



Opportunities, recent trends and challenges of integrated biorefinery: Part II



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ABSTRACT

Availability of cost-competitive biomass conversion technologies plays crucial role for successful realization of biorefinery for sustainable production of fuels and organic chemicals from biomass. The present article provides an outline of opportunities and socio-techno-economic challenges of various biomass processing technologies. The biomass processing technologies were classified into three broad categories: thermochemical, chemical and biochemical. This review article presents an overview of two potential thermochemical conversion processes, gasification and fast pyrolysis, for direct conversion of lignocellulosic biomass. The article further provides a brief review of chemical conversion of triglycerides by transesterification with methanol for production of biodiesel. The highly productive microalgae as an abundant source of triglycerides for biodiesel and various other fuels products were also reviewed. The present article also provides an outline of various steps involved in biochemical conversion of carbohydrates to alcoholic bio-fuels, bio-ethanol and bio-butanols and conversion of nature's most abundant aromatic polymer, lignin, to value-added fuels and chemicals. Furthermore, an overview of production of hydrocarbon fuels through various biomass processing technologies such as hydrodeoxygenation of triglycerides, biosynthetic pathways and aqueous phase catalysis in hydrocarbon biorefinery were highlighted. The present article additionally provides economic comparisons of various biomass conversion technologies.

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Abbreviations: APD/H, aqueous phase dehydration/hydrogenation; APR, aqueous phase reforming; BTL, biomass-to-liquids; CBP, consolidated bioprocessing; FFA, free fatty acid; FTS, Fisher-Tropsch synthesis; GVL, γ -valerolactone; 5-HMF, 5-hydroxymethylfurfural; HDO, hydrodeoxygenation; LCB, lignocellulosic biomass; LtL, lignin-to-liquid; MTG, methanol to gasoline; 4-PD/H, four-phase dehydration/hydrogenation; SSF, simultaneous saccharification and fermentation; toe, tons of oil equivalent

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1. Introduction

The energy and chemical security of the world is extremely important for sustainability of human civilization. The world is currently facing severe energy crisis due to incessant increase of energy demands and gradual depletion of fossil fuels. Therefore, there is a growing need of shifting dependency away from finite fossil fuels to carbon neutral renewable resources like biomass. The biomass being origin of fossil fuels provides wonderful opportunities to meet societal needs of both fuels and organic chemicals. Therefore, new manufacturing concepts are developing continuously for production of fuels, organic chemicals, polymers, and materials from biomass using complex processing technologies. These manufacturing concepts are analogous to today's integrated petroleum refinery and petrochemical industry commonly known as biorefinery [1–3].

Considering tremendous forthcoming potential of biorefinery, a comprehensive overview of possible opportunities and challenges of various biorefinery systems were presented in the previous article [1]. Moreover, various sources of biomass and their availability and chemical structure, classification of biorefinery and a roadmap of platform chemicals from carbohydrates were thoroughly reviewed [1]. The biorefinery was classified into three broad categories based on chemistry of biomass: triglyceride, sugar and starchy and lignocellulosic [1]. The present article provides comprehensive review of opportunities and socio-techno-economic challenges of various biomass processing technologies in biorefinery. The biomass processing technologies are generally classified into three broad categories depending on their conversion technologies: thermochemical, chemical and biochemical. The present article provides an overview of advancements of thermochemical conversion of lignocellulosic biomass (LCB) through gasification and fast pyrolysis, chemical conversion of triglycerides by transesterification with methanol and biochemical conversion of carbohydrates of sugar and starchy biomass and LCB to alcoholic bio-fuels, bio-ethanol and bio-butanols. Moreover, an overview of biorefinery based on highly productive microalgae as novel feedstock and conversion of nature's most abundant low-value aromatic polymer, lignin, to useful fuels and chemicals were highlighted in the present article.

The traditional biorefinery was mainly envisaged through a set of bio-fuels and platform chemicals containing oxygen heteroatoms in their structure [1]. The production of hydrocarbon fuels and building block chemicals from biomass in integrated hydrocarbon biorefinery is highly desirable to enable use of existing petroleum refinery and petrochemical industry infrastructures. The present article further provides an overview of various

biomass processing technologies in hydrocarbon biorefinery including hydrodeoxygenation (HDO), microbial processing and aqueous phase catalysis. Moreover, economic comparisons of various biomass conversion technologies were elaborated in the present article.

2. Thermochemical conversion processes

Gasification and fast pyrolysis are two potential thermochemical processes for direct conversion of LCB as outlined below.

2.1. Gasification

The biomass gasification is a potential technology to generate synthesis gas, heat and electricity. In gasification, the biomass is converted to combustible gas mixture consisting of H₂, CO, CO₂, CH₄, N₂ (for gasification with air) and traces of higher hydrocarbons in the temperatures range of 1073–1173 K [4–5]. The gasification is a combination of pyrolysis and partial oxidation. The heat required for endothermic pyrolysis is generated by partial oxidation of biomass using air or oxygen. The gasification of biomass is generally carried out using air as usage of oxygen involves additional costs of its separation from air. The technology of gasification of biomass by air however suffers from drawback of low heating value (4–7 MJ m⁻³) of resulting synthesis gas that limits its application for boiler, engine and turbine operation only [6]. Though biomass gasification by oxygen has potential to produce synthesis gas with improved heating value (10–18 MJ m⁻³); the economics however favors use of hydrocarbons (natural gas, C₂–C₅ and naphtha) and inexpensive coal as feedstock [5]. The detailed review of biomass gasification can be found elsewhere [5,7–9].

2.1.1. Gasification and pyrolysis regimes

The gasification and pyrolysis of biomass is usually described using three different regimes based on severity: primary (below 773 K), secondary (973–1123 K) and tertiary (1123–1273 K) as shown in Fig. 1 [10]. The products distribution in each regime depends on oxygen level, steam-to-biomass ratio, pressure and time-temperature history of solids and gases. In primary regime, solid biomass is converted to gases and oxygenated vapors for low pressure gasification; whereas it is primary oxygenated liquids in high pressure gasification. In secondary regimes, oxygenated vapors undergo cracking forming olefins, aromatics, H₂, CO, CO₂ and H₂O [8]. The primary oxygenated liquids however undergo condensation under high pressure to form condensed liquids

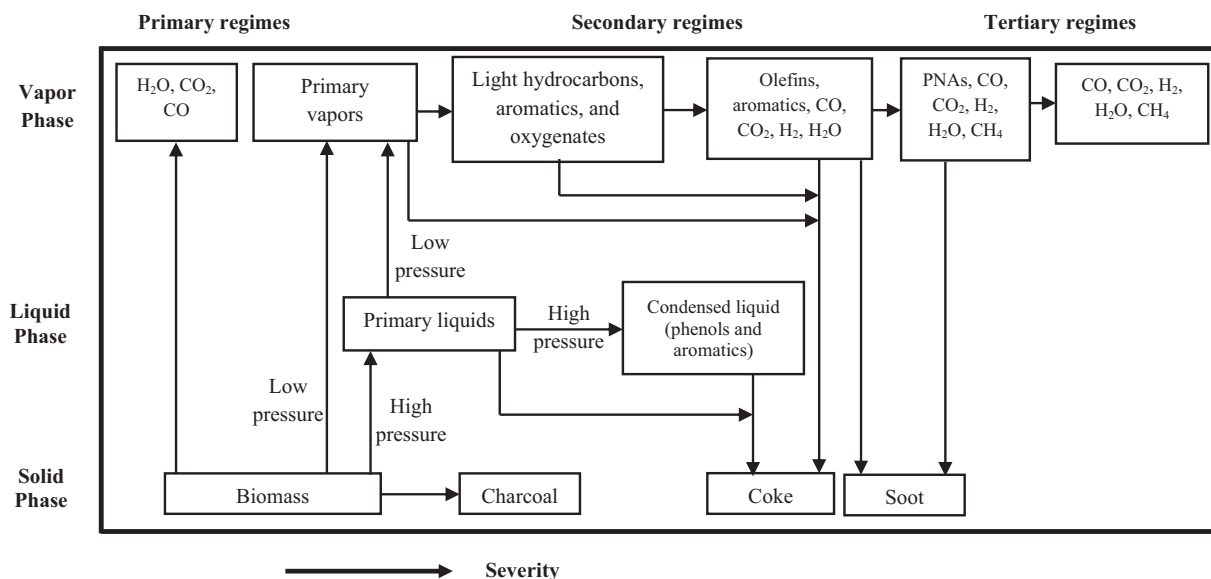


Fig. 1. The gasification and pyrolysis pathways [13].

consisting of phenols, aromatics and coke. In tertiary regime, secondary regime products further transformed to H_2 , CO, CO_2 , H_2O and polynuclear aromatics. The polynuclear aromatics condense to form tars [7]. Soot and coke also forms in secondary and tertiary regimes. The thermolysis of liquids and organic vapors is responsible for formation of coke. The nucleation of intermediate chemical species produced at high temperatures yields soot in gas phase.

2.1.2. Catalytic steam gasification

The presence of tars and methane in the resulting synthesis gas are two serious concerns of biomass gasification that restricts its application for power generation only [11]. The presence of tars in synthesis gas affects gasification efficiency and causes blocking and fouling of process equipments [12]. The presence of methane makes synthesis gas unsuitable as feedstock for Fisher-Tropsch synthesis (FTS). Tom Reed made a classical statement based on his long experience in the area of biomass gasification as outlined below [13].

While a great deal of time and money has been spent on biomass gasification in the last two decades, there are very few truly commercial gasifiers, operating without government support or subsidies, day in, day out, generating useful gas from biomass. The typical project starts with new ideas, announcements at meetings, construction of the new gasifier. Then it is found that the gas contains 0.1–10% ‘tars’. The rest of the time and money is spent trying to solve this problem. Most of the gasifier projects then quietly disappear. In some cases the cost of cleaning up the experimental site exceeds the cost of the project. Thus ‘tars’ can be considered the Achilles heel of biomass gasification. In the gasification of coal, a more mature technology, the ‘tars’ (benzene, toluene, xylene, coal tar) are useful fuels and chemicals. The oxygenated ‘tars’ from biomass have only minor use. With current environmental and health concerns, we can no longer afford to relegate ‘tars’ to the nearest dump or stream.

The high gasification temperature above 1273 K, though favours tars reduction, leads to agglomeration of ash that forces to keep gasification temperature below 1023 K [7]. By use of suitable catalysts, it is however possible to operate gasifier at such low temperature with simultaneous reduction of tars to a significant extent. It was reported that efficiency of biomass

gasification can be increased by ~10% by use of catalysts alone [12]. The catalytic gasification is generally carried out using two different approaches [12].

- (i) In primary approach, catalysts are mixed with biomass prior to gasification to promote tars elimination reactions within the gasifier. This approach is most preferred as it eliminates the need of hot-gas cleaning.
- (ii) In secondary approach, catalysts are placed in a reactor downstream of gasifier that operates under conditions different from gasifier. This approach is mainly used for reforming of methane and higher hydrocarbons.

Three different types of catalysts are generally used for catalytic biomass gasification: (i) dolomite, (ii) alkali and other metals and (iii) nickel. The inexpensive dolomite is most preferred primary catalyst as it is easily disposable and can substantially reduce tars. On the other hand, usage of alkali metals (carbonates of Na, K and Cs and borax) as primary catalyst poses serious disposal problems. The nickel being most widely used industrial catalyst for steam reforming is mainly used for hot gas cleaning. The catalytic biomass gasification using steam attracted substantial consideration in recent times for production of synthesis gas with relatively higher hydrogen contents for applications of both highly efficient electric power generation and feedstock for FTS [14].

2.1.3. Biomass-to-liquid

Biomass-to-liquid (BTL) is normally referred to synthetic fuels produced from biomass derived synthesis gas using FTS. The BTL technology enables production of large varieties of synthetic fuels including gasoline, diesel, heating oil, jet fuel, synthetic natural gas, methanol, dimethyl ether, ethanol [15,16] and higher alcohols [17,18]. The low temperature FTS (473–523 K) is generally used for production of jet fuel and diesel; whereas high temperature FTS (573–623 K) is used to produce gasoline range hydrocarbons [19]. The Fe and Co-based materials are commonly used as catalyst for FTS [20]. However, excepting methanol, dimethyl ether and synthetic natural gas; BTL technology is suffering from poor selectivity to fuel products [19]. Moreover, FTS requires synthesis gas with H_2/CO mole ratio in the range of 1.7–2.15. The synthesis gas obtained from biomass gasification is normally enriched in CO

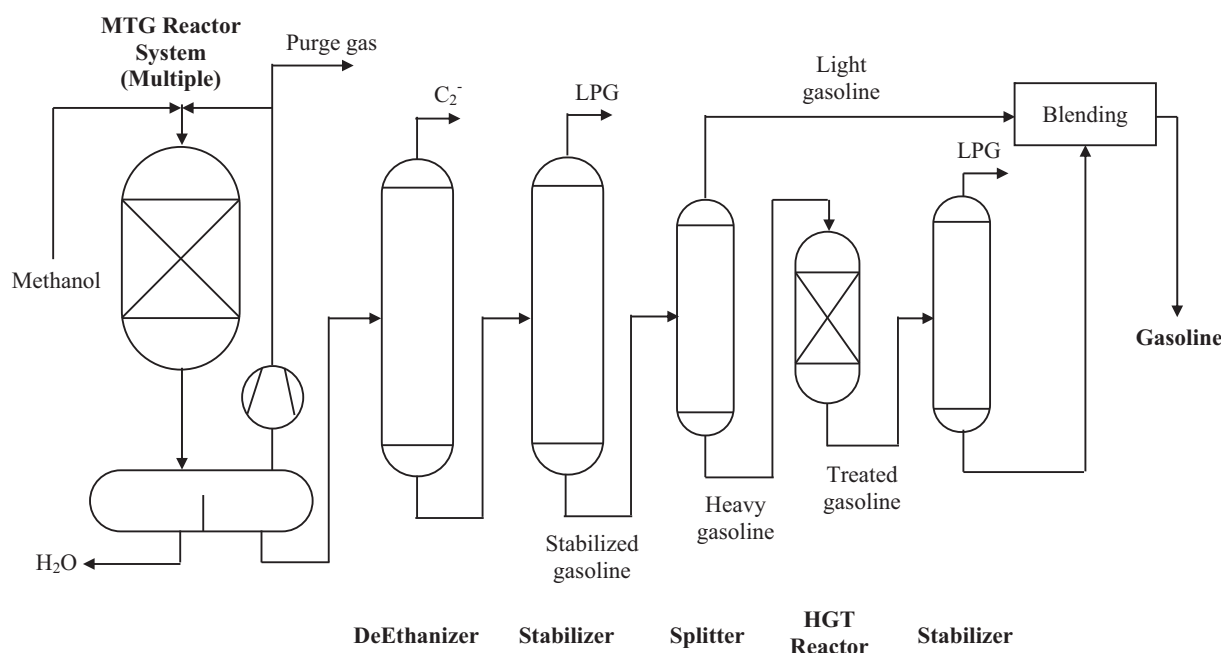


Fig. 2. Methanol-to-gasoline process flow diagram [24].

($H_2/CO=0.5$) because of higher oxygen contents in LCB [21]. The adjustment of H_2/CO mole ratio of synthesis gas by water gas shift reaction is thus necessary to suite its specific FTS applications. The integrated biomass gasification and BTL technology is generally gigantic in nature involving various capital-intensive intermediate and downstream processes such as hot gas cleaning, steam reforming, water gas shift reaction, FTS, hydrocracking and products separation [22]. The non-concentric nature of biomass also poses the biggest challenge for biomass gasification. All these factors make biomass gasification economically unviable.

The integrated biomass gasification and BTL technology progressed significantly as one can observe from technological initiatives by giant industries in the world. The Sasol's high temperature FTS based on fused-iron catalyst to produce gasoline range hydrocarbons in a bubbling fluidized-bed reactor is most promising one [23]. ExxonMobil developed a process for conversion of methanol (produced from synthesis gas) to gasoline (MTG) [24] (Fig. 2). The stoichiometric conversion of methanol to hydrocarbons is the associated advantage of this process. The main concern of MTG is that it produces gasoline with high aromatic contents which is unacceptable as per current gasoline specifications.

2.2. Fast pyrolysis

Fast pyrolysis of biomass has tremendous prospective over BTL because of its simplicity, lesser equipment requirements (only reactor) and hence lesser capital investments [21]. These attributes led this technology economically favorable on small scale (i.e. 50–100 t of biomass/day) appropriate to build and distribute portable units close to biomass source thereby eliminating expensive transportation of biomass [19]. The cost of biomass was reported to be \$22/dry tons for a fast pyrolysis plant capacity of 24 t/day; whereas cost of biomass became double (\$44/dry tons) for increasing capacity to 1000 t/day [19].

The pyrolysis is the thermal disintegration of organic materials at modest temperatures into solid, liquid and gas in absence of oxygen or in presence of significantly less oxygen required for complete combustion [25]. The fast pyrolysis of biomass with high heating rate (773 K/s) is generally used to obtain liquids in high

yield commonly known as bio-oils. The key to maximize yield of bio-oils in fast pyrolysis are rapid heating, high heat transfer rates, reactor operating temperature of ~ 773 K and rapid cooling of the pyrolysis vapors. The rapid heating and quenching of intermediate vapors (with vapor residence time < 1 s) prevents further break down of high molecular weight species into gaseous products (Fig. 1). The rapid reaction rate on the other hand minimizes char formation. The ease of transportation, storage and upgradation of bio-oils makes fast pyrolysis an effective method for densification of voluminous biomass in decentralized biorefinery [26]. Among various types of reactors, the fluidized bed reactor seems to be most economical and readily scalable and hence quite commonly used for fast pyrolysis of biomass. Realizing the importance, several review articles were published on fast pyrolysis of biomass [25,27,28].

A representative distribution of products from a fast pyrolysis reactor operated to maximize yield of bio-oils is 65 wt% bio-oils, 10 wt% water, 12 wt% char and 13 wt% gas [19]. The relative yields of gas, liquid and char however depends strongly on types of biomass, rate of heating and quenching, reaction conditions, reactor design and biomass alkali contents. The biomass alkali contents have significant impact on bio-oils composition as it catalyzes cracking to low molecular weight species as well as ring opening reactions [19]. The bio-oil is the mixture of more than 300 identified chemical compounds with considerable variation of physical properties and chemical compositions depending on types of biomass. The woody biomass typically produces mixture of 30% water, 30% phenolics, 20% aldehydes and ketones, 15% alcohols and 10% miscellaneous compounds [2]. It apparently seems that bio-oils could be a potential feedstock for varieties of chemicals. However, separation of compounds of very low concentration from mixtures of large number of chemical compounds of many classes is practically impossible by fractional distillation or extraction. However, bio-oils can be upgraded to get specific types of chemicals in high concentrations. Vispute and Hubber recently developed a process to upgrade aqueous fraction of bio-oils by aqueous phase dehydration/hydrogenation (APD/H) using 4%Pt/SiO₂-Al₂O₃ as catalyst producing C₁-C₆ alkanes with 42–48% of theoretical yield [29].

Table 1
Comparison of characteristics of bio-oil and catalytically upgraded bio-oil with crude oil [32].

| | Raw bio-oil | HDO of bio-oil | Zeolite cracking of bio-oil | Crude oil |
|-------------------------------|-------------|----------------|-----------------------------|-----------|
| Upgraded bio-oil | | | | |
| Y_{Oil} (wt%) | 100 | 21–65 | 12–28 | – |
| $Y_{Water\ phase}$ (wt%) | – | 13–49 | 24–28 | – |
| Y_{Gas} (wt%) | – | 3–15 | 6–13 | – |
| Y_{Carbon} (wt%) | – | 4–26 | 26–39 | – |
| Oil characteristics | | | | |
| Water (wt%) | 15–30 | 1.5 | – | 0.1 |
| pH | 2.8–3.8 | 5.8 | – | – |
| ρ (kg m^{-3}) | 1050–1250 | 1200 | – | 860 |
| 323 KPa s | 0.04–0.1 | 0.001–0.005 | – | 0.18 |
| HHV (MJ kg^{-1}) | 16–19 | 42–45 | 21–36 | 44 |
| C (wt%) | 55–65 | 85–89 | 61–79 | 83–86 |
| O (wt%) | 28–40 | < 5 | 13–24 | < 1 |
| H (wt%) | 5–7 | 10–14 | 2–8 | 11–14 |
| S (wt%) | < 0.05 | < 0.005 | – | < 4 |
| N (wt%) | < 0.4 | – | – | < 1 |
| Ash (wt%) | < 0.2 | – | – | 0.1 |
| H/C | 0.9–1.5 | 1.3–2.0 | 0.3–1.8 | 1.5–2.0 |
| O/C | 0.3–0.5 | < 0.1 | 0.1–0.3 | –0 |

The bio-oils can also be used as liquid transportation fuels. However, high water and oxygen contents, immiscibility with petroleum fuels, low heating value (~ 40 – 45% of hydrocarbon fuels), poor storage stability due to unsaturated compounds and high corrosiveness due to organic acids mainly acetic and formic acid leads bio-oils unacceptable as transportation fuels [6,8]. These factors limit its applications only as direct boiler firing, some types of turbines and large diesel applications after significant modifications [30]. The removal of oxygen of bio-oils is thus necessary to increase volatility and thermal stability and reduce viscosity for use as fuels. The following methods are commonly used to upgrade bio-oils.

- (i) Steam reforming: The steam reforming of whole bio-oils or water soluble fractions of bio-oils is a potential approach for production of synthesis gas using metal catalysts supported on metal oxides [31]. The synthesis gas will provide a source of hydrogen for upgrading bio-oils by HDO.
- (ii) Hydrodeoxygenation: HDO of bio-oil is carried out in presence of high hydrogen pressures (75–300 bars) in the temperature range of 523–723 K to eliminate oxygen heteroatoms in the form of water [32]. The high hydrogen pressure ensures high solubility of hydrogen in bio-oils and hence reduces coke formation. Numerous metal catalysts are used for HDO of bio-oils with notable being commercial hydrotreating catalysts such as Co–MoS₂ and Ni–MoS₂ supported on γ -Al₂O₃.
- (iii) Zeolite upgrading: The zeolite upgrading is carried out in the temperature range of 573–873 K under atmospheric pressure in absence of hydrogen to remove oxygen in the form of CO, CO₂ and water [32]. The components of bio-oils undergo series of reactions including dehydration, cracking and aromatization with catalytic cracking being dominating one.

The suitability of a process for practical consideration is primarily governed by yields and characteristics of the products. The principal product from HDO is oils (Table 1) [32]. On the contrary, main product from zeolite upgrading seems to be carbon with low yield of oils. As observed from the table, oxygen contents of resultant oils decreased to < 5 wt% for HDO and 13–24 wt% for zeolite upgrading. The decrease of oxygen contents resulted enhancement of HHV and pH and reduction of viscosity compared to bio-oils. HDO thus seems to be promising method over zeolite

upgrading because of higher potential yield of oils with characteristics closer to crude oils. However, HDO is associated with consumption of large amount of expensive hydrogen. HDO of whole bio-oils is also unsuitable for co-processing in existing petroleum refinery infrastructures due to its high acidity and water solubility and immiscibility with petroleum products. Pre-processing of bio-oils is thus required to reduce acidity and improve miscibility with hydrocarbons before its processing in typical refinery units.

The catalytic pyrolysis of biomass has enormous forthcoming potential to improve composition of bio-oils thereby avoiding costly upgradation [33]. Various types of catalysts (HZSM-5, mesoporous materials (MCM-41 MSU SBA-15), FCC catalysts, α - and γ -Al₂O₃ and transition metals (Fe/Cr)) have been examined so far for catalytic pyrolysis of biomass [34–35]. Carlson et al. recently reported production of aromatics from catalytic fast pyrolysis of biomass in single reactor with short residence time (< 2 min) in the temperature range of 673–873 K using ZSM-5, silicate, β -zeolite, SiO₂–Al₂O₃ and Y-zeolite as catalyst [36]. Highest percentage of aromatic products (ca. 30%) was observed for ZSM-5. The yield of aromatics can be favored by appropriate selection of catalyst, high heating rates and high ratio of catalyst/intermediate chemical feed. The approximate distribution of aromatics from a variety of feedstocks (glucose, cellulose, cellobiose and xylitol) were 10% benzene, 20% toluene, 40% naphthalene, 15% ethylbenzene and xylenes and remainder being mostly indanes and substituted benzenes containing three additional carbon atoms (such as mesitylene and ethyl methyl benzene).

Sooner fast pyrolysis is going to be leading thermochemical biomass processing technology due to its favorable credentials as one can see from recent technological advancements in this area. In 2008, UOP and Ensyn Corporation created a joint venture called Envergent Technologies for conversion of forest and agricultural waste to bio-oils through the RTP[®] process (rapid thermal processing) [37,38]. According to RTP technology, biomass is rapidly heated to approximately 773 K in absence of oxygen with hot sand in a circulating fluidized bed reactor and then rapidly cooled. The process occurs in less than two seconds. The joint venture of Dutch bio-fuels startup Bioecon and Khosla Ventures called Kior is currently developing catalytic cracking process for converting agricultural waste directly into “biocrude” a mixture of small hydrocarbon molecules that can be processed into fuels like gasoline or diesel in existing oils refineries [39].

3. Chemical conversion process

3.1. Transesterification

The transesterification of triglycerides with methanol is a promising chemical conversion process for production of biodiesel. The biodiesel have been widely accepted all over the world as potential bio-fuel with properties suitable for blending with petrodiesel. The blending of biodiesel with petrodiesel offers benefits of reduction of engine emissions (hydrocarbons, CO, particulate matter and SO₂) (though it increases NO_x) due to presence of oxygen in its structure (~11 wt%) [40–43]. The global annual production of biodiesel was 15.7 million m³ in 2009 and projected to nearly three-fold increase to 45.3 million m³ by 2020 [44]. The top five biodiesel producing countries in the world are Germany, US, France, Argentina and Brazil. Sofiprotéol's (an European leader in biodiesel production) group companies, (Oleon and Novance) France, are leading producer of renewable products (fatty acids, fatty alcohols, esters, glycerol, etc.) from vegetable oils and animal fats [45].

The transesterification is carried out in presence of either alkali, acid (homogeneous and heterogeneous) or enzymes (lipase) as catalyst under mild temperatures (323–353 K). The methanol is most commonly used as alcohol for transesterification reaction due to its suitable physicochemical properties, low cost, mild reaction conditions and ease of phase separation [46]. The transesterification reaction catalyzed by acid is usually slower compared to alkali and hence high alcohol to triglycerides mole ratio (> 15:1) is needed to drive equilibrium towards formation of esters [47]. On the other hand, enzyme catalyzed transesterification reaction offers advantages of mild reaction conditions, lesser sensitivity to free fatty acid (FFA) and water and ease of products recovery and catalyst recycling [48,49]. The slow rate of reaction, inhibition by methanol, exhaustion of enzyme activity and high cost of enzymes however barred its industrial application [50,51]. The alkali catalyzed transesterification reaction is quite commonly used using inexpensive NaOH as catalyst because of its high reactivity. Considering enormous potential of biodiesel, numerous review articles were published addressing technological advancements in this area [40–42,47,50–55]. Some of the major socio-techno-economic challenges of transesterification process are outlined briefly in the present article.

3.1.1. Feedstock

The selection of appropriate feedstock is very much important as it accounts for 60–80% of cost of biodiesel production [52,56]. At present, price of biodiesel is almost double of petrodiesel [56]. Currently, more than 95% of biodiesel is produced from edible oils such as rapeseed and sunflower oil in Europe, soybean oil in USA and palm oil in tropical countries [46,52]. The excessive use of edible oils for biodiesel necessitates sacrificing large fraction of arable lands that will eventually lead to food crisis and economic imbalances. The use of low-cost feedstocks such as non-edible oils, waste cooking oils and animal fats is thus needed for cost-competitive and sustainable production of biodiesel [57,58]. Though non-edible oils (e.g. mahua, karanja, neem, etc.) and animal fats are comparatively cheaper; but often contain large amounts of FFA that require multiple chemical steps or alternative approaches for its processing thereby increasing costs of production from such feedstocks [59]. Furthermore, animal fats are usually composed of high molecular weight saturated fatty acids and generally exist in solid state at room temperature thereby increasing difficulty in its conversion [52]. India has estimated annual production potential of about 20 million tons of natural non-edible oil seeds with only a few percentage of utilization [60]. Utilization of these non-edible oils entirely for biodiesel can

merely fulfill ~6% of country's annual consumption of transportation fuels in 2009–2010 (assumption: yield of biodiesel = 1 m³ of biodiesel per 4 t of seeds; density = 860 kg m⁻³). In India cultivation of jatropha having low FFA content in non-agricultural lands have emphasized to serve biodiesel industries [61]. Additionally ~20% of annual transportation fuels requirements can be met by cultivation of jatropha in identified plantation area of 13.4 million hectares. To fulfill whole transportation fuels requirements of India in 2009–2010 by biodiesel alone, ~45% of arable lands needs to be diverted for cultivation of jathopha which is completely unacceptable [1].

3.1.2. Feedstock quality

The triglycerides and methanol should be substantially anhydrous to prevent soap formation by hydrolysis of triglycerides followed by saponification of resultant fatty acids. The triglycerides should be free of FFA (acid value less than 1) to reduce consumption of NaOH by saponification reaction and minimize soap formation [59]. The water formed by reaction of FFA and methanol also inhibits transesterification reaction. The soap formation lowers the yield of esters and renders downstream separation of ester and glycerol and water washing difficult because of formation of emulsion. The non-edible oils, animal fats and waste cooking oils usually contain high percentage of FFA that makes unsuitable for their conversion to biodiesel by alkali catalyzed transesterification reactions [40,62]. The waste cooking oils are generally contaminated with moisture and various undesirable chemical compounds due to thermoxidative and hydrolytic reactions of vegetable oils during cooking [48]. This mandates pretreatment of waste cooking oils before transesterification reaction with added costs and process complexity.

3.1.3. Biodiesel purification

The biodiesel is mainly contaminated with residual catalysts, water, unreacted alcohol, free glycerol, soap and mono- and di-glycerides. The presence of mono- and di-glycerides are due to incomplete triglyceride conversion to esters and cause escalation of pour point and cloud point [47,63]. The removal of such contaminants is thus essential to meet standard specification of biodiesel and to ensure safe operation of diesel engines. The glycerol phase usually contains water, salts, unreacted alcohol and unused catalyst. The purification of glycerol is also very much important for its downstream conversion to value-added chemicals, synthesis gas or fuels additives to improve economics of biodiesel industries [64].

3.1.4. Fuel quality

Physicochemical properties of biodiesel primarily depend on fatty acid composition of triglycerides. The cetane number of biodiesel is generally higher than petrodiesel due to presence of oxygen and long hydrocarbon chain in its structure [63,65]. The cetane number of biodiesel is function of chain length and degree of unsaturation and branching [43,66]. The biodiesel produced from animal fats is normally of higher cetane number because of longer carbon chains length with more degree of saturation [63]. Additionally, viscosity, cloud point and pour point (15–25 K higher) of biodiesel are higher than petrodiesel. The higher proportion of unsaturated esters in biodiesel leads to formation of insoluble products by hydrolytic, oxidative and polymerization reactions causing problems within fuel system especially in injection pump [50]. But higher proportion of saturated esters results unfavorable cold flow properties [43,53,65]. Maintaining an appropriate proportions of saturated and unsaturated esters in biodiesel is thus important to trade-off between stability and cold flow properties [40]. Because of all these reasons, application of

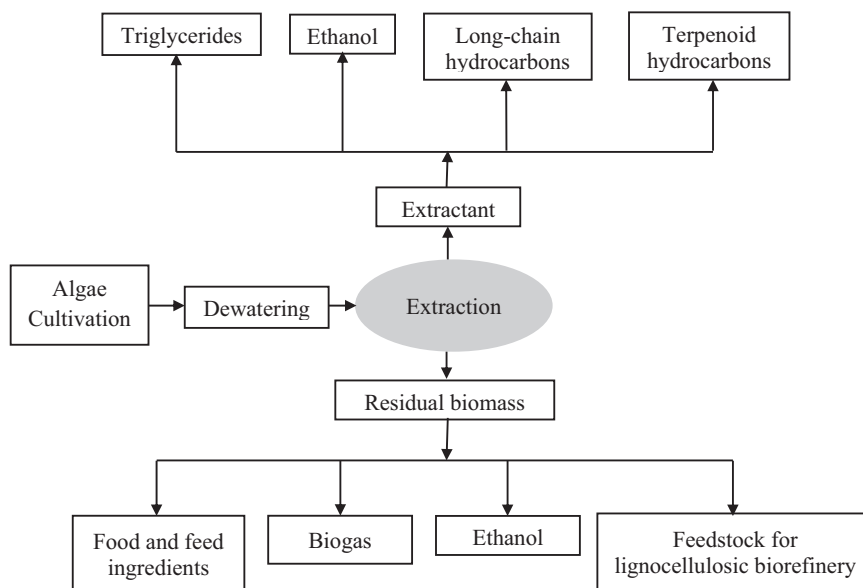


Fig. 3. Prospective avenues of microalgal biorefinery.

biodiesel is limited to blending with petrodiesel to an extent of 20% (B20) without engine modifications [40].

3.2. Microalgal biorefinery

The diversion of large fractions of arable lands for cultivation of oils crops is key bottleneck for successful realization of biodiesel. The microalgae as a source of triglycerides have enormous potential for complete replacement of transportation fuels with nominal sacrificing of arable lands. The rapid biomass growth rate, high oils productivity per hectare, high oils contents and non-requirement of arable lands are primary reasons for such extraordinary promises [66–67]. The microalgae commonly double their biomass within 24 h [67]. The oils contents can be up to 80 wt% of dry biomass with 20–50 wt% oils contents being common [67,68]. Considering only 30 wt% oils contents, annual biodiesel productivity from microalgae could be about 43.4 and 31.5 t of oil equivalent (toe)/hectares for photobioreactor and raceway ponds respectively compared to merely 1.29 toe/hectares from oils crops [1]. The simple calculation showed that less than 2% of arable lands are sufficient to meet entire transportation fuels requirements of India in 2009–2010 by biodiesel without adverse impact on food supply and other agricultural products [1]. However, such high biodiesel productivity has been reported based on short-term trials. Average annual microalgal biomass productivity of about $0.020\text{--}0.022\text{ kg m}^{-2}\text{ d}^{-1}$ ($\cong 18.8\text{--}20.7$ toe/hectares for 30 wt% oils contents) has been achieved so far in small scale trials in open raceway ponds [69]. Considering such realistic microalgal biomass productivity, the whole transportation fuels requirements of India can be realized by $\sim 3\%$ of arable lands only. By use of only $\sim 3\%$ of the US cropping area, transportation fuels requirements of US can be fulfilled by biodiesel [70]. The area equivalent to surface area of Portugal is sufficient to replace all transportation fuels of Europe by biodiesel [71].

Microalgae fixes solar energy in the form of biomass and oxygen using CO_2 and inexpensive growth medium containing water and inorganic nutrients (nitrates, phosphates, iron and some trace elements). The microalgae needs much less water compared to energy crops and can be cultivated in fresh water, saline water from sea, lakes, rivers and aquifers or waste water derived from municipal, agricultural and industrial activities [70,72]. The use of sunlight and CO_2 released as flue gas from nearby power plants or

chemical industries for microalgae cultivation will help to reduce expenses [73]. The open raceway pond and enclosed tubular photobioreactor are generally used for large scale production of microalgae [67,74–76]. The photobioreactor is advantageous over raceway pond due to its higher volumetric productivity (13 fold more compared to raceway pond), higher biomass concentrations (30 times greater than raceway ponds), lesser contaminations, reduced CO_2 losses and better control of culture condition at expense of higher cost of infrastructure, operation and maintenance [67,77]. To achieve improved productivity, reactors design and operation should be performed carefully to minimize biomass sedimentation on wall of the reactor, control of dissolved oxygen level to prevent photo-oxidative damage of microalgal cells, excessive rise of pH in the downstream of reactor due to consumption of CO_2 and temperature variations.

Despite having enormous potentials, commercial scale production of microalgae is currently limited due to excessive cost of production [78]. The collection and dewatering and extraction of oils are two major expensive steps in the process of microalgae production. The separation of small individual cell of microalgae ($3\text{--}30\text{ }\mu\text{m}$ diameter) from diluted biomass streams ($< 3\text{ kg m}^{-3}$) needs large capacity centrifuge making the process highly energy-intensive [79]. The analysis revealed that dewatering step alone consumes $\sim 69\%$ of total energy input [80]. Prior to centrifugation or filtration, flocculation followed by sedimentation and flotation will reduce harvesting costs substantially [71,79,81]. To extract oils from microalgae, cells are first disrupted and oils are then extracted with organic solvents (hexane or chloroform) [77]. Since, oils are present inside relatively small microalgae covered by a thick cell wall; very harsh conditions are needed to break cells for extraction of oils [71]. The scale of production also governs cost of bio-fuels from microalgae. It was reported that increase in scale of production by 3 orders of magnitude will decrease the cost of production by a factor of 10 [71].

The economics can be further improved by recovering oxygen and utilizing residual biomass in an integrated biorefinery to produce bulk chemicals, food and feed ingredients (Fig. 3) [82,83]. The conventional thermochemical conversion technologies such as gasification, fast pyrolysis and direct combustion can be used to produce synthesis gas, bio-oils and electricity respectively [81]. The biochemical conversion processes such as anaerobic digestion and yeast fermentation can be used to produce

Table 2
Features of most commonly used pretreatment methods.

| Methods | Process description | Effects |
|------------------------------|--|---|
| Steam explosion | Biomass undergo explosive decomposition by saturated steam at 433–533 K and 0.69–4.83 MPa for several seconds to few minutes before bringing the biomass back to atmospheric pressure. | The hemicellulose (80–100%) undergoes hydrolysis by released acetic acid and other acids and lignin is removed to a limited extent. The inhibitory compounds are generated. |
| Liquid hot water | The biomass is cooked with hot liquid water (473–503 K) at high pressure (> 5 MPa) for ~15 min with solid loading < 20 wt%. | 40–60% of biomass is dissolved with 4–22% of cellulose, entire hemicellulose and 35–60% of the lignin. Low or no formation of inhibitors. |
| Ammonia fiber explosion | The biomass is cooked with liquid ammonia (1–2 kg of ammonia/kg of dry biomass) at 363 K and 1.12–1.36 MPa for ~30 min. | Small amounts of hemicellulose or lignin is removed. The hemicellulose is deacetylated and degraded to oligomeric sugars. No inhibitors formation. |
| Ammonia recycled percolation | The aqueous ammonia (10–15 wt%) at 423–443 K is passed through biomass with velocity of 1 cm/min and residence time of 14 min. The ammonia is separated and recycled. | The aqueous ammonia causes depolymerization of lignin and cleavage of lignin-carbohydrate linkages, removes some hemicellulose and decrystallizing cellulose. |
| Dilute acid | The biomass is contacted with dilute H ₂ SO ₄ (< 4 wt%) at ~1 MPa for several seconds to minutes. Continuous: 5–10 wt% solids at 433–473 K. Batch: 10–40 wt% solids at 393–433 K. The H ₂ SO ₄ is neutralized by lime. | The dilute H ₂ SO ₄ hydrolyzes hemicellulose to xylose and other sugars which are further dehydrated to furfural and HMF. |
| Lime | The biomass is treated with lime (~0.5 kg/kg dry biomass) for few hours to days at ambient conditions. The lime is neutralized by CO ₂ and recovered as insoluble CaCO ₃ . | The acetyl and uronic acid substitutions of hemicellulose and lignin are removed. |

biogas and ethanol respectively [81,84–86]. The low lignin and hemicellulose contents of residual biomass are associated benefits of production of alcoholic bio-fuels from such feedstock. These bio-fuels can be used for generating electricity to power cultivation and oils extraction process. The residual biomass containing significant amount of proteins, carbohydrate and other nutrients can also be utilized to produce animal feed [87].

The fatty acid composition of algal oils is highly influenced by specific growth conditions and types of algal strains [65,88]. In general, algal oils are chemically quite similar to vegetable oils and composed of mixture of unsaturated fatty acids such as palmitoleic (16:1), oleic (18:1), linoleic (18:2) and linolenic acid (18:3) together with saturated fatty acids such as palmitic (16:0) and stearic (18:0) [65,89]. The fatty acid composition of algal oils for some of the strains are broader consisting of both lighter (C₁₂–C₁₄) and heavier fatty acids (C₂₀–C₂₂) [65,66]. Many algal strains possess huge amounts of saturated fatty acids leading to poor cold flow properties of biodiesel [88]. For some of the algal species, microalgal oils are quite rich in polyunsaturated fatty acids with four or more double bonds which make it susceptible to oxidation during storage [88,90–91]. Other than fish oils, microalgae can also be used as potential source of polyunsaturated fatty acids especially docosahexaenoic acid and eicosapentaenoic acid [79,81,92–94]. In addition to triglycerides, algae provides potential avenues to synthesize multitude of fuels products [95] such as photobiologically produced hydrogen [96,97], ethanol [85,98–99], long-chain hydrocarbons (> C₂₂) [100,101] and terpenoid hydrocarbons [100–102] (Fig. 3). The low concentration of these fuels products still remains as challenge for their successful commercialization.

4. Biochemical conversion processes

The steps involved in the production of alcoholic bio-fuels from starchy biomass are enzymatic hydrolysis of carbohydrates, fermentation of resultant sugars and products separation/purification. However, access of carbohydrates of LCB is hindered by protective plant cell wall composed of lignin that requires additional expensive pretreatment step in the process of its conversion to alcoholic bio-fuels. Brief overviews of these steps are outlined below.

4.1. Pretreatment

The pretreatment of LCB is required to remove lignin and hemicellulose, increase porosity and disrupt crystalline structure of cellulose which is otherwise inactive for subsequent enzymatic hydrolysis [103–106]. The several methods including physical (mechanical comminution), physicochemical (steam explosion, hydrothermolysis, ammonia fiber explosion (AFEX)), chemical (lime, dilute acid) or their combinations are generally used for pretreatment of LCB [107–112]. The features of most commonly used pretreatment methods are outlined in Table 2. The majority of cellulose of LCB is recovered as solid in all pretreatment methods. The hemicellulose and lignin are however either solubilized or recovered as solid together with cellulose depending on types of pretreatment methods. In AFEX, entire biomass is recovered as solid [103]. In dilute acid pretreatment, significant fraction of hemicellulose is hydrolyzed and recovered with liquid fraction while cellulose and lignin are recovered as solid [106,109]. In lime pretreatment, only lignin is solubilized and recovered as liquid; while entire carbohydrates recovered as solid are available for production of alcoholic bio-fuels [109].

The type and severity of pretreatment methods are generally selected based on nature and chemical compositions of biomass, cost involved and degree of recovery of carbohydrates. The mechanical comminution is generally not preferred because of huge energy requirements. The high temperature pretreatment is inappropriate for agricultural residues and hardwoods with low lignin and high pentose contents to prevent thermal degradation of pentose sugars [109]. On the other hand, high temperature pretreatment like steam explosion can be used for softwood having low pentose contents [109]. The AFEX is ineffective for biomass with high lignin contents [104]. The formation of various inhibitory compounds such as furfuraldehydes (HMF and furfural), weak acids (acetic, formic and levulinic acid), soluble phenolics and lignin degradation products (cinnamaldehyde, p-hydroxybenzaldehyde and syringaldehyde) is another bottleneck of steam explosion, acid and alkali pretreatments that mandates additional detoxification steps to remove these compounds [113,114]. The recent economic analysis of ethanol production from corn stover revealed that dilute acid pretreatment provides least product value among four pretreatment methods: dilute-acid, 2-stage dilute-acid, hot water and AFEX [115]. The success of alcoholic bio-fuels largely depends on availability of low cost pretreatment methods [116].

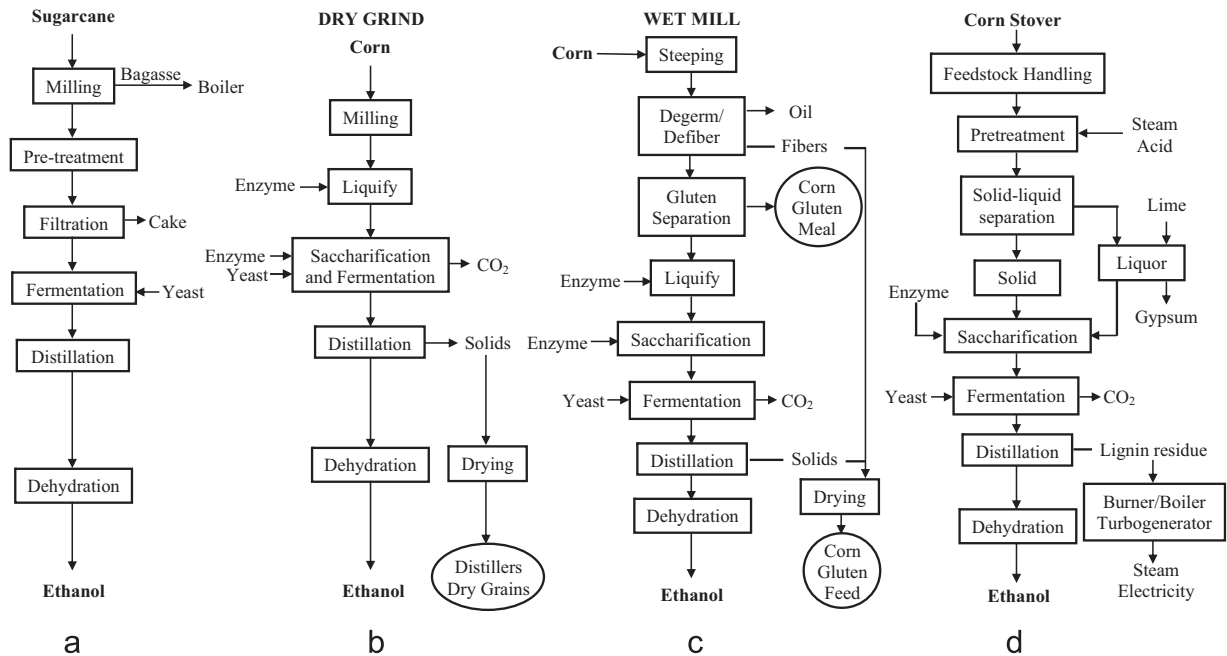


Fig. 4. Schematic process flow diagram ethanol production from (a) sugarcane [222], (b) corn by dry grind [224], (c) corn by wet milling [224] and (d) corn stover [222].

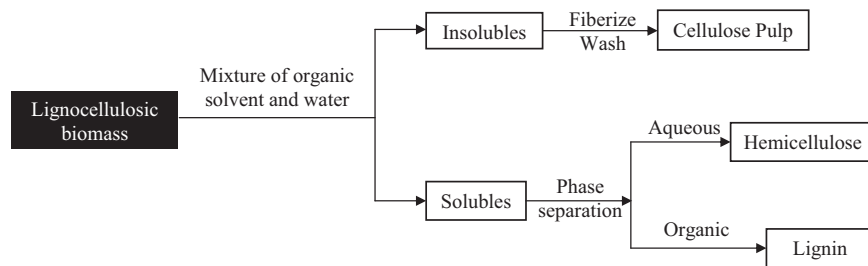


Fig. 5. Clean fractionation process [136].

4.2. Hydrolysis

The enzymatic hydrolysis is most commonly used for starchy biomass in spite of slower rate than acid hydrolysis due to its high specificity, mild reaction conditions and lesser propensity of formation of inhibitory products [105,114]. The starch kernels are first broken down to liquefied starch containing dextrans and small amounts of glucose by α -amylase at 363–383 K. The liquefied starch is then subjected to saccharification at 323–333 K using glucoamylase.

The solid residue containing mainly cellulose and remaining hemicellulose and lignin recovered after pretreatment of LCB are hydrolyzed to monomeric sugars either enzymatically (pH=4.8 and 318–323 K) using cellulase (for cellulose) and hemicellulase (for hemicellulose) or chemically using sulfuric acid or other mineral acids [117,118]. The acid hydrolysis is generally carried out using either dilute acid (1.5% H₂SO₄ at 473–513 K) or concentrated acid (30–70% H₂SO₄ at 313 K). The dilute acid hydrolysis is carried out in two stages: hydrolysis of hemicellulose (~80%) at lower temperature below 473 K followed by hydrolysis of cellulose at higher temperature (above 493 K) for maximum yield of sugars. Despite fast reaction, acid hydrolysis is generally not preferred due to corrosion of process equipments, degradation of released hexose and pentose sugars to HMF and furfural respectively, expensive recovery of acid and removal of degradation products and generation of chemical waste during neutralization of acid [114,119].

4.3. Fermentation

In separate hydrolysis and fermentation, hydrolysate containing monosaccharides are fermented by yeast or bacteria to either ethanol [105,120–122] or butanols by ABE (Acetone–Butanol–Ethanol) fermentation [123–126]. The hydrolysate obtained from sugar and starchy biomass containing only hexose sugars is usually fermented to ethanol by many naturally occurring organisms (traditionally Baker's yeast). The hydrolysate obtained from LCB contains both pentose (xylose and arabinose) and hexose sugars (glucose, galactose and manose). The fermentation of pentose sugars still remains as challenge. Only a few strains are available for fermentation of pentose sugars to ethanol. The most promising yeast species identified so far are *Candida shehatae*, *Pichia stipitis* and *Pachysolen tannophilus* [127].

The fermentation of hexose and pentose sugars is combined in single unit commonly known as co-fermentation to reduce process complexity [128,129]. The co-fermentation is carried out using either a genetically engineered microorganism for concurrent fermentation of hexose and pentose sugars or co-culture where two different microorganisms are cultured together and simultaneously exist in the same medium. Slow fermentation rates of pentose sugars compared to hexose sugars, high sensitivity to inhibitors, carefully regulated oxygen requirement and low product tolerance prohibited commercial application of co-fermentation [127]. The improvement of stains by genetic engineering is the key for effective utilization of pentose sugars to

boost overall economics of alcoholic bio-fuels from LCB. Inbicon recently demonstrated co-fermentation for production of bio-ethanol at their demonstration plant in Kalundborg, Denmark using specially developed microorganisms and the technology is ready for licencing [130].

To reduce capital investments, saccharification and fermentation are generally integrated in single unit commonly known as simultaneous saccharification and fermentation (SSF) with hydrolysis being rate determining step [113]. The SSF typically lasts for 3–6 days [131]. Additionally, integration helps to prevent product inhibition of hydrolytic enzymes [131]. The consolidated bioprocessing (CBP) provides another opportunity for biological conversion of LCB to alcoholic bio-fuels at lowermost cost. In CBP, four steps involved in the transformations of pretreated LCB to alcoholic bio-fuels are integrated in single unit [132–134]. (1) Production of saccharolytic enzymes, (2) hydrolysis of carbohydrates, (3) fermentation of hexose sugars and (4) fermentation of pentose sugars. It was estimated that total projected costs for biological processing of LCB to ethanol for an advanced process featuring on-site dedicated cellulase production in combination with simultaneous saccharification with co-fermentation was 49.9 \$ m⁻³ [133]. The production cost was more than four times of projected cost of CBP (11.1 \$ m⁻³).

4.4. Products separation

The concentration of alcohols in fermentation broth is normally very low. For example, fermentation product of SSF typically contains 4–4.5% ethanol [131]. The typical concentration of n-butanol in ABE fermentation broth is ~13 kg m⁻³ [126]. The separation of alcohols from such diluted aqueous solution to anhydrous grade alcohols by distillation is highly energy intensive. The cost of separation can be reduced by using advanced separation processes such as pervaporation or hybrid separation processes. The residue left after separation of alcohols containing lignin, unreacted cellulose and hemicellulose and other components is usually concentrated for use as fuel to power the process. The schematics of process flow diagram for production ethanol from various feedstocks are shown in Fig. 4. The overall economics of alcoholic bio-fuels can be improved by proper recovery and better utilization of lignin and hemicellulose, use of improved microorganism and advanced separation processes and process integration.

4.5. Clean fractionation

The foremost weakness of the methods being currently used for pretreatment of LCB is their inability to segregate biomass into its constituent fractions (cellulose, hemicellulose and lignin) preserving their chemical natures [135]. This impeded proper and complete utilization of all three fractions of biomass. Recently, researchers at National Renewable Energy Laboratory (NREL) developed an efficient pretreatment method called clean fractionation to segregate LCB into three fractions using mixture of an organic solvent and water (Fig. 5) [136]. The cellulose being insoluble in the mixture of organic solvent and water is isolated as solid. The hemicellulose being dissolved in aqueous phase is difficult to purify. However, aqueous hemicellulose can be converted into more concentrated solution or isolated as solid. The organic solvent containing dissolved lignin is evaporated to recover lignin as solid. This technology allows decentralized processing of wide variety of LCB into three fractions with little variation in chemical composition that can be easily stored, transported and processed individually to varieties of value-added chemicals or fuels in centralized biorefinery.

4.6. Bio-ethanol based biorefinery

The bio-ethanol is recognized as one of the most promising bio-fuels in the world. At present, ethanol alone accounts for ~94% of global bio-fuels production with Brazil and US together contributing ~78% of world's ethanol production [137]. The high octane number of ethanol (RON=96 and MON=78) permits its blending with gasoline to improve combustion characteristics. The presence of structural oxygen and negligible sulfur contents in ethanol leads to reduction of particulate matters, hydrocarbons, CO, NO_x and SO_x in exhaust gases [21,122]. The broader flammability limits, higher flame speeds and higher heats of vaporization of ethanol allows higher compression ratio and shorter burn time which in turn leads to theoretical efficiency advantages over gasoline in internal combustion engine [122].

At present, commercial ethanol production is predominantly based on edible sugar and starchy biomass; for example, sugarcane in Brazil, corn grains in USA and wheat and sugar beets in European Union countries. The world's largest producer of sugars and sugarcane, Brazil has been producing bio-ethanol from sugars and combined heat and power from sugarcane bagasse in large scale [138]. It was reported that whole corn grains currently available in US would be required to materialize 2020 federal mandates of renewable fuels by corn based ethanol alone [139]. Shifting dependency away from food materials to non-edible feedstocks such as LCB for ethanol production is thus necessary. The commercial cellulosic ethanol production is however limited due to high cost of production (almost twice of corn ethanol) [140]. Beta Renewables recently inaugurated world's first commercial scale biorefinery plant in Northern Italy for the production of 0.075 million m³ year⁻¹ bio-ethanol from agricultural residues [141]. For plant capacity of 0.262 million m³ of ethanol per annum (equivalent to more than 2000 metric dry tons of corn stover per day), the economic analysis revealed that feedstock, pretreatment, products separation and cellulase enzyme are major cost controlling factors contributing 31, 19, 12 and 9% of ethanol selling price respectively [142]. Moreover, the distillation can merely concentrate ethanol to just below azeotropic point (95 mol%). So specialized separation techniques (e.g. molecular sieve, azeotropic distillation, lime drying etc.) are needed additionally to produce fuel grade ethanol.

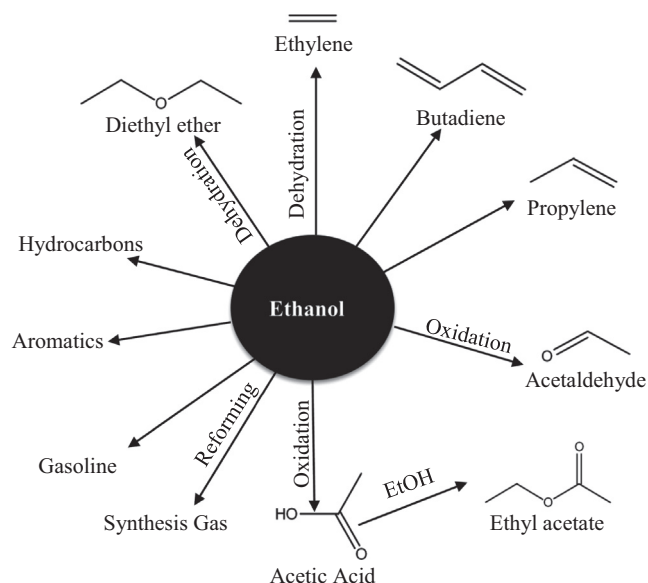


Fig. 6. Fuels and chemicals from ethanol.

The key challenges of ethanol as fuel are its incompatibility with existing internal combustion engine and gasoline infrastructures, corrosiveness and toxicity to ecosystems, high hygroscopicity and complete miscibility with water. The corrosive properties limit its blending with gasoline to limited extent only to avoid corrosion of metallic components in tanks and deterioration of rubbers and plastics in existing internal combustion engine. The blending with gasoline is associated with increasing risk of soil and groundwater contamination due to its miscibility with water. The complete miscibility of ethanol with water also increases solubility of ethanol-gasoline blend. The ethanol phase separates from gasoline once water contamination exceeds saturation limit [21]. These factors limit blending of ethanol with gasoline to the extent of 5–15% (v/v) without engine modifications. Ethanol-enriched gasoline such as E85 requires specially designed engines designated as flexible-fuel vehicles that are currently being used only in few countries like Brazil and Sweden [21]. In addition, ethanol contains about 35 wt% oxygen in its structure resulting in lesser energy density per unit volume (23.4 GJ m^{-3}) compared to gasoline (34.4 GJ m^{-3}) [143]. Therefore, blending of ethanol with gasoline leads to lesser fuel mileage compared to gasoline (for example E85 operates with 30% lesser fuel mileage) [21]. The lesser fuel mileage together with small price variance between E85 and regular gasoline discouraged purchase of E85 cars or fuels so far.

The ethanol provides wonderful opportunities to produce hydrocarbon fuels and varieties of chemicals besides its applications as fuel/fuels additives that led to consider it as one of the top priority platform chemicals in integrated biorefinery (Fig. 6). The ethanol can be converted into diethyl ether, ethylene, higher hydrocarbons or aromatics over zeolite catalysts especially HZSM-5 [144–153]. The selective production of above products is possible by choosing appropriate temperature. It was reported that diethyl ether is dominant product in the temperatures range of 423–473 K. The higher temperature (473–573 K) leads to formation of ethylene as primary product. The higher hydrocarbons become predominating products at temperatures above 573 K.

At temperatures above 623 K, significant fractions of hydrocarbons are aromatics. The ethanol-to-gasoline process provides another opportunity to produce gasoline range hydrocarbons primarily consisting of C_7 – C_{10} monocyclic aromatics together with C_2^+ alkanes [154]. Recently, Brazilian Braskem inaugurated its first commercial-scale ethanol-to-ethylene plant to produce 0.2 million tons per annum of green polyethylene from sugarcane ethanol [155]. The ethanol can be transformed to varieties of C_2 commodity chemicals. The ethanol is dehydrogenated to acetaldehyde with 100% selectivity using inexpensive Cu catalysts at mild temperatures and ambient pressure [156]. This process allows simultaneous production of renewable hydrogen and acetaldehyde in a simple and clean one-step reaction. The dilute ethanol is converted to acetic acid by aerobic oxidation using supported Au catalysts at moderate temperatures (423 K) and pressures [157]. The propylene is second most important building block chemical in petrochemical industry after ethylene. The propylene can also be produced from ethanol by dehydration to ethylene, partial dimerization of the latter to butene followed by metathesis of C_2 and C_4 olefins to yield propylene [158]. The ethanol can also be transformed to butadiene – another important petrochemical building block chemical [159].

4.7. Bio-butanol based biorefinery

In 2005, David Ramey first drove his unmodified car across USA fueled exclusively by butanol [160]. Since then bio-butanols have drawn renewed attention as bio-fuel due to its superior fuel qualities over ethanol and biodiesel such as compatibility with existing internal combustion engines, lesser miscibility with water, lesser vapor pressure, octane rating similar to gasoline (RON=96 and MON=78), higher energy density and better blending ability with gasoline [161,162]. In addition, existing ethanol production facilities can be retrofitted for production of butanol with only minor modifications.

The bio-butanol is produced by ABE fermentation of carbohydrates using solventogenic clostridia. The ABE fermentation is

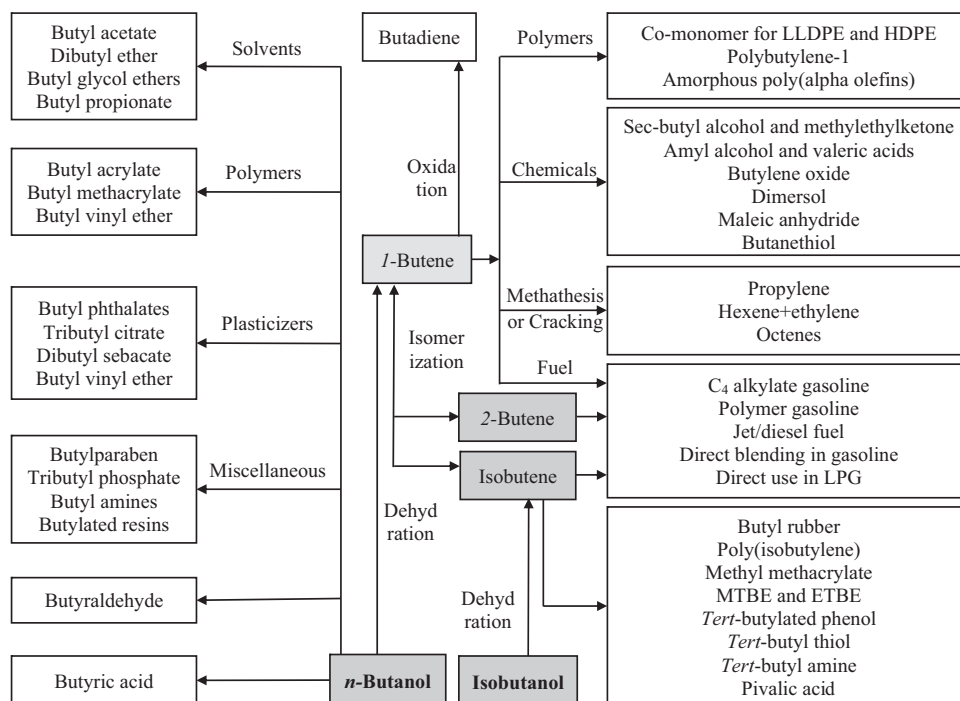


Fig. 7. Derivative potentials for butanols [162].

usually carried out in a series of batch fermenters (residence time up to 21 days) with periodic addition of seed culture forming acetone, *n*-butanol and ethanol [126]. Typical solvent concentration in ABE fermentation broth is $\sim 20 \text{ kg m}^{-3}$ (butanol:acetone:ethanol=6:3:1) from $55\text{--}60 \text{ kg m}^{-3}$ of substrate with butanol concentration of $\sim 13 \text{ kg m}^{-3}$ and products yields of $\sim 0.35 \text{ kg kg}^{-1}$ of sugar [124,126]. The hydrogen produced as by-product (typically about 1/10th of mass of butanol) in ABE fermentation can be used to generate heat and power or as renewable chemical feedstock [126]. The isobutanol having lesser toxicity and higher octane number and same essential fuel potentials as *n*-butanol has been deliberated as one of the promising bio-fuels in future [126,163]. Furthermore, isobutanol undergoes phase separation spontaneously from aqueous broth because of its low water solubility thereby eliminating the need of additional energy-intensive separation steps [143].

The excessive costs of sugar and starchy biomass, products inhibition of fermenting microorganisms and energy intensive products recovery are key bottlenecks for commercialization of ABE fermentation. The products inhibition of fermenting microorganisms results low butanol titer in the fermentation broth. Low butanol titer forces reduced sugars loadings and increased water usage which in turn results large processing volumes. The economics of ABE fermentation can be improved by use of world's most abundant and cheap cellulosic biomass. The recent economic analysis for production capacity of 10,000 t of *n*-butanol per annum showed that use of glucose required 37% lesser fixed capital investment compared to other cellulosic and non-cellulosic feedstocks [164]. However, unitary production cost of *n*-butanol from glucose is four times higher than sugarcane and cellulosic feedstocks. The microorganisms with improved solvent titers and butanol-to-solvent ratio, cheap product recovery techniques (e.g. adsorption, gas stripping, liquid–liquid extraction, pervaporation, aqueous two-phase separation, supercritical extraction etc.) and in-situ product removal methods to alleviate end product tolerance will enable ABE fermentation economically feasible [123].

At present, *n*-butanol has wide range of market potentials as solvent and derivatives (Fig. 7) [124,162]. The isobutanol has also broad petrochemicals markets as solvent and feedstocks for synthetic rubber, plastics and polyesters. The butenes are one of the important petrochemical building block chemicals. The dehydration of butanols using acidic catalysts yields butenes in high yield [165–167]. The butenes are then dimerized using zeolites, NiO dispersed on silica, sulfated titania or ion exchange resins as catalyst that can be subsequently isomerized to branched alkenes for blending with gasoline [168–170]. Alternatively, butanols can be dehydrated to butenes followed by oligomerized of butenes with degree of polymerization of 3–5 and isomerized to branched hydrocarbons in the boiling range of gasoline or diesel [171,172]. Recently, Bond et al. demonstrated oligomerization of butene–CO₂ mixture in a fixed bed reactor using acid catalysts (HZSM-5 and amberlyst 70) at 443–523 K and 1–36 bars [173]. More than 90% butene conversion with 95% selectivity to liquid alkenes having eight or more carbon atoms was reported.

The incentives of bio-butanol as fuels and chemicals feedstock motivated giant industrialists to develop commercial processes for its production from biomass as well as its downstream conversion. The most notable is Butamax™ Advanced Bio-fuels – a joint venture of BP and Dupont. They are currently developing technology for production of butanol from corn using genetically engineered yeast [174]. The Cobalt Bio-fuels raised \$25 million equity to accelerate commercialization of *n*-butanol [175]. Green Biologics Ltd. (GBL)'s UK proprietary technology are currently being used to produce C₄ alcohols, carboxylic acids and derivatives from a variety of LCB [176]. Recently, Albemarle Corporation awarded a contract

Table 3

Comparison of properties of LtL oil with typical Milled Wood Lignin (MWL), flash pyrolysis product of biomass and fossil fuels [183].

| Property | MWL | Flash pyrolysis oil | Heavy fuel oil | Light fuel oil | LtL oil |
|------------------------------|-------|---------------------|----------------|----------------|----------|
| C (wt%) | 59.2 | 54–58 | 85 | 85 | 76–83 |
| H (wt%) | 6 | 5.5–7.0 | 11 | 13 | 9–13.5 |
| O (wt%) | 34.5 | 35–40 | < 1.0 | 0.4 | 5–10 |
| S (wt%) | < 0.2 | < 0.2 | 1 | 1 | < 0.2 |
| H/C | 1.2 | 1.15–1.55 | 1.55 | 1.8 | 1.3–1.8 |
| O/C | 0.44 | 0.6–0.73 | 0.01 | 0 | 0.05–0.1 |
| Ash (wt%) | 2–3 | 0–0.2 | 0.1 | 0 | 0–0.2 |
| pH | – | 2.5 | – | – | – |
| ρ (kg m ⁻³) | – | 1200–1300 | 900 | 900 | 940–1000 |
| HHV (MJ kg ⁻¹) | 24.2 | 21–25 | 42.5 | 44.5 | 35.6–44 |

Table 4

Zeolite upgrading of Alcell® lignin using HZSM-5 catalyst [185].

| | 773 | 823 | 873 | 873 | 873 | 923 |
|----------------------------|------|------|-----|------|------|------|
| Temperature (K) | 773 | 823 | 873 | 873 | 873 | 923 |
| WHSV (h ⁻¹) | 5 | 5 | 2.5 | 5 | 7.5 | 5 |
| Yield (wt%) | | | | | | |
| Gas | 11 | 19 | 51 | 54 | 58 | 68 |
| Liquid | 39 | 43 | 34 | 30 | 22 | 11 |
| Char + coke | 50 | 38 | 15 | 16 | 20 | 21 |
| Major liquid product (wt%) | | | | | | |
| Benzene | 8.6 | 9.4 | 9.3 | 13.6 | 14.5 | 14.4 |
| Toluene | 33.1 | 36.7 | 31 | 42.4 | 41.9 | 43.7 |
| Xylene | 31.5 | 33 | 25 | 22.7 | 24.8 | 21 |
| Ethyl benzene | 3 | 2.1 | 2.2 | 1.9 | 1.5 | 1.3 |
| Propyl benzene | 4.2 | 2.5 | 3.7 | 1.3 | 1.5 | 1 |
| C ₉ aromatics | 9 | 5.1 | 6.4 | 6 | 3.1 | 3 |

to complete its first bio-jet fuel production from bio-*n*-butanol provided by Cobalt Technologies [177]. Their research team is focused on conversion of *n*-butanol to 1-butene followed by oligomerization of 1-butene into jet fuel based on process developed at Naval Air Warfare Center Weapons Division. Another company, Gevo successfully demonstrated fermentation and isolation of isobutanol in commercial fermenters (946 m³) and cleared registration of isobutanol with US EPA as fuel additive [178].

4.8. Utilization of lignin

In biorefinery, the lignin remains as most unutilized fraction of LCB so far. The lignin generated as by-product in pulp and paper industry are generally used as low-grade fuel for boiler to generate heat or steam to power pulping process [179]. Lignin accounts for 10–30 wt% of LCB which is equivalent to $\sim 40\%$ of its energy contents. Hence economics of biorefinery depends largely on availability of cost-effective process for conversion of low-value lignin to value-added fuels and chemicals. The isolation of lignin from LCB resembling its native chemical structure and free of sulfur still remains a biggest challenge. The physico-chemical properties and structure of isolated lignin differ significantly depending on nature of extraction methods [179]. For example, aliphatic sulfonic acid functional group becomes part of the lignin backbone in sulfite pulping process making it highly water soluble. Kraft lignin contains small number of aliphatic thiol groups. The sulfur free lignin finds many industrial thermosetting polymer applications such as polyurethane foams, epoxy resins and substitute of phenolic resins and bio-dispersants [179]. Lignin can also be used as a potential source of low-cost carbon fibers to replace synthetic polymers (such as polyacrylonitrile) and steel in

domestic passenger vehicles with lightweight but strong carbon fiber-reinforced plastics that significantly reduces vehicle weight [180].

Several approaches are also adopted for conversion of lignin to fuels and chemicals. The lignin is chemically very stable high molecular weight phenylpropane biopolymer (600–15000 kDa) and hence harsh reaction conditions are generally required to break down its polymeric structure [181]. Base catalyzed depolymerization to partially depolymerized lignin followed by catalytic partial HDO to a mixture of monomeric and polymeric alkylated phenols and mild hydrocracking is one such approach to produce fuel products compatible with gasoline [181,182]. The above process can be terminated after HDO stage to obtain phenolic building block chemicals.

The solvolysis in presence of hydrogen donating solvents such as formic acid and 2-propanol is another approach for simultaneous depolymerization and HDO in single step to produce mixture of monomeric alkylated phenols and aliphatic hydrocarbons compatible with gasoline/diesel commonly known as lignin-to-liquid (Ltl) oil [183,184]. Kleinert and Barth recently studied solvolysis of different lignin at 653 K using formic acid as hydrogen donating solvent, methanol/isopropanol as co-solvent and dimethyl carbonate/water as methylating agent [183]. The Ltl oils consist of low molecular weight mono- to oligo-alkylated phenols with C₁–C₄ alkyl groups and C₈–C₁₀ aliphatics. The H/C ratio of the oils was increased to some extent with significant decrease of O/C ratio indicating simultaneous depolymerization and HDO. The bulk composition of Ltl oil was close to petroleum fuels (Table 3).

The lignin being phenolic in structure can be considered as a perfect feedstock for aromatics. Thring et al. studied zeolite upgrading of Alcell[®] lignin in a fixed bed reactor using HZSM-5 catalyst at 773–923 K with WHSV of 2.5–7.5 h⁻¹ as shown in Table 4 [185]. With increasing temperature, the gas yield was increased and yield of solid was decreased. The maximum yield of liquid was 43% at 823 K. The major liquid components were benzene, toluene, xylene, ethyl benzene and propyl benzene. The major hydrocarbons components of the gas were propane and propylene. Such low-molecular weight gases could be used to produce synthesis gas by steam reforming, alkylated gasoline, propane fuels or olefins by dehydrogenation [180].

5. Hydrocarbon biorefinery

The existing liquid transportation fuels are composed of mixture of hydrocarbons with different molecular weights, chemical structures and degree of branching (C₄–C₁₂ for gasoline, C₉–C₂₃ (average C₁₆) for diesel and C₈–C₁₆ for jet fuel) [186]. The physico-chemical properties of bio-fuels (biodiesel and bio-ethanol) produced in traditional biorefinery allow its blending with petroleum based fuels as oxygenate additives to a limited extent only for its application in existing internal combustion engines. The existing infrastructures developed considering properties of hydrocarbon fuels are also unsuitable for bio-fuels [21]. Therefore, production of hydrocarbon analogous transportation fuels from biomass is quite desirable due to its superior energy density, stability and combustion characteristics over bio-fuels. The production and downstream transformation of oxygenated platform chemicals in traditional biorefinery are based on completely new chemistry which is unsuitable with existing petrochemical industry infrastructures. Therefore, production of hydrocarbon building block chemicals from biomass is quite desirable for faster realization of biorefinery. Therefore, new manufacturing concepts are being evolved continuously to produce an array of hydrocarbon fuels and building block chemicals from biomass through complex

processing technologies commonly known as hydrocarbon biorefinery. The significant advancements have been made on production of hydrocarbons fuels through microbial processing, aqueous phase catalysis and HDO of triglycerides [140]. The hydrocarbon biorefinery offers following advantages [19].

- (i) The hydrocarbon biorefinery takes advantages of existing infrastructures (including engines, fueling stations, distribution networks and storage tanks) and production systems of petroleum refineries and petrochemical industries.
- (ii) There will be no penalty in fuel mileage as hydrocarbon fuels derived from biomass are energy equivalent to petroleum derived fuels.

5.1. Traditional approach

The hydrocarbon fuels and building block chemicals are also produced in traditional biorefinery. For example, synthesis gas is produced by gasification of LCB or steam reforming of alcoholic bio-fuels or bio-oils. The synthesis gas is subsequently transformed to hydrocarbon fuels and organic chemicals through FTS. The bio-oils produced by fast pyrolysis of LCB are upgraded to liquid transportation fuels by HDO. The biogas consisting mainly of methane and CO₂ is produced by anaerobic digestion of waste biomass [187–189]. The propylene produced during zeolite upgrading of lignin as by-product could be a potential renewable feedstock for hydrocarbon biorefinery. The hydrocarbon biorefinery can be envisaged through alcoholic bio-fuels as well. For example, bio-ethanol and bio-butanols are dehydrated to corresponding olefins in high yield using acid catalysts [150,165–167,190]. The ethylene and butylene can be subsequently oligomerized to gasoline or diesel range hydrocarbons. Further research efforts are however needed for manufacturing of hydrocarbon fuels, olefins and aromatics from carbohydrates in single step with high yield.

5.2. Hydrodeoxygenation of triglycerides

The triglycerides contain aliphatic hydrocarbon backbone of 8–24 linear carbon atoms with majority being 16 and 18 [191]. The removal of oxygen heteroatoms from triglycerides should ideally produce linear hydrocarbons with boiling range (boiling point: *n*-C₁₆=560 K; *n*-C₁₈=589 K) similar to conventional diesel (boiling range=513–593 K) for direct application in diesel engines. The oxygen heteroatoms of triglycerides can be eliminated by either (1) pyrolysis in absence of any catalyst in the temperatures range of 573–773 K under atmospheric pressures [192], (2) catalytic cracking over various zeolite catalysts (HZSM-5, MCM-41, SiO₂–Al₂O₃ etc.) in the temperature range of 623–773 K [193–195] or (3) catalytic HDO under high hydrogen pressure. The substantial losses of carbons in the form of light hydrocarbon gaseous products and low yield of liquid hydrocarbon fuels (gasoline and diesel) are primary bottlenecks of pyrolysis and catalytic cracking of triglycerides [196].

The HDO of triglycerides is most preferred technology to produce diesel range hydrocarbons in high yields commonly known as green diesel. This technology allows use of existing petroleum refinery infrastructure with possibility of co-processing. In recent times, significant research progress has been made on HDO of various triglycerides (sunflower oil, rapeseed oil, jatropha oil, waste cooking oil, etc.) and fatty acids and their esters over different metals catalysts (Pt, Ni, Pd, Ni–Mo, Co–Mo, Pt–Pd, Pt–Re, Ni–W) dispersed on various supports (γ -Al₂O₃, CNT, Al-SBA-15, SAPO-31, γ -Al₂O₃–BEA, SiO₂–Al₂O₃, HY, USY and HZSM-5) [197–203].

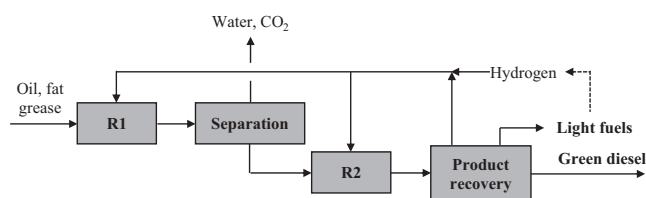


Fig. 8. Simplified ecofining process flow diagram [204].

Table 5

Comparison of fuel qualities of biodiesel, FT diesel and green diesel with diesel [204].

| | Diesel (ULSD) | Biodiesel | Green diesel | FT diesel |
|--------------------------------------|---------------|-----------|--------------|---------------|
| Oxygen (wt%) | 0 | 11 | 0 | 0 |
| Specific gravity | 0.84 | 0.88 | 0.78 | 0.77 |
| Sulfur (ppm) | < 10 | < 1 | < 1 | < 1 |
| Heating value (MJ kg ⁻¹) | 43 | 38 | 44 | 44 |
| Cloud point (K) | 268 | 268–288 | 253–293 | Not available |
| Cetane | 40 | 50–65 | 70–90 | > 75 |
| Stability | Good | Marginal | Good | Good |

Both sulfided and non-sulfided NiMo and CoMo catalysts are most commonly used for HDO of triglycerides.

Recently, UOP developed a two-stage hydrorefining process called UOP/Eni Ecofining™ for green diesel production from plant-derived non-edible oils (Fig. 8) [204,205]. In the first stage, triglycerides are saturated and completely deoxygenated by catalytic HDO (R1) to produce paraffins as primary products. The primary deoxygenation reaction by-products are propane, water and carbon dioxide. In the second stage, resultant paraffins are subjected to catalytic hydro-isomerisation (R2) to branched paraffins-rich diesel fuel. This step is used to adjust cold flow properties of the diesel. The propane produced during UOP/Eni Ecofining™ process as by-product could be used as gaseous fuel or transformed to propylene by dehydrogenation reaction for use as hydrocarbon building block chemical. The green diesel is superior in properties compared to biodiesel and similar to FT diesel in terms of both composition and combustion properties (Table 5). UOP has also developed and commercialized technology for conversion of non-edible oils and wastes to Honeywell Green Jet Fuel™ that successfully powered a number of bio-fuel demonstration flights meeting all aircraft specification without any aircraft modifications [206].

5.3. Biosynthetic pathways

The novel concepts of production of hydrocarbon fuels and organic chemicals in the biological plants itself are gradually nucleating to circumvent cost-intensive processing of biomass in industrial plants. This approach is not quite unusual as natural rubber (polyisoprene) is being traditionally produced from plants itself. Biosynthetic pathways is thus an attractive approach to produce short-chain, branched-chain and cyclic alcohols, alkanes, alkenes, esters and aromatics [207]. For example, isoprene is synthesized naturally in plants, animals and bacteria [207–209]. The isoprene units can be recombined to produce a large variety of compounds with different molecular weights and degree of branching for applications as gasoline, diesel and jet fuel [143]. Many naturally occurring microorganisms also synthesize linear C₁₄–C₂₅ hydrocarbons. These hydrocarbons are suitable as fuel after mild hydrocracking and hydro-isomerization. However, low hydrocarbon contents (no more than 10 wt% of dry biomass) of microbial cells is primary bottleneck for large scale production of

hydrocarbon-rich biomass using native microorganisms [207]. The genetic and metabolic engineering is the key to improve microbial systems with higher hydrocarbon contents. Recently, companies such as Amyris and LS9 successfully developed a process to convert C₅ and C₆ sugars using genetically altered microorganisms to produce farnesene – C₁₅ hydrocarbon oil [210,211]. Being oil, it forms a separate phase and floats on top of fermentation broth. This makes recovery and purification of hydrocarbon relatively easy similar to separating cream from milk. Through various finishing steps, farnesene is converted into diesel, surfactant used in soaps and shampoos, cream used in lotions, a number of lubricants and varieties of other useful chemicals.

5.4. Aqueous phase catalysis

The energy intensive separation of ethanol and butanols from dilute aqueous fermentation broth is one of the major challenges in the process of production of alcoholic bio-fuels. Alternatively, aqueous sugars can be converted to hydrogen by aqueous phase reforming (APR) or alkanes that spontaneously separates from aqueous phase by APD/H [159,212–218]. The APD/H is carried out in single step using bifunctional catalysts containing acidic sites for dehydration of carbohydrates to oxygenated hydrocarbons and metallic sites for hydrogenation of resultant oxygenated hydrocarbons. The APD/H occurs in aqueous phase itself thereby eliminating the need of concentrating aqueous carbohydrates and hence improving overall thermal efficiency of the process.

Huber et al. demonstrated production of alkanes from aqueous sorbitol using Pt/Pd supported SiO₂–Al₂O₃ catalyst [219]. The hydrogen required for hydrogenation reaction was produced by APR of aqueous sorbitol in the same reactor. The APD/H of aqueous sorbitol however resulted formation of C₅–C₆ hydrocarbons. These hydrocarbons are highly volatile and hence unsuitable as liquid fuel or fuels blend. Therefore, increasing molecular weight by C–C bond forming reactions such as aldol-condensation is essential for production of gasoline and diesel range of hydrocarbons. However, sugars do not undergo aldol-condensation as carbonyl group undergoes intra-molecular reactions to form ring structures [212]. However, the hexose and pentose sugars can be dehydrated to 5-hydroxymethylfurfural (5-HMF) and furfural respectively using acidic catalysts with more than 90% yield [213]. The 5-HMF and furfural however cannot undergo self aldol-condensation due to lack of α-H atom. The possible alternatives to increase carbon number are (1) partial hydrogenation of 5-HMF and furfural to generate α-H atom in their structure to enable self aldol-condensation and (2) cross aldol-condensation of these compounds with α-H bearing carbonyl compounds such as acetone (by-product of ABE fermentation).

Recently, Huber et al. developed a four step catalytic process for conversion of biomass-derived carbohydrates to liquid alkanes (C₇–C₁₅) (Fig. 9) [212]. (1) The hexose and pentose sugars were first dehydrated to 5-HMF and furfural respectively. (2) The furfural and 5-HMF were then reacted with acetone by base-catalyzed (mixed Mg–Al-oxide) aldol-condensation at room temperature to monomers and dimers. (3) The monomers and dimers were then subjected to hydrogenation to saturate double bonds. The hydrogenation helps to minimize coke formation on Pt/SiO₂–Al₂O₃ catalyst in the subsequent four-phase dehydration/hydrogenation (4-PD/H) reactor and to increase solubility of condensed products in water. (4) The saturated monomers and dimers were then converted to straight-chain alkanes by 4-PD/H reactor. Xing et al. extended above work to pentose sugars for production of diesel and jet fuel range alkanes [218] (Fig.9b). The combined xylose hydrolysis and dehydration were conducted in biphasic batch reactor at 433 K and 220 psig using water–THF as solvent and HCl as catalyst. Almost complete conversion of xylose with more

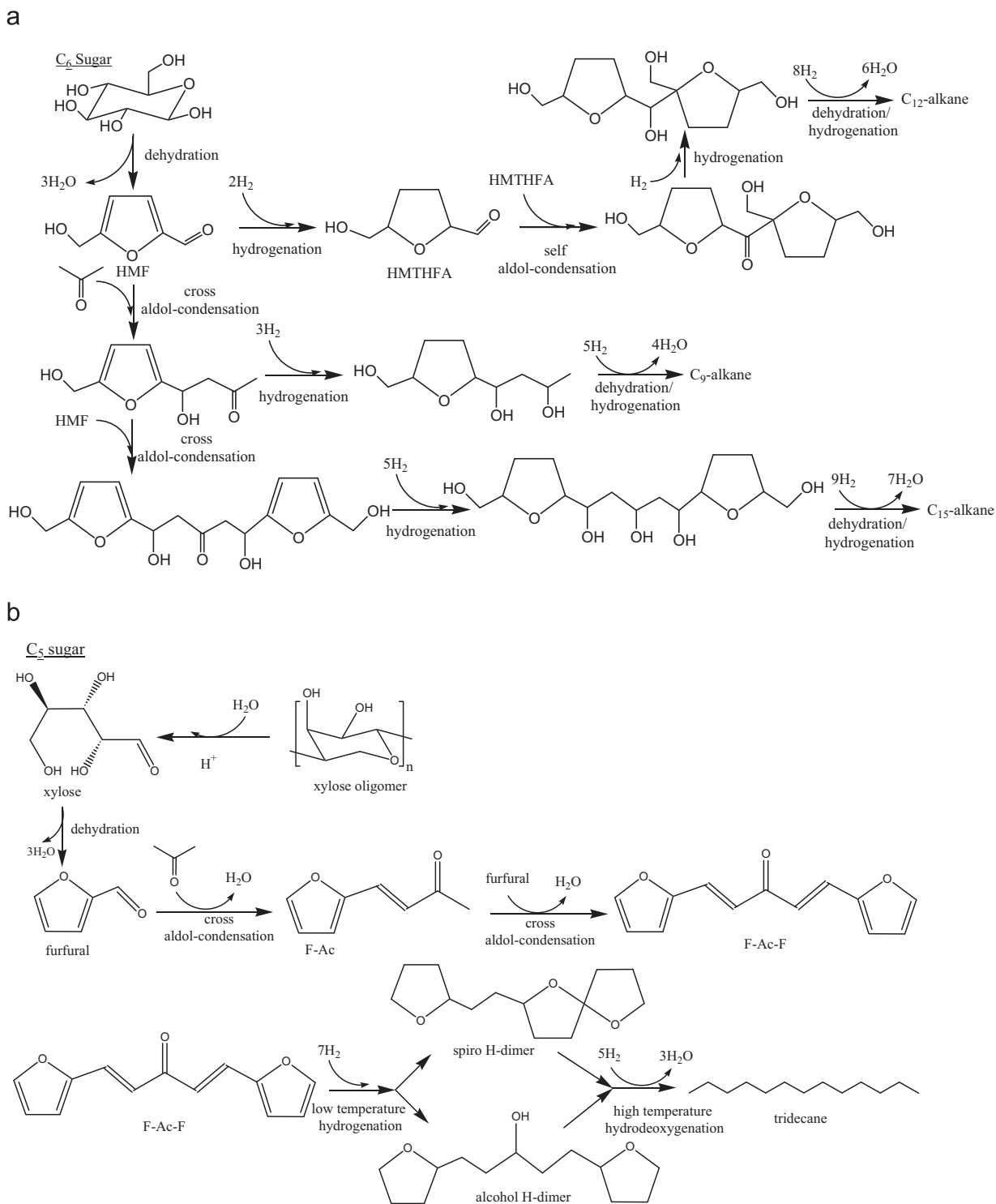


Fig. 9. Reaction pathways for the conversion of biomass-derived (a) glucose [212] and (b) xylose [218] into liquid alkanes.

than 80% selectivity to furfural (F) was reported at HCl/xylose molar ratio more than 2.4. The aldol-condensation of furfural in THF with stoichiometric amount of acetone (Ac) (molar ratio of furfural to acetone=2) was conducted in a batch reactor at 298–353 K using NaOH as catalyst. Almost complete conversion of furfural with more than 95% yield of F-Ac-F was reported at NaOH/furfural ratio of 0.37 and mass ratio of organic to aqueous phase of 5.1:1. F-Ac-F dimer in THF was then hydrogenated in a batch reactor at 383–398 K using 5wt%Ru/C catalyst to saturate all three kinds of double bonds (alkene C=C, furan C=C and

ketone C=O bonds). The HDO of mixed hydrogenated dimers in THF was conducted in a plug flow reactor at 533 K and 900 psig over 4 wt%Pt/SiO₂-Al₂O₃ catalyst. The yield of jet and diesel fuel range alkanes was 91% with tridecane and dodecane being 72.6% and 15.6% respectively.

Recently, Kunkes et al. catalytically converted aqueous glucose and sorbitol to hydrophobic organic liquid containing mixtures of monofunctional organic compounds (such as alcohols, ketones, carboxylic acids and alkanes containing 4–6 carbon atoms) as well as heterocyclic tetrahydrofuran and tetrahydropyran using Pt-Re/C

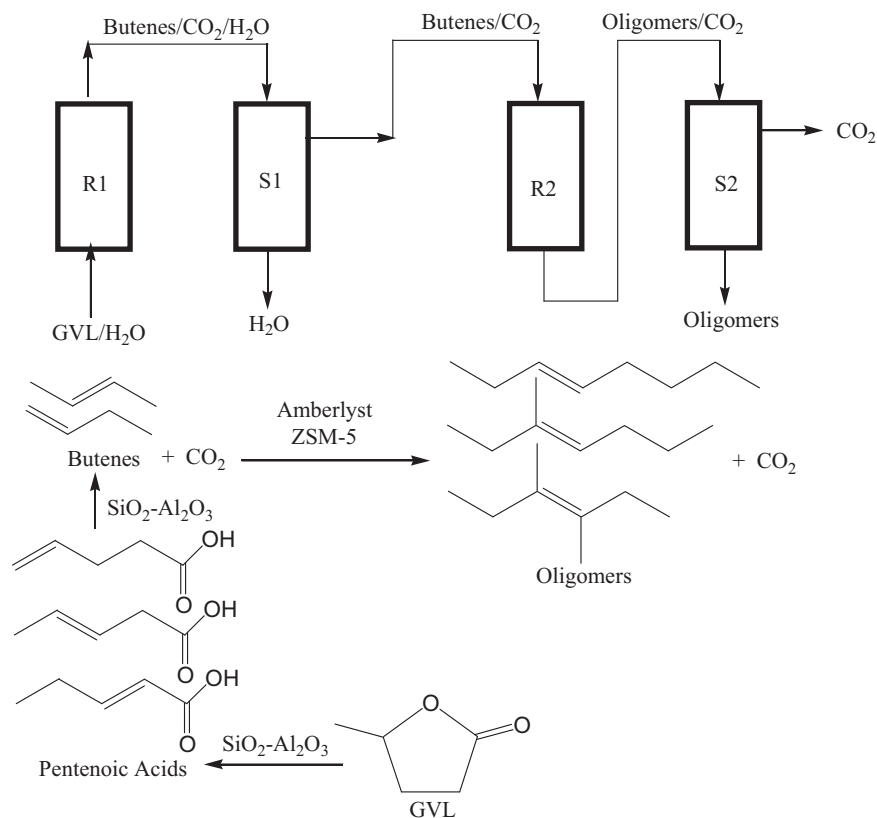


Fig. 10. Reaction pathways and process for conversion of GVL to butenes and CO₂ followed by oligomerization of butenes [173].

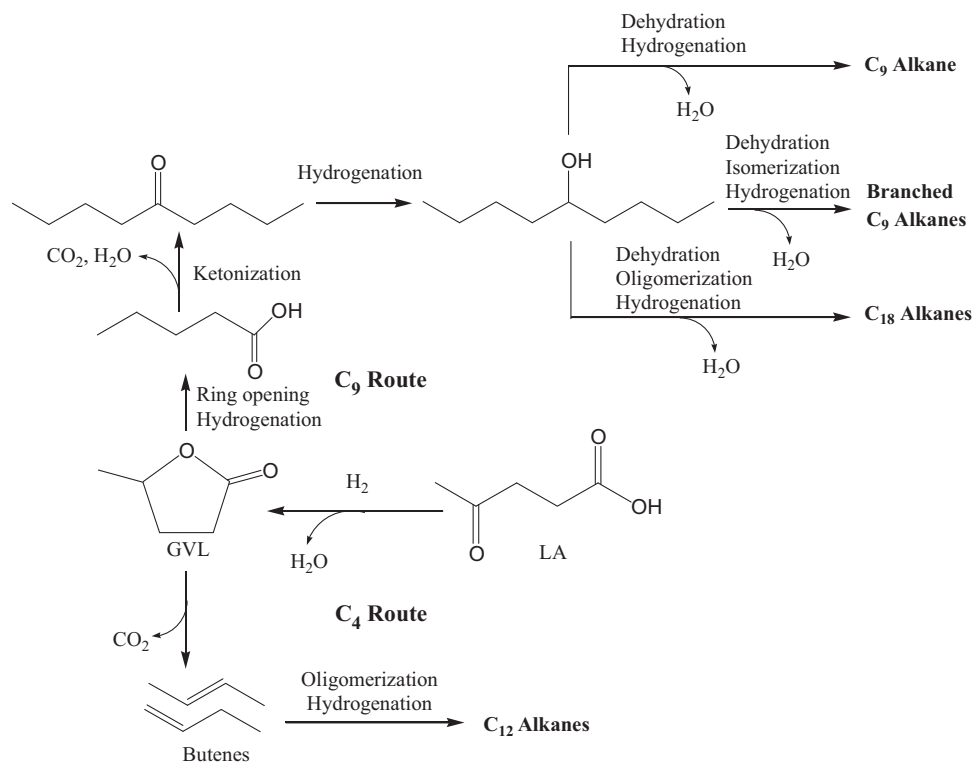


Fig. 11. Reaction pathways for conversion of levulinic acid into liquid hydrocarbon fuels [21].

catalyst at 503 K and 18–27 bars [220]. The H₂ required for deoxygenation reactions was generated in situ by APR. The monofunctional organic compounds provide a potential source of reactive intermediates for fine chemicals and polymers or can be

converted to gasoline, diesel and jet fuels range hydrocarbons. As first catalytic approach, organic liquid was converted to aromatics by hydrogenation of ketones to alcohols (at 433 K and 55 bars H₂ pressure over 5 wt% Ru/C) followed by heating to 673 K

Table 6The economic comparison of six different processes with plant size of 0.17 MM m³ per year bio-fuel [222].

| Feedstock | Ethanol Corn | Ethanol Sugarcane | Ethanol (biochem) Corn stover | Ethanol (thermochem) Corn stover | Butanol Corn | Diesel Soybean |
|---|---|----------------------|----------------------------------|-------------------------------------|--------------------|---|
| Feedstock cost (\$ m ⁻³) | 237.8 ^a ; 190.2 ^b | 245.7 | 134.7 | 150.6 | 649.9 ^c | 583.8 |
| Total production cost (\$M yr ⁻¹) | 74 | 58 | 64 | 58 | 88 | 121 |
| Total project investment (\$M) | 131 | 88 | 183 | 241 | 276 | 23 |
| Production cost (\$ m ⁻³) | 404.2 | 340.8 | 391.0 | 348.7 | 517.8 | 673.6 |
| Energy density (MJ m ⁻³) | | | 21274 | | 27826 | 33321 |
| Production cost with energy equivalent to gasoline (\$ m ⁻³) | 615.5 | 515.1 | 594.4 | 528.3 | 602.3 | 655.1 ^d ; 723.8 ^e |

^a Dry mill.^b Wet mill (maize).^c Shelled corn.^d Equivalent to gasoline.^e Equivalent to diesel.

at atmospheric pressure over H-ZSM-5. The organic liquid was converted to paraffins (25%), olefins containing 3–4 carbon atoms (29%) and aromatics (38%). The aromatic fraction was composed of 12% benzene, 37% toluene, 30% xylenes or ethyl benzene and 22% C₃–C₆ substituted benzene. To produce diesel-fuel range components, the organic liquid was passed over bifunctional CuMg₁₀Al₇O_x catalyst to achieve C–C coupling of C₄–C₆ ketones and secondary alcohols by aldol-condensation (at 573 K and 5 bars with 20 cm³ (STP) min⁻¹ H₂ co-feed with WHSV of 0.4 h⁻¹). The 45% of feed carbons were converted to condensation products containing between 8 and 12 carbon atoms and one or no oxygen atoms that was subsequently converted to corresponding alkanes by HDO using Pt/NbOPO₄ catalyst. Ketonization is an effective approach when organic phase is rich in carboxylic acids. For example, conversion of 40 wt% glucose over Pt-Re/C at 483 K and 18 bars leads to an organic phase containing 40% of feed carbon with 30% C₄–C₆ carboxylic acids. This organic phase was then ketonized in a fixed bed reactor over CeZrO_x catalyst. The yield of C₇⁺ products were subsequently increased by aldol-condensation of resulting ketones.

The aqueous phase catalysis can also be used to produce liquid hydrocarbons through platform chemicals. For example, Bond et al. recently developed an integrated two step approach to convert γ -valerolactone (GVL) to alkenes with molecular weights appropriate for application as transportation fuels (Fig. 10) [173]. The aqueous GVL solution was first catalytically decarboxylated to an initial mixture of isomeric butenes and CO₂ in a fixed bed reactor over acidic SiO₂–Al₂O₃ catalyst at 468–673 K and 1–36 bars. More than 95% GVL conversion to butenes was observed. After separation of water with an inter reactor separator, butene–CO₂ mixture was oligomerized in second fixed bed reactor over H-ZSM-5 and Amberlyst 70 catalysts at 443–523 K and 1–36 bars. More than 90% of butene conversion with 95% selectivity to liquid alkenes containing eight or more carbon atoms was reported.

Serrano-Ruiz et al. catalytically converted aqueous levulinic acid into liquid hydrocarbon transportation fuels (Fig. 11)[21]. The aqueous levulinic acid was first hydrogenated to water-soluble GVL which was then upgraded to liquid hydrocarbons following two different pathways: C₉ and C₄ route. Following C₉ route, GVL was converted to 5-nonanone over water-stable multifunctional Pd/Nb₂O₅ catalyst. 5-Nonanone was subsequently hydrogenated to corresponding alcohol that was processed by three different approaches. (1) The alcohol was converted into linear *n*-nonane through hydrogenation/dehydration over bifunctional metal–acid catalyst Pt/Nb₂O₅. (2) The alcohol was dehydrated and isomerized in single step over USY zeolite to produce mixture of branched C₉

alkenes with appropriate molecular weight and structure for use in gasoline after hydrogenation to corresponding alkanes. (3) The alcohol was dehydrated to C₉ alkene that was subsequently oligomerized over Amberlyst 70 to C₁₈ alkanes (after hydrogenation) for diesel applications. Following C₄ route, GVL undergone decarboxylation at elevated pressures (36 bars) over SiO₂–Al₂O₃ catalyst, producing butene isomers and CO₂ followed by oligomerization of butene in a second reactor over H-ZSM5 and Amberlyst 70 catalyst yielding a distribution of alkenes centered around C₁₂.

6. Economics of biorefinery

The manufacturing costs primarily governed by (1) feedstock cost, (2) processing cost and (3) scale of production. Lange recently evaluated economics of fuels from various feedstocks (LCB, sugar and starchy biomass, vegetable oils, crude oils and natural gas) based on first two factors [221]. The vegetable oils, though expensive (\$13–18/GJ or \$500–700/t), are easy to process due to its simplicity in chemical structure and low functionality. On the other hand, LCB are quite cheap (\$2–4/GJ or \$34–70/t dry); but its processing is quite expensive because of its complex chemical composition. The economics of bio-fuels derived from vegetable oils are thus governed by feedstock cost; whereas those derived from LCB are dominated by technology. The cost of fuels produced from petroleum is largely dominated by feedstock cost; whereas those obtained from natural gas (e.g. MeOH by FTS) are mainly controlled by technology. The economics of bio-fuels derived from sugar and starchy biomass lies intermediate to these two extremes. At the moment, bio-fuels are expensive than petroleum derived fuels. However, the bio-fuels are expected to be competitive with petroleum derived fuels only at high crude oils prices say \$50–75/bbl.

The scale of production also controls overall manufacturing costs in chemical process industry significantly. The two-fold increase in plant capacity is known to reduce manufacturing cost by 20–25% [221]. The scale of production in biorefinery is mainly limited by biomass availability and its collection logistics; not by its conversion technology. The high transportation cost of biomass from long collection radius generally impedes large scale operation of biorefinery. Therefore, there is a need to trade-off between scale of production and biomass transportation cost for biorefinery. In fact, some of the biorefinery processes, for example, fast pyrolysis is economical at small scale.

Tao and Aden analyzed manufacturing costs of bio-fuels from various feedstocks for USA during 2006–2007 for plant size of

0.17 MM m³ per annum as shown in Table 6 [222]. The production costs of bio-ethanol from corn, sugarcane, corn stover (biochem) and corn stover (thermochem) were \$404.2, \$340.8, \$391.0 and \$348.7 m⁻³ respectively. As observed from the table, feedstock contributes ~60% of manufacturing cost for corn compared to ~70% for sugarcane and ~40% for corn stover. The feedstock cost depends on geographical location as well. For example, sugarcane costs in Brazil is as low as \$79.3 m⁻³ of ethanol which makes sugarcane ethanol more economical in Brazil than USA [222]. Among all bio-fuels, manufacturing cost of soyabean diesel is highest. This is largely attributed to feedstock cost that alone accounts for ~75–95% of overall production cost. The production cost of bio-butanol from shelled corn is \$517.8 m⁻³. The feedstock cost is higher than butanol production cost due to co-product credit.

The minimal project investment is required for production of biodiesel. The project investment is highest for bio-fuels from corn stover. The huge project investment required for bio-butanol is largely attributed to complex downstream separation process. For conversion of wood chips by thermochemical process (gasification) to ethanol, it was reported that tars reforming and synthesis gas conditioning is largest cost contributing factor that accounts for 28% of overall cost [223]. On the other hand, for biochemical conversion of corn stover to ethanol, pretreatment alone accounts for 19% of overall manufacturing cost [223]. The improvements of tars reforming and synthesis gas conditioning in case of gasification and pretreatment for biochemical conversion of LCB are essential to boost overall economics of the biorefinery.

7. Conclusions

The biorefinery offers plenty of opportunities to produce an array of fuels and organic chemicals from biomass. The biorefinery can be envisaged through various biomass conversion technologies including thermochemical conversion of LCB through gasification and fast pyrolysis, chemical conversion of triglycerides by transesterification with methanol and biochemical conversion of carbohydrates to bio-ethanol and bio-butanols or HDO, microbial processing and aqueous phase catalysis in hydrocarbon biorefinery. The biomass gasification provides an avenue to produce range of fuels and organic chemicals through synthesis gas. The biomass gasification however seems to be economically unviable due to huge capital investment. The catalytic gasification is a potential alternative with enhanced efficiency. The fast pyrolysis is a promising thermochemical conversion process of LCB due to its simplicity, low capital investments and economic viability at small scale. The transesterification of vegetable oils is a potential technology for production of biodiesel. The requirements of huge quantity of vegetable oils together with their edible nature are primary bottlenecks of this technology. The highly productive microalgae offers an abundant source of triglycerides for biodiesel if technological progress results cost-effective harvesting and extraction of oils from microalgae. The alcoholic bio-fuels are generally produced through fermentation of carbohydrates of sugar and starchy biomass. The production of alcoholic bio-fuels from world's most abundant, cheap and non-edible LCB are still limited due to higher costs of production. Sooner hydrocarbon biorefinery is going to be the dominating technology if technological advancements result competitive production cost.

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