNGAS DERIVED FUELS

In thermochemical conversion, the entire biomass is converted into gases, which are then synthesized into the desired chemicals or used directly [17]. Syngas is the name given to a gas mixture containing different quantities of CO and H<sub>2</sub>. The name comes from its uses as an intermediate in producing Synthetic Natural Gas – SNG. Methods for producing syngas includes: steam reforming of natural gas or liquid hydrocarbons to produce hydrogen, coal, biomass or waste gasification. Gasification can use materials with no other application such as biomass and organic wastes. Moreover, combustion at high temperatures removes corrosive ash like chlorine and potassium, allowing a purified gas to be produced [17].

Normally, there are three main gasification types for biomass: pyrolysis, partial oxidation and steam reforming. Under ideal conditions, gases obtained after biomass gasification by pyrolysis, partial oxidation or steam reforming are carbon monoxide and hydrogen. Cellulose conversion as feedstock is done based on following relations:



Gas energy content after biomass gasification may vary from low (3,92 – 11,78 MJ/m<sup>3</sup>), medium (11,78 – 27,48 MJ/m<sup>3</sup>) and high (27,48 – 39,26 MJ/m<sup>3</sup>) [1]. Biomass gasification chemistry is similar with that of coal, in the sense that both processes have as result a mixture of same essential gases. Thermodynamic equilibrium of specific gases concentrations in the mixture depends on the amount of carbon, hydrogen and oxygen, temperature and pressure.

Pyrolysis represents the thermal decomposition of biomass, and primary products resulting after the process are gas, oil, tar and water [6]. Many of the conversion processes can be classified as partial oxidation processes in which biomass needs less than the stoichiometric amount of oxygen for a complete combustion. In some gasification units, air is mixed with steam for the whole process to take place through steam-carbon reactions to form hydrogen and carbon monoxide.

Table 4 Comparison of four major thermochemical conversion processes [17].

Process	Temperature [°C]	Pressure [MPa]	Catalyst	Drying
Liquefaction	250-330	5-20	Essential	Not required
Pyrolysis	380-530	0.1-0.5	Not required	Necessary
Combustion	700-1400	>0.1	Not required	Not essential, but may help
Gasification	500-1300	>0.1	Not essential	Necessary

Table 4 compares the four major biomass thermochemical conversion processes. It also shows the typical range of their reaction temperatures.

Figure 4 shows routes for transportation fuels and chemicals production from syngas. The fuels produced from syngas include hydrogen by the water gas-shift reaction, methanol by methanol synthesis, alkanes by Fischer-Tropsch Synthesis, isobutane by isosynthesis, ethanol by fermentation, or with homogeneous catalysts and aldehydes or alcohols by oxosynthesis.



Methanol is a platform chemical used to produce a range of other chemicals and fuels including olefins, gasoline, dimethyl ether, methyl tert-butyl ether, acetic acid, and formaldehyde [6].

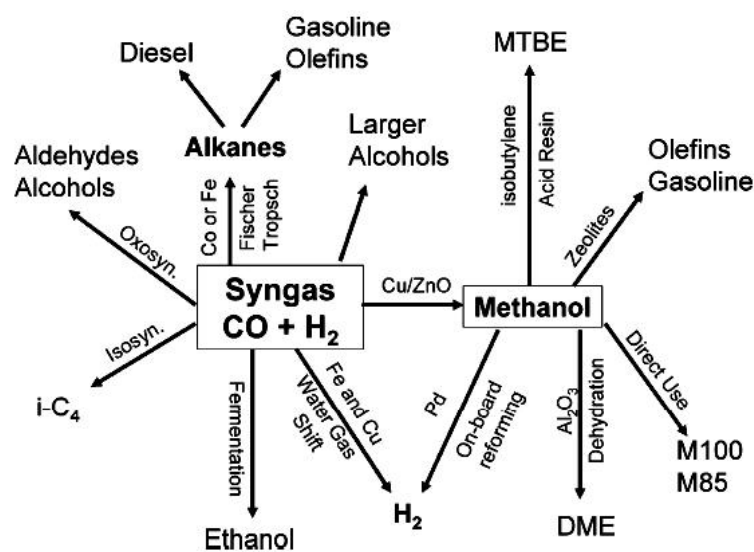


Figure 4. Syngas derived fuels (from [18])

## CONCLUSION

The EU road transport sector accounts for more than 30% of the total energy consumption in the Community. It is 98% dependent on fossil fuels with the crude oil feedstock being largely imported and thus extremely vulnerable to oil market disturbance. It is expected that 90% of the increase of CO<sub>2</sub> emissions between 1990 and 2010 will be attributable to transport [19].

Internal combustion engines will continue to be the dominant transport technology available in 2030, using mostly liquid fuels produced from both fossil and renewable sources. Biodiesel, ethanol and syngas derived fuels provide the best option to replace fossil fuels in the transportation industry. The composition of biodiesel may not be exactly the same as their equivalence from petroleum, but they perform the same task. Ethanol derived from biomass is either used as the sole fuel or mixed with gasoline in spark ignition engines. The bulky and inconvenient form of biomass is a major barrier to a rapid shift from fossil to biomass fuels. Unlike gas or liquid, biomass cannot be handled, stored, or transported easily, especially in its use in transportation. This provides a major motivation for the conversion of solid biomass into liquid or gaseous fuels. Pilot scale units prove the feasibility of the main fuels produced from biomass, either by biochemical or thermochemical routes.

Between 2000 and 2030, energy demand for passenger transport will increase by 14%, whereas freight transport will increase by 74%. Based on this growth, the study predicts a strong increase in the need for middle distillate fuels for transportation, diesel fuel mainly for road transport, and kerosene for aviation. The demand for diesel fuel is forecast to grow by 51% from 2000 to 2030, due to the strongly growing need for freight transport services and an increasing number of diesel passenger cars. Gasoline consumption, on the other hand, is expected to even shrink in the last decade of the time period. For kerosene, an increase of nearly 60% has to be expected [19]. Processes and equipment, used in biomass conversion to biofuels, are subject of continuous technological developments, so nothing ends here.

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