Progress and recent trends in biofuels

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Abstract

In this paper, the modern biomass-based transportation fuels such as fuels from Fischer–Tropsch synthesis, bioethanol, fatty acid (m)ethylester, biomethanol, and biohydrogen are briefly reviewed. Here, the term biofuel is referred to as liquid or gaseous fuels for the transport sector that are predominantly produced from biomass. There are several reasons for biofuels to be considered as relevant technologies by both developing and industrialized countries. They include energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector. The term modern biomass is generally used to describe the traditional biomass use through the efficient and clean combustion technologies and sustained supply of biomass resources, environmentally sound and competitive fuels, heat and electricity using modern conversion technologies. Modern biomass can be used for the generation of electricity and heat. Bioethanol and biodiesel as well as diesel produced from biomass by Fischer–Tropsch synthesis are the most modern biomass-based transportation fuels. Bio-ethanol is a petrol additive/substitute. It is possible that wood, straw and even household wastes may be economically converted to bio-ethanol. Bio-ethanol is derived from alcoholic fermentation of sucrose or simple sugars, which are produced from biomass by hydrolysis process. Currently crops generating starch, sugar or oil are the basis for transport fuel production. There has been renewed interest in the use of vegetable oils for making biodiesel due to its less polluting and renewable nature as against the conventional petroleum diesel fuel. Biodiesel is a renewable replacement to petroleum-based diesel. Biomass energy conversion facilities are important for obtaining bio-oil. Pyrolysis is the most important process among the thermal conversion processes of biomass. Brief summaries of the basic concepts involved in the thermochemical conversions of biomass fuels are presented. The percentage share of biomass was 62.1% of the total renewable energy sources in 1995. The reduction of greenhouse gases pollution is the main advantage of utilizing biomass energy.

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Keywords: Fischer–Tropsch synthesis; Steam reforming; Biohydrogen; Bio(m)ethanol; Biodiesel; Bio-oil

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1. Introduction

The term bio-fuel is referred to as liquid or gaseous fuels for the transport sector that are predominantly produced from biomass. Bio-fuels are generally considered as offering many priorities, including sustainability, reduction of greenhouse gas emissions, regional development, social structure and agriculture, security of supply [1]. Worldwide energy consumption has increased 17 fold in the last century and emissions of CO₂, SO₂ and NOₓ from fossil-fuel combustion are primary causes of atmospheric pollution [2]. Known petroleum reserves are estimated to be depleted in less than 50 years at the present rate of consumption [3]. In developed countries there is a growing trend towards employing modern technologies and efficient bio-energy conversion using a range of bio-fuels, which are becoming cost-wise competitive with fossil fuels [4].

Biomass has been recognized as a major world renewable energy source to supplement declining fossil fuel resources [5,6]. Biomass appears to be an attractive feedstock for three main reasons. First, it is a renewable resource that could be sustainably developed in the future. Second, it appears to have formidably positive environmental properties resulting in no net releases of carbon dioxide (CO₂) and very low sulfur content. Third, it appears to have significant economic potential provided that fossil fuel prices increase in the future [7]. Lignocellulosic bio-methanol have such low emissions because the carbon content of the alcohol is primarily derived from carbon that was sequestered in the growing of the bio-feedstock and is only being re-released into the atmosphere [8].

Transport sector is major consumer of petroleum fuels such as diesel, gasoline, liquefied petroleum gas (LPG) and compressed natural gas (CNG). This sector is likely to suffer badly because of following reasons: (a) Prices of petroleum in global market are raising trend; (b) Petroleum reserves are limited and it is monopoly of some oil-importing countries and rest of the world depends on them; (c) Number of vehicles based on petroleum fuels is on increase worldwide. Many research programs recently focus on the development of concepts such as renewable resources, sustainable development, green energy, eco-friendly process, etc. in the transportation sector. In developed countries there is a growing trend towards employing modern technologies and efficient bio-energy conversion using a range of biofuels, which are becoming cost-wise competitive with fossil fuels [9]. Advantages of bio-fuels are the following: (a) Bio-fuels are easily available from common biomass sources; (b) They are represent a CO₂ cycle in combustion; (c) Bio-fuels have a considerable environmentally friendly potential; (d) There are many benefits the environment, economy and consumers in using bio-fuels; and (e) They are biodegradable and contribute to sustainability [10].

Currently, biomass converts to bio-oil by fast pyrolysis and then the bio-oil converts to hydrogen (H₂) by catalytic steam reforming [11–13]. The yield of H₂ that can be produced from biomass is relatively low, 16–18% based on dry biomass weight [14]. Only the carbohydrate-derived bio-oil fraction produced from biomass undergoes reforming. At present, the amount of biomass-derived bio-oil available for reforming is rather limited, but a viable way to increase the production of H₂ in a biomass-based plant could be co-reforming of bio-oil with natural gas [15]. If the purpose were to maximize the yield of liquid products resulting from biomass pyrolysis, a low temperature, high heating rate, short gas residence time process would be required. If the purpose were to maximize the yield of fuel gas resulting from biomass pyrolysis, a high temperature, low heating rate, long gas residence time process would be preferred [16].

The Fischer–Tropsch Synthesis (FTS) produces hydrocarbons of different length from a gas mixture of H₂ and CO (syngas) from biomass gasification called as bio-syngas. The fundamental reactions of synthesis gas chemistry are methanol synthesis,
FTS, oxo synthesis (hydroformylation), and methane (CH₄) synthesis [17]. The FTS process is a process capable of producing liquid hydrocarbon fuels from bio-syngas. The large hydrocarbons can be hydrocracked to form mainly diesel of excellent quality. The process for producing liquid fuels from biomass, which integrates biomass gasification with FTS, converts a renewable feedstock into a clean fuel.

The products from FTS are mainly aliphatic straight-chain hydrocarbons (CₓHᵧ). Besides the CₓHᵧ also branched hydrocarbons, unsaturated hydrocarbons, and primary alcohols are formed in minor quantities. The product distribution obtained from FTS includes the light hydrocarbons CH₄, ethene (C₂H₄) and ethane (C₂H₆), LPG (C₃–C₄, propane and butane), gasoline (C₅–C₁₂), diesel fuel (C₁₃–C₂₂), and light and waxes (C₂₃–C₃₃). The distribution of the products depends on the catalyst and the process parameters such as temperature, pressure, and residence time. The FTS was extensively investigated by many researchers [17–22].

Vegetable oils from renewable oil seeds can be used when mixed with diesel fuels. Pure vegetable oil, however, cannot be used in direct-injection diesel engines, such as those regularly used in standard tractors, since the vegetable oil cooking occurs after several hours of use. Conversion of the vegetable oils and animal fats into biodiesel has been undergoing further development over the past several years [23–28]. Biodiesel represents an alternative to petroleum-based diesel fuel. Chemically speaking, biodiesel is a mixture of mono-alkyl esters of fatty acids, most often obtained from extracted plant oils and/or collected animal fats. Commonly accepted biodiesel raw materials include the oils from soy, canola, corn, rapeseed, and palm. New plant oils that are under consideration include mustard seed, peanut, sunflower, and cottonseed. The most commonly considered animal fats include those derived from poultry, beef, and pork [29].

Ethanol is the most widely used liquid biofuel. It is an alcohol and is fermented from sugars, starches or from cellululosic biomass. Most commercial production of ethanol is from sugar cane or sugar beet, as starches and cellululosic biomass usually require expensive pretreatment. It is used as a renewable energy fuel source as well as being used for manufacture of cosmetics, pharmaceuticals and also for the production of alcoholic beverages. Ethyl alcohol is not only the oldest synthetic organic chemical used by man, but it is also one of the most important. In an earlier study [30], physiological effects of inhibitors on ethanol from lignocellulosic materials and fermentation strategies were comprehensively investigated.

2. Global biofuel scenarios

Renewable resources are more evenly distributed than fossil and nuclear resources, and energy flows from renewable resources are more than three orders of magnitude higher than current global energy use. Today's energy system is unsustainable because of equity issues as well as environmental, economic, and geopolitical concerns that have implications far into the future [31].

According to International Energy Agency (IEA), scenarios developed for the USA and the EU indicate that near-term targets of up to 6% displacement of petroleum fuels with biofuels appear feasible using conventional biofuels, given available cropland. A 5% displacement of gasoline in the EU requires about 5% of available cropland to produce ethanol while in the USA 8% is required. A 5% displacement of diesel requires 13% of USA cropland, 15% in the EU [32].

The dwindling fossil fuel sources and the increasing dependency of the USA on imported crude oil have led to a major interest in expanding the use of bio-energy. The recent commitment by the USA government to increase bio-energy three-fold in 10 years has added impetus to the search for viable biofuels. The EU have also adopted a proposal for a directive on the promotion of the use of bio-fuels with measures ensuring that bio-fuels account for at least 2% of the market for gasoline and diesel sold as transport fuel by the end of 2005, increasing in stages to a minimum of 5.75% by the end of 2010 [33]. Fig. 1 shows main biomass conversion processes. Fig. 2 shows resources of main liquid biofuels for automotives. Fig. 3 shows the shares of alternative fuels compared to the total automotive fuel consumption in the world as a futuristic view.

3. Biohydrogen from biomass by steam reforming

Biomass is a mixture of structural constituents (hemicelluloses, cellulose and lignin) and minor amounts of extractives which each pyrolyze at different rates and by different mechanisms and pathways. All biomass materials can be converted to energy via thermochemical and biological processes. Biomass gasification has attracted the
highest interest among the thermochemical conversion technologies as it offers higher efficiencies in relation to combustion, whereas flash pyrolysis is still in the development stage [34]. It is believed that as the reaction progresses the carbon becomes less reactive and forms stable chemical structures, and consequently the activation energy increases as the conversion level of biomass increases [35].

Biomass gasification can be considered as a form of pyrolysis, which takes place in higher temperatures and produces a mixture of gases with H$_2$ content ranging 6–6.5% [36,37]. H$_2$ can be produced from biomass via two thermochemical processes: (1) gasification followed by reforming of the syngas, and (2) fast pyrolysis followed by reforming of the carbohydrate fraction of the bio-oil. In each process, water–gas shift (WGS) is used to convert the reformed gas into H$_2$, and pressure swing adsorption is used to purify the product.

Power generation from gaseous products from biomass gasification is found to be the most promising biomass gasification technology. Gasification technologies provide the opportunity to convert renewable biomass feedstocks into clean fuel gases or synthesis gases. The synthesis gas includes mainly H$_2$ and carbon monoxide (CO) which is also called as syngas. Bio-syngas is a gas rich in CO and H$_2$ obtained by gasification of biomass [38].
Currently, H₂ is most economically produced from natural gas. The most studied technology for H₂ production is steam-CH₄ reforming, in which CH₄ reacts with steam to produce a mixture of H₂, CO₂ and CO.

3.1. Steam-reforming process

In the steam-reforming reaction, steam reacts with hydrocarbons in the feed to predominantly produce CO and H₂, commonly called synthesis gas. Steam reforming can be applied various solid waste materials including, municipal organic waste, waste oil, sewage sludge, paper mill sludge, black liquor, refuse-derived fuel, and agricultural waste. Steam reforming of natural gas, sometimes referred to as steam CH₄ reforming is the most common method of producing commercial bulk H₂. Steam reforming of natural gas is currently the least expensive method of producing H₂, and used for about half of the world’s production of H₂.

H₂ production from carbonaceous solid wastes requires multiple catalytic reaction steps: For the production of high purity H₂, the reforming of fuels is followed by two water gas-shift reaction steps, a final CO purification and CO₂ removal. Steam reforming, partial oxidation and autothermal reforming of CH₄ are well-developed processes for the production of H₂. Stepwise steam reforming of CH₄ for production of CO-free H₂ has been investigated at various process conditions by Choudhary and Goodman [39]. The process consists of two steps involving the decomposition of CH₄ to CO-free H₂ and surface carbon in the first step followed by steam gasification of this surface carbon in the second step. The amount of CO-free H₂ formed in the first step. The mixture of gases can be separated and CH₄-rich gas mixture returned to the first step [39]. Steam, at high temperatures (975–1375 K) is mixed with CH₄ gas in a reactor with a Ni-based catalyst at 3–25 bar pressure to yield CO and H₂. Steam reforming is the process by which CH₄ and other hydrocarbons in natural gas are converted into H₂ and CO by reaction with steam over a nickel catalyst on a ceramic support. The H₂ and CO are used as initial material for other industrial processes.

\[
\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2 \quad \Delta H = +251 \text{ kJ/mol.} \tag{1}
\]

It is usually followed by the shift reaction:

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \quad \Delta H = -42 \text{ kJ/mol.} \tag{2}
\]

The theoretical percentage of H₂ to water is 50%. The further chemical reactions for most hydrocarbons that take place are

\[
C_n\text{H}_m + n\text{H}_2\text{O} \rightleftharpoons n\text{CO} + (m/2 + n)\text{H}_2. \tag{3}
\]

It is possible to increase the efficiency to over 85% with an economic profit at higher thermal integration. There are two types of steam reformers for small-scale H₂ production: conventional reduced-scale reformers and specially designed reformers for fuel cells.

Commercial catalysts consist essentially of Ni supported on a-alumina. Mg-promoted catalysts showed a greater difficulty for Ni precursor’s reduction besides different probe molecules (H₂ and CO) adsorbed states. In the conversion of cyclohexane, Mg inhibited the formation of hydrogenolysis products. Nonetheless, the presence of Ca did not influence the metallic phase. The impregnated Ni/MgO-catalyst performed better than the other types [40].

Comparison with other biomass thermochemical gasification such as air gasification or steam gasification, the supercritical water gasification can directly deal with the wet biomass without drying, and have high gasification efficiency in lower temperature. The cost of H₂ production from supercritical water gasification of wet biomass was several times higher than the current price of H₂ from steam CH₄ reforming. Biomass was gasified in supercritical water at a series of temperature and pressure during different resident times to form a product gas composed of H₂, CO₂, CO, CH₄, and a small amount of C₂H₄ and C₂H₆ [41].

The yield of H₂ from conventional pyrolysis of corncob increases from 33% to 40% with increasing of temperature from 775 to 1025 K. The yields of H₂ from steam gasification increase from 29% to 45% for (water/solid) = 1 and from 29% to 47% for (water/solid) = 2 with increasing of temperature from 975 to 1225 K. Fig. 4 shows comparisons for the yield of H₂ from supercritical fluid extraction (SFE), pyrolysis and steam gasification [(water/solid) = 2] of beech wood at different temperatures. Distilled water was used in the SFE (the critical temperature of pure water is 647.7 K). From Fig. 4, the yield of H₂ from SFE was considerably high (49%) at lower temperatures. The pyrolysis was carried out at the moderate temperatures and steam gasification at the highest temperatures [42].
3.2. Fuels from bio-syngas via Fisher–Tropsch synthesis (FTS)

The FTS for the production of liquid hydrocarbons from coal-based synthesis gas has been the subject of renewed interest for conversion of coal and natural gas to liquid fuels [43]. The use of iron-based catalysts is attractive due to their high FTS activity as well as their WGS reactivity, which helps make up the deficit of H₂ in the syngas from modern energy-efficient coal gasifiers [44]. The FTS for the production of transportation fuels and other chemicals from synthesis has attracted much attention due to the pressure from oil supply [45]. The interest in use of iron-based catalysts stems from its relatively low cost and excellent WGS reaction activity, which helps to make up the deficit of H₂ in the syngas from coal gasification [46–48]. Hydrocarbon synthesis from biomass-derived syngas (bio-syngas) has been investigated as a potential way to use biomass [49]. Only biomass offers the possibility to produce liquid, carbon neutral, transportation fuels [50]. The FTS is used to produce chemicals, gasoline and diesel fuel. The FT products are predominantly linear hence the quality of the diesel fuel is very high. Since purified synthesis gas is used in the FTS all the products are S- and N-free [51]. Suitable economic conditions given, the FTS is an alternative route to liquid fuels and chemicals. Being S- and N-free and low in aromatics, the fuels are more environment friendly than those produced from crude oil. In particular, the production of environment friendly high-quality diesel fuel is an attractive application of the FTS [52].

The FTS-based gas to liquids (GTL) technology includes the three processing steps namely syngas generation, syngas conversion and hydroprocessing. In order to make the GTL technology more cost-effective, the focus must be on reducing both the capital and the operating costs of such a plant [53]. For some time now the price has been up to $60 per barrel. It has been estimated that the FT process should be viable at crude oil prices of about $20 per barrel [54,55]. The current commercial applications of the FT process are geared at the production of the valuable linear olefins and of fuels such as LPG, gasoline, kerosene and diesel. Since the FT process produces predominantly linear hydrocarbons the production of high-quality diesel fuel is currently of considerable interest [56]. The most expensive section of an FT complex is the production of purified syngas and so its composition should match the overall usage ratio of the FT reactions, which in turn depends on the product selectivity [57]. The industrial application of the FT process started in Germany and by 1938 there were nine plants in operation having a combined capacity of about 660 × 10³ t per year [58].

According to operating conditions the FTS always produces a wide range of olefins, paraffins and oxygenated products (alcohols, aldehydes, acids and ketones). The variables that influence the spread of the products are temperature, feed gas composition, pressure, catalyst type and promoters [57].

The high-temperature fluidized bed FT reactors with iron catalyst are ideal for the production of large amounts of linear-olefins. As petrochemicals they sell at much higher prices than fuels. The olefin content of the C₃, C₅–C₁₂ and C₁₃–C₁₈ cuts are typically 85%, 70% and 60%, respectively [57].

The Al₂O₃/SiO₂ ratio has significant influences on iron-based catalyst activity and selectivity in the process of FTS. Product selectivities also change significantly with different Al₂O₃/SiO₂ ratios. The selectivity of low molecular weight hydrocarbons increases and the olefin to paraffin ratio in the products shows a monotonic decrease with increasing Al₂O₃/SiO₂ ratio. Table 1 shows the effects of Al₂O₃/SiO₂ ratio on hydrocarbon selectivity [47]. Recently, Jun et al. [48] studied FTS over Al₂O₃ and SiO₂ supported iron-based catalysts from biomass-derived syngas. They found that Al₂O₃ as a structural promoter facilitated the better dispersion of copper and potassium and gave much higher FTS activity. The reaction results from FTS with balanced syngas are given in Table 2 [48].
More recently, there has been some interest in the use of FTS for biomass conversion to synthetic hydrocarbons. The bio-syngas consists mainly of H₂, CO, CO₂ and CH₄. Although the composition of bio-syngas is not suitable for direct using in the FTS, it can be tailored by CH₄ reforming, WGS reaction and CO₂ removal. To maximize the utilization of C sources, the steam reforming of bio-syngas with additional natural gas feedstock can be considered [58–62]. Hydrocarbon synthesis from bio-syngas has been investigated as a potential way to use biomass. The FTS was established in 1923 by German scientists Franz Fisher and Hans Tropsch. The main aim of FTS is synthesis of long-chain hydrocarbons from CO and H₂ gas mixture. The FTS is described by the set of equations [63,64]:

\[ n\text{CO} + 2n\text{H}_2 \rightarrow (n\text{CH}_2-) + n\text{H}_2\text{O}, \]  
\[ n\text{CO} + (2n + 1)\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+1} + n\text{H}_2\text{O}, \]  
\[ n\text{CO} + (n + m/2)\text{H}_2 \rightarrow \text{C}_n\text{H}_m + n\text{H}_2\text{O}, \]

where \( n \) is the average length of the hydrocarbon chain and \( m \) is the number of H₂ atoms per carbon. All reactions are exothermic and the product is a mixture of different hydrocarbons in that paraffin and olefins are the main parts.

Cobalt (Co) catalysts have the advantage of a higher conversion rate. The Co catalysts are in general more reactive for hydrogenation and produce therefore less unsaturated hydrocarbons and alcohols compared to iron catalysts. In the FTS

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Effects of Al₂O₃/SiO₂ ratio on hydrocarbon selectivity</th>
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</thead>
<tbody>
<tr>
<td>Hydrocarbon selectivities (wt%)</td>
<td>100Fe/6Cu/5K/25SiO₂</td>
</tr>
<tr>
<td>CH₄</td>
<td>6.3</td>
</tr>
<tr>
<td>C₂–4</td>
<td>24.5</td>
</tr>
<tr>
<td>C₅–₁₁</td>
<td>26.8</td>
</tr>
<tr>
<td>C₁₂–₁₈</td>
<td>21.9</td>
</tr>
<tr>
<td>C₁₉⁺</td>
<td>20.5</td>
</tr>
</tbody>
</table>

Reaction condition: 523 K, 2.0 MPa, H₂/CO = 2.0, and gas stream velocity: 2000 h⁻¹. Source: Ref. [47].

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Reaction results from FTS with balanced syngas (H₂-supplied bio-syngas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>CO₂</td>
</tr>
<tr>
<td>82.9</td>
<td>0.3</td>
</tr>
<tr>
<td>88.2</td>
<td>28.9</td>
</tr>
</tbody>
</table>

Reaction conditions: Fe/Cu/Al/K (100/6/16/4), CO/CO₂/Ar/H₂ (6.3/19.5/5.5/69.3), 1 MPa, 573 K and 1800 mL/(gcat h). Source: Ref. [48].
one mole of CO reacts with two moles of H2 in the presence Co-based catalyst to afford a hydrocarbon chain extension (–CH2–). The reaction of synthesis is exothermic ($\Delta H = -165$ kJ/mol):

$$CO + 2H_2 \rightarrow -CH_2- + H_2O \quad \Delta H = -165 \text{ kJ/mol}.$$ (7)

The –CH2– is a building stone for longer hydrocarbons. A main characteristic regarding the performance of the FTS is the liquid selectivity of the process [65]. For this reaction given with Eq. (7) is necessary a $H_2/CO$ ratio of at least 2 for the synthesis of the hydrocarbons. When iron (Fe)-based catalysts are used with WGS reaction activity the water produced in the reaction (2) can react with CO to form additional H2. The reaction of synthesis is exothermic ($\Delta H = -204$ kJ/mol). In this case a minimal $H_2/CO$ ratio of 0.7 is required:

$$2CO + H_2 \rightarrow -CH_2- + CO_2 \quad \Delta H = -204 \text{ kJ/mol}.$$ (8)

Typical operation conditions for the FTS are a temperature range of 475–625 K and pressures of 15–40 bar, depending on the process. The kind and quantity of liquid product obtained is determined by the reaction temperature, pressure and residence time, the type of reactor, and the catalyst used. Catalysts and reactors have been extensively investigated for liquid phase FTS [66–68]. Iron catalysts have a higher tolerance for sulfur, are cheaper, and produce more olefin products and alcohols. However, the lifetime of the Fe catalysts is short and in commercial installations generally limited to 8 weeks.

The design of a biomass gasifier integrated with a FTS reactor must be aimed at achieving a high yield of liquid hydrocarbons. For the gasifier, it is important to avoid CH4 formation as much as possible, and convert all carbon in the biomass to mainly CO and CO2 [67]. The gas cleaning is an important process before FTS. Gas cleaning is even more important for the integration of a biomass gasifier and a catalytic reactor. To avoid poisoning of FTS catalyst, tar, hydrogen sulfide, carbonyl sulfide, ammonia, hydrogen cyanide, alkali and dust particles must be removed thoroughly [65].

Synthetic FTS diesel fuels can have excellent autoignition characteristics. The FTS diesel is composed of only straight chain hydrocarbons and has no aromatics or sulfur. Reaction parameters are temperature, pressure and $H_2/CO$ ratio. FTS product composition strongly influenced by catalyst composition: product from Co catalyst higher in paraffins and product from Fe catalyst higher in olefins and oxygenates [69].
4. Bioethanol

Carbohydrates (hemicelluloses and cellulose) in plant materials can be converted to sugars by hydrolysis process. Fermentation is an anaerobic biological process in which sugars are converted to alcohol by the action of microorganisms, usually yeast. The resulting alcohol is ethanol. The value of any particular type of biomass as feedstock for fermentation depends on the ease with which it can be converted to sugars.

Anaerobic digestion of bio-wastes occurs in the absence of air, the resulting gas called as biogas, is a mixture consisting mainly of CH₄ and CO₂. Biogas is a valuable fuel which is produced in digesters filled with the feedstock like dung or sewage. The digestion is allowed to continue for a period of from 10 days to a few weeks [69].

Cellulose is a remarkable pure organic polymer, consisting solely of units of anhydro glucose held together in a giant straight chain molecule. Cellulose must be hydrolyzed to glucose before fermentation to ethanol. Conversion efficiencies of cellulose to glucose may be dependent on the extent of chemical and mechanical pretreatments to structurally and chemically alter the pulp and paper mill wastes. The method of pulping, the type of wood, and the use of recycled pulp and paper products also could influence the accessibility of cellulose to cellulase enzymes [70]. Cellulose is insoluble in most solvents and has a low accessibility to acid and enzymatic hydrolysis. Hemicelluloses (arabinoglycuronoxylan and galactoglucamannans) are related to plant gums in composition, and occur in much shorter molecule chains than cellulose. The hemicelluloses, which are present in deciduous woods chiefly as pentosans and in coniferous woods almost entirely as hexosanes, undergo thermal decomposition very readily. Hemicelluloses are derived mainly from chains of pentose sugars, and act as the cement material holding together the cellulose micells and fiber [71]. Hemicelluloses are largely soluble in alkali and, as such, are more easily hydrolyzed.

Bioethanol is a fuel derived from renewable sources of feedstock; typically plants such as wheat, sugar beet, corn, straw, and wood. Bioethanol is a petrol additive/substitute. It is possible that wood, straw and even household wastes may be economically converted to bioethanol. Bioethanol can be used as a 5% blend with petrol under the EU quality standard EN 228. This blend requires no engine modification and is covered by vehicle warranties. With engine modification, bioethanol can be used at higher levels, for example, E85 (85% bioethanol).

Bioethanol can be produced from a large variety of carbohydrates with a general formula of (CH₂O)n. Fermentation of sucrose is performed using commercial yeast such as Saccharomyces cerevisiae. Chemical reaction is composed of enzymatic hydrolysis of sucrose followed by fermentation of simple sugars [73]. First, invertase enzyme in the yeast catalyzes the hydrolysis of sucrose to convert it into glucose and fructose.

\[ C_{12}H_{22}O_{11} \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6 \]  \hspace{1cm} (9)

Second, zymase, another enzyme also present in the yeast, converts the glucose and the fructose into ethanol.

\[ C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 \]  \hspace{1cm} (10)

Gluco-amylase enzyme converts the starch into d-glucose. The enzymatic hydrolysis is then followed by fermentation, distillation and dehydration to yield anhydrous bioethanol. Corn (60–70% starch) is the dominant feedstock in starch-to-bioethanol industry worldwide.

Carbohydrates (hemicelluloses and cellulose) in lignocellulosic materials can be converted to bioethanol. The lignocellulose is subjected to delignification, steam explosion and dilute acid pre-hydrolysis, which is followed by enzymatic hydrolysis and fermentation into bioethanol [74–77]. A major processing step in an ethanol plant is enzymatic saccharification of cellulose to sugars through treatment by enzymes; this step requires lengthy processing and normally follows a short-term pretreatment step [78]. Fig. 6 shows the flow chart for the production of bioethanol from cereal grain or straw.

Hydrolysis breaks down the H₂ bonds in the hemicellulose and cellulose fractions into their sugar components: pentoses and hexoses. These sugars can then be fermented into bioethanol. The most commonly applied methods can be classified in two

<table>
<thead>
<tr>
<th>America</th>
<th>Asia</th>
<th>Europe</th>
<th>Africa</th>
<th>Oceania</th>
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</thead>
<tbody>
<tr>
<td>22.3</td>
<td>5.7</td>
<td>4.6</td>
<td>0.5</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Source: Ref. [74].
groups: chemical hydrolysis (dilute and concentrated acid hydrolysis) and enzymatic hydrolysis. In the chemical hydrolysis, the pretreatment and the hydrolysis may be carried out in a single step. There are two basic types of acid hydrolysis processes commonly used: dilute acid and concentrated acid.

The biggest advantage of dilute acid processes is their fast rate of reaction, which facilitates continuous processing. Since 5-carbon sugars degrade more rapidly than 6-carbon sugars, one way to degrade sugar degradation is to have a two-stage process. The first stage is conducted under mild process conditions to recover the 5-carbon sugars while the second stage is conducted under harsher conditions to recover the 6-carbon sugars.

Concentrated sulfuric or hydrochloric acids are used for hydrolysis of lignocellulosic materials. The concentrated acid process uses relatively mild temperatures, and the only pressures involved are those created by pumping materials from vessel to vessel. Reaction times are typically much longer than for dilute acid. This process provides a complete and rapid conversion of cellulose to glucose and hemicelluloses to 5-carbon sugars with little degradation. The critical factors needed to make this process economically viable are to optimize sugar recovery and cost effectively recovers the acid for recycling. The solid residue from the first stage is dewatered and soaked in a 30–40% concentration of sulfuric acid for 1–4 h at low temperatures, the contents are separated to recover the sugar and acid. The sugar/acid solution from the second stage is recycled to the first stage to provide the acid for the first stage hydrolysis [69].

The primary advantage of the concentrated acid process is the potential for high sugar recovery efficiency. The acid and sugar are separated via ion exchange and then acid is re-concentrated via multiple effect evaporators.

5. Biodiesel

Vegetable oil (m)ethyl esters, commonly referred to as “biodiesel,” are prominent candidates as alternative diesel fuels. The name biodiesel has been given to transesterified vegetable oil to describe its use as a diesel fuel [79]. There has been renewed interest in the use of vegetable oils for making biodiesel due to its less polluting and renewable nature as against the conventional diesel, which is a fossil fuel leading to a potential exhaustion [80]. Biodiesel is technically competitive with or offer technical advantages compared to conventional petroleum diesel fuel. The vegetable oils can be converted to their (m)ethyl esters via transesterification process in the presence of catalyst. Methyl, ethyl, 2-propyl and butyl esters were prepared from vegetable oils through transesterification using potassium and/or sodium alkoxides as catalysts. The purpose of the transesterification process is to lower the viscosity of the oil. Ideally, transesterification is potentially a less expensive way of transforming the large, branched molecular structure of the bio-oils into smaller, straight chain molecules of the type required in regular diesel combustion engines.

Transesterifications of vegetable oils in supercritical methanol are carried out without using any catalyst. A few studies have been conducted via non-catalytic transesterification with supercritical methanol (SCM) [81–87]. Saka and Kusdiana [82] and Demirbas [79] have firstly proposed that biodiesel fuels may be from vegetable oil. A novel process of biodiesel fuel production has been developed by a non-catalytic supercritical methanol method. Compared with the catalytic processes under barometric pressure, the supercritical methanol process is non-catalytic, purification of products is much simpler, shorter reaction time, more environmentally friendly and lower energy use. However, the reaction requires temperatures of
525–675 K and pressures of 35–60 MPa [82,84].

Table 5 shows the comparisons between catalytic methanol process and supercritical methanol method for biodiesel from vegetable oils by transesterification. Fig. 7 shows non-catalytic biodiesel production in supercritical alcohol.

The most important variables affecting the methyl ester yield during the transesterification reaction are molar ratio of alcohol to vegetable oil and reaction temperature. Biodiesel has become more attractive recently because of its environmental benefits. The viscosity values of vegetable oils are between 27.2 and 53.6 mm²/s whereas those of vegetable oil methyl esters are between 3.59 and 4.63 mm²/s [86,87]. The flash point values of vegetable oil methyl esters are highly lower than those of vegetable oils. Biodiesel is an environmentally friendly fuel that can be used in any diesel engine without modification.

The bio-diesel esters were characterized for their physical and fuel properties including density, viscosity, iodine value, acid value, cloud point, pour point, gross heat of combustion and volatility. The biodiesel fuels produced slightly lower power and torque, and higher fuel consumption than no. 2 diesel fuel. Biodiesel is better than diesel fuel in terms of sulfur content, flash point, aromatic content and biodegradability [88].

If the biodiesel valorized efficiently at energy purpose, so would be benefit for the environment and the local population, job creation, provision of modern energy carriers to rural communities, avoid urban migration and reduction of CO₂ and sulfur levels in the atmosphere.

The cost of biodiesels varies depending on the base stock, geographic area, variability in crop production from season to season, the price of the crude petroleum and other factors. Biodiesel has over double the price of petroleum diesel. The high price of biodiesel is in large part due to the high price of the feedstock. However, biodiesel can be made from other feedstocks, including beef tallow, pork lard, and yellow grease [86].

With cooking oils used as raw material, the viability of a continuous transesterification process and recovery of high-quality glycerol as a biodiesel by-product are primary options to be considered to lower the cost of biodiesel [88,89]. The vegetable oil fuels were not acceptable because they were more expensive than petroleum fuels. With recent increases in petroleum prices and uncertainties concerning petroleum availability, there is renewed interest in vegetable oil fuels for diesel engines.

Most of the biodiesel that is currently made uses soybean oil, methanol, and an alkaline catalyst. The high value of soybean oil as a food product makes production of a cost-effective fuel very challenging. However there are large amounts of low-cost oils and fats such as restaurant waste and animal fats that could be converted to biodiesel. The problem with processing these low-cost oils and fats is that they often contain large amounts of free fatty acids.
(FFA) that cannot be converted to biodiesel using an alkaline catalyst [84,90].

A review of 12 economic feasibility studies shows that the projected costs for biodiesel from oilseed or animal fats have a range US$0.30–0.69/l, including meal and glycerin credits and the assumption of reduced capital investment costs by having the crushing and/or esterification facility added onto an existing grain or tallow facility. Rough projections of the cost of biodiesel from vegetable oil and waste grease are, respectively, US$0.54–0.62/l and US$0.34–0.42/l. With pre-tax diesel priced at US$0.18/l in the US and US$0.20–0.24/l in some European countries, biodiesel is thus currently not economically feasible, and more research and technological development will be needed [84,91].

6. Biomethanol

Methanol can be used as one possible replacement for conventional motor fuels. It has been seen as a possible large volume motor fuel substitute at various times during gasoline shortages. It was often used in the early part of the century to power automobiles before inexpensive gasoline was widely introduced. Synthetically produced methanol was widely used as a motor fuel in Germany during the World War. Methanol is commonly used in biodiesel production for its reactivity. Methanol can be used as one possible replacement for conventional motor fuels. The use of methanol as a motor fuel received attention during the oil crises of the 1970s due to its availability and low cost. Problems occurred early in the development of gasoline–methanol blends. As a result of its low price some gasoline marketers over blended. Many tests have shown promising results using 85–100% by volume methanol as a transportation fuel in automobiles, trucks and buses (Table 6).

Methanol, also known as “wood alcohol.” Sustainable methods of methanol production are currently not economically viable. Methanol is produced from synthetic gas or biogas and evaluated as a fuel for internal combustion engines. The production of methanol is a cost-intensive chemical process. Therefore, in current conditions, only waste biomass such as old wood or bio-waste is used to produce methanol [92].

Methanol is poisonous and burns with an invisible flame. Methanol has just like ethyl alcohol a high octane rating and hence an Otto engine is preferable. Most processes require supplemental oxygen for the intermediate conversion of the biomass into a synthesis gas (H₂ + CO). A readily available supply of H₂ and oxygen, therefore, should improve the overall productivity of biomass-derived methanol [93].

Before modern production technologies were developed in the 1920s, methanol was obtained from wood as a co-product of charcoal production and, for this reason, was commonly known as wood alcohol. Methanol is currently manufactured worldwide by conversion or derived from syngas, natural gas, refinery off-gas, coal or petroleum:

\[
2H_2 + CO \rightarrow CH_3OH. \tag{11}
\]

The chemical composition of syngas from coal and then from natural gas can be identical with the same H₂/CO ratio. A variety of catalysts are capable of causing the conversion, including reduced NiO-based preparations, reduced Cu/ZnO shift preparations, Cu/SiO₂ and Pd/SiO₂, and Pd/ZnO [94,95].

Methanol is currently made from natural gas but can also be made using biomass via partial oxidation reactions [96]. Biomass and coal can be considered as a potential fuel for gasification and further syngas production and methanol synthesis [95]. Adding sufficient H₂ to the synthesis gas to convert all of the biomass into methanol carbon than double the methanol produced from the same biomass base [97]. Waste material can be partially converted to methanol, which the product yield for the conversion process is estimated to be 185 kg of methanol per metric ton of solid waste [98,99].

<table>
<thead>
<tr>
<th>Methanol</th>
<th>Biomethanol</th>
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<tbody>
<tr>
<td>Catalytic synthesis from CO and H₂</td>
<td>Catalytic synthesis from CO and H₂</td>
</tr>
<tr>
<td>Natural gas</td>
<td>Distillation of liquid from wood pyrolysis</td>
</tr>
<tr>
<td>Petroleum gas</td>
<td>Gaseous products from biomass gasification</td>
</tr>
<tr>
<td>Distillation of liquid from coal pyrolysis</td>
<td>Synthetic gas from biomass and coal</td>
</tr>
</tbody>
</table>

Table 6
Main production facilities of methanol and biomethanol
Agriculture-(m)ethanol is at present more expensive of synthesis ethanol from ethylene and of methanol from natural gas [100].

Biomass resources can be used to produce methanol. The pyrolygeneous acid obtained from wood pyrolysis consists of about 50% methanol, acetone, phenols and water [98,101]. As a renewable resource, biomass represents a potentially inexhaustible supply of feedstock for methanol production. The composition of bio-syngas from biomass for producing methanol is presented in Table 3. Current natural gas feedstocks are so inexpensive that even with tax incentives renewable methanol has not been able to compete economically. Technologies are being developed that may eventually result in commercial viability of renewable methanol.

Methanol from coal could be a very important source of liquid fuel in the future. The coal is first pulverized and cleaned, then fed to a gasifier bed where it is reacted with oxygen and steam to produce the syngas. Once these steps have been taken, the production process is much the same as with the other feedstocks with some variations in the catalyst used and the design of the converter vessel in which the reaction is carried out. Methanol made using synthesis gas (syngas) with H2 and CO in a 2:1 ratio (Table 3). The syngas was transformed to methanol in a fixed catalyst bed reactor. Coal-derived methanol has many preferable properties as free of sulfur and other impurities, could replace petroleum in transportation, or be used as a peaking fuel in combustion turbines, or supply a source of H2 for fuel cells. The technology for making methanol from natural gas is already in place and requires only efficiency improvements and scale-up to make methanol an economically viable alternative transportation fuel [102].

In recent years, a growing interest has been observed in the application of methanol as an alternative liquid fuel, which can be used directly for powering Otto engines or fuel cells [103]. The feasibility of achieving the conversion has been demonstrated in a large-scale system in which a product gas is initially produced by pyrolysis and gasification of a carbonaceous matter. Syngas from biomass is altered by catalyst under high pressure and temperature to form methanol. This method will produce 100 gallons of methanol per ton of feed material [104].

The gases produced can be steam reformed to produce H2 and followed by WGS reaction to further enhance H2 production. When the moisture content of biomass is higher than 35%, it can be gasified in a supercritical water condition [105]. Supercritical water gasification is a promising process to gasify biomass with high moisture contents due to high gasification ratio (100% achievable) and high H2 volumetric ratio (50% achievable) [106–108]. H2 produced by biomass gasification was reported to be comparable to that by natural gas reforming [109]. The process is more advantageous than fossil fuel reforming in consideration of environmental benefits. It is expected that biomass thermochemical conversion will be one of the most economical large-scale renewable H2 technologies.

The strategy is based on producing H2 from biomass pyrolysis using a co-product strategy to reduce the cost of H2 and concluded that only this strategy could compete with the cost of the commercial hydrocarbon-based technologies [110]. This strategy will demonstrate how H2 and bio-fuel are economically feasible and can foster the development of rural areas when practiced on a larger scale. The process of biomass to activated carbon is an alternative route to H2 with a valuable co-product that is practiced commercially [111].

The simultaneous production of bio-methanol (obtained by the hydrogenation of CO2 developed during the fermentation of sugar juice), in parallel to the production of bio-ethanol, appears economically attractive in locations where hydro-electricity is available at very low cost (~0.01$KWh) and where lignocellulosic residues are available as surpluses.

The gas is converted to methanol in a conventional steam-reforming/WGS reaction followed by high-pressure catalytic methanol synthesis:

\[ CH_4 + H_2O \rightarrow CO + 3H_2. \]  \hspace{1cm} (12)

\[ CO + H_2O \rightarrow CO_2 + H_2. \]  \hspace{1cm} (13)

Eqs. (12) and (13) are called as gasification/shift reactions.

\[ CO + 2H_2 \rightarrow CH_3OH \]  \hspace{1cm} (14)

or

\[ CO_2 + 3H_2 \rightarrow CH_3OH + H_2O. \]  \hspace{1cm} (15)

Eqs. (14) or (15) are methanol synthesis reactions. Fig. 8 shows production of biomethanol from carbohydrates by gasification and partial oxidation with O2 and H2O.

The energy value of residues generated worldwide in agriculture and the forest-products industry
amounts to more than one-third of the total commercial primary energy use at present [112]. Bio-energy supplies can be divided into two broad categories: (a) organic municipal waste and residues from the food and materials sectors; and (b) dedicated energy crops plantations. Bio-energy from biomass, both residues and energy crops, can be converted into modern energy carriers such as H₂, methanol, ethanol or electricity [113].

Methanol can be produced from biomass essentially any primary energy source. Thus, the choice of fuel in the transportation sector is to some extent determined by the availability of biomass. As regards the difference between H₂ and methanol production costs, conversion of natural gas, biomass and coal into H₂ is generally more energy efficient and less expensive than conversion into methanol [113].

7. Bio-oil

The term bio-oil is used mainly to refer to liquid fuels. There are several reasons for bio-oils to be considered as relevant technologies by both developing and industrialized countries. They include energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector.

Bio-oils are liquid or gaseous fuels made from biomass materials, such as agricultural crops, municipal wastes and agricultural and forestry by-products via biochemical or thermochemical processes. They can substitute conventional fuels in vehicle engines—either totally or partially in a blend [114]. The organic fraction of almost any form of biomass, including sewage sludge, animal wastes and industrial effluents, can be broken down through anaerobic digestion into CH₄ and CO₂ mixture called as “biogas” [115]. Biogas is an environment friendly, clean, cheap and versatile fuel [116].

Pyrolysis/cracking, defined as the cleavage to smaller molecules by thermal energy. H₂ can be produced economically from woody biomass [117]. Biomass can be thermally processed through gasification or pyrolysis to produce H₂. The main gaseous products from biomass are the following [118–122]:

\[
\text{Pyrolysis of biomass} \rightarrow \text{H}_2 + \text{CO}_2 + \text{CO} + \text{Gaseous and liquid hydrocarbons}, \quad (16)
\]

\[
\text{Catalytic steam reforming of biomass} \rightarrow \text{H}_2 + \text{CO}_2 + \text{CO}, \quad (17)
\]

\[
\text{FTS of (H}_2 + \text{CO)} \rightarrow \text{Gaseous and liquid hydrocarbons.} \quad (18)
\]

The conventional pyrolysis of biomass is associated with the product of interest that is the high charcoal content, but the fast pyrolysis is associated with the products of interest are tar, at low temperature (675–775 K) [123–126], and/or gas, at high temperature [127].

8. Conclusion

The term biofuel is referred to as liquid fuels for the transport sector that are predominantly produced from biomass. Biofuels include energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector. The Fischer–Tropsch synthesis (FTS) uses various catalysts to produce linear hydrocarbons and oxygenates, including unrefined gasoline, diesel, and wax ranges. Co catalysts have the advantage of a higher conversion rate and a longer life. The Co catalysts are in general more reactive for hydrogenation and produce therefore less unsaturated hydrocarbons and alcohols compared to iron catalysts.
Most traditional biofuels, such as ethanol from corn, wheat, or sugar beets, and biodiesel from oil seeds, are produced from classic agricultural food crops that require high-quality agricultural land for growth. Bioethanol is a petrol additive/substitute. Bioethanol can be produced from plentiful, domestic, cellulose biomass resources such as herbaceous and woody plants, agricultural and forestry residues, and a large portion of municipal solid waste and industrial waste streams. Production of bioethanol from biomass is one way to reduce both the consumption of crude oil and environmental pollution.

Biodiesel is an environmentally friendly alternative liquid fuel that can be used in any diesel engine without modification. There has been renewed interest in the use of vegetable oils for making biodiesel due to its less polluting and renewable nature as against the conventional petroleum diesel fuel. Due to its environmental merits, the share of biofuel in the automotive fuel market will grow fast in the next decade. There are several reasons for biofuels to be considered as relevant technologies by both developing and industrialized countries.

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