

Selected Thermo-Chemical Biorefining: Evaluation of the Current Trends and Progressions

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ABSTRACT

The review paper embodies the current trends and advancements involved in the transformation of biomass to enhanced products, bioenergy, and chemicals. Some selected chemical process like the slow-fast pyrolysis, catalytic fast pyrolysis, hydrothermal liquefaction, transesterification and lignin valorization by depolymerization are aptly suited for biorefinery processing, and were discussed in this review. The (catalytic) fast pyrolysis and hydrothermal liquefaction are quite similar, but differ in their feedstock preparations, reactor configuration and thermal or energy optimization. The review covers the biomass selection, chemical conversion techniques and most importantly the required heterogeneous catalysts (where applicable). The work further suggests the superiority of dedicated chemicals over drop-in and smart drop-in chemicals, due the complete usage of biomass. Relative to the oil refinery process, biorefining is quite novel and accompanied by its drawbacks. These challenges range from catalyst poisoning and deactivation to energy intensiveness and eventually as being cost-ineffective. The challenge encountered in biorefinery is in the economic feasibility, as it is inferred from this review that the pre-treatment process takes up to about 20% of the conversion cost. Although the biorefinery plant employ lignocellulosic biomass, but study shows that the use of biomass is largely under-utilized. The solid products/ wastes from pyrolysis for example, can be utilized as source of energy for the process. In the pursuit for sustainability, it is essential to ensure a balance-energy-mix, where every other type of energy will have a role to play to avoid dependence on only one solution for the future. Therefore, in contrast to the dwindling fossil fuels, it can be generally speculated that the future for biorefining is bright. It was concluded that with vast knowledge on the suitable heterogeneous catalysts and proper optimization of process parameters (temperatures, pressure, and reactant species); some of the biorefining processes will result into a significant increase in industrial fuels and bio-based drop-in chemicals leading towards commercialization.

Keywords: biorefining, pyrolysis, transesterification, depolymerization, valorization, deactivation, biomass, hydrothermal liquefaction, lignin and catalysts

INTRODUCTION

Biorefining encompasses the selection, conversion and/or processing of biomass into value-added products, specifically, fuels and chemicals. Just like the refinery process converts oils to light and heavy hydrocarbon fuels and further into useful chemicals, the biorefinery utilize several known chemical processes into the valorization of biomass to chemicals. Elliot (2004) suggests that most chemicals from petroleum, used in food additives, clothing fibers, plastics in cars and paints, can as well be obtained from the biorefinery process. In recent years, aromatics, for example, gained its major boost in demand, as it is a major feedstock in the chemical industry (Reif et al., 2020). To ensure meeting this high Benzene,

Toluene and Xylene (BTX) demand, the depolymerization of lignin-fraction from wood, by the Diels-Alder reaction pathway has been utilized (Maneffa et al., 2016; Reif et al., 2020). Pyrolysis oil, for example, has shown to contain about 400 different compounds, where the feed composition determine its chemical properties (Yaman, 2004). The monolignols obtained from lignin depolymerization contain mainly alcohols. These monomers (which basically includes G - coniferyl alcohol, H - p-coumaryl alcohol and S - sinapyl alcohol) (Crocker and Santillan-Jimenez, 2020), transforms into chemicals of better-quality such as vanillin, vanillic acid and syringaldehyde, which have high market value (Song et al., 2018). The demand for biofuels relies on its transmissibility, which is the ease with which the fuel has transported to the higher its demand. The production and demand for biogas

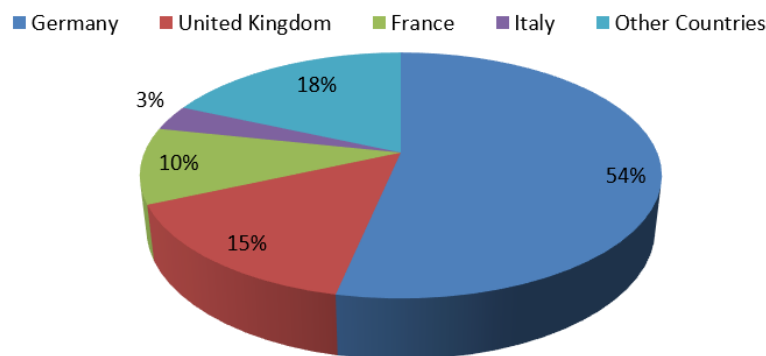


Figure 1. Units of biogas produced in Europe (Capodaglio and Bolognesi, 2019)

(which contain chiefly methane) are huge in Europe, and its use varies from cooking to heating (Capodaglio and Bolognesi, 2019) (**Figure 1**).

Ma et al. (2012) estimate that about an approximate value of 0.73 billion agricultural deposits produced per annum can correspond to 12000 trillion KJ of energy. The processing of first-generation biofuels was ineffective in Asia, as it couldn't fulfill the energy requirements for its population. Also, the outsized population in Asia (particularly China), was enough drawback for first-generation biofuels feedstock to thrive, as it competes greatly with human food. Within the searches of the authors of this work, there hasn't been a review that tackles specifically, thermo-chemical biorefinery processes and emphasizes more on their most perceived procedural drawbacks coupled with techno-economic analysis.

Therefore, the objective is to recognize emerging technologies, clarify problems, elucidate the techno-economic analysis of thermochemical processes, underline comprehensive comparisons between related thermochemical processes, evaluate research progress as it examines the most common biorefinery processes and finally, provides a feasible solution to the prevailing disadvantages encountered. This review would add to the continued drive towards energy and environmental sustainability.

OVERVIEW OF SOME SELECTED PROCESSES FOR BIOMASS UPGRADING

The earliest (or first-generation) forms of biomass for fuels were plants, which competes greatly with food for humans. There has been a drift from the first to the second and third generation, which doesn't compete with human food, has come to stay. Biomass required for processing, can either be lingo-cellulosic biomass like corn cobs, corn stover, straw, husks and sugarcane bagasse. Other forms include algae, fats and oils, are reliable and easily sourced alternatives to declining fossil fuels (Morales et al., 2020). The significant drift from the petroleum-based products to bio-based products is as a result of improved biorefining techniques. Over the years, the massive advancements from slow to fast pyrolysis, to the addition of multiple catalysts to help result in stable products, to lignin depolymerization. The US Department of Energy envisaged that within 2020-2050, biomass should make up about 10% - 50% (respectively) of the basic chemical building blocks of bio-based products (Elliott, 2004).

Irrespective of the low yields of bio-products from biorefining, researchers continue to devise new chemical techniques and approach, to improve on the yields and product quality. The scope of this paper covers both thermal and catalytic selected biorefinery process like Biomass gasification, Slow to fast pyrolytic processes, Transesterification of lipids, lignin depolymerization and Catalytic fast pyrolysis. In the generation of pyrolysis oil by pyrolysis, there are investigations that the liquid can either be used directly in the application, of subjected to further upgrading or processing. The side biochar is not left behind; it is also applied in the industry as solid fuels or specifically in purification (Onay and Kockar, 2008). The Hydrodeoxygenation (HDO) process is applied to convert bio-oil to fuel. The process is still not efficient, due to the unstable bio-oil produced. The need to produce thermally stable bio-oil lead to the introduction of catalysts in the pyrolytic process (Crocker and Santillan-Jimenez, 2020), making the pyrolysis either ex-situ or in-situ. Recently, researcher's attention has moved into the valorization of lignin and it was found to be useful (Song et al., 2018). Lignin which is structural glue in the plant secondary cell wall is formed from radical polymerization of monolignols. The bonding pattern is formed by the radical linking of the monolignols by radical polymerization. Therefore, to valorize valuable products like vanillic acid and syringaldehyde, the bonding pattern has to be depolymerized. When vegetable oil is transesterified, a blend of glycerin and fatty acids alkyl esters is formed. This is only possible in the presence of a catalyst (alkali or acid), when an alkanol reacts with a triglyceride. According to Demirbas (2003), this process of transesterification is commonly used. The base-catalyzed process executes speedily compared to the acid catalyzed process, making it the most preferred. The pyrolysis oil is a dark brown organic liquid, composed of several compounds such as oligomers, alkanols, alkanals, phenols and carboxylic acids, etc. Rahman et al. (2018) suggests the drawbacks for the use of the promising bio-oil, which involves thermal and chemical instability, high viscosity, high moisture and corrosiveness. Compared to the heating value of fossil fuels, which take a range from 40 to 45 MJ/Kg, the pyrolysis oil is relatively small. The higher heating value (HHV) for bio-oil ranges from 16.79-19MJ/Kg which is as a result of moisture and oxygenated components present, thereby making the pyrolysis oil not fit for use directly as transportation fuels (Taarning et al., 2011).

The spectrum of selected thermo-chemical processes from lipids and lignocellulosic biomass, adapted from Ma et al.

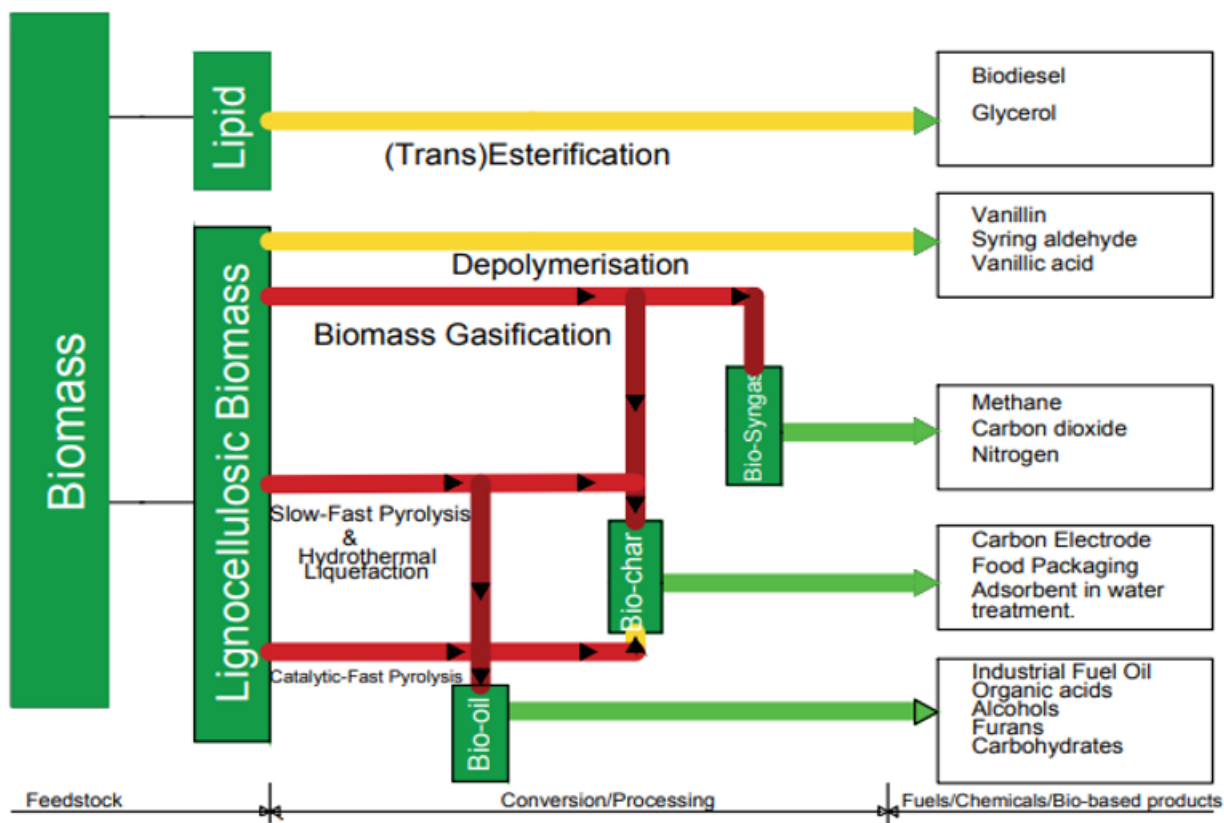


Figure 2. The spectrum of thermo-chemical processes

(2012) shown in **Figure 2**, involves the process pathways of how fuels and chemicals are made from biogenic feedstock. The flowsheet properly extends from the biomass or bio-path process (Green), through either a catalytic (Yellow) or thermal (Red) process to ensure the proper conversion of biomass.

It is paramount to differentiate between the different pathways involved and chemicals obtained from biomass utilization. These chemicals are more efficient, of high product quality, and more expensive compared to their petroleum-based counterparts. These quality products from biogenic sources can be classified into Drop-ins, Smart Drop-ins and Dedicated Chemicals. The process tracks taken for the transformation are called pathways. Hence, the conventional pathway follows the track taken to convert natural gas, petroleum and ash or coal to valuable products. **Figure 3** shows a schematic description of biological- and petroleum-based pathways to chemicals.

Bio-based drop-in chemicals are structurally similar to chemicals based on petroleum (Gerardy et al., 2020). Drop-ins use the biomass as a raw material and at an early stage join the traditional pathway. Compared to petroleum-based alternatives, they are manufactured in greater quantities and therefore costlier (Carus et al., 2017). Ethene, polyethene, polypropene and Polyethene terephthalate (PET) are examples of drop-ins. Smart drop-ins' chemicals are a particular subdivision of drop-in chemicals; the approach involves initially using the biomass-related method until at a late stage joining the traditional pathway. Generally, smart drop-ins are lower in quantity. Ethanoic acid, propenoic acid, adipic acid, butadiene and Isoprene are examples, etc. An entirely different direction from the traditional pathway follows dedicated bio-based chemicals. They may not have similar equivalents based on

fossils. They are used to manufacture high quality products that can't be manufactured by conventional chemical process (Carus et al., 2017). Compared to the others, the dedicated chemicals are more powerful as they use not only carbon but also the whole biomass, which includes carbon, nitrogen, hydrogen and oxygen. Therefore, the use of the complete biomass represents a high efficiency of biomass use (BUE) (Iffland et al., 2015). The comparison of various chemical groups from the use of biomass is shown in **Table 1**.

TRENDING SELECTED PROCESSES FOR THERMO-CHEMICAL BIOREFINING AND THEIR CHEMICALS

Biomass Gasification

Biomass gasification encompasses the incomplete oxidation of biomass, to a mix of combustible gases. The biomass ranges from agricultural residue, wood to coal, while the mixtures of gases (called syngas) are methane, carbon dioxide and hydrogen. Other wastes could be biochar, coal tar and ashes etc. According to the World Bioenergy Association (WBA), gasification originated in the 1800s as a process used to produce town gas, used in cooking and lightening. Hence, it is not a new technology (World Bioenergy Association, 2015). Gasification lost its attention, but regained it in the World War II, as a result of the shortage in liquid fuels available then (Kirkels and Verbong, 2011). Gasification process is safe, effective and highly organized method of biorefining with a wide variety of applicability offered by feedstock. The feedstock applications primarily include heating, electricity,

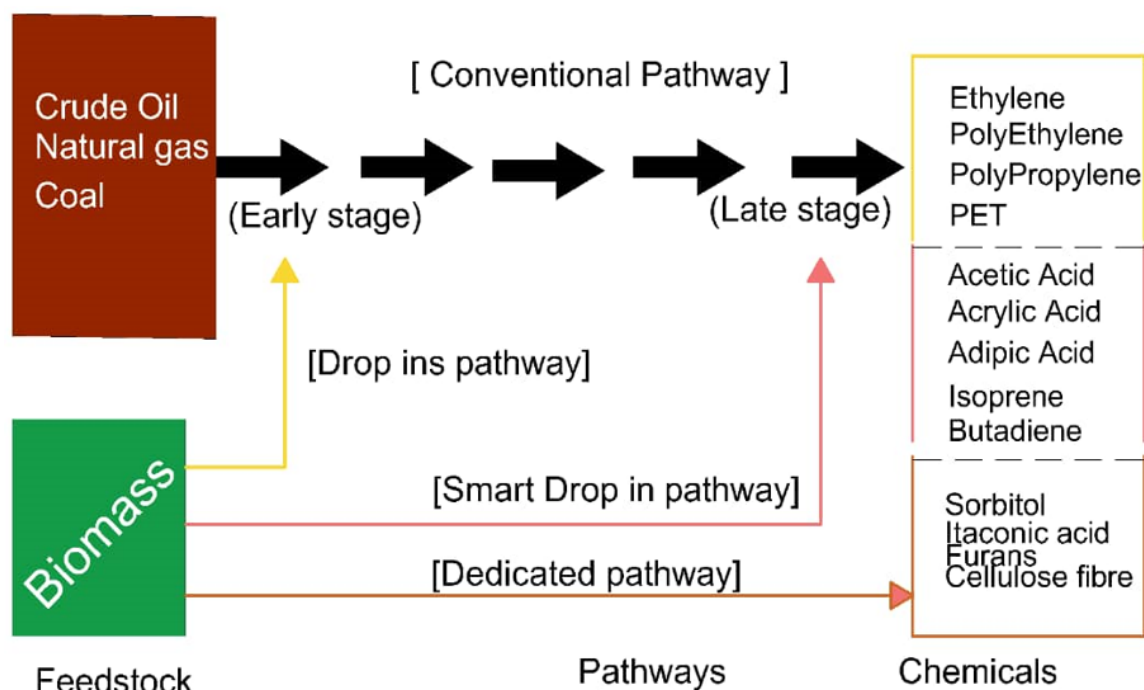


Figure 3. Schematic descriptions of bio- and petroleum-based pathways to chemicals

Table 1. Assessments of different chemical class from biomass utilization

Chemicals	Biomass Utilization Efficiency (BUE)	Petroleum Equivalence	Product Quantity	Product Quality	Pathway Efficiency	Cost (compared to petroleum-based products)
Drop-ins	< 100%	Yes	Large	Better	Efficient	Expensive
Smart Drop-ins	< 100%	Yes	Small	More Better	More Efficient	Expensive
Dedicated	100%	No	Medium/Large	Novel	Most Efficient	Expensive

chemicals and fuels for transport. Wood, mainly dominant in Canada, Finland, Sweden and the USA, is the most used feedstock for biomass gasification as the USA becomes the leading region (Kirkels and Verbong, 2011). The goal was to seek for a potential substitute for natural gas or transportation fuels. De Lasa (2011) proposes that biomass gasification process generates very minute levels of particles, together with a small amount of NO_x and SO_x when measured up with fossil fuels. Although the unwanted particulate poses a challenge to the biomass gasification process, it can as well be utilized effectively. The tar is thermally transformed when the gasifier operates at elevated temperatures; even at additional 1000°C it's difficult to completely remove tars (Morales-Delarosa and Campos-Martin, 2014). As opposed to the use of increase temperature to reduce the tar formation, the increased temperature can also make the process highly not economically feasible (Asadullah et al., 2001).

The introduction of catalysts can be approached in two groups, the first group, which is the chief catalysts, is positioned in the gasifier, while inside the reactor, the other group of catalyst is placed. The major challenge in the use of varied catalysts in catalyst biorefining technique, such as catalytic fast pyrolysis, is the presence of coke, which is capable of deactivating the catalysts. Using a nickel catalyst for example in a gasifier (De Lasa et al., 2011) works perfectly on time. When in the gasifier for long, it deactivates due to the deposition of carbon and prolonged sintering (Bulushev and Ross, 2011; De Lasa et al., 2011). The combined use of nickel

catalyst with either dolomite or olivine seemed promising, after about 60hours of operations (Bulushev and Ross, 2011). This for sure has been effective for pilot-scale production using the biomass gasification process (Pfeifer et al., 2004). Biomass required for gasification is usually of great amount, to get a significant large energy application. Several technologies have been advanced over the years to manage biomass feedstock usage. A set-up, in form of a co-gasification technique with coal or co-combustion with natural gas in an associated cycle is an alternative approach to properly manage the use of the biomass feedstock (Kirkels and Verbong, 2011). Due to the enormous energy required in a gasifier, the risk and cost of setting up the process seem quite outrageous (Maithel, 2009). **Figure 4** shows a plot of several fuels (solid, liquid and gaseous fuel) against their respective calorific values. From the plot, their average calorific value is high for gases and relatively low for solids, and an intermediate value for the liquid form.

Most deposits, bagasses and waste are basically used for production of power and heat generation in the industries (specifically, sugar industry) in East Africa. The heating rate for most biomass fuels is 10-16 MJ/kg (Parasnis, 2010). Residues and organic wastes have shown to be the widely used biomass basis, but arguably, the economic value of bioenergy crops has increased remarkably.

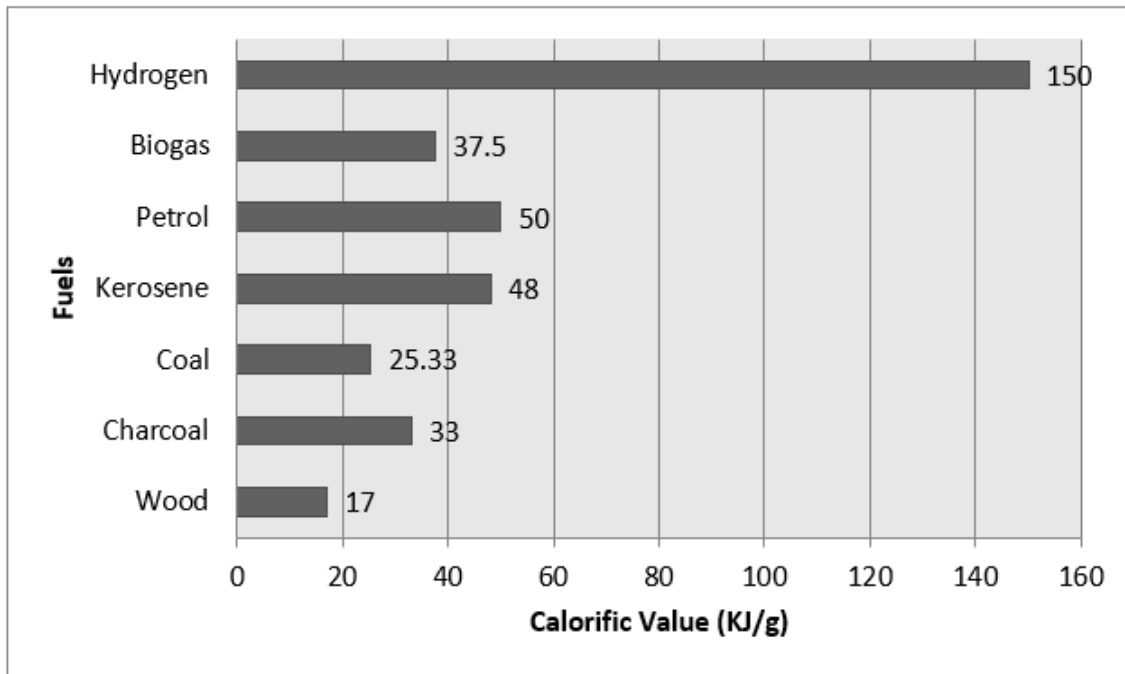


Figure 4. Sample substance heating value

Table 2. Wt % of bio-products generated from fast pyrolysis using different biomass

Biomass	Pyrolysis Type	Temp Range [°C]	Heating Rate [°C/s]	Bio-char [Wt %]	Bio-oil [Wt %]	Gas [Wt %]	Ref
Sewage Sludge	Fast	500	0.17	-	45.2	7.2	Cao et al. (2010)
Grape Bagasse	Fast	350 – 600	0.83	33.0	23.81	30.01	Demiral and Emine (2010)
Wood waste	Fast	500	0.17	-	39.7	22.2	Cao et al. (2010)
Corn cob	Fast	700	85	20.2	54.2	21.3	Huiyan et al. (2008)
Pig compost	Fast	500	0.17	-	44.4	8.4	Cao et al. (2010)

Slow/Fast Pyrolysis

The thermal breakdown of lignocellulosic biomass composed mainly of the long polymeric chain of cellulose, hemicellulose and lignin is carried out under certain operating conditions in an oxygen-deficient environment to yield different products. The products which consist of condensable liquids (bio-oils, tar and water), residual solids (bio-char) and gases (like CO₂, H₂, CO and hydrocarbons like CH₄, C₂H₄, C₂H₆) depend on the method of pyrolysis, the characteristics of the biomass and the operating conditions giving rise to different pyrolytic processes like the slow and fast pyrolysis. Slow pyrolysis also known as conventional pyrolysis or carbonization is one of the oldest types of pyrolysis. This method dates as far back as human history until the early 1900s where coal, acetic acid, methanol and ethanol were obtained from the slow pyrolysis of wood (Generation, 2019). It is characterized by a slower heating rate usually < 1°C/S, a lower pyrolysis temperature ranging from 300°C to 600°C and a longer residence time. Slow pyrolysis maximizes the production of biochar and gases which can be condensed into a liquid. In order to obtain sufficient bio-char, biomass with large particle size (5 - 50 mm), little ash content, high lignin content and fixed carbon should be used (Yaning et al., 2019). Bio-char is valued for its carbon storage ability and has also proven to be useful in soil amendment due to its hygroscopic and porous nature. Bio-oil obtained from pyrolysis are good sources of renewable fuels (they are CO₂ neutral) and are also

good feedstock for the production of chemicals such as bio-lime (Czernik and Bridgwater, 2004). In contrast, fast pyrolysis is ideal for the production of gaseous and liquid products. It is most commonly used for research and real-life application and is characterized by a high rate of heating, the gas residence time of a few seconds and an instant cooling of the vapour produced (Pfitzer et al., 2016). Careful selection of the feedstock must be done to maximize the pyrolysis oil yield. The moisture content should be around 10% or lower and the biomass should be reduced to fine particles usually < 1mm to increase the rate of disintegration leading to a greater yield (up to 70%) of bio-oil. The ideal feedstock for fast pyrolysis is one with a substantial amount of hemicellulose, cellulose substrate and extractives as they easily decompose to yield condensable vapours and gases. Biomass like wheat straw, corn cob and barley straw is good bio-oil feedstock whereas, walnut shell, nutshell and hazelnut shell are good feedstock for bio-char production because of their rich lignin content (Chowdhury et al., 2017). Tables 2 and 3 shows the percentage distribution of the products obtained from fast and slow pyrolysis respectively using different biomass.

Catalytic Fast Pyrolysis

Pyrolysis which involves the non-oxidative heating of organic materials is a process involved in the conversion of lignocellulosic biomass to a dark liquid called bio-oil (Crocker and Santillan-Jimenez, 2020). Conventional operating

Table 3. Wt % of bio-products generated from slow pyrolysis using different biomass

Biomass	Pyrolysis Type	Temp Range [°C]	Heating Rate [°C/s]	Bio-char [Wt %]	Bio-oil [Wt %]	Gas [Wt %]	Ref
Thistle	Slow	550	0.67	54.1	24.7	18.1	Gercel (2011)
Bamboo biomass	Slow	300	0.17	80	4	16	Laidy et al. (2014)
Live Oak	Slow	500	0.5	22 - 28	44-54 (tar)	18 - 30	Safdari et al. (2019)
Spark berry	Slow	500	0.83 - 0.5	26.1	50.2 (tar)	29.1	Amini et al. (2019)
Yaupon	Slow	500	0.83 - 0.5	27.3	48.9 (tar)	20.5	Amini et al. (2019)

conditions for pyrolysis are usually a temperature of 500°C and pyrolysis pressure of 1atm. The fast pyrolysis seems advantageous, because of the high yield of bio-oil and its corresponding bio-char. The bio-oil is usually thermally unstable, which limits its commercial use. Zhang et al. (Zhang et al., 2007) Suggests that bio-oil possesses a higher viscosity, poor volatility, lower heating value due to 35-40% oxygen content. The presence of oxygen poses a great challenge to biomass-derived products, obtained from lignocellulosic biomass. To address this challenge, this excess oxygenated compounds needs to be removed. The viable approach to the removal of oxygen from biomass-derived molecule is deoxygenation, which could be in form of decarbonylation/decarboxylation (deCOx) and hydrodeoxygenation (HDO). The hydrodeoxygenation (HDO) of lipids (specifically, vegetable oils), basically composed of triglycerides to alkanes, oleic and linoleic acids with C=C bonds is required to generate quality biofuels (Serrano-Ruiz and Dumesic, 2011). Although, HDO seems to be environmentally friendly, because it removes CO₂ and H₂O compared to deCOx reaction. The HDO process joins the C-O/C=O bond thus maintaining the carbon chain length (Lin et al., 2018). This is only made possible, by the introduction of metallic catalyst. Transition metal carbides (TMCs) have emerged as promising HDO catalysts. Robinson et al. (2016) investigated bifunctional catalysts specifically for the HDO reaction of bio-oil and its derivatives from biomass, with a target on the reactivity and how it is influenced by catalyst structures.

Ma et al. (2012) carefully outlined several catalytic chemical processes used in the enhancement of bio-oil to energy and chemicals. Bio-oil physico-chemical properties are highly unstable, which hinders its application. Hence there is a need for upgrading (Bunch et al., 2018). The Catalytic fast pyrolysis (CFP) involves catalytic processing of pyrolysis vapors either in situ (where pyrolysis and catalysis take place in same reactor vessel) or ex-situ (where the pyrolysis and catalysis take place in a separate reactor) (Crocker and Santillan-Jimenez, 2020). Each methodological approach comes with its drawbacks. The catalytic fast pyrolysis over zeolites (HZMS-5), through acid-catalyzed dehydration, at the active sites of the catalyst (zeolite) cellulose produces anhydro-sugar (Carlson et al., 2009). Hence, the anhydro-sugar is further converted into lighter olefins of C₂-C₆ forms, via oligomerization, decarboxylation and decarbonylation, and ultimately, the lighter olefins come together to produce aromatics, via aromatization of olefins (Rahman et al., 2018). Furans go through a succession of catalytic decarbonylation and oligomerization reactions and then generate aromatics (monocyclic and polycyclic) together with olefins through hydrocarbon group mechanism. Zeolite, which is a framework

of mainly silica (SiO₂) and alumina (Al₂O₃), is the most applicable catalyst for CFP (Crocker and Santillan-Jimenez, 2020).

Dong et al. (2012) propose that, due to complicated structure of phenyl propane monomers, called guaiacyl, syringyl, and p-hydroxyphenyl, lignin has the least susceptibility during catalytic pyrolysis. Raman et al. (2018) have clearly outlined several factors which may be essential to enhance the value of bio-oil yields. The presence of oxygenating species, increased viscosity and low energy density etc. are some of these restrictions. The amount of bio-oil generated, is heavily dependent on the catalyst properties i.e., pore size, crystallite size and chemical structure, as well as operating conditions, plays a very important role. Moreover, the yield and quality of bio-products of catalytic pyrolysis rely on the composition of biomass, the mode of reaction and the operating condition (ranging from residence time, heating rate, temperature, the particle dimensions or size of biomass and form of catalysts, etc.). In the context of zeolites, bio-oil deoxygenation is a function of the Silica/Alumina (Si/Al) ratio and needs modifying the mesoporous zeolites with a decreasing Si/Al ratio for higher bio-oil and chemical yields. As a competent technique for generating high-quality bio-oil and chemicals from biomass substrates, Catalytic co-pyrolysis is used. Feedstock rich in hydrogen content is used in co-pyrolysis as a co-feeder. It is also possible to minimize oxygenating components and mutagenic polyaromatic hydrocarbons in bio-oil produced, by catalytic co-pyrolysis of the biomass feedstock with a hydrogen-loaded co-feeder (Crocker and Santillan-Jimenez, 2020; Rahman et al., 2018).

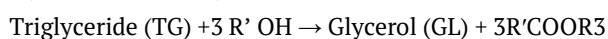
(Trans)esterification

A traditional method to manufacture biodiesel is transesterification, which can also be called alcoholysis. It is known to be the most efficient way to turn big triglyceride molecules into smaller, straight-chain fatty acid ester molecules. According to Zhang et al. (2003), the molecular weight will decrease by a factor of eight to one-third that of oil and viscosity, as well as increase its volatility. In vegetable oil transesterification, in the presence of a strong acid or alkali catalyst (acid-catalyzed or alkali-catalyzed processes), triglycerides react with alcohol, creating a mixture of methyl ester (FAME) and glycerol fatty acids. The transesterification is a stable response and basically, the conversion occurs by mixing the reactants uniformly (Demirbas, 2003). On the other hand, excess alkanol is used to increase alkyl esters yields and to allow proper separation from the glycerol formed (Anusi et al., 2018a, 2018b), and biodiesel yield increases with reaction time and is best at an elevated temperature of 60°C when palm kernel oil (PKO) has been transesterified. Transesterification

Table 4. Oil content for biodiesel feedstock (Baskar and Aiswarya, 2016)

Type of Oil	Feedstock	Oil content %
Edible	Soybean	15-20
	Sunflower	25-35
	Coconut	63-65
	Palm	30-60
Non-edible	Jatropha seed	35-40
	Neem oil	20-30
	Castor	53
Other sources	Rubber seed	40-50
	Sea mango	54
	Cottonseed	18-25

is therefore dependent on hydrodynamics, the power of the catalyst and the quality of the feedstock.



Biodiesel's merits outweigh its demerits, and thus, making it a good alternative to fuels from petroleum and have led to its use, especially in areas that are environmentally sensitive and where feedstock is readily available. Biodiesel high flash point of 150°C makes it safer to transport, less volatile and also safer to treat than diesel oil. Biodiesel offers lubricating properties capable of reducing engine abrasion and prolonging engine life (Von Wedel, 1999). It is understood that transesterification reactions are acid-catalyzed, alkali-catalyzed, or catalyzed by enzymes. As a consequence of its effectiveness, acid and alkali-catalyzed transesterification reactions have long been used. As for the enzyme-catalyzed reaction, an increased reaction time is required compared to the other two (Watanabe et al., 2001). The draw back to the commercialization of biodiesel is due to its high cost of production, as the feedstock pretreatment plant alone, is enough to affect the return on investment of the entire process (Zhang et al., 2003). This shows that the biodiesel industry has not completely seen the light. Biodiesel typically costs over US\$ 0.5/L, compared to US\$ 0.35/L for diesel from petroleum source (Lott, 2002). But still, there is a major downside to petroleum diesel. For several years, the use of these petroleum diesel sources of energy has resulted in an increase in global warming (Ogunwole, 2012).

Gashaw and Teshita (2014) suggests that transesterification is a conventional method introduced to minimize the viscosity during biodiesel synthesis, done in the presence of an alkanol. However, several factors such as reaction temperature and time, the molar ratio of alcohol, and catalyst concentration, affect the biodiesel production by transesterification. The production cost of biodiesel occupies about 75%, which make up feedstock and catalysts (Capodaglio and Bolognesi, 2019). Biodiesel is a blend of fatty acid methyl esters obtained from both edible and non-edible oil, as shown in **Table 4** (Baskar and Aiswarya, 2016).

Glycerol is the other product that comes from the transesterification process. Compared to the purified clear form, glycerol obtained from transesterification is typically very crude, dark and viscous. The method for purifying crude glycerol requires isopropyl alcohol (IPA) neutralization, glycerol concentration, decolorization and glycerol concentration, which ultimately results in refined glycerol (Muniru et al., 2016). Glycerol can be used for the manufacture of lubricants, cosmetics, paper, plastics, paints, etc. as a

feedstock. Its application varies considerably, as it is essential for both fine and heavy chemical manufacturing. A distilled or processed glycerol is commonly advertised on the market as 99.5-99.7% pure (Saifuddin et al., 2014). Glycerol in its pure form can be used in the food and pharmaceutical industries after transesterification with a high yield of crude glycerol, which can further be oxidized, reduced, halogenated, etherified and esterified to achieve different product chemicals (Javani et al., 2012).

Lignocellulosic Biomass Depolymerization

Lignin is known to act as structural glue between the cellulose and the hemicellulose of secondary cell wall of plants. Lignocellulosic biomass is compound blend of natural polymers - these materials contain cellulose within the range of 35-50%, hemicelluloses occupying 25-30%, and lignin 15-30% - firmly merged by both physical and chemical interactions (Rubin, 2008). Technical lignin is generated from chemical or laboratory process such as pulping and can be used in the generation of fuels. These lignins could be any of lignosulfonate, Kraft and organosolv lignin. The complication of the lignocellulosic biomass makes it hard for chemical transformations. In sugar, for example, cellulose hydrolysis needs a severe condition to occur, conditions such as the use of concentrated acids at high temperatures, but the β -glycosidic linkages of the sugar molecules contained in cellulose or lignocelluloses are powerfully sheltered by the firm packing of cellulose chains in micro fibers, resulting into difficulty in hydrolysis (Morales-Delarosa and Campos-Martin, 2014). Monolignols obtained from lignin depolymerization contain mainly alcohols. These monomers (G - coniferyl alcohol, S - sinapyl alcohol and H - p-coumaryl alcohol), combine by radical polymerization to form a bonding pattern called β -Aryl ether (β -O-4). In lignin depolymerization, the aim is to depolymerized (or delignify) the bonding pattern, β -Aryl ether (β -O-4), which is formed by radical linking of lignin monomers. The depolymerization of β -Aryl ether (β -O-4) is due to the presence of benzylic alcohol, to produce aromatic monomers (Crocker and Santillan-Jimenez, 2020). The β -Aryl ether (β -O-4) is abundant in lignin and takes up to about 60% structural linkages, followed by the β -5 and β - β as well as other minor units (Song et al., 2018). It is reported that the depolymerization process needs a rigorous reaction condition like high temperature and pressure, extended reaction time and involve the use of corrosive chemicals (Forsythe et al., 2013).

Lignin has a convoluted make-up with low reactivity, according to Chio et al. (2019), which restricts its use, hence

Table 5. Selected examples of Base catalyzed depolymerized lignin at different conditions (Rößiger et al., 2018)

Feedstock	Base Catalysts	Reaction Parameters		Products and Composition
		Reaction Conditions	Reaction Systems	
Organosolv lignin beech Wood and lignoboost craft lignin	5% Lignin in 1-5 wt % NaOH - Solution	250 bar; 5, 10, 15min at 250-340°C	Plug-flow reactor, Continuous mode	Oil content produced \leq 23 wt%
Organosolv lignin	2.5-10 wt%, 2.5 wt % NaOH-solution	250-315 bar, retention time 2-15 min at 240-340°C	Continuous mode of a Plug-flow reactor	\sim 22 wt % oil and \sim 15 wt% oligomers
Steam explosion hemp lignin	5 wt % lignin in NaOH solution	90-130 bar at 300-330°C	Batch wise mode of operation	About 11 wt % monomer species
Softwood indulin lignin	10 wt % lignin in a solution of 5 wt % NaOH	LHSV 1.4-4 h ⁻¹ at 270-315°C	Plug flow reactor at Continuous mode of operation	solid product \leq 70 wt% and some organic compounds
Residue from corn stover	10 wt % lignin, 2-4 wt % NaOH solution	270-300°C	Batch wise mode of operation	Soluble fractions \leq 78 wt %

the reason it's burned off as energy. However, the reactivity of the structural lignin is much lower than that of the lignin fragment, due to the reactive site being obstructed by the complex lignin formation. The sources of chemicals from lignin are very impressive, as the aliphatic and aromatic hydroxyl groups are major components and active sites in technical lignin. In chemical manufacturing, scientific lignin is extracted from industrial by-products that can be used as well as feedstock. Thus, about 30% of petroleum-based polyols have been substituted by technical lignin for the production of polyurethane (Cateto et al., 2008). Several catalysts ranging from acids, bases, metallic catalysts and ionic liquids are used for lignin depolymerization. Acid-catalyzed depolymerization is widely researched but has its related challenges (Chio et al., 2019).

A lot of metallic catalysts also have been investigated which includes noble metals (Ru, Pd, Pt, and Ti except Ni), cheap metals (Cu, Mo, Al, Fe, Zn), their combination and alloy (Zhai et al., 2017). Chio et al. (2019) in their work displayed the efficacy of Ru in specifically converting corn stalk lignin to 4-ethylphenol and 4-ethylguaicol with the yields of 3.10wt% and 1.37wt% at 275°C, 90min, 2 MPa. Song et al. (2018) employed Au nanoparticles (NPs) and Li-Al layered double hydroxide (LDH) as support, and it showed an outstanding result in oxidation of the benzylic group. The applications of metallic catalysts in lignin depolymerization can be limited by catalyst deactivation and low conversion rate (around 50-60%). Due to the deactivation of the catalysts, it is not cost-effective, especially when compared to acid or base which can almost completely convert lignin to other valuable chemicals in the course of the reaction (Chio et al., 2019). The most prevalent method for lignin depolymerization is the oxidative depolymerization. It involves breaking the β -Aryl ether (β -O-4) linkage pattern. Hydrogen peroxide and other oxidants are used in oxidation, which shows how cheap the process can be. The over-oxidation could increase the complexity of the lignin structure, which cause a difficulty of separating the products. Notwithstanding, biocatalyst require comparatively moderate reaction conditions when it compares to others. The biocatalysts involved specifically for biomass treatments and lignin depolymerization have been understudied for decades (Jennings et al., 2017). It is envisaged that the use of strong bases, like KOH, NaOH can transform and produce more depolymerized products rather than the weak bases, like Ca(OH)₂ and LiOH (Evans et al., 1996). Selected examples of

Base catalyzed depolymerized lignin at different conditions are shown in **Table 5**.

Hydrothermal Liquefaction

An emerging thermo-chemical process is the Hydrothermal Liquefaction (HTL), it basically involves the conversion of wet biomass, or organic materials in any form (including algae) into biocrude, biochar and gases, such as H₂, CO₂ and CH₄ (Castello et al., 2018). This process takes place at about 250-450°C and at a pressure of 100-350bar, with their respective catalysts as shown in **Table 6**. Several configurations have been set up for the HTL process, which can either take effect as a batch or continuous process. The relatively simplistic approach of the continuous configuration makes it heavily reported by literatures compared to the batch techniques (Toor et al., 2011; Zhu et al., 2015a, 2015b). In the batch approach, an autoclave is used as the batch reactor. The wet feedstock is fed into the autoclave, set at required temperature and further heated to a required time in the presence of a catalyst, after which the products are collected. Comparing the pyrolysis process with the HTL, Elliot et al. (1993) proposed that the HTL process is superior and differ in both biomass preparation and reactor configurations as shown in **Table 7**. According to Castello et al. (2018), there are several drawbacks with the batch technique, and this includes difficulty in coupling temperature and pressure, thermal transition, different contacting pattern and ultimately, HTL requires a systematic energy optimization which only be achieved in a continuous configuration.

ADVANCEMENTS, TECHNO-ECONOMIC ANALYSIS AND CHALLENGES ON BIOREFINING

The circular economy was invented as a feasible alternative to the present model of economic growth that promoted the system of "produce, consume, dispose." A remarkable approach was considered to be the implementation of biorefining as a strategy to achieve the circular economy principle as it would serve as a solution to the disadvantages surrounding waste generation by anthropological practices. Life cycle assessment (LCA) is a scientific methodology used to systemically analyze the environmental impact created after the useful life of a product, service or process (Ubando et al.,

Table 6. HTL biomass selection and operating conditions

Biomass	Catalysts	Reaction Conditions (bar/°C)	Reactor type/configurations	Residence Time (min)	References
Pomace, Yeast	K ₂ CO ₃ and ZrO ₂	200-250/330-400	Tubular/Continuous	1-30	Hammerschmidt et al. (2011)
Algae	-	200/350	Stirred	15	Barreiro et al. (2015)
Microalgae	-	200/350	-	27-50	Elliott et al. (2014)
Sewage sludge	Na ₂ CO ₃	86-148/275-305	Column/Continuous	90	Molton et al. (1986)
Wood	-	207/330-340	Tubular	19-100	Thigpen and Berry (1982)
Fungi	-	270/300-400	Tubular	11-31	Suesse et al. (2016)
Fractions of MSW	-	100/250-310	N/A	60-120	Caretta et al. (2013)
Aspen wood	NiMo/Al ₂ O ₃	-	Tubular	-	Jensen et al. (2017)
Pine/Spruce	NiMo/Al ₂ O ₃	-	Tubular	-	Jensen et al. (2017)
Digested grains	K ₂ CO ₃	250/250-350	Tubular (Bench)	20	Mørup et al. (2015)

Table 7. Comparison between Hydrothermal liquefaction and fast (catalytic) pyrolysis

Hydrothermal Liquefaction				Fast (Catalytic) Pyrolysis			
Biomass	Catalysts	Design conditions	References	Biomass	Catalysts	Design conditions	References
Sewage Sludge	Na ₂ CO ₃	86-148 bar, 275-305°C, Continuous column	Molton et al. (1986)	Pine wood	N/A	500°C	Howe et al. (2015)
Digested Grain	K ₂ CO ₃	250bar, 250-350°C and Tubular	Mørup et al. (2015)	Pine wood	H-ZMS	520°C, in-situ technique	Paasikallio et al. (2014)
Pine	NiMo/Al ₂ O ₃	Tubular configurations	Jensen et al. (2017)	Beech wood	H-ZMS	520°C, in-situ technique	Paasikallio et al. (2016)
Wood	-	207bar, 330-340°C, Tubular	Thigpen and Berry (1982)	Sewage sludge	N/A	500°C	Cao et al. (2010)
Yeast	K ₂ CO ₃ and ZrO ₂	200-250bar, 330-400°C and Tubular	Hammerschmidt et al. (2015)	Grape Bagasse	N/A	350-600°C	Demiral and Ayan (2010)
Algae	-	200bar, 350°C and stirred	Barreiro et al. (2015)	Wood waste	N/A	500°C	Cao et al. (2010)

2019). This impact check begins at the point of extraction of raw materials through to processing/manufacturing, transportation and distribution, usage and disposal. Lifecycle assessment is very important in today's pursuit for sustainability as it critically evaluates and compares products, processes or services thereby helping us choose those with the least impact on the environment. For life-cycle environmental impacts, feedstocks have quite an immeasurable effects on biofuels produced. These impacts are made obvious amongst agricultural feedstocks, as lignocellulosic biomasses, from the point of extraction to the biorefinery plants. Lange (2007) suggests that the cost of both technology and feedstock used affects the conversion of biomass to biofuels. Important factors need to be considered in the setting up of a biorefinery; even more important is the techno-economic analysis, which is evaluated by several parameters such as production cost and income. It is pertinent to note that the price of some parameters greatly depends on the production technology, just as the cost variation for feedstock is also related to the purity of the product. Mandegari et al. (2017) suggested that these parameters are connected to several indicators such as total manufacturing cost, net present value, payback period, fixed capital cost, and break-even price and after-tax rate of return. Pedersen et al. (2017) evaluated the economic feasibility of gasoline equivalents production through hydrothermal liquefaction of aspen wood, by means of three different case scenarios. According to their research, sensitivity analysis predicts that the biocrude yield from the HTL process is the most responsive parameter for the fuel production cost; other important economic parameters are feedstock price, thermal energy, and these parameters helps in the performance of the HTL process.

The key issues to be addressed by the assessments of renewable resources for sustainable production of energy, oils, chemicals and polymers are of growing demands, gradual reduction of fossil fuels, an increase in the price of crude oil and environmental degradation (Rostrup-Nielsen, 2005). With the International Energy Agency's estimated biofuel production of approximately 25% in 2024 (IEA, 2019), bioenergy would certainly make a major contribution to the global energy mix, and biorefining will be an exceptional tool in achieving sustainable growth. Biorefining was first described as a process in the 1990s (Maity, 2014) and has since developed, although it is still evolving. The International Energy Agency (IEA) describes it as the sustainable processing of biomass into a continuum of bio-based and bio-energy products that are marketable (IEA Bioenergy - Task 42, 2019). The goal of biorefinery, as suggested by Cherubini (2010), is to increase the use of biomass and to reduce the waste and pollution connected with its transformation into bioenergy and bio-based goods.

Since initiation, biorefining processes have continued to advance. Biomass feedstock selection, policies, technologies and refining processes are constantly being investigated to utilize the intrinsic potentials available therein. Some of the biggest and most recent advancements in the biorefining process include:

- i. Sustainable government policies: According to Herman et al. (2011), government policies have always been important for promoting sustainable socio-economic development. In their current guiding principles affecting the market permeation of biomaterials stated that biofuels for transportation is supported regionally

by the EU biofuels directive and nationally by the US Energy Policy Act (2005) (Herman et al., 2011). Also, the German Renewable Energy (GRE) Law is another policy strengthening electricity and biofuel generation and distribution from biomass (REN21, 2009). It also accounts for about 46% of the fuel used in municipal heating in 2013 (Ericsson and Werner, 2016).

- ii. The introduction of big data analytics in biorefineries in line with the new industrial era (industry 4.0): As the world population continues to increase, amounting to about 7 billion, there is need for a large volume of products (chemicals, energy, fuels, etc.) to meet demand sustainably. In the fast world, big data analytics coupled with machine learning is improving the overall biorefining process. Biorefineries are generally integrated with several units requiring constant monitoring of several process parameters by plant personnel. The commencement of platforms like Enterprise Manufacturing Intelligence (EMI) streamline the process of contextualizing process data which is shown for easy visualization for knowledge-driven decisions, giving birth to smart biorefineries that would be effective in the nearest future (Chiang et al., 2017).

Challenges of biorefining are:

- i. There are varied biomass feedstocks available for biorefining processes which can be grouped as; agricultural residues, algae, forestry residue, waste streams and non-reusable carbon sources. This variety comes with huge disproportions that make it difficult to create a system that can accommodate all feedstocks in a single class. There are four biorefinery systems, which are green refineries, lingo-cellulosic feedstock biorefinery, whole-crop biorefinery and two-platform concept (Roland and Jean-Michel, 2013). This has continued to impose challenges because while the conversion of corn/sugarcane to bioethanol and waste to biogas have been well-studied and established other biomass processing routes featuring the second and third-generation biofuels using agricultural, forest, municipal waste and algae are still ongoing research and development. And as such, they are commercially non-competitive (Ralph et al., 2010; Roland, A. L. and Jean-Michel, 2013).
- ii. Technological advancement is another factor with enormous impact on biorefining. The knowledge gap with the second and third-generation biofuels is greatly wide. According to Ralph et al. (2010), improved research techniques and technology would help in the understanding of feedstock including the production, transportation, storage and refining processes (including biochemical, chemical and thermochemical). Lignocellulosic biomass is the next most plentiful polymer; yet, it is being under-utilized despite. Hence, lignin is generally burned to provide power/heat as opposed to its economical use in the production of chemicals, fuels, and other products (Yamakawa et al., 2018). This is attributed to the difficult nature of lignin which inhibits cellulose and hemicellulose hydrolysis (Akhar et al., 2016).

Interestingly, pre-treatment or preparation processes constitute about 20% of the conversion cost (Mafe et al., 2015) and until cost-effective and environmentally soothing pre-treatment technologies are established. Hence, lignin-based products will continue to be economically infeasible (Baruah et al., 2018).

- iii. Accessibility of biogenic feedstock all year round for commercial-scale production and the danger connected with land use.
- iv. Land use, afforestation and water: The issue of land for arable purpose, afforestation and water remains one of the biggest challenges of biofuel because till date majority of biofuels produced worldwide are derived from first and second generation sources. According to a report carried out by Organisation for Economic Co-operation and Development (OECD) in 2019, 25% of sugarcane and 14% of global maize would be used in the production of bioethanol by 2028. This simply means that vast land mass would be used to cultivate sugarcane and maize for industrial purpose which could lead to food scarcity or undue increase in food price. Several thousands of forests are been destroyed to be able to provide feedstock (lignocellulosic biomass) for the production of biofuel.

CONCLUSION AND OUTLOOK

In the last decade, biofuels such as bioethanol, biodiesel and bio-gasoline have become an issue of global importance as man tries to fight environmental degradation and global climate change. According to World Energy Council (2016), bioethanol and biodiesel are the two common types of biofuel and are expected to increase globally to 140 billion litres and 46 billion litres respectively by 2029. Various models of biofuels have been proposed from first generation down to the fourth generation, some operational others still developing. Canada is still considered to be a major biofuel producer in the world producing over 250 million liters of biofuel annually (Mabee, n.d.). One would only wonder how other continents like Asia, Africa and few other developing countries are working towards energy sustainability.

For biorefining process to be a success, it involves proper understanding of the feedstock selection (biomass), processes (chemistry and technology) involved and finally the bio-based products (fuels and chemicals) to be achieved. The forthcoming biorefinery will have a huge influence on society as fossil-based resources become inadequate and more costly, it is even projected that biorefinery would overwhelm the petroleum refinery. Therefore, to properly maintain the balance of demand to energy, the use of biomass to complement petroleum, is the only known alternative to meet society demands in supplying new hydrocarbon-based chemical products. The beauty of biorefining is that it incorporates not just the prolificacy and involvement of the fine and heavy chemical industries, but it also places agriculture (afforestation) at the forefront of the economy. The need for afforestation and non-food crop cultivation would eventually pick up drastically. Even though the technological impediments for biomass gasification are much, it cannot be

denied that the products are useful, as attention for both gasification and pyrolysis should concentrate mainly on product enhancements. The lignin component which is the least utilized of the biomass fractions is often viewed as a fuel to drive the processing systems, but it is also a possible basis of aromatic chemical products. Other thermochemical processes like gasification and pyrolysis should concentrate on the scaling up and integration with current plants (Umenweke, Great, 2020). The pretreatment process of the lignocellulosic biomass has to be maintained properly in a cost-effective way, for commercialization. Furthermore, if attention should shift towards the second-generation biofuels (lignocellulosic biomass), composed of rice husk, corn stovers, energy grasses etc. due to its non-competitiveness as food crops or materials, it would make the conversion of biomass to energy a very promising venture to embark. As biofuel continues to advance, there is no doubt that this new drive towards clean energy will open a world of opportunities some of which includes:

- The need for R & D: There is need to bridge the gap between the realities of today and the possibilities of tomorrow. For example, even though it is possible to mass culture algae for oil production, the cost of production is still reasonably high due to the advanced technology involved (Benemann, 2008). It is possible for cost effective measures to be implemented and technologies deployed to allow for competitiveness in this method of biofuel generation.
- Waste Water: More opportunities would be presented with respect to water treatment and purification as almost all biofuel production is water dependent. This is obviously an aspect of biofuel production researchers need to look into, to ensure the biomass valorization process is highly environmental friendly in almost every aspect.

ABBREVIATIONS

Mtoe- Million Tonnes of Oil Equivalent, BTX- Benzene Toluene Xylene, HDO- Hydrodeoxygenation, WBA - World Bioenergy Association, CFP- Catalytic Fast Pyrolysis, HZSM-5- H-form of Zeolite Silicony Mobile -5, PKO- Palm Kernel Oil, IPA- Isopropyl Alcohol, NPs- Nanoparticles, LDH-Layered Double Hydroxide, LHSV-Liquid hourly space velocity. SO_x- Sulphur oxides, NO_x-Nitrogen oxides, EMI-Enterprise Manufacture Intelligence, GRE-German Renewable Energy, LCA-Life Cycle Assessments, HTL-Hydrothermal Liquefaction.

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