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Review

A review on the current state of the art for the production of advanced liquid biofuels

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Abstract: Recent socio-political and economic factors encourage development of bioenergy and biofuels. The aim of this paper is to provide an updated review of the most promising technologies for sustainable production of advanced liquid biofuels, specifically transportation fuels. The focus is on second generation biofuels since they do not compete with land required for arable and pastoral use; therefore, first generation biofuels are not included in this review. Upon evaluation the authors recognise the most promising liquid biofuels to include bioethanol, biobutanol, biodiesel, green diesel, biomethanol, dimethyl ether, bio-oil, and biojet fuel. The order of the paper follows a specific structure. Initially, a detailed description, including physical and chemical properties, is given for each liquid biofuel. Then a review of production pathways for each fuel is given, including details regarding the feasibility of integrating it into the current liquid fuel infrastructure. Furthermore, a discussion of the challenges associated with current production pathways is provided.

1. Introduction

The need for energy security, as well as, environmental concerns, are the main drivers behind the growth of bioenergy and consequently biofuels, in recent years. In 2009 the EU issued a mandatory environmental directive, Renewable Energy Directive 2009/28/EC, regarding renewable energy, to address environmental problems that have arisen from the use of fossil fuels in energy generation. This directive specified that 20% of all energy in the EU-27 should be from renewable sources, with 10% of road transport energy coming from biofuels, by the end of 2020. Moreover, in 2012, an amendment of the directive required that first generation derived biofuels should be limited to 5%, reinforcing the need for further development of second-generation advanced biofuels. A report from the International Renewable Energy Agency (IRENA) projects a scenario with 22% of transportation fuels coming from liquid biofuels and biogas by 2050 (Figure 1) [1].
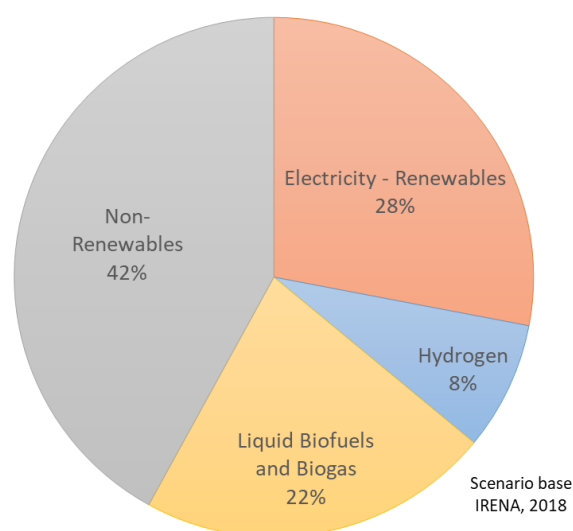

Figure 1. Transport energy consumption (2050) [1].

In addition to changes in legislation, the use of fossil fuels releases greenhouse gases (GHG) into the atmosphere and contributes to the atmospheric CO_2 concentration, which is directly related with climate change. Subsequently, there is renewed interest in the production of liquid biofuels from biomass since their use has the potential to reduce CO_2 emissions [2]. "First generation" biofuels can contribute to CO_2 emissions reduction, but they compete with land used for arable and pastoral farming; therefore, first generation biofuels are not included in this review. "Second generation" liquid biofuels are produced from non-food biomass, including agricultural and forest biomass residues, dedicated energy crops, lignocellulosic fraction of municipal and industrial solid waste [3]. Furthermore, waste vegetable oils and waste animal fats can be used for the generation of liquid biofuels. The same type of biomass can generate different sustainable liquid fuels depending on the applied technology. Figure 2 illustrates the fuels discussed in this paper. Challenges associated with the production of such fuels include cost effectiveness and technical issues.
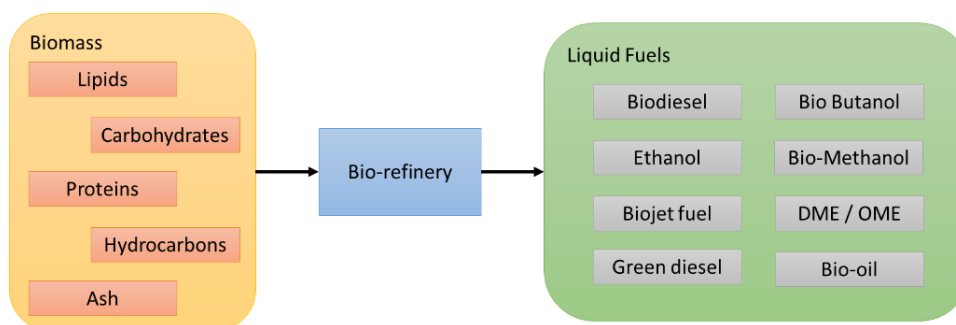
Figure 2. Liquid fuels from biomass.

Advanced liquid biofuels that are studied in this review include bioethanol, biodiesel, bio-methanol, dimethyl-ether, bio-oil, biobutanol, and biojet. Such biofuels (i.e. biodiesel and bioethanol) are characterized either by their ability to blend with existing petroleum fuels, or by their ability to be used in existing internal combustion engines. To preserve the integrity of engine manufacturer warrantees and ensure the same engine combustion, emissions, and performance output, second generation liquid biofuels are required to have similar properties to existing petroleum fuels. These properties among others include heating value, octane number, viscosity, water content, and flash point. Figure 3 shows how fossil fuels can be replaced by sustainable biofuels and their application.
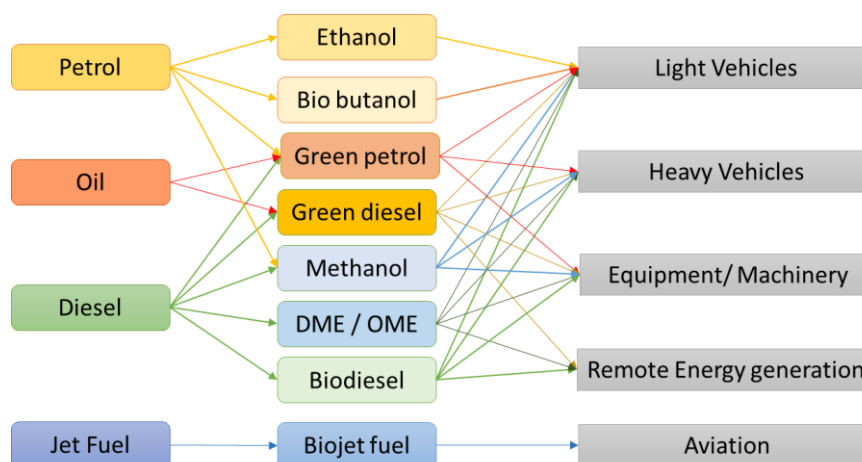

Figure 3. Fossil fuel replacement and applications [4].

In order to produce biofuels, researchers are developing and improving different pathways that can be divided into two main conversion routes, thermochemical or biochemical. The most studied biochemical routes are fermentation and transesterification processes, the most studied thermochemical routes are pyrolysis, gasification, and Fischer Tropsch processes. The sustainability of the pathways for the production of liquid biofuels significantly depends on the type of feedstock used and the end product specifications. Therefore, there is no best pathway or solution to produce renewable liquid fuels. This paper aims to provide an up to date review on the most promising second generation liquid biofuels and the sustainable pathways for their production. Challenges concerning the commercialisation of these biofuels are also discussed.

2. Advanced liquid biofuels

2.1. Bioethanol

Bioethanol is commonly produced from the fermentation of sugars and can be used as a petrol substitute to fuel spark ignition engines. Another pathway is through fermentation of syngas. Petrol is a liquid consisting of C_4–C_{12} hydrocarbons and is produced by cracking crude oil. Ethanol can be used in its pure form (E-100) or blended with petrol. It should be noted that the use of pure ethanol (E-100) requires engine modifications to overcome issues associated with fuel compression, timing of injection, and engine corrosion. Bioethanol can be blended up to 10% and 15 % with petrol according to the requirements in the EN 15376 and ASTM D4806 specifications, respectively. The important properties of pure ethanol (E100) and its 10% blend with petrol (E10) can be seen in Table 1 and are compared with pure petrol.

Table 1. Key properties of petrol, ethanol (E-100), and 10% ethanol to petrol blend (E-10) [5].

Properties	Petrol	E-100	E-10
Viscosity mm^2/s	0.48–0.84	1.57 (20 ℃)	0.53 (30 ℃)
Flash Point ℃	−65	13	−40
RON ℃	86.4–100	108.6–114	87.4–94
MON ℃	80–98.8	89.7–112	86–99.9
Octane number	86–94	98–100	-
Cloud point ℃	−22	-	8
Pour point ℃	(−17)–(−19)	-	0
MJ/Kg	41.9–44.4	26–30	33.19–44.22

It can be observed that pure ethanol has a higher octane number than petrol suggesting that it has higher anti knocking properties. The flashpoint of ethanol and the blend is also higher than petrol making the fuel safer to handle during transport. Moreover, ethanol has a lower heating value.

There are two processing routes for the conversion of lignocellulosic biomass into bioethanol: Fermentation of carbohydrates resulting from the hydrolysis of biomass into bioethanol and the fermentation of syngas. The alcohol produced from the fermentation of carbohydrates or syngas can be subjected further to ethanol dehydration, oligomerization, distillation, and hydrogenation to produce liquid biofuels, such as biojet fuel and green diesel.

2.1.1. Biochemical fermentation

Bioethanol is currently produced from starch/sugar based biomass such as wheat and corn, but issues arise concerning the sustainability of such feedstocks since they compete with human food [6]. Alternative, lignocellulosic biomass can be used for the production of ethanol, but additional technological steps are required, making the process more complicated and costly. Another shortcoming of bioethanol production from sugars is that the process of fermentation is lengthy, usually taking hours or days to complete.

Either acid or enzymatic hydrolysis (also known as saccharification) is required to convert the hemicellulose and cellulose constituents of lignocellulosic biomass into fermentable sugars. The lignin, cellulose, and hemicellulose structure, form a chemical and physical barrier preventing the access of enzymes and the hydrolysis of biomass to produce fermentable sugars. This requires the separation of lignin from the biomass structure, reduction in the crystallinity of cellulose, and alterations in the surface area and porosity of the biomass [7]. Hydrolysis of cellulose and hemicellulose results in the generation of mainly hexoses (glucose) and pentoses, respectively, although some hexoses can also be obtained from hemicellulose.

The main steps for the production of bioethanol from lignocellulosic biomass are pretreatment and/or detoxification, hydrolysis, fermentation, and product recovery [8]. Crushing the feedstock and mixing it with water is required prior to pretreatment to generate slurry. Zhu et al. concluded that the selection of the appropriate pretreatment technology significantly depends on feedstock type [9]. Biochemical fermentation of carbohydrates resulting from the hydrolysis of biomass takes place under the presence of specific microorganisms (yeast or bacteria) at temperatures of up to approximately 38 ℃ with either a batch, fed-batch, or continuous mode bioreactor. The selection of appropriate microorganisms depends on pretreatment conditions, fermentation conditions, and reactor configuration. Furthermore, the hydrolysate of lignocellulosic biomass can contain mixtures of sugars, such as pentoses and hexoses, and the desirable microorganisms should be able to convert both type of sugars. Zabed et al. presented a comprehensive overview on the technological approaches and microbial contribution to the conversion of lignocellulosic biomass into ethanol [8]. Following pretreatment and hydrolysis the sugars released are then fermented by the relevant microorganisms and converted into ethanol. The microorganisms can be acquired from yeast, bacteria, and filamentous funghi and are chosen based on the ethanol yields that they can achieve in addition to the inhibitor tolerance.

Ethanol yields depend on the biomass structure, pretreatment method, type of sugars (five or six carbon sugars), concentration of sugars in the hydrolysates, type of microorganisms, and the fermentation process conditions. The integration of hydrolysis and fermentation is also an important step to achieve process sustainability and high ethanol yields. De Silva et al. investigated the use of carnauba straw residue to produce ethanol by the simultaneous saccharification and fermentation (SSF) process [10]. The SSF approach involves both cellulose hydrolysis and fermentation of hexose sugars in a single reactor. The pretreatment methods applied on the sample included hydrothermal (HT), alkaline (AL), and acid-alkaline (AA) treatment. It was shown that the AL pretreatment resulted in the most efficient removal of lignin and hemicellulose. Moreover, enzymatic hydrolysis of the AL treated sample converted 64.43% to sugars. The maximum ethanol concentration was achieved by using Kluyveromyces marxianus ATCC-36907 cultivated at 45 ℃ and generated 7.53 g/L of ethanol. Further work by Nguyen et al. studied the effectiveness of popping pretreatment in the saccharification process and its consequent effect on bioethanol yields, using coffee beans, cassava starch, and coconut [11]. Results revealed that saccharification efficiencies, after enzymatic hydrolysis, were increased significantly in all the popping-pretreated samples compared to the non-pretreated samples. The total fermentable sugars after pretreatment reached values up to 22.6 g/L, in comparison with the samples without pretreatment, which only achieved maximum values of 7.8 g/L.

Nguyen et al. also investigated the effect of separate hydrolysis and fermentation (SHF) and SSF processing on bioethanol production and foundthe SSF process more promising than the SHF process [11]. In their study ethanol conversion yields from the popping-pretreated sample (mixture of

coffee beans, cassava starch, and coconut) using the SSF approach reached 88.1%, which is significantly greater than the yields of 76.8% (9.5 g/L) achieved by the SHF process. The SSF configuration was previously shown to be more effective in terms of ethanol concentration and conversion yields, in the conversion of corn stover and loblolly pine, when compared with SHF [12]. Ethanol yields of 84% (17.3 g/L) and 77% (15.4 g/L) were achieved from the SSF processing of corn stover and loblolly pine, respectively, while the yields were lower (76% for corn stover and 67% for loblolly pine), for the SHF processing. Dahnum et al. also study the influence of SHF and SSF on ethanol yields using empty fruit bunch [13]. Similar to the previous studies the SSF approach produced the highest concentration of ethanol.

Cotana et al. investigated the potential of the SHF and semi-simultaneous saccharification and fermentation (SSSF) configurations for ethanol production using cardoon [14]. Steam explosion was the pretreatment method selected for the study. Similar to the previous studies the SSSF process displayed better results in terms of ethanol yields and length of the process. Another study used delignified coconut waste and cactus to compare the SSF and SSSF approach [15]. Similar, to Cotana et al., the SSSF configuration resulted in higher ethanol yields (up to 89.15%) when compared to SSF.

Ishola et al. examined the potential of the simultaneous saccharification, filtration, and fermentation (SSFF) process of spruce chips on ethanol yields [16]. This process configuration involves the combination of SHF and SSF, with fermentation broth circulated between the hydrolysis and fermentation vessels. The samples were chemically pretreated with SO_2 impregnation and exposed to a pressure of 22 bars, and a temperature of 215 ℃ for 5 minutes. Approximately, 31.1 g/L of ethanol was produced in the hydrolysis reactor after 96 hours of processing, which corresponds to 85.0% of the theoretical yield.

Another configuration for ethanol production is simultaneous saccharification and co-fermentation (SSCF) which involves both cellulose hydrolysis and fermentation of hexose and pentose sugars in a single reactor. Liu et al. used a dry biorefining approach including dry acid pretreatment, disk milling, and biodetoxification of corn stover, wheat straw, rice straw, sugarcane bagasse, and poplar sawdust to maximise the potential of SSCF [17]. The most promising feedstock was wheat straw, which produced 101.4 g/L of ethanol.
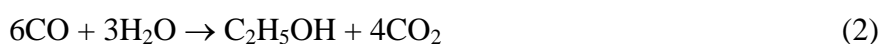
Consolidated bioprocess (CBP) is another process configuration, where hydrolysis and fermentation take place in the same vessel simultaneously, as well as, producing the required hydrolytic enzymes within the process [18]. Horisawa et al. investigated the potential of direct ethanol production from wood chips in a single reactor under anaerobic conditions using the white rot fungus Schizophyllum commune NBRC 4928 [19]. This fungus was selected due its ability to produces enzymes that degrade all biomass constitutes including lignin, cellulose and hemicellulose. Initial tests were performed with polysacchatides and monosaccharides to determine the fungus's ability to produce ethanol from various types of sugar. Results show that the rate of saccharification was slower for polysacchatides fermentation. Concerning the fermentation of wood chips, successful delignification and ethanol production were achieved by also adding the lignin-degrading fungus T. cucumeris IWA5b to the culture. The study demonstrated that the combined use of lignin and polysaccharide degrading fungi was successful and that direct ethanol production from lignocellulosic biomass, without pretreatment, could be feasible. Huang et al. also demonstrated the feasibility of producing ethanol directly from sugarcane bagasse (without pretreatment) using the Recombinant Trichoderma reesei Strain HJ48 [20]. The maximum ethanol concentration produced

was 3.1 g/L after 120 hours of cultivation. Recent work by Loaces et al. showed that Arundo donax biomass can be converted into ethanol by a genetically modified E. coli under a SSF process configuration. It should be noted that the biomass was pretreated with 2% sulfuric acid in mild conditions [21].

2.1.2. Fermentation of syngas

Another pathway for production of ethanol is through fermentation of syngas. Lignocellulosic waste materials can be converted initially through gasification into a gas mixture (syngas) consisting of carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2), methane (CH_4), water vapour, and short chain hydrocarbon gases [22]. During gasification, all biomass components are utilised, including lignin, which is the main advantage of the process when compared with saccharification fermentation where only hemicellulose and cellulose are consumed.

The fermentation of syngas involves mixing together carbon monoxide, hydrogen, and carbon dioxide, which are converted into acetate, followed by ethanol. Typical reactions are the following:

$$4CO + 2H_2O \rightarrow CH_3COOH + 2CO_2 \tag{1}$$

$$6CO + 3H_2O \rightarrow C_2H_5OH + 4CO_2 \tag{2}$$

$$6H_2 + 2CO_2 \rightarrow C_2H_5OH + 3H_2O \tag{3}$$

Syngas produced from gasification contains impurities, such as nitrous oxide, alkali compounds, and tars. Impurities can affect microbial activities and the pH of the fermenting broth, which could lead to cell toxicity, thus gas cleaning is required prior to fermentation. The optimum temperature range for the mesophilic bacteria is 37–40 °C, whereas for the thermophilic bacteria the range is 55–80 °C. The process takes place under strict anaerobic conditions. The most promising microorganisms are acetogens, such as C. carboxidivorans and A. bacchi, which can metabolize CO, CO_2, and H_2 to alcohols and organic acids [23,24]. These microorganisms use two metabolic steps, an acidogenic, and a solventogenic. The acidogenic step involves the main bacterial growth where acids are produced with little or no production of alcohols. The generation of ethanol occurs in the solventogenic step in which alcohol is produced from the formed acids or to a lesser extent, directly from syngas consumption.

Syngas fermentation was performed using a two-stage continuous system with two stirred tank reactors connected in series by Abubackar et al. [25]. The effectiveness of the microorganism clostridium carboxidivorans on the production of acids and alcohols was investigated in continues mode. Syngas ($CO:CO_2:H_2:N_2$; 30:10:20:40; vol%) was supplied at a constant flow rate while a nutrient medium was provided at different flow rates (8.1–30 ml/h). The bioreactors were maintained at different pH levels to enhance acidogenesis (pH 6) and stimulate solventogenesis (pH 5). The highest ethanol concentration was 1.51 g/L and it was achieved for medium flow rates of 22 ml/h. Previous work by Fernández-Naveira et al. used the same medium as mentioned previously to investigate the conversion of syngas by Clostridium carboxidivorans into hexanol, butanol, and ethanol (H-B-E fermentation) [26]. Syngas with composition of $CO:CO_2:H_2:N_2$ (20:20:10:50) was provided continuously at 10 mL/min using a two-stage continuous system with two stirred tank reactors connected in series. The maximum concentrations of ethanol, butanol, and hexanol, were achieved at a pH of 5.75 and were 2.7 g/L, 1.9 g/L, and 0.85 g/L, respectively.

Devarapalli et al. investigated the use of Clostridium ragsdalei, which is another acetogen microorganism, for the conversion of syngas into ethanol [27]. A trickle bed reactor was utilised as the fermentation bioreactor while a syngas mixture of $CO:CO_2:H_2:N_2$ (38:28.5:28.5:5), as well as, the medium, were fed continuously. The highest ethanol concentration (5.7 g/L) was accomplished at 200 ml/min of liquid flow rate and 4.6 sccm syngas flow rate. An interesting approach to enhance ethanol production during syngas fermentation was to use biochar as a medium to serve as nutrients to the Clostridium ragsdalei since it contains mineral and metals [28]. The study compared four fermentation media containing biochar from switchgrass, forage sorghum, red cedar, and poultry litter, with a standard yeast extract medium. Syngas fermentations were conducted in 250 mL bottle reactors at 150 rpm and 37 ℃ with syngas containing $CO:H_2:CO_2$ (40:30:30) by volume. The poultry litter derived biochar medium showed the highest ethanol improvement (58.9%) in comparison to the yeast medium. It is believed that this is due the high release of Na, K, Ca, Mg, S and P from the biochar derived medium.

The use of a mixed culture in a corn steep liquor containing A. bacchi strain CP15 and C. propionicum was also researched [29]. Syngas fermentation with cell recycle was performed in a 7 L continuous stirred tank reactor with a syngas composition of $CO:CO_2:H_2:N_2$ (20:15:5:60) by volume. The mixed culture medium was able to produce 8 g/L, 6 g/L and 1 g/L of ethanol, n-propanol and n-butanol, respectively.

2.2. *Biobutanol*

Biobutanol (C_4H_9OH) can be used as a petrol substitute since its properties are comparable to petroleum derived petrol. It can be produced from lignocellulosic biomass via the process of fermentation. Similar to the fermentation of lignocellulosic biomass to ethanol (mentioned in Section 2.1.1) pretreatment steps are also required. The important properties of pure biobutanol can be seen in Table 2 and are compared with pure petrol.

Table 2. Key properties of petrol and biobutanol [30,31].

Properties	Biobutanol	Petrol
Boiling point (℃)	118	200
Freezing point (℃)	−89	−40
Density (kg/m³)	810	760
Heat of vaporization (MJ/kg)	0.43	0.36
Energy density (MJ/L)	30	32
Cetane no	~25	5–20
Flash point (℃)	35	−42
Auto-ignition temperature (℃)	397	257

2.2.1. Biobutanol production pathways

Biobutanol can be produced by the same pathways as bioethanol; Figure 4 illustrates the production routes of bioethanol and biobutanol. As mentioned previously, butanol is produced simultaneously with ethanol from the fermentation of sugars or syngas [26,28]. Biobutanol

production from fermentation of syngas including recent technological advances was discussed in the bioethanol section. With regards to fermentation of sugars, the conventional pathway for biobutanol production is the acetone-butanol-ethanol (ABE) fermentation route using the microorganism Clostridium acetobutylicum. The main challenge is the recovery of butanol from the fermentation broth, since it is difficult to exceed 2% (v/v), while ethanol can reach yields of up to 15% (v/v).
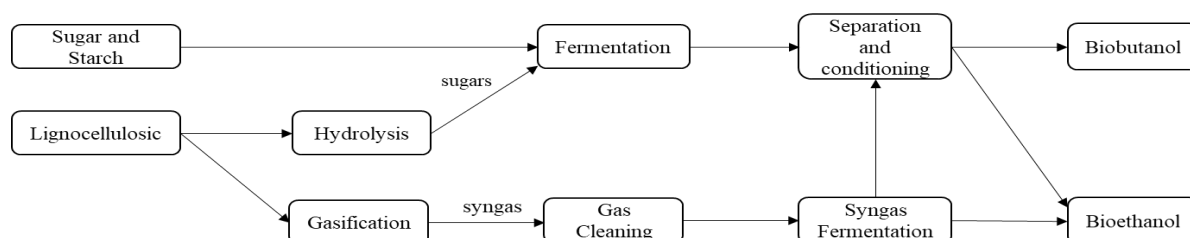

Figure 4. Bioethanol and biobutanol simplified production route.

Xue et al. investigated the potential of Jerusalem artichoke stalk (JAS) as a feedstock for microbial butanol production and the vapour stripping-vapor permeation (VSVP) process for butanol recovery [32]. JAS was subjected initially to alkaline pretreatment followed by enzymatic hydrolysis to achieve delignification and fermentable sugar release. It was found that 11.8 g/L of butanol was produced under the optimum conditions using a Clostridium microorganism. Moreover, the VSVP process proved to be more productive for butanol recovery from the fermentation broth, than conventional pervaporation process. Further work by Xue et al. [33] reviewed the problems and advances in butanol production by Clostridium acetobutylicum to achieve process feasibility. It was concluded that in-situ product recovery techniques can lead to a reduction in the production cost of biobutanol, since the continuous removal and purification of inhibitory products during fermentation, results in the generation of ABE in a concentrated solution. Furthermore, genome editing of Clostridium acetobutylicum could lead to a significant improvement in biobutanol yields.

2.3. Biodiesel

Biodiesel can be defined as fatty acid methyl/ethyl ester (FAME and FAEE) derived from transesterification and esterification of vegetable oils or animal fats and alcohol (methanol or ethanol), usually in the presence of a basic, acid, or enzyme catalyst [34]. Currently, first generation biodiesel is produced on a large scale and is blended with fossil derived diesel. It is regulated by the standards ASTM D6751 and EN 14214. Table 3 shows the key properties and differences between regulated biodiesels and fossil diesel.

Table 3. Key properties of biodiesel and fossil diesel.

Properties	Biodiesel (ASTM D6751)	Biodiesel (EN 14214)	Fossil diesel
Density 15 ℃ (kg/m^3)	880	860–900	820–850
Viscosity @ 40 ℃ (cSt)	1.9–6.0	3.5–5.0	2.04–3.23
Calorific value (MJ/kg)	-	35	42–48

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Properties	Biodiesel (ASTM D6751)	Biodiesel (EN 14214)	Fossil diesel
Acidity total (mgKOH/g)	Max. 0.50	Max. 0.5	0.02
Cetane number (min)	Min. 47	Min. 51	Min. 40
Iodine number (max)	-	120	-
Flash point (℃)	Min. 93	Min. 120	Min. 52
Pour point (℃)	−15 to 10	-	−35 to −15
Cloud point (℃)	−3 to 12	-	−15 to 5
Cold filter plugging point (℃)	19	Max. 5	5
Copper strip corrosion (3 h–50 ℃)	Max. 3	Min. 1	Max. 3
Sulphur % (ppm)	Max. 15	Max. 10	Max. 15
Sulphated ash % (m/m)	Max. 0.02	Max. 0.02	Max. 0.01
Oxidation stability (min, 110 ℃)	3	6	-

Compared to fossil diesel, biodiesel has low sulphur and aromatics content, high biodegradability, low stability (which can be increased with the addition of antioxidants) [35] and high NOx emissions when burned [36].

2.3.1. Transesterification/esterification

Biodiesel is produced through the transesterification/esterification reaction. The oil (triglycerides and free fat acids (FFA)) reacts with an alcohol (usually methanol) in the presence of a catalyst (mainly alkaline) to form alkyl esters (fatty acid methyl ester (FAME) when reacted with methanol) and glycerol or water. The exemplified reactions are below:

$$\text{Triglycerides} + 3 \text{ alcohol} \rightarrow 3 \text{ ethyl esters} + \text{glycerol} \qquad (4)$$

$$\text{Fatty acid} + \text{alcohol} \rightarrow \text{ethyl ester} + \text{water} \qquad (5)$$
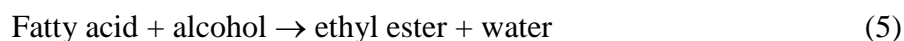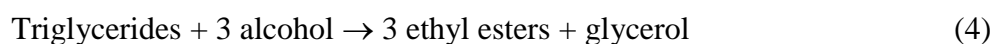
Many studies have been performed to identify the best catalyst for biodiesel production. The most commonly used catalysts are the alkaline ones (NaOH and KOH), however they require less water and FFA in the oil, so this route is limited by the feedstock properties. Waste cooking oil, for example, has a large amount of FFA and is not suitable for this route. Therefore, more catalytic routes have been developed including heterogeneous catalysts, acid catalysts, and enzymes [37]. The latest studies focus on the use of heterogeneous catalysts from biological waste because of their high activity, tolerance to water, non-toxicity, and enviromental benefits [38].
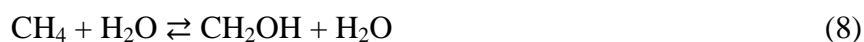
Other studies have focussed on eliminating catalysts all together by using supercritical fluids including, subcritical hydrolysis for lipid extraction integrated into supercritical esterification and, direct supercritical transesterification. The advantage of these approaches is their high tolerance to water and FFA, therefore they are more suitable for cooking oil and wet biomass (algae). However, their efficiency and economic feasibility need to be improved in order to make these technologies viable for larger scale applications [39].

2.4. Green diesel

Another biofuel that can be blended or replace fossil diesel is green or renewable diesel [40]. Green diesel is derived from the diesel fraction of upgraded bio-oil or Fischer–Tropsch (FT) wax. In this case, green diesel, has not been derived from the transesterification process and can be obtained by hydroprocessing (HDO), followed by cracking or isomerisation, of bio-oil or FT wax. This technology will be explained further in Section 2.6.2 and Section 2.8.1.2. However, it is not commonly used yet, as its production costs are higher when compared to biodiesel, and operating conditions are more complex (higher temperatures and pressures). Green diesel has a higher cetane number (around 70–90) when compared to biodiesel (50–65) and diesel (40) and a higher range of cloud point (from −20 to 20 ℃) due to isomerisation after the HDO step [41]. Thus, it is more stable. Moreover, green diesel has a higher calorific value, lower oxygen content, lubricity, density, and viscosity when compared with biodiesel [42].

2.5. Biomethanol

Biomethanol is an alcohol (CH_3OH) that can be produced by catalytic (usually copper, zinc or chromium oxides) hydrogenation of syngas (carbon monoxide and carbon dioxide) or biogas (methane) [43,44]. Its production can be divided into 3 reactions:

$$CO + 2H_2 \rightleftarrows CH_3OH \text{ (two stages: } CO + H_2 \rightleftarrows CH_2O \text{ followed by } CH_2O + H_2 \rightleftarrows CH_3OH) \quad (6)$$

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O \quad (7)$$

$$CH_4 + H_2O \rightleftarrows CH_2OH + H_2O \quad (8)$$

The reactions occur at 200–300 ℃ and 50–100 bar and the use of catalysts are required in order to force thermodynamic equilibrium for methanol production. The recycling of the unreacted gas and the required cooling systems (due to the exothermic nature of the reaction) are responsible for the main costs of the synthesis process [45].

2.5.1.   Hydrogenation of syngas

For methanol synthesis, the syngas ratio (H_2/CO_2) is required to be higher than 2. Thus, cleaning of syngas is carried out before methanol generation in order to optimize its composition. Furthermore, syngas contains impurities, such as sulphur and chlorides that can be harmful to the environment and/or deactivate the catalyst [46]. Another way of optimising the process is the conversion of CO to CO_2 using a water gas shift catalyst or a catalytic membrane reactor immediately after the gasification process [47]. CO_2 is then converted to methanol by catalytic hydrogenation. The produced biomethanol also requires a purification step in order to meet specifications. This process can be realised at a competitive price when biomethanol is used as a biofuel blend and methanol can be directed to the production of other fuels such as biodiesel, DME, and OME [47]. Biomethanol production can be simplified with the approach presented in Figure 5 below:
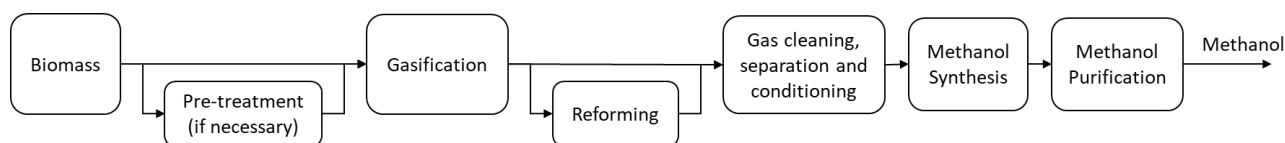
Figure 5. Biomethanol simplified production route.

It has been shown that biomethanol has a competitive cost production and GHG emissions reduction when compared to methanol production from fossil fuels [48]. Biomethanol can be used as direct blending with petrol and maritime fuel, for transesterification, and as feedstock for DME/OME synthesis [49].

2.6. DME/OME

Poly (oxymethylene) dimethyl ethers (OME) and dimethyl ether (DME) are diesel substitutes and can be used in compression ignition engines without major modifications. Biomethanol can be used as feedstock for the generation of OME/DME. The DME structure is CH_3OCH_3, while OME is $H_3CO(CH_2O)_nCH_3$, with n from 2 to 8, preferably 3 to 5 for diesel replacement [48]. The properties of these fuels in comparison with diesel are presented in Table 4 [49,50].

Table 4. Key properties of DME and OME.

Properties	DME	OME	Fossil diesel
Molecular weight	46.07	76–196.2	96
Density 20 ℃ (kg/m^3)	660	960–1105	800–840
Viscosity @ 40 ℃ (cSt)	0.12–0.15	0.64–1.75	2–4
Calorific value (MJ/kg)	28.5	18.5–23.3	42.5
Cetane number (min)	55–60	60–90	Min. 40

DME has a high oxygen content, low viscosity, low lubrication, and LHV when compared to fossil diesel fuel [51]. DME has already been tested in diesel engines; information regarding emissions and performance are established. When compared to diesel combustion, DME emits lower levels of particulate matter, HC, and nitrous oxides (NOx) [51], but also has inferior performance (due to the lower LHV) [52]. OME does not contain impurities and has a cetane number higher than conventional diesel, but it has a lower HHV. Costs analysis confirms that OME production could be even cheaper than diesel production [50].

2.6.1.   DME production pathways

The main pathway for DME production is methanol dehydration in a catalytic gas-phase reactor followed by purification and distillation [53]. Common catalysts used are solid-acid catalysts, such as alumina, zeolites, $AlPO_4$, and CuO/ZrO_2. DME synthesis usually occurs in slurry or fixed bed reactors, but the process can also take place in fluidized-bed reactors, coupled and dual type, as well as, membrane reactors [54]. The reaction of the commercialised process is presented below:

$$2 \, CH_3OH \rightarrow CH_3OCH_3 + H_2O \tag{9}$$
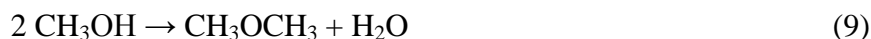
A promising route that is currently being studied is DME production in a one stage reactor. DME can be produced directly from syngas, at 250–400 ℃ and pressures higher than 10 bar, in an exothermic reaction using a bi-functional catalyst that is able to synthesise methanol followed by DME. The process is strongly influenced by the presence of water, H_2/CO ratio, CO_2 content, and reaction temperature [56].

2.6.2. OME production pathways

For OME production, the methanol is utilised by a metal oxide catalytic process (or with silver catalyst) to produce formaldehyde as shown in the reactions below:

$$CH_3O + 1/2 \, O_2 \rightarrow CH_2O + H_2O \tag{10}$$

$$CH_3O \rightarrow CH_2O + H_2 \tag{11}$$

From the formaldehyde, trioxane is produced with the use of sulphuric acid ($3CH_2O \rightarrow (CH_2O)_3$) and methylal is produced by a reaction-distillation process with an acidic heterogeneous catalyst ($2CH_3OH + CH_2O \rightleftarrows CH_3O\text{-}CH_2O\text{-}CH_3 + H_2O$) [50]. The most used catalysts are liquid catalysts (mineral acid (H_2SO_4) or ionic liquids) and heterogeneous catalysts (ion exchange resin, carbon marerial, solid superacid, zeolite and others) [55].

The catalytic steps involved in OME synthesis is the main drawback of the process. Therefore, further research has been undertaken aiming to simplify the process with more efficient and feasible catalysts [57].

Further optimisations regarding the feasibility of the DME/OME routes has been investigated in regards to the optimization of the gasification and methanol process. Parvez (2018) showed that CO_2-enhanced gasification resulted in better energy efficiency and less environmental impact when producing DME compared to conventional gasification [56].

2.7. Bio-oil

Bio-oil is the primary product from the process of pyrolysis, which can be obtained from the thermal decomposition of lignocellulose biomass with rapid heating in the absence of oxygen followed by rapid quenching of the vapour products. It is a multicomponent mixture consisting of hundreds of different sized molecules obtained from the depolymerisation and fragmentation of cellulose, hemicellulose, and lignin [57]. A typical compound distribution in bio-oil includes acids, esters, alcohols, ketones, aldehydes, sugars, furans, hydrocarbons (such as alkene, aromatics), phenols (such as phenols, anisoles, catechols, guaiacols, syringols), water, and fragments of cellulose and lignin [58,59]. The composition and yields of bio-oil are significantly dependent on the process operating parameters, reactor configuration, and feedstock type.

Bio-oil can be used as a substitute for fuel oil or diesel in many industrial boilers, furnaces, and static engines for heat and power generation. The USA has developed the ASTM D7544, which covers the specification of pyrolysis liquid produced from biomass for use in various types of fuel-burning equipment.

Significant upgrading of bio-oil is required to meet engine specifications, since its physiochemical properties vary significant from those of conventional fossil fuels (Table 5). The main reason for the differences between bio-oil and transportation fuels is the high content of oxygen in bio-oil, which tends to resemble its original biomass [60]. Furthermore, it is immiscible with fossil fuels, because of its high polarity and hydrophilic nature. The indigenous undesired properties of bio-oil that makes it unsuitable as a transportation fuel are given below:

- Low heating value,
- Immiscible with fossil transportation fuels,
- Acidity,
- High oxygen content,
- High viscosity,
- High water content,
- High solid content.

Bio-oil can be used in other applications, such as a food flavouring and chemical production, however our focus is on its potential as a biofuel for transportation.

Table 5. Typical physical properties of fast pyrolysis bio-oils and mineral oils [61].

Analysis	Typical wood derived bio-oil	Fossil diesel	LFO Motor/heating EN590
Water, wt.%	20–30	~0	~0
Stability	Unstable[*]		
Viscosity (40 ℃), cSt	15–35	2.04–3.23	2.0–4.5
Density (15 ℃), kg/dm^3	1.10–1.30^c	0.820–0.850	Max. 0.845
Flash point, ℃	40–110^d	Min. 52	Min.60
Pour point, ℃	−9–36	−35−15	−5 min
LHV, MJ/kg	13–18^c	42–48	42.6
Distillability	Non-distillable	Distillable	Distillable

[*]Polymerisation occurs during heating for prolonged periods.

2.7.1. Bio-oil production pathways

Pyrolysis is defined as the thermal decomposition of organic matter in the complete absence of oxygen (usually nitrogen). Pyrolysis takes place in the temperature range 280–850 ℃ depending on the nature of the feedstock, the desired products, and the particular pyrolysis process employed. Depending on the heating rate and vapour phase residence time, pyrolysis can be classified into several categories. Slow pyrolysis is a batch process characterised by long vapour residence time (5–30 min), slow heat transfer rates up to 2 ℃/s, and low reactor temperatures ranging from 300–500 ℃. Intermediate pyrolysis is carried out in the temperature range 300–500 ℃ with heat transfer rates up to 1000 ℃/s. Fast pyrolysis is a continuous process and requires high heat transfer rates (>1000 ℃/s), short vapour residence time (1 s), and a relatively high temperature (450−600 ℃). Moreover, feedstock drying is necessary in fast pyrolysis, while slow and intermediate pyrolysis process feedstocks with higher moisture levels. Even though fast pyrolysis produces the highest bio-oil yields (up to 75 wt.% expressed on biomass basis), it has been shown that intermediate pyrolysis

can produce better quality of bio-oil (low tar yield and viscosity) [62]. The processes described above occur under atmospheric pressure.

In addition to the previous categorisation, hydrogen can be used instead of an inert nitrogen environment. Hydropyrolysis takes place under a pressurised hydrogen atmosphere, which results in the reduction of unsaturated hydrocarbons and formation of fewer compounds in the bio-oil with higher selectivity [63]. It seems that the presence of hydrogen avoids the random thermal cracking that takes place under a nitrogen environment and promotes the systematic bond cleavage in the structure of biomass, thus increasing the quality of the produced bio-oil. Pressurised water can also be used to achieve the thermochemical conversion of biomass into bio-oil in a process termed hydrothermal liquefaction [64]. Typical operating temperatures are 250–374 °C and operating pressures from 4–22 MPa. Another promising pyrolysis mode is microwave pyrolysis [65]. The fundamental difference here is that microwave waves heat the biomass particles from within and not by external heat transfer from a high temperature heat source.

2.7.2. Upgrading of bio-oil

- Catalytic hydrotreatment

The process takes place at high pressure (up to 200 bar) and moderate temperature (up to 400 °C) in the presence of a heterogeneous catalyst. A hydrogen source is necessary to achieve the removal of the oxygenated compounds in bio-oil, such as ketones and carboxylic acids, and to produce an oil suitable to be used as a feedstock in a biorefinery or blend with diesel. Hydrotreatment rejects oxygen as water by catalytic reaction with hydrogen [66].

$$(CH_2O) + H_2 \rightarrow Catalyst \rightarrow (CH_2) + H_2O \tag{12}$$
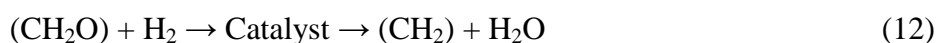
Gollacota et al. summarised the following different type of reactions that occur during the process: Hydrodeoxygenation, hydrogenation, hydrogenolysis, hydrocracking, dehydration, and decarboxylation [67]. Hydrotreating (HT) gives a naphtha-like product that requires further refining to produce transport fuels, such as aviation fuel and green diesel [68].

Commonly applied catalysts for the hytrotreating of bio-oil or bio-oil model compounds are alumina or aluminosilicate supported sulfided CoMo and NiMo catalysts. This review focuses on the upgrading of actual bio-oil, thus work regarding bio-oil model compounds is not discussed further. The main work involving the testing of sulphided CoMo or NiMo catalysts on wood derived bio-oil was conducted in the 1980s and 1990s [69,70]. Their results showed that even though the catalysts were effective in the enhancement of bio-oil, several issues, such as low upgraded bio-oil yields and catalyst deactivation caused by carbon/coke deposition, required further research. The disadvantage of alumina as a support material for the HT catalysts was its instability at high temperatures in the high water environment of the bio-oil. Thus, carbon-supported sulphided CoMo and NiMo catalysts were also tested as HT catalysts by Elliot et al. [71].

Alternatively, noble metals have been tested, dispersed on active charcoal supports or metal oxides, for the HT of bio-oil [72–74]. Wildschut et al. used Ru, Rh, Pd and Pt over different supports to assess their effect on the deoxygenation of bio-oil in comparison with conventional HT catalysts. It was found that the Ru/C catalyst was greater than the HT catalysts with reference to bio-oil yields (up to 60 wt.%) and deoxygenation level (up to 90 wt.%). The type of catalyst precursor on catalyst

performance was also found to play a role on the HT of bio-oil [76]. However, the high cost of noble metals significantly affects the industrialisation of the process.

Inexpensive non-sulphided transition metal catalysts over various support materials, such as aluminosilicate and zeolite, have been studied for their HDO activity for bio-oil upgrading. Ni-based catalysts with three different support materials (active carbon, SBA-15 and Al-SBA-15) and their catalytic effects were tested with poplar derived bio-oil by Oh et al. [75]. The Ni/SBA-15 catalyst was found to show the highest degree of deoxygenation and upgraded bio-oil yields by 47.7 wt.%.

Xu et al. investigated the effect of a non-sulphided bimetallic catalyst, MoNi/γ-Al$_2$O$_3$, for upgrading of pine sawdust derived bio-oil [76]. The catalyst seemed to improved pH and water content, but the oxygen content was not reduced significantly. The influence of the non-sulphided bimetallic FeCo/SiO$_2$ catalyst, as well as, the monometallic Co/SiO$_2$ and Fe/SiO$_2$ catalysts, on deoxygenation of pine sawdust derived bio-oil was also tested [77]. The bimetallic Fe-Co/SiO$_2$ catalysts decreased the upgraded bio-oil yields (23.85–26.94 wt.%) and increased the gas yields (10.35–22.90 wt.%). The bimetallic catalysts showed an improvement on HDO performance over the monometallic catalysts, but they produced lower upgraded bio-oil yields (23.85–26.94 wt.% in comparison of 31.23–33.91 wt.%).

Furthermore, activated carbon supported Ni, Co and Mo phosphide catalysts have been shown to be promising for HT [78]. Guo et al. investigated the effect of phosphorus content on the deoxygenation of bio-oil by varying the metal/P ratio [79]. It was found that the addition of phosphorous to a certain level resulted in the improvement of H$_2$ consumption, upgraded oil yields, and increased the degree of deoxygenation. The Ni-based catalysts seemed more promising than Co-based catalysts with regards to hydrogenation and HDO activities.

- Zeolite cracking

Zeolite catalysts can be used to improve the quality of bio-oil in two configurations. One mode is in-situ upgrading which involves the integration of catalysts into the pyrolysis system. The other configuration involves catalytic upgrading as a downstream (decoupled) process. The process takes place under atmospheric pressure and does not require the presence of hydrogen. The reactions described for the HT process also take place in zeolite cracking, but the cracking reactions are the primary ones. Zeolite cracking rejects oxygen as CO$_2$ and H$_2$O, generating liquid hydrocarbon products through the remaining hydrocarbon fraction [80].

$$C_1H_{1.33}O_{0.43} + 0.26\,O_2 \rightarrow 0.65\,CH_{1.2} + 0.34\,CO_2 + 0.27\,H_2O \qquad (13)$$
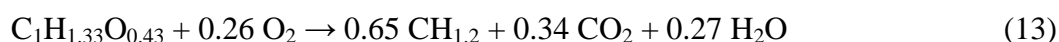
ZSM-5 has been used extensively as a catalyst by a number of researchers to improve the quality of bio-oil. Comprehensive work was performed by Williams and Horne to study the effect of ZSM-5 on pyrolysis product yields and chemical distribution using a fluidised bed reactor [81]. The catalyst was placed at the reactor freeboard as a fixed bed (in-situ configuration). Results showed that the oil yields were reduced from 40.4 to 5.5 wt.% of biomass, while a reduction was also observed in the molecular weight (from 30–1300 u to 50–600 u) of the bio-oil. The chemical distribution of the bio-oil was also affected, particularly the formation of monocyclic aromatic hydrocarbons and polycyclic aromatic hydrocarbons (PAH).

Furthermore, the influence of ZSM-5 temperature has been investigated. Catalytic experiments were performed over a range of temperatures from 400–600 ℃ [82]. It was found that the total liquid

yields, molecular weight and oxygenated compounds (such as phenols and benzenediol) in bio-oil were reduced. On the contrary, the concentration of aromatic hydrocarbons and PAH were increased. Li et al. also investigated the effect of catalytic reaction temperature (390, 410, 450, 470, 500, or 550 ℃) and WHSV (1 to 5 h^{-1}) on bio-oil using ZSM-5 [83]. The reactor configuration involved a fluidized bed reactor for pyrolysis coupled with a secondary fixed bed reactor for upgrading. It was observed that acid and ketones were reduced, whereas hydroxybenzene and monocyclic or dicyclic aromatic hydrocarbons were increased. Both researchers found that as catalytic temperature increased the upgraded bio-oil yields decreased while the opposite trend was observed for the gas yields. This is due the decomposition of bio-oil to light gases and carbon at higher temperatures. It should be noted that it is necessary to establish the optimum degree of cracking, where a sufficient amount of oxygen is removed but the yields of upgraded bio-oil are not too low. Catalytic fast pyrolysis (CFP) bio-oils with different organic oxygen contents (4–18 wt.%) were prepared in a bench-scale dual fluidized bed reactor system by ex-situ CFP of southern pine over HZSM-5, and the oils were subsequently hydrotreated over a sulphided CoMo catalyst at 170 bar [84].

The main properties for the catalytic activity of zeolite catalysts are their shape selectivity and acidity. The limitations of the pore size (5A) of H-ZSM-5 in the case of large molecules justified further research using zeolite materials with larger pore size, such as MCM-41 and zeolite Y.

Williams and Horne [85] studied the effect of different zeolite structures and activated alumina on bio-oil. Regarding the product yields, stainless steel balls, Na-ZSM-5, H-ZSM-5, Y and activated alumina showed a reduction in organic liquid yields (blank run—40.41%) of 11.80, 6.01, 5.47, 1.13 and 3.12 respectively, expressed on wt.% of biomass feed. The overall conclusions were that all the zeolites produced hydrocarbons (aromatic and PAHs); Y-zeolite formed higher PAHs levels compared to the other catalysts; ZSM-5 was the most effective catalyst; hydrocarbon yields were low, when expressed on wt.% of biomass feed.

Extensive work related to the acidity and metal incorporation of catalysts was conducted by Antonakou et al. [86]. Pyrolysis experiments using Al-MCM-41 catalysts with various acidities (Si:Al ratios of 20, 40, 60) and metal containing Al-MCM-41catalysts (Cu, Fe and Zn) were conducted using a bench scale fixed bed reactor. An increase was observed in the amount of phenols and hydrocarbons in bio-oil, while the opposite effect occurred for the oxygenated compounds. It should be highlighted that a reduction in acids, carbonyls, and heavy compounds was also observed. The organic yields, though, decreased by about 9 wt.% (on biomass basis) when catalysts were applied.

Metal oxide catalysts have also been tested for their catalytic effect on pyrolysis oils [87,88]. The effect of ZnO on bio-oil was studied by Nokkosmäki et al. in a fluidised bed reactor with capacity of 1 kg/h^{-1}, with the catalytic fixed bed reactor connected into the side stream of the reactor system [89]. The pyrolysis reaction temperature was 525 ℃, while the catalytic reaction temperature was 400 ℃. Results revealed that the ZnO derived bio-oil had lower viscosity thus indicating an improvement in stability. Putun et al investigated the effect of MgO on pyrolysis product yields [90]. A fixed bed reactor was used with the catalyst placed as a bed material inside the reactor. Oxygen content of the treated bio-oil was reduced from 9.56% to 4.90% when different amounts of catalysts were applied.

- Filtration

    Bio-oil contains impurities, such as alkali metals and particulates, which cause problems in certain applications. Hot-vapour filtration can be used to reduce the solid content of the oil to less than 0.01% and the alkali content to less than 10 ppm [82,89]. However, bio-oil requires further upgrading since the primary reason for its immiscibility with fossil fuels is its oxygen content.

- Supercritical fluids (SCFs)

    A fluid is defined as supercritical when its pressure and temperature go beyond its critical point and it has the ability to dissolve materials that are not normally soluble in either the liquid or gaseous phase of the SCFs. In the case of bio-oil production, the use of SCF organic solvents, results in an oil with higher caloric values, lower viscosity, and higher yields [90]. Typical SCFs organic solvents have been identified by Baloch et al. and include ethanol, butanol, acetones, methanol, n-hexanol, 2-propanol, and 1,4-di-oxane [91].

- Solvent addition/esterification

    Esterification can reduce the acidity of bio-oil by removing the carboxylic acids. The reaction takes place in the presence of a catalyst and a solvent to generate esters. Catalysts used for esterification are solid acid, solid alkali, and ionic liquid ion exchange resins [92–94].

- Emulsification (emulsions)

    Emulsification is a physical method for upgrading bio-oil. Homogenous emulsion of bio-oil with diesel can be achieved by agitation with an emulsifier [95].

2.8. Biojet fuel

    Biojet fuel or renewable aviation fuel is a biomass derived fuel and contains hydrocarbons with a boiling range similar to fossil jet fuel (170–300 °C). Fossil jet fuel is composed of approximately 20% paraffin, 40% isoparaffin, 20% naphthenes and 20% aromatics. Depending on the pathway, biojet fuel does not always contain aromatic compounds. Mixtures of up to 50% biojet fuel with aviation fossil fuels have been established as a standard to overcome this issue. Biojet fuel is only certified if it has similar properties with fossil jet fuel, such as energy content and density. Some characteristics of biojet fuel (according to ASTMD 7566) that are similar to fossil jet fuel are presented in Table 6 [96].

Table 6. Key properties of biojet fuel (ASTMD7566).

Properties	Biojet fuel
Acidity,total (mgKOH/g)	0.1 max
Flash point (℃)	38 min
Density @15 ℃ (kg/m^3)	775–840
Freezing point (℃), max	−40 JetA; −47 JetA1
Viscosity @ −20 ℃ (cSt)	8, max
Net heat of comb (MJ/kg)	42.8, min

2.8.1. Conversion pathways for biojet fuel generation

Certified biojet fuel can be blended up to 50% with conventional aviation fossil fuel according to the requirements in the ASTM D7566 specification. The following processes have been certified by the standard for production of renewable aviation fuel.

2.8.1.1. Hydroprocessed renewable jet fuels (HRJ)

HRJ also known as hydroprocessed esters and fatty acids (HEFA) are paraffinic liquids with the chemical formula C_nH_{2n+2}. HRJs are produced by the hydrodeoxygenation of triglyceride-based feedstocks, followed by isomerisation and cracking, forming fuels equivalent to conventional aviation fossil fuel. The use of bio-oil as a triglyceride-based feedstock is not yet certified.

The triglyceride-based feedstock is firstly converted to lineal long chain hydrocarbons, under high pressure and temperature in the presence of hydrogen and a solid catalyst (hydrodeoxygenation, see Section 2.6.2); by-products formed are water, carbon monoxide, and carbon dioxide. Isomerisation and cracking convert the lineal long chain hydrocarbons into the hydrocarbon chains that are in the range C_8 to C_{16} (biojet fuel). Light gases, naphtha, and green diesel are produced in addition to biojet fuel. In comparison to fossil fuels, HRJ fuels possess a higher cetane number, lower aromatic content, lower sulphur content, and potentially lower GHG emissions.

The hydrotreating process has been demonstrated at pilot plant level by UOP Honeywell for the production of renewable jet fuel using second-generation oils as feedstock [97]. It should be noted that information concerning the type of catalyst involved in the UOP Honeywell process is not publicly available. There are few studies in literature focussing on hydrotreating of sustainable feedstocks for biojet fuel production. Promising work has been performed by Robota et al. regarding the conversion of algal triglycerides to biodiesel and HEFA jet fuel fractions [98]. The proposed process involves deoxygenation, hydrogenation, and hydro isomerisation using a 3% Pd/carbon, a 0.5% Pt/alumina, and a 0.5% Pt/US-Y zeolite catalyst, respectively. Choi et al. studied the use of a Pt/TiO$_2$ catalyst with a W addition for the deoxygenation of Jatropha fatty acid derived from Jatropha oil by hydrolysis [99]. The deoxygenation reaction was carried out in a fixed-bed reactor without the presence of hydrogen producing saturated hydrocarbons (C17 and C15) with a degree of deoxygenation of 86%.

Zhao et al. investigated the upgrading of non-edible sunflower oils over a ZSM-5 catalyst in a fixed-bed reactor, at three different reaction temperatures (450 ℃, 500 ℃ and 550 ℃), followed by distillation [100]. The maximum conversion efficiency of sunflower oils to hydrocarbon fuels

was 30.1% and was realised at 550 ℃. Even though the properties of the hydrocarbon fraction were improved after upgrading and distillation, further refining is required to remove the remaining oxygen atoms. Liu et al. used Ni supported on moderate acidic zeolites to produce biojet fuel from castor oil by hydroprocessing in a continuous-flow fixed-bed microreactor followed by isomerization and hydrocracking [101]. The main observation of this work was that the acid strength of zeolite had an important role in the conversion of castor oil into biojet range alkanes. It should be mentioned that the oils produced meet all of the basic jet-fuel mixing requirements according to ASTM D7566. The conversion of waste cooking oil to jet biofuel has also been researched with nickel-based mesoporous zeolite Y catalyst [102]. Moreover, NiMo, CoMo, and NiW sulfide catalysts were also applied during hydrodeoxygenation of waste cooking oil [103]. During both studies the deoxygenation of cooking oil was achieved and converted into jet range alkanes, but further investigation is required to achieve higher fuel yields.

2.8.1.2. Fischer Tropsch fuels (FT fuels)

FT fuels are biomass derived hydrocarbon fuels, which are produced from the catalytic conversion of syngas. The integration of gasification with Fisher Tropsch synthesis shows great potential as a sustainable route for production of biodiesel and biojet fuel from biomass [104–107]. Process temperature varies from 700–1000 ℃ and requires a gasifying agent, such as steam or air. The process is carried out under atmospheric pressure typically with a fixed bed gasifier which is categorised as either updraft, downdraft, or crossdraft [108].

Fischer Tropsch technology involves conversion of syngas into long chain hydrocarbon products, either straight or branched. FT synthesis occurs in two temperature ranges, a low temperature FT (LTFT) and a high temperature FT (HTFT), which range between 200–240 ℃ and 300–350 ℃, respectively [109]. The low temperature process uses either iron or cobalt catalysts, while the high temperature process uses iron-based catalysts [110,111]. Pressures range from 10–60 bar. Typical reactor types are circulated fluidised bed and fluidised bed for HTFT and tubular fixed bed and slurry phase for LTFT [109].

FT synthesis converts the gasification gas mixture into a mixture of light (C_1–C_4), naphtha (C_5–C_{11}), diesel (C_{12}–C_{20}) and heavier hydrocarbons/wax (>C_{20}) [112,113]. The latter requires further catalytic hydrocracking to produce biojet fuel and green diesel. Liquid product yields from FT synthesis can be up to 95%. This crude FT product requires further processing for the synthesis of the FT fuel. The composition of the crude FT product strongly depends on the H_2/CO ratio, the catalyst, pressure, and temperature process conditions. Furthermore, cracking and isomerization of the crude FT product generates FT fuel with hydrocarbon chains that are in the range C_8–C_{16}, corresponding to biojet fuel.

Recent work by Hillestad et al. demonstrated the feasibility of a power and biomass plant for the production of Fischer-Tropsch biojet fuel compared to a conventional Biomass-to-Liquid (BtL) process [114]. It was shown that the carbon efficiency of a conventional BtL process can be increased from 38% to more than 90%. This was achieved by adding hydrogen from high temperature steam electrolysis in a solid oxide electrolysis cell (SOEC), with high temperature steam generated from the hot syngas. Moreover, SOEC produces oxygen, which is supplied as oxidant in the gasifier, thereby eliminating the need for a cryogenic air separation unit. Previously, Viguié et al. presented the BioTfueL project, which produces biojet fuel and green diesel from second generation

feedstocks [115]. This project focuses on the original concept of co-processing (biomass and fossil feedstock). The selection of the appropriate catalyst for hydrocracking of crude FT is also an important parameter to achieve process feasibility. Hanaoka et al. produced biojet fuel by hydrocracking an FT product derived from woody biomass via gasification [116]. The maximum jet fuel yield was 29.1 C-mol% with a Pt-loaded zeolite catalyst with particle size of 7.6 nm.

2.8.1.3. Synthetic isoparaffin (SIP) fuels from fermented hydroprocessed sugar

SIP fuels, were formerly known as direct-sugar-to-hydrocarbon (DSHC) fuels. The process involves the biochemical fermentation of carbohydrate sugars to hydrocarbon fuels through purification and hydroprocesing, without producing ethanol first. The sugars can be derived from the hydrolysis of biomass or from direct sugar sources such as sugar cane residues. Blends of 10% volume of SIPs with aviation fossil fuels are permitted by ASTM D7566.

2.8.1.4. Alcohol to jet (ATJ) fuels

ATJ fuels are produced by thermal and biochemical fermentation of carbohydrates obtained from the hydrolysis of biomass. The sugars extracted by hydrolysis are fermented, followed by distillation to get bio alcohol. Direct use of alcohol as jet fuel requires engine modification, thus further processing needs to occur to produce a suitable jet fuel. The next steps are alcohol dehydration, oligomerisation, hydrogenation followed by distillation to produce a biojet fuel similar to fossil aviation fuel. Additionally, the process produces naphtha and diesel. Lanzatech is the world's first large scale ATJ facility producing commercial quantities of fuel in the UK [117]. The commercial facility will convert ethanol produced from waste to biojet.

2.8.1.5. Other biojet fuels

Other promising pathways for biojet fuel production that are not yet certified by the standard are:
- Catalytic hydro-thermolysis (CH) fuels, also termed hydrothermal liquefaction. The same process is followed as described for the SIPs, but it involves catalytic conversion of sugars instead of biochemical fermentation.
- Hydro-treated depolymerized cellulosic jet (HDCJ), also known as fast pyrolysis with upgrading to jet fuel.
- Gas fermentation process. Instead of catalytically upgrading FT syngas to biojet fuel, it is also possible to ferment syngas to liquid biofuels. The cooled syngas can be fermented to ethanol or butanol by acetogenic bacteria followed by oligomerisation and hydrogenation to produce biojet fuel.

3. Evaluation of production pathways for second generation advanced biofuels

Various pathways have been developed for the production of second generation liquid biofuels. This review considers only sustainable feedstocks that do not compete with food production including sugar and starch crop residues, lignocellulosic biomass and waste, and non edible oils (or fats). Figure 6 illustrates the fuels and their production routes.
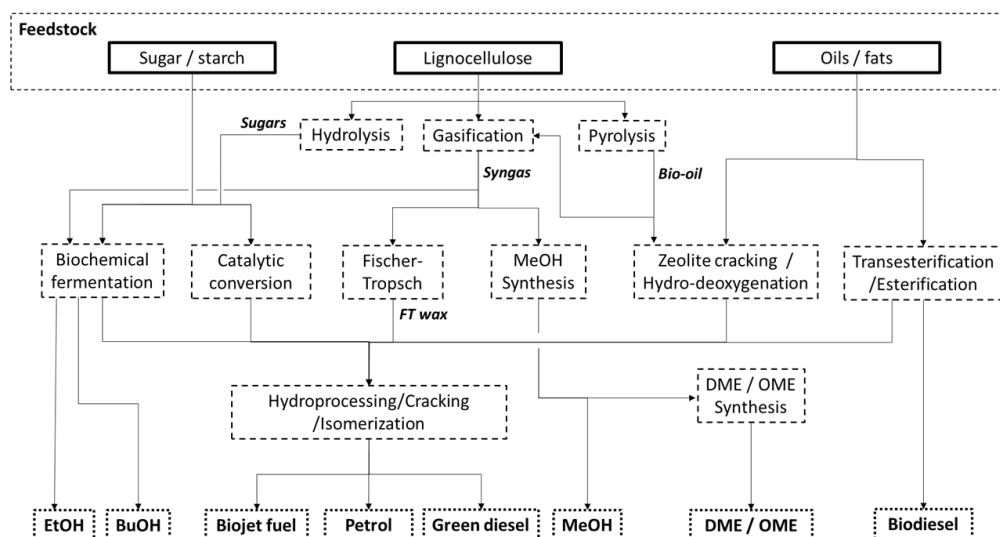
Figure 6. Pathways for the production of advanced liquid biofuels.

Sugar and starch type agricultural residues are converted through biochemical fermentation to bioethanol or biobuthanol. Further processing through hydroprocessing and cracking/isomerization produces biojet fuel and green diesel. Another approach for the latter fuels using sugar and starch feedstocks is through catalytic conversion followed by hydroprocessing and cracking/isomerization. Lignocellulosic feedstocks can be converted to sugars by hydrolysis, syngas by gasification or bio-oil by pyrolysis. The produced syngas can be directed to biochemical fermentation, Fisher-Tropsch and biometanol synthesis. Biomethanol (generated from the methanol synthesis) can be used directly as biofuel or to generate DME and OME. Pyrolysis derived bio-oil can be subjected to further processing through zeolite cracking or hydro-deoxygenation to produce a de-oxygenated bio-oil which after cracking/isomerization produces biojet fuel, petrol, and green diesel. Oils and fats can be directed either to zeolite cracking and hydro-deoxygenation or to transesterification and esterification, to generate green diesel and biodiesel, respectively. A comparison of the main advantages and disadvantages of the technological pathways for second generation liquid biofuels are summarised in Table 7.

Table 7. Comparison of technological routes for biofuels generation.

Product	Pathway	Advantages	Challenges
Ethanol	Biochemical fermentation from sugars	Well-developed route Acid/enzymatic step allows for feedstock diversification	Development of microorganisms to be able to convert both type of sugars Research on process integration is required to achieve process feasibility
	Fermentation of syngas	All biomass components are utilised, including lignin	Syngas conditioning is required
Butanol	Biochemical fermentation from sugars	Simultaneous process with ethanol production	Product recovery process
	Fermentation of syngas		

Continued on next page

Product	Pathway	Advantages	Challenges
Biodiesel	Catalytic Transesterification	Well-developed route Market ready for the product	Catalyst developed for first generation oils
	Supercritical Transesterification	High feedstock tolerance	Expensive process when compared to the catalytic route
			Extreme conditions and high energy demand (more development needed)
Green diesel	Bio-oil upgrading (HDO and HC)	Less feedstock limitation Similarity with fossil diesel	Bio-oil production technology challenges Catalyst
Biomethanol	Gasification + MeOH Synthesis	Cost competitive with methanol from fossil fuels Developed market for the product	Gasification process challenges Syngas conditioning
DME/OME	DME/OME Synthesis	Used as diesel replacement Not expensive	Inferior performance compared to the fossil fuel Challenges from the methanol production
Petrol	Hydroprocessing followed by cracking/isomerisation	Several production routes	Further development on processing of bio-oil Low yields, is produced as a by-product
Biojet fuel	Hydroprocessing of triglycerides	Cost competitive than the other biojet routes	Cost of catalysts and hydrogen Limited feedstock tolerance Product refining
	Biochemical fermentation of sugars to hydrocarbons	Fewer technological steps than ATJ fuels	Product refining
	Biochemical fermentation of sugars to ethanol followed by hydrogenation	Less feedstock limitation	Product refining
	FT synthesis	All biomass components are utilised, including lignin	Cost of FT synthesis

The technoeconomic feasibility of a production pathway chosen for fuel production is dependant on a number of different factors, such as market demand, feedstock availability, and market readiness in each location. Location on its own is also an important factor, influencing both the feedstock supply chain and plant construction and commissioning costs. In Brazil the abundance of arable land, as well as, the availability of sugar cane and bagasse, has lead to the dominance of bioethanol in the Brazilian market. In addition to geographical, political influence has also been an important driver of the bioethanol market in Brazil today, where public policy has helped to create the largest flexible-fuel fleet in the world [118].

Feedstock availability is another important parameter affecting process feasibility. Thus pathways that allow for feedstock diversification present an important advantage when compared with technologies that can only process limited feedstocks. One of the most significant advantages of thermochemical technologies (see Table 7), such as gasification and pyrolysis, is the high diversity of feedstock, from waste (household, food, municipal, sewage sludge) to animal manure, including

forest and agricultural biomass residues. Hamelinck and Faaij estimated the feedstock costs as 45–58% of the total fuel production costs, highlighting the importance of feedstock flexibility [119]. Biofuels production costs are highly dependent on feedstock price [120], which can vary considerable with the type, season, and country. Consequently, technologies that use a variety of feedstocks are attractive, allowing the most economical feedstock to be used at any given time.

Additional technological steps required to address end user product specifications, will further increase the overall costs and need to be taken into consideration. For example, the addition of the hydrolysis (acid/enzymatic) step to the biochemical route to process lignocellulosic biomass results in higher costs and technological complexity but it allows for feedstock flexibility. The effect of economies of scales is also a significant factor in biofuel production costs, thus a comprehensive technoeconomic study is required to assess the feasibility of each route to produce a specific biofuel [121].

Further factors that require consideration are market readiness and technological maturity. Many of the presented technologies are commercially mature because they have been successfully applied for many years to first generation biofuels. Technologies such as gasification which only requires small modifications in order to produce second generation biofuels. Gasifiers are already commercially spread around the world; there are more than 270 operational plants, mostly in Asia and Australia, and over 100 more currently under construction [122]. On the other hand, some technologies, such as biochemical fermentation, require further modifications to produce second generation biofuels. These additional technological steps make the process costlier and more complicated, and are therefore hindering its commercial adoption.

Taking into consideration factors such as technological maturity, the market, feedstock availability and location, each technology presents its own advantages and disadvantages. As a result a detailed process design and technoeconomic analysis is required to assess the feasibility of any route to produce a specific biofuel.

4. Conclusions

The transition from fossils fuels to advanced liquid biofuels will have an enormous impact on global climate change due to the resulting reduction in GHG emissions. The production of advanced liquid biofuels cannot rely solely on a specific process since each technology strongly depends on biomass feedstock composition. To add to this complexity, the final product obtained from each technology and feedstock varies in quality and type. The integration of technologies and variety into the biomass supply chain can overcome some/all of the issues associated with cost and product quality.

Conflict of interest

The authors declare no conflict of interest.

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