

**ABSTRACT**

The increasing research and development of biofuels production has dominated spectrum of science and engineering in recent years. In this paper, a review of literature on recent advances in this area of biofuels production technologies, including green diesel synthesis, and other technologies namely; advance biofuels production, process intensification, biorefinery concept and integrated energy system approach are reviewed. The choice of technology largely depends on feedstock nature and composition, targeted biofuels and economics of the production technology. Therefore, challenges associated with feedstock availability has been intensively compiled providing alternative sources like waste, biomass and oils. Challenges associated with technology, profitability and energy density of biofuels and products are highlighted. The conclusion is that, these recent advances provide wider view into production of biofuels and its flexibility in both science and engineering would ensure marketability of biofuels.

**Keywords:** Biodiesel, Bio-oil, Feedstock, conversion technology, Yield.

**1.0 INTRODUCTION**

Energy availability, affordability and its renewability are some fundamental points dominating the debate on sustainable development. Energy and clean environment have transitioned into sustainable development indicators in country's economic evaluation. Although, according to neoclassical economists, energy is not considered as a factor of production; yet, there is association between the GDP and primary energy consumption, suggesting that; GDP growth is driven by country's energy demand (EIA, 2019) as shown in Fig. 1. Recalling that, the rate of fossil fuels utilization is by far much higher than its natural regeneration, leading to its shortage due to excessive depletion (Shemfe et al. 2015). There is existing gap between energy production and energy consumption needing to be addressed.

Consequently, the embryonic development of biofuels as response to both energy and environmental security was not unanticipated. According to Pierie *et al.* (2015), the carbon footprint reduction, total energy return on investment and environmental impacts of these biofuels, defined their energy efficiency and sustainability. For example, in conducting the sustainability analyses of particular biofuels feedstock, evaluating its renewability, availability, economic feasibility and supply chain management would have to be considered. In addition, the process energy efficiency, which is defined by the ratio of the energy output (EO) and the energy consumption ratio (Chen *et al.*, 2015); must be put into cognizance. Thus, in ensuring biofuels' sustainability, the careful selection of the feedstock, its suitable conversion technologies into valuable fuels and chemicals; and its long-term environmental impacts are critical factors to be well thought-out.

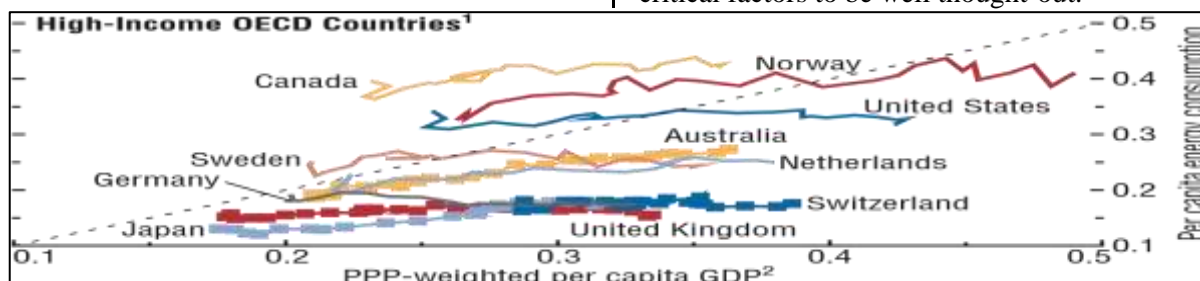


Fig. 1: World's per capital energy consumption relating to per capital GDP (EIA, 2019)

## 2.0 FORMS OF BIOFUELS

A biofuel could best be defined as any form of fuel (solid, liquid or gas) derived from biomass and accordingly, its application can be in household energy (cooking, heating), for electricity generation or in transportation sector (Ayres and Voudouris, 2014). In this regards, literature has availed different fuel materials qualified to be referred to as biofuels, including Biodiesel, Biocrude oil, Pyrolysis oil, Bioethanol, Biogas, Bio-butanol, Biohydrogen, Biomethanol, EBTE1 & EBTE2, DME and Synthesis gas to mention but a few. Interestingly, more biofuels are been discovered by the day. Recently, Green diesel (Srifa et al., 2015, Ahmed et al., 2020) and Furanic fuels (Addepally and Thulluri et al., 2015) have been added to the saturated literature pool. Therefore, it becomes increasingly difficult to keeping a universal definition of this concept, owing to the complexity in its chemistry and processing. Although, biorefinery concept has been well articulated, the need for in-depth knowledge of the individual biofuels, with regards to its production chemistry, kinetics and most importantly its economics will boost the whole biofuels industry.

Biomass energy obtained from biomass materials including specific energy crops, agricultural waste, animal and human waste and food waste, is today considered as one of the best alternative fuels sources (Anh et al., 2021). Meritoriously, biodiesel and its precursor, biocrude oil, are amongst the intensively investigated biofuels. Both fuels are obtained from biomass sources. The subsequent sub-sections of this review focus on the current and advances in the production of biodiesel and bio-oil as the major products of the biomass processing, towards proper integration into the biorefinery concept. Well established literature knowledge is avoided.

## 3.0 ADVANCES IN BIOFUELS PRODUCTION AND TECHNOLOGIES

Basically, four advanced approaches are been explored in current biofuels production, namely (1) advance biofuels production (2) process intensification (3) biorefinery concept and (4) integrated energy system approach. These are briefly discussed below.

## 3.1 Advance Biofuels Production

In discussing the current state of biofuels, the emergence of advance biofuels is briefly discussed here. Within few years back, new biofuels are introduced into the research and market of biofuels. Recently, n-butanol emerged as promising biofuels, synthesized via the conversion of principally pentose's liquor, and said to have contained longer hydrocarbon chain, making it miscible with either gasoline or diesel, even with significant GHG emission reduction (Pereira *et al.*, 2015).

Also, monomeric sugars and carbohydrate containing biomass are converted into highly aromatic and *iso*-paraffinic fuels via two-step hydrolysis followed by aqueous phase catalytic reforming. According to Wang *et al.*, (2015) sorbitol is converted into mono-functionalized oxygenated intermediates in the first stage of the reaction and proceeds to form jet fuel via aromatization of the intermediates. Aromatic, alcohol and alkane fuels are blended with gasoline to form gasohols for spark ignition engines. Such alcohol fuels have superior advantages over conventional gasoline including high oxygenation, lean flammability and octane number on one side and lower C/H ratio, heating value and boiling point as well (Agarwal *et al.*, 2015).

Green diesel (also called *syn-diesel*) is receiving appreciable attention recently. Literature has shown that green diesel is produced via two-step reaction. The oxygen contained in straight vegetable, fats and animals oils is removed via hydrogen catalyzed deoxygenation reaction, competing side-by-side with decarboxylation, decarbonylation and hydro-deoxygenation (Liu *et al.*, 2015). Based on the catalyst(s) selectivity, diesel boiling-range paraffin is formed, with water, propane and carbon dioxide as major by-products, which could be pressure removed from the green diesel, then, the green diesel is selectively hydro-isomerized further to C<sub>15</sub>-C<sub>18</sub> alkane grade diesel using catalytic hydrogen with yield of 81% (Kiatkittipong *et al.*, 2013). Detailed mechanism indicated that the green diesel is a

product formed via sequential reactions involving the deoxygenation of individual components.

### 3.2 Process Intensification and Solvent Engineering

As stated earlier, the increasing innovations, complex chemical/process interactions and the uncertainties in the composition of products make the bioenergy production much complex. Thus, Process intensification (PI) emerged as a way of strategic elimination of unwanted reactions, reducing size of processing plant and objectively optimized the desired product and equally making the process cleaner and energy-efficient, which will improved the production economics (Oh *et al.*, 2012). PI could be categorized into method-PI and equipment-PI.

Method-PI is aimed at development of simple, yet energy and cost effective process of biofuels production, which may perhaps involve the combination of two or more processes running side-by-side. Reactive Distillation in biodiesel production for example, is emerging method-PI involving continuous product separation as the reaction is taking place, thereby increasing the reaction surface. Reactive distillation has advantages including eliminating catalyst requirement, improved selectivity and enable rerun, which is proceeding via pseudo-homogeneous second order mechanism.

Molecular distillation is again another method-PI development in biofuels production. This low temperature filtration and vacuum distillation results in the separation of distillates based on their molecular moieties. Boffito and Rivas, (2020) reported the molecular distillation of bio-oil into phenolic, acidic, ketonic and esters as light distillates, while aldehydes and sugars were collected as heavy distillates. Fig. 2 presents the schematic diagram for molecular distillation of bio-oil into different products. On the overall, PI is aimed at improving the economics of biofuels production by reducing the energy, time and materials costs, without compromising the yield and product quality.

Similarly, break-through in solvent, catalysis and reaction engineering had demonstrated interesting approaches towards improving process effectiveness. Because; most biofuels production processes proceed by liquid-solvent extraction mechanism, the partition coefficient of such processes could be solvent engineered. Notably, in supercritical alcohol and supercritical carbon dioxide, to enhance hydrophobicity, needed for both biodiesel and bio-oil production. Solvent engineering such as co-solvent (Alhassan *et al.*, 2014), and synergetic co-liquefaction effects within the reaction intermediates (Johannes *et al.*, 2015) will improve the economics of biofuels production.

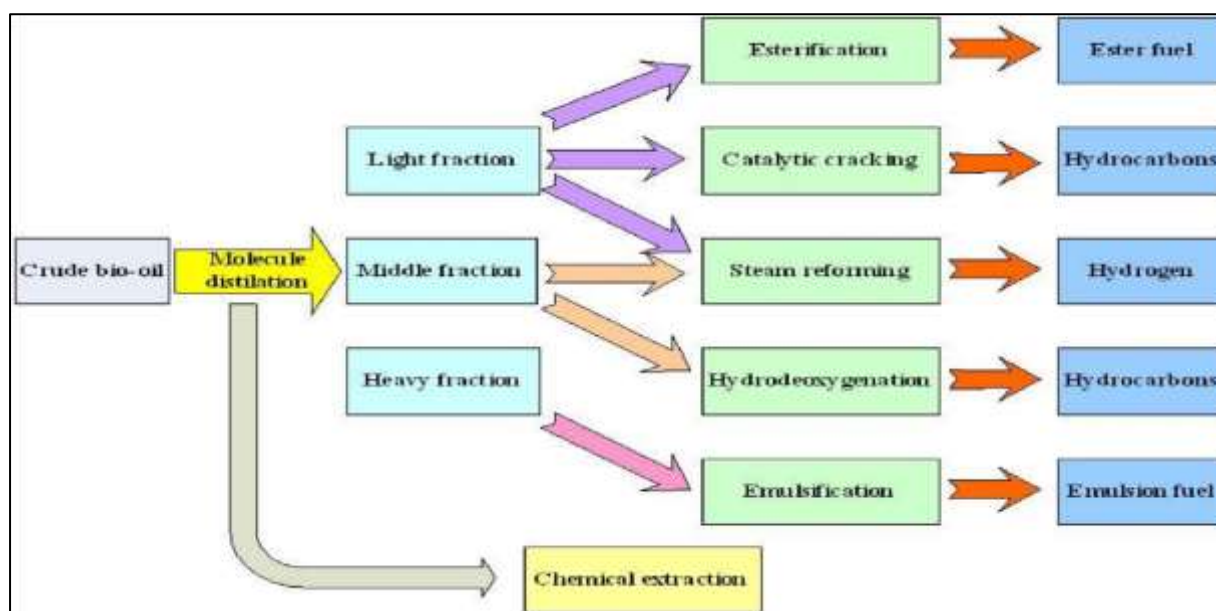


Fig. 2: Schematic diagram of Molecular Distillation of bio-oil (Adopted from Shurong Wang, 2013)

### 3.3 Integrated Renewable Energy System (IRES)

Integrated Renewable Energy System (IRES), involves a robust identification and optimization of the precise energy requirements under given scenario, considering environmental factors and availability. Thus, giving a design scenario specific approach in maximizing the best energy way out by combination of different energy sources including renewables. Recently, Hurtado *et al.*, (2015) demonstrated the suitability of such IRES; consisting biomass gasification system, solar component and battery bank as system back-up was sufficient in providing up to 98% energy stability.

It is believed that through IRES, both energy preservation and efficiency; thus curtails the need for energy storage prerequisite, increases consistency of power supply and quality from different renewable energy sources. According to Chauhan and Saini (2014), the evaluation of the energy production of IRES requires the inclusion of all factors determining the recurring and nonrecurring costs and the total life span of the system. This is defined as the ratio of the sum of annual cost of system to the system annual electricity production.

### 3.4 Biorefinery Concept

Biorefinery is a pinnacle of simple and advanced technologies put together in converting biomass

material into sustainable fuels, intermediates and chemical products with little or no waste (Rawat *et al.*, 2013), while the unconverted residues are also incorporated into the value chain. The complex nature of biomass biorefining did not permit universally accepted definition as well as classification of the concept. Initially, biorefinery was classified as *classical biorefinery* and *integrated biorefinery*.

Nowadays, biorefinery concept is classified into *energy-driven* and *chemicals/materials-driven* biorefineries. The classification could be based on the platform type, feedstock type and technology used in processing. Typically, a biorefinery consists of biochemical, chemical and thermo-chemical processes running side-by-side. Therefore, biomass processing using biorefinery is expected to ensure only useful products are produced in such a manner that pollutants, waste and losses are limited, in what is referred to as an *atom economy model*. In so doing, modern biorefineries are designed to accommodate all feedstock and produce wide variety of products. Since biomass is said to have contained economically viable molecules and compounds such as waxes, dyes, flavonoids, volatile fatty acids and polyphenols with cosmetics and semi-chemicals values (Pfaltzgraff and Clark, 2014) in addition to large fuels and fuels additives.

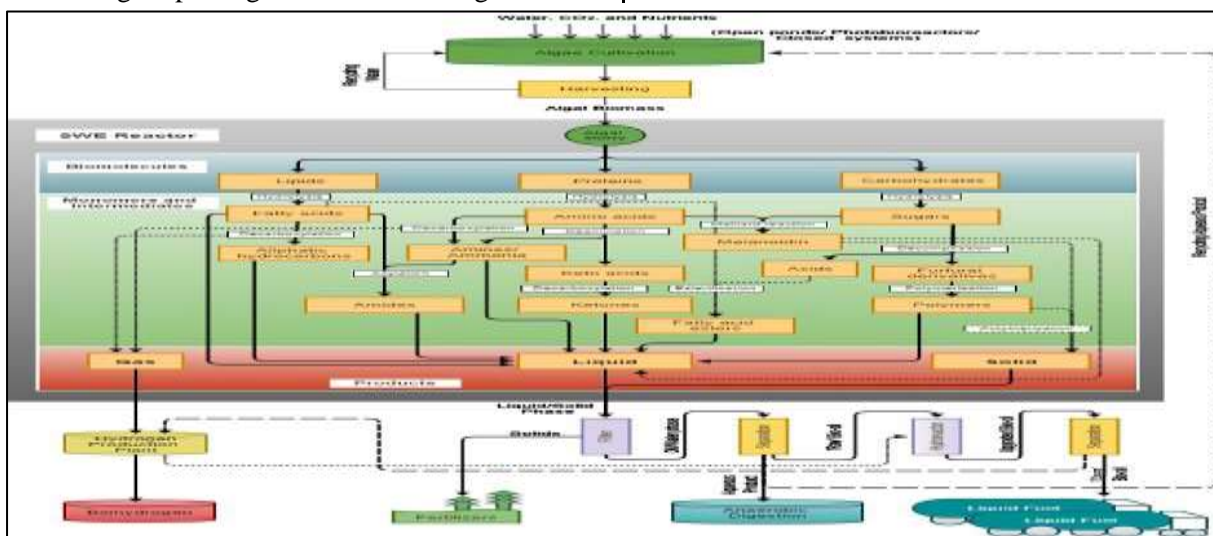


Fig. 3: Schematic diagram of a classical Algae Biorefinery (From Thiruvankadam *et al.*, 2015)

According to Holm-Nielsen and Ehimen (2014) the major considering factors during the design of an integrated biorefinery are the sources, type and composition of biomass, the techno-economic costs of the feedstock, the conversion and integration technologies as well as the final energy recovery of the biorefinery. Biorefinery products are formed via three basic steps; condensates products are formed by physical processes such as condensation and solvent differential interaction; non-condensates are formed via catalytic reaction processes like deoxygenation, carbonylation and reforming, while the final products are formed through advance chemical processes such as polymerization. Fig. 3 presents the classical algae biorefinery. For the aforementioned reasons, the need for inclusive investigations of the individual production processes and the synergetic and antagonistic interactions of the major components is inevitable.

Biodiesel and bio-oil production from different feedstock have been explored using biorefinery concept. It was demonstrated that, biodiesel and bio-oil production have similar biorefinery.

#### 4.0 BIOFUELS SUSTAINABILITY AND ECONOMICS

It is estimated that the renewable energy will be among the leading energy sources by 2020. In achieving this, the sustainability of the industry has to be assured. Biofuels sustainability indicators are evaluated based on its environmental and socio-economic impacts. The impacts on energy security, trade volume, socio well-being, natural conservation and carbon foot prints put together the sustainability of biofuels. In addition, biomass energy ensures job security through rural revitalization (Arinsola *et al.*, 2014). The sustainability of biofuels is discussed based on three sustainability indicators, namely; feedstock, environmental and economic sustainability.

##### 4.1 Feedstock Sustainability

Although there is unlikely available biomass to replace fossil fuel energy, comprehensive study of the bottom-up biomass availability potentials from different countries suggested the increasing biofuels supply potentials, specifically in

transportation fuel, which will be sourced from biomass, agricultural residue and energy crops (Deng *et al.*, 2015). Greater than 80% total cost of most biofuels is the cost of feedstock cultivation, transportation, sorting and pretreatment (Ayres and Voudouris, 2014; Arinsola *et al.*, 2014; Rawat *et al.*, 2013). According to Atabani *et al.*, (2013), more than 450 seed oil species had already been reported in the literature with many more that followed afterwards. Generally, feedstock could be classified into two broad continuums as 1) *Dedicated energy crops* and 2) *Waste and residue materials*.

The first and second generation biofuels are produced from specific energy crops. Such crops are rich in particular energy compound, which is easily converted into designated fuel based on the energy content of the crop. Sugar crops are prominent in low carbon components; found to be suitable in making ethanol fuels, as suitable gasoline substitutes, while oil crops are suitable for alkyl esters (biodiesel) production as diesel substitute, owing to their long chain (Addepally *et al.*, 2015). Algae biomass is increasingly becoming attractive and reliable feedstock for biofuels production. On per hectare basis, algae was found to be twenty times more productive than oil crops and can produce up to 220 times higher triglyceride content than oil crops, in addition to faster growth rate and high lipid content (Rawat *et al.* 2013). To this end, algae are likely the most convenient biomass for the production of different fuels (biodiesel, bio-hydrogen and bio-oil), secondary chemicals and fertilizer as presented in Fig. 3.

Assessment based on all performance indicators, algae has shown promising environmental impacts, excellent energy and carbon out-print and good production economic. Similarly, other aquatic biomass such as water hyacinth are equally promising feedstock (Pierie *et al.*, 2015; Wang *et al.*, 2015). Waste and residue are also gaining increasing global attention as feedstock for bioenergy production. Waste cooking oil (WCO), a largely available waste is been explored as suitable feedstock for biofuels because it is much cheaper than vegetable oils (VO). In a detailed review by Talebian-Kiakalaieh *et al.* (2013), it showed the advantages of WCO over

other VOs and animal fats as feedstock for biodiesel production including low acidity and cost; since feedstock accounts for 75-80% of the total biodiesel production cost. However, the authors were quick to elaborate the challenging issue with WCO such as increasing pre-treatment owing to high impurities resulting from the cooking process. In spite of these challenges, WCO has a bright future in the bioenergy market.

Waste sludge (SW) is yet another promising feedstock for biodiesel and bio-oil production. The high lipid contents of WS suggested their suitability in biodiesel production with impressive economics, as long as some challenges associated with its high free fatty acid (FFA) could be addressed. Recently, Olkiewicz *et al.* (2016) successfully produced biodiesel from WS using ionic liquids (ILs) catalysts with 90 % yield obtained under optimized conditions. In addition, important chemical constituents like cellulose and protein could be recovered from WS using suitable solvents, which helps the economics of such feedstock.

Food waste (FW), is another attention-grabbing feedstock which was said to possess functionalized fragments in its composition, it showed valorization characteristics. Intermediates and new application products include bio-fuels, renewable chemicals and intermediate materials are produced from FW. According to Uckun Kiran *et al.* (2014), FW contain components present in both biomass and algae; thus starch, lipids, organic acids, protein, lignin, cellulose, hemicellulose and residual are the major compounds in FW. This suggested the increasing interest in FW conversion into fuels and bio-chemicals. Microbial lipids from FW can be converted into high energy biodiesel and bio-oil as surrogates to VO; owing to its similar fatty acids composition.

In conclusion, feedstock is an integral part of biofuels production and economics. Generation by generation, feedstock from different biomass including cellulosic, algae, waste sludge, wastewater and waste papers have demonstrated suitable biofuels potentials. However, until date, seed oils have been the major source of biodiesel, while lignocellulosic biomass is most suitable for bio-oil production.

#### 4.2 Economic Sustainability

Achieving a low carbon economy in a few years to come depends on the viability of the so-called “*low carbon economy*”. A recent study conducted by Scarlat *et al.* (2015) has projected the current bio-economy market cutting across biofuels, biopharmaceutical, enzymes, forestry, aquaculture and other strands of the market to about €2.4 billion and providing about 22 million job opportunities within the European Union only. The main factor in economic sustainability of biofuels is its energy recovery. This is defined as the ratio of the energy required in the total biomass conversion to total energy that could be recovered from the combustion of such a fuel, while also taking into consideration, the heat recovery and losses (Hognon *et al.*, 2015). The evaluation of such net energy ratio requires the understanding of the mass, energy and elemental balances at each step of the entire process. In addition to this, total investment costs at every step, including fixed and working capital, start-up and maintenance costs needed to be considered. Finally, the operating cost including labor, electricity, raw materials and other expenses would give the final economic points of the process.

Interestingly, recent studies conducted by considering high energy price situation and side-by-side to a non-cellulosic scenario, demonstrated the existence of an integrated agriculture–energy link, in the near future (Han *et al.* 2016). This complex heterogeneity exists within the energy and agricultural commodities scenario. The up to date developments in applied energy economics (also referred to as *applied econometrics*), suggested that the established energy economic research approaches are the *co-integration and unit root testing*; and *Granger causality*, and *long-run estimation* (Smyth and Narayan, 2014).

To this end, proper eco-efficiency assessment is based on economic, environmental performances and total output value (commercial-worth) of each bioenergy product obtainable from the bioenergy system to be evaluated. According to Silalertruksa *et al.* (2015), the eco-efficiency is the ratio of the final product(s)/valuable chemical(s) to that of the environmental impact.

Thus; the eco-efficiency system output of a bioenergy system is given by;

$$\text{Eco - efficiency} = \frac{\text{Gross value added (US\$)}}{\text{Total GHG emissions (kg CO}_2\text{eq)}} \quad (1)$$

## 5.0 PROSPECTS AND CHALLENGES OF BIOFUELS PRODUCTION

### 5.1 Prospects of Biofuels Production

The future prospects of biofuels production and commercialization could best be described by a two-tailed prospect picture. The entire industry is ventured with prospects and challenges. The development of well-defined technologies targeting significant value addition of products and by-products, will undoubtedly give way to

emerging markets in the industry. Such technology intensification, like every other emerging technology, is both scientifically and economically challenging. On the other hand, the future of biofuels industry also depends on the number of useful products obtainable from the industry. The conversion of the products and by-products of the biofuels industry into value added chemicals will increase the production economics (Yan *et al.*, 2014). Fig. 4 presents the different pathways for the conversion of fatty acid methyl esters into value added chemicals. For example, one of the value additions is the production of volatile fatty acids which are fuel rich products and stabilizers as well.

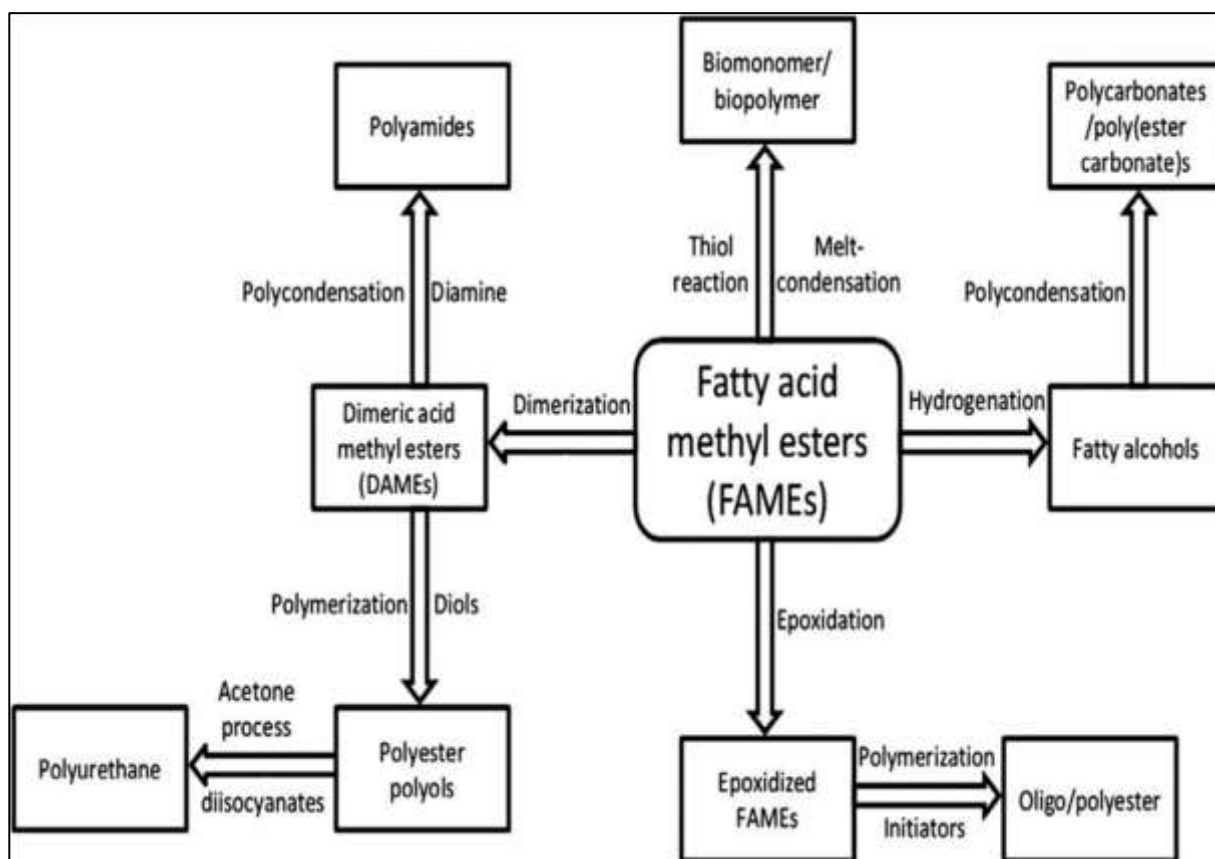


Fig. 4: Schematic conversion pathways for value added chemicals (From Yan *et al.*, 2014)

### 5.2 Challenges in Biofuels Production

The increasing interest in biofuels research has unavailable address some of the major challenges of biofuels industry. In this thesis, the challenges are classified into feedstock, production technologies and economics of the products. It was stated earlier that the greatest challenges are revolved around feedstock and its conversion

technologies. The increasing price of raw materials for biofuels production is alarming. Recently, production of fuels and chemical from waste materials has proven to be sustainable in terms of feedstock availability, environmental friendly with regards to landfill management and reducing methane emission. Investigation of additional feedstock will undoubtedly reduce the

pressure on energy crops and microalgae. However, the uncertainties in fluctuating feedstock availability and price need to be addressed.

## 6.0 CONCLUSIONS

It is an undisputable fact that conversion of biomass and other feedstock into biofuels is contributing significantly in World energy production. Bio-oil and biodiesel in particular are becoming major sources of renewable energy worldwide. However, the major challenges in the final product are associated with their poor stability, combustion and transportation properties, which translate into poor energy content and energy efficiency. Biomass including and lignocellulose biomass, would play significant roles in fuels and chemicals industry. Biodiesel and its precursor, bio-oil are source of transportation fuels and chemicals via transesterification and hydrothermal liquefaction processes, respectively.

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