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Current Status in the Conversion of Lignocellulosic Biomass to Liquid (BtL) Biofuels

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ABSTRACT

Petroleum and other liquid fuels are currently the dominant source of global transportation energy. However, the rapid increase in energy demand, the extensive use of fossil fuels and the urgent need to reduce the carbon dioxide emissions (CO₂) have raised concerns in the transportation sector. This brings lignocellulosic biomass into limelight to sustain the supply liquid biofuels as potential substitutes for conventional fossil fuels in the in the transportation sector. Currently, a growing number of liquid biofuels are evaluated for commercial exploitation, such as bioethanol, biodiesel, biomethanol, and reformulated gasoline components. This article reviews the existing conversion technologies and most recent developments for the production of second-generation liquid biofuels from lignocellulosic biomass. There are two basic conversion routes for the conversion of lignocellulosic biomass to biofuels – thermochemical (pyrolysis, liquefaction, torrefaction and gasification) and biochemical (fermentative pathways). Syngas fermentation has been presented as an advanced biomass conversion technology that converts syngas to higher alcohols in the presence of mesophilic and thermophilic microorganisms.

Keywords: Lignocellulosic biomass, biofuels, Thermochemical conversion, biochemical conversion, second-generation technologies.

1.0 INTRODUCTION

Conventional petroleum and other liquid fuels are currently the dominant source of global transportation energy. However, the rapid increase in energy demand, the extensive use of fossil fuels and the urgent need to reduce the carbon dioxide emissions (CO₂) have raised concerns in the transportation sector (Ibarra-Gonzalez and Rong, 2019). Production of liquid transportation fuels from alternative renewable and sustainable sources have become the ultimate solution to overcome tackle the dual challenges of depletion of fossil fuels and climate change. As the production of liquid biofuels through 'first-generation' biofuels technologies appear unsustainable because of the potential stress that their production places on food commodities, the conversion of lignocellulosic biomass to liquid (BtL) transportation fuels through 'second generation' technologies seems to be a promising path and presents advantages fossil fuels (Naik *et. al.*, 2010).

Biomass to liquid (BtL) conversion of lignocellulosic is based on the utilization of dry biomass via thermochemical and biochemical conversion routes. Different raw materials can be

used as feedstock for lignocellulosic biofuels; these include agricultural residues (e.g., corn stover, corn cobs, wheat straw, sugarcane straw, bagasse, etc.), forestry residues (woody biomass), and municipal solid waste or dedicated energy crops (e.g., switchgrass, miscanthus, and willow) planted in non-productive areas. Lignocellulosic biomass is chemically composed of cellulose, hemicellulose and lignin that can be transformed into energy-dense components for use as fuels or chemicals.

Therefore, development of BtL systems is critical to increase the potential of this resource in a sustainable passion. Many efforts have been made on the conversion of raw lignocellulosic biomass or its components to hydrocarbons through various strategies (Han *et. al.*, 2019). Conversion of lignocellulosic biomass to BtL transportation fuels, such as, bioethanol, biobutanol, and biodiesel can be accomplished through various thermochemical and biochemical conversion routes (Refaat, 2012).

There are major steps for the conversion of lignocellulosic biomass to liquid transportation fuels, these include; feedstock selection and preparation, feedstock pre-treatment, production of

bio-oil, upgrading of bio-oil to transportation fuels and recovery of value-added products (Ibarra-Gonzalez and Rong, 2019). This is shown in Fig. 1.

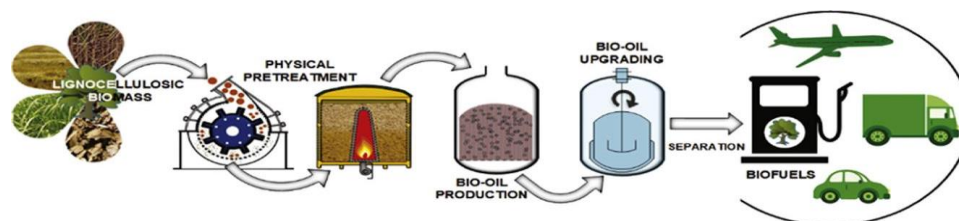


Figure 1: Lignocellulosic biomass conversion to liquid biofuels (Han, *et. al.*, 2019)

Generally, biofuels demand is projected to increase in 2050 for the achievement of stable atmospheric CO₂ concentration at 450 ppm with second-

generation biofuels accounting for about 90% of all biofuels (Eisentraut, 2010).

Table 1: List of selected liquid biofuels, technologies, status and engine applications Antizar-Ladislao and Turrión-Gomez, 2008)

Biofuels	Description	Technology	Status	Engine application
Bioethanol	Ethanol produced from biomass and/or the biodegradable fraction of waste	Microbial	Industrial	Pure/blend
Biodiesel	A methyl-ester produced from vegetable oil, animal oil or recycled fats and oils of diesel quality, for use as biofuel	Physical/chemical (enzymatic)	Industrial (Laboratory)	Pure/blend
Biomethanol	Methanol produced from biomass, for use as Biofuel	Thermochemical/ microbial	Pilot plant	Pure/blend (MTBE/biodiesel)
Bio-ethyl-tertbutyl-ether (bio-ETBE)	Produced from bioethanol. The percentage by volume of bio-ETBE that is calculated as biofuel is 47%	Chemical/microbial	Industrial	Blend
Bio-methyltertio-Butylether (bio-MTBE)	Produced from biomethanol. The percentage by volume of bio-MTBE that is calculated as biofuel is 36%			
Bio-dimethylether (bio-DME)	Produced from biomass, appropriate biofuel for power generation			
Synthetic Biofuels	Synthetic hydrocarbons or mixtures of synthetic hydrocarbons which have been produced from biomass	Microbial and physical (gasification) to produce syngas	Industrial	Gas turbine

Fisher-Tropsch
process to
produce synthetic
biofuel

Albeit production of second-generation biofuels is in the demonstration stage, sustainable production of second-generation biofuels requires sufficient supply of biomass; therefore, surplus agricultural land for intensive agricultural production of biomass feedstocks is essential. Studies have shown that large potentials are estimated for the

Sub-Saharan Africa and Latin America (Fink and Medved, 2011). However, apart from Brazil, significant investments in technological improvement, new infrastructure and capacity building in the agricultural sector are needed for sustainable production of second-generation biofuels.

Table 2: Properties of some liquid biofuels (Gupta, et. al., 2010)

Properties	Biodiesel	Diesel	Gasoline	Bioethanol	Biomethanol	Bio-oil
Density (kg/m ³)	860-900	827.4	720-800	794-810	796	984-1250
Kinetic viscosity (cSt at 40 °C)	3.5-5	1.7283	5	1.4-1.7	1.4-1.7	32-45
Flash point (°C)	120-180	44		13	11	56-130
Cloud point (°C)	-3 to -12	-6		-	-	-
Pour point (°C)	-15 to 5	-16		-117	-161	-35 to -10
LHV (MJ/kg)	39-41	43	42.9	25-26	20	13-18
HHV (MJ/kg)	37.528	42.612	43.448	26.952	22.7	
Ignition temperature	177	250		423	463	580
Cetane no.	48-60	45-55	5.20	8	5	10
Stoichiometric air/fuel ratio	13.8	14.6	14.5	9.79	06:01	34:01:00
C (% , w/w)	77-81	80.33		52.2	37.5	32-48
H ₂ (% , w/w)	12	14		13.1	12.6	7-8.5
N ₂ (% , w/w)	0.03	1.76		-	-	<0.4
O ₂ (% , w/w)	9-11	1.19		34.8	49.9	44-60
S (% , w/w)	<0.03	<0.4		-	-	<0.05

Currently, different conversion routes for the production of second-generation biofuels are being investigated – in which the two main options are (1) Bio-chemical route (fermentation) and (2) Thermochemical routes (pyrolysis, gasification, methanation, FT-process, and biomethanol formation). These processes are classified into: a) primary and b) secondary conversion processes. The application of the conversion process depends on the kind of desired biofuel to be produced. These conversion processes are discussed in the following sub-sections.

2.0 PRIMARY CONVERSION PROCESSES

These processes primarily convert biomass feedstock to solid, liquid or gaseous biofuels that may lead to the formation of different synthetic biofuels.

2.1 Bio-oil – Pyrolysis process

Pyrolysis is one of several means of production of BtL biofuel from lignocellulosic biomass. It is the process of thermal conversion of organic matter

using a catalyst in the absence of oxygen. Pyrolysis is typically defined as the thermochemical decomposition of biomass feedstock at medium (300–800°C) to high temperatures (800–1300°C) in an inert atmosphere. The products of liquid, syngas, and solid are all actually valuable fuels and are defined as bio-oil, biosyngas, and biochar, respectively. Pyrolysis oil (bio-oil) is observed to have a lower viscosity and flash point than diesel fuel (Saleem *et al.*, 2015). However, unlike conventional fuel oil, bio-oil increases in viscosity with time because of polymerization (Basu, 2018). Product of pyrolysis is a mixture of several hydrocarbons, which allows production of fuel and chemicals through appropriate refining methods. The heating value of the liquid produced is a little lower or in the same range (13–18 MJ/kg) as that of the parent biomass. It contains a much higher amount of oxygen (~50%) than does most fuel oil. It is also heavier (specific gravity ~1.3) and more viscous. Bio-oil is not self-igniting like fuel oil, and as such it cannot be blended with diesel for operating a diesel engine. Based on the operating conditions such as heating rate, pyrolysis temperature, and residence time, conventional electric pyrolysis can be generally classified into three subclasses: (1) slow pyrolysis, (2) fast pyrolysis, and (3) flash pyrolysis (Table 3). Furthermore, catalytic pyrolysis, microwave pyrolysis, vacuum pyrolysis, and hydro pyrolysis are also reported in some publications (Baskar *et*

al., 2019). For slow pyrolysis, the heating rate, pyrolysis temperature, and residence time are <1°C/s, 300–700°C, and >450 s, respectively. For fast pyrolysis, they are 10–300°C/s, 550–1250°C, and 0.5–20 s, respectively. For flash pyrolysis, they are >1000°C/s, 800–1300°C, and <0.5 s, respectively (Zhang, *et al.*, 2019). Baskar *et al.*, (2019) reported that the recent advances in upstream processing for the generation of biomass and oil have given a space for the establishment of biofuels to a great extent. However, major challenge lies in the development of cost-effective extraction and purification methods, as the extraction of oil from these types of sources is energy intensive, which concurrently increases the overall production cost. According to Basu (2018), bio-oil is a good source of some useful chemicals and may be subjected to hydrocracking to produce gasoline and diesel. The maximum yield of bio-oil from pyrolysis may be increased to as high as 80% (dry weight) through proper choice of heating rate and pyrolysis temperature, and evacuation of product from the reaction zone. The author reported that a slower heating rate, a lower pyrolysis temperature, and a longer residence time maximize the yield of solid char. It was found that a higher heating rate, a higher pyrolysis temperature, and a shorter residence time maximize the gas yield. A higher heating rate, an intermediate pyrolysis temperature, and a shorter residence time maximize the liquid yield.

Table 3: Biomass Pyrolysis Using Different Technologies (Zhang, *et al.*, 2019).

Pyrolysis	Operating Conditions	Results
Slow pyrolysis	Temperature: 300–700°C Vapour residence time: 10–100 min Heating rate: 0.1–1°C/s Feedstock size: 5–50 mm	Biooil: ~30 wt% Biochar: ~35 wt% Gases: ~35 wt%
Fast pyrolysis	Temperature: 400–800°C Vapor residence time: 0.5–5 s Heating rate: 10–200°C/s Feedstock size: <3 mm	Biooil: ~50 wt% Biochar: ~20 wt% Gases: ~30 wt%
Flash pyrolysis	Temperature: 800–1000°C Vapor residence time: > 0.5 s Heating rate: > 1000°C/s Feedstock size: < 0.2 mm	Biooil: ~75 wt% Biochar: ~12 wt% Gases: ~13 wt%

Compared with the other thermochemical technologies such as liquefaction and combustion, pyrolysis generally has the following advantages:

1. High bio-oil yield – may be as high as 75%;

2. High content of carbon;
3. Low nitrogen and sulfur contents;
4. High HHV of bio-oil - e.g., 42 MJ/kg, which is comparable with those of fossil fuels;
5. The residence time is generally short, which decreases the operational cost;
6. The desired product (bio-oil, biosyngas, or bio-char) could be produced by adjusting the operational parameters; and
7. The bio-oil could be easily stored or transported.

Currently, a new pyrolysis technology, microwave-assisted pyrolysis, has been developed and widely used. The technology has drawn serious attention because of its advantages (Table 3) over the conventional electric pyrolysis due to the different heat and mass transfer mechanisms (Kazmi and Clark, 2012; Saleem *et. al.*, 2015).

Table 3: Comparison of microwave assisted pyrolysis with the conventional pyrolysis (Zhang, *et. al.*, 2019).

Microwave-Assisted Pyrolysis	Conventional Electric Pyrolysis
Conversion of energy	Transfer of energy
Noncontact heating	Contact heating
Hot spot	No hot spot
Selective	Nonselective
Lower thermal inertia and faster response	Higher thermal inertia and slower response
Lower energy consumption	Higher energy consumption
Rapid heating	Slow heating
Shorter reaction times	Longer reaction times
Volumetric heating	Superficial heating
Higher level of control	Lower level of control
Improved product yields	Lower product yields

2.2 Biosyngas – Gasification Process

Gasification technology is a thermochemical biomass conversion process through which biomass is converted into synthesis gas (a mixture of CO and H₂) by subjecting it to high temperatures (800–900°C) in the presence of limited supply of oxygen. After cleaning, the gas is used for the production of power (fuel for running diesel generators) or utilized as a chemical platform for the production of methanol, dimethyl ether (DME), and olefins (Fisher-Tropsch synthesis). Biomass gasification has attracted intense interest among the biomass thermochemical conversion technologies as this offer higher combustion efficiency. Production of bio-based methanol and DME based on biomass gasification technology has been successfully demonstrated in recent times (Zhang, *et. al.*, 2010). Biosyngas derives from biomass gasification technology can achieve conversion efficiency of around 40% in biomass integrated gasification and combined cycle (Sims *et. al.*, 2010).

There are three routes for the conversion of biomass to syngas namely catalytic, non-catalytic,

and steam gasification processes. Low operational temperature is required during catalytic process, whereas a very high temperature of operation (up to 1300 °C) is required for the noncatalytic process. Syngas mainly consists of hydrogen (H₂), methane (CH₄), nitrogen (N₂), carbon dioxide (CO₂) and carbon monoxide (CO) (Table 4). Syngas can be either be burnt directly or transformed to other gaseous or liquid fuels. BtL technology also utilizes biomass-derived syngas, and the process is based on the well-known Fisher-Tropsch synthesis for the production of liquid fuels (gasoline, diesel, heating oil, jet fuel, etc.). However, there are several drawbacks of BtL ranging from poor quality (low H₂/CO ratio) of biomass-derived syngas (improved by water-gas-shift reaction), poor selectivity to olefins (the desirable fuel products), catalyst poisoning, low heating value of gas, tar, and methane formation (can damage process equipment in long-term operation), and complicated cleaning steps (needed for the removal of CO₂, CH₄, tars, etc.). So, it is economically more attractive to use inexpensive natural gas and coal as feed rather than biomass for producing syngas.

Table 4: A typical composition of Biosyngas (Sims *et. al.*, 2010)

Components	Composition (%)
CO	22-36
CO ₂	22-32
H ₂	21-30
CH ₄	8-11
Ethane	0.16-0.22
Benzene/toluene/xylene	0.84-0.96
Tar	0.15-0.24

2.3 Torrefaction Process

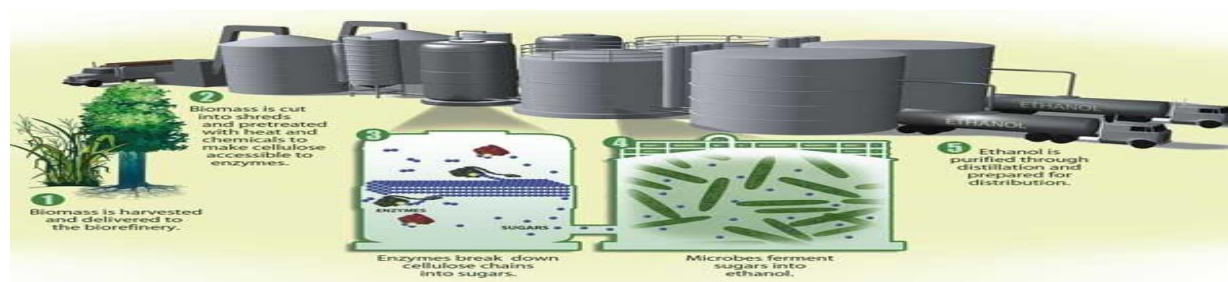
Torrefaction is a thermochemical process that converts dry biomass to solid (biocoal) biofuel at temperature ranging between 200 to 300°C in the absence of oxygen under atmospheric conditions. The characteristics of a torrefaction process are given in Bergman (2005). Research findings have shown that torrefaction technique has been used for the pre-treatment (Deng *et. al.*, 2009; Yan, *et. al.*, 2009) and improving the value and fuel properties of a wide range of biomass feedstocks (Bridgeman, and Jones, 2008) for thermochemical conversion.

2.4 Liquefaction Process

This is also a thermochemical process that converts biomass to small highly reactive fragments that can be converted to oil through polymerisation. The process occurs at a low temperature and high-pressure conditions. Comprehensive description of the process and its advantages compared with pyrolysis process can be found in Zhang, *et. al.*, (2010)

2.5 Advanced Fermentation

Advanced fermentation is a biochemical process for the conversion of lignocellulosic biomass to bioethanol. The process involves the microbial and enzymatic digestion of lignocellulosic materials (cellulose and hemicellulose) into simple sugars through pre-treatment and hydrolysis processes. The sugars are then fermented into alcohol, and the lignin produced is used as an energy source to drive the process. The principal organism involved in the production of bioethanol is the yeast *Saccharomyces cerevisiae*. Studies have shown that the organism-based fermentation has shown good yield for ethanol from sugar or starch crops. The ethanol yield for some biomass feedstocks is given in Table 5. Bioethanol production from lignocellulosic biomass feedstocks require a number of operations which includes; pre-treatment of the feedstock, enzyme production and hydrolysis, fermentation, and finally ethanol recovery (Figure 2).

Figure 2: Lignocellulosic bioethanol conversion processes (Han *et. al.*, 2010).

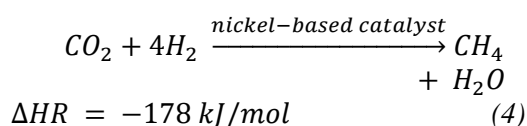
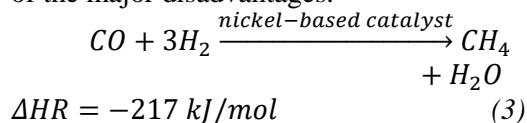
Production of advanced bioethanol from lignocellulosic biomass usually requires expensive pre-treatment of biomass feedstock. Physical, chemical, physiochemical, and biological pre-treatment methods have been applied to several

lignocellulosic materials to enhance their digestibility during fermentation process (Gelfand, *et al.*, 2013). Lignocellulosic bioethanol yield from different biomass feedstocks is given in Table 5.

Table 5: Bioethanol from lignocellulosic (Naik, *et. al.*, 2010)

Feedstocks	Bioethanol yield, litres/tonne biomass
Cane bagasses	424

al., 2005). However, heat removal and carbon formation during the methanation process are some of the major disadvantages.



3.4 Biomethanol Synthesis

Like the aforementioned processes (FT- process, methanation, and Carbo-V), biosyngas produced

from the gasification of cellulosic biomass can be converted to biomethanol (Figure 4). However, compared to FT- synthesis, biomethanol production requires a slightly different H_2/CO ratio. Biomethanol is a liquid fuel and needs additional safety measures due to its poisonous nature and burns with an invisible flame. Studies have demonstrated methanol production from biomass to be a feasible option to fossil fuels, and the biomass to biomethanol conversion efficiencies have been estimated to be on the order of 60% (Galindo and Badr 2007; Amigun, *et. al.*, 2010; Amigun, *et. al.*, 2011).

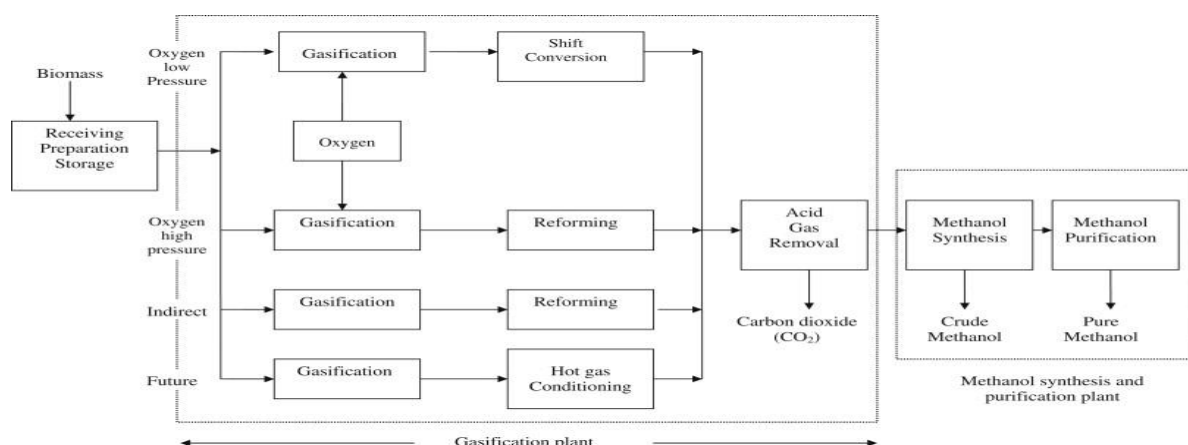


Figure 4: Production of Biomethanol from cellulosic biomass (Galindo and Badr, 2007)

3.5 Bio-DME Synthesis

Bio-dimethylether (Bio-DME – CH_3OCH_3) production process is very similar to that of biomethanol. There are two possible routes for the production of bio-DME. (1.) Bio-DME can be produced from pure methanol by means of catalytic dehydration process, which chemically separates the methanol from water. (2.) Bio-DME can also be produced directly from biosyngas, which involves gasification and synthesis processes. Biosyngas is first converted into biomethanol in the presence of copper-based catalyst, which is subsequently dehydrated in the presence of another different catalyst (e.g. silica-alumina) resulting in the production of bio-DME. Bio-DME is a gaseous fuel with overall conversion efficiency of about 38% (Zhang, *et. al.*, 2010), much less toxic than biomethanol (Sims, *et. al.*, 2008; Wu, *et. al.*, 2007) and has the same empirical formula as ethanol (C_2H_6O), but different structural formula. Bio-

DME has large potential for being produced in commercial quantities, it is convenient to store and transport, low emissions, and its physical and chemical properties are very similar to those of liquefied petroleum gas (LPG) (Lee, *et. al.*, 2009). It is a good alternative for transportation and power generation.

4.0 CONCLUSION

Lignocellulosic biomass such as agricultural residues, dedicated energy crops, forestry residues, municipal solid wastes have great potential to provide liquid biofuels in a sustainable fashion and provide a sustainable solution to the increasing energy demands. Conversion of lignocellulosic biomass to BtL transportation fuels, such as, bioethanol, biobutanol, and biodiesel can be accomplished through various thermochemical and biochemical conversion routes. Sustainable production of second-generation biofuels requires

sufficient supply of biomass; therefore, surplus agricultural land for intensive agricultural production of biomass feedstocks is essential. Moreover, efficient thermochemical and biochemical conversion technologies are required to convert lignocellulosic biomass to liquid biofuels. While, pyrolysis and liquefaction are efficient in generating bio-oils, gasification

produces syngas that can be further converted to liquid biofuels.

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