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A Review of Bio-jet Production Pathways

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Abstract

With the imminent depletion of fossil fuels in the near future, there is a dire need for developing new technologies to produce alternate fuels from renewable sources. The other fossil fuel dependent sectors do not have stringent norms compared to the aviation sector, which requires a 'drop-in' fuel with properties similar to that of existing aviation fuel. While this endeavor has been ongoing for many decades, it has received renewed attention in recent years with many commercially viable solutions being made available. The feedstock for these alternate fuels is derived from renewable resources such as plant oils, animal fat, byproducts of industrial processes and municipal waste. Each of these feedstocks requires a different production pathway, resulting in long chain alkane or liquid hydrocarbon fuel with properties similar to that of conventional aviation fuel. The different production pathways, along with their merits, demerits and recent advances have been presented here.

Keywords: Fossil fuels; Renewable energy sources; Fischer-tropsch method; Bio-jet; Petroleum; Carbon dioxide; Polysaccharides; Microbial fermentation; Lignocellulose biomass; Trans-esterification; Camelina, jatropha and algae; Alcohol dehydration, Oligomerization and hydrogenation; Triglycerides and unsaturated fatty acids

Introduction

Fossil fuels currently provide for the majority of the energy market and remain one of the more sought after resources world over. However, being non-renewable, their supply is limited, and these resources will be depleted before the end of the century Shafiee & Topal [1]. Analyzing the current rate of consumption, production and existing reserves, many researchers have estimated the duration for which fossil fuels will remain a viable source of energy De Almeida & Silva [2], Kjärstad & Johnsson [3] and Sorrell & Miller et al, [4]. This energy crisis has fueled the quest for an alternate source of fuel, which can replace fossil fuels, especially for powering the transportation sector. The energy sector has found solace and comfort in renewable energy sources such as hydro, wind, solar and thermal. However, these sources cannot be used to power the entire transportation sector, at best they can be used as supplements. The transportation sector will be best served by the advent of a 'drop-in' fuel which can replace existing fossil fuels without requiring any modifications to the existing infrastructure or engines. These fuels should be derived from renewable sources, using sustainable manufacturing methods. Of the transportation sector, the aviation sector has the most stringent fuel norms ASTM International Ministry of Defence [5]. requiring very strict adherence to fuel properties. Following the approval of drop-in' fuels, produced using Fischer-Tropsch method, by ASTM International Association IAT [6]. many commercial airlines have been using bio-jet blended in varying proportions with conventional aviation fuel (International Civil Aviation Organization, n.d.). The flights have been a success with minimal change in engine performance, prompting other aviation agencies to explore this route further. The objective of the work presented here is to review the various sources and the associated methods, using which Bio-jet can be produced, thus bringing to light future production pathways.

Feedstock for Bio-Jet

The feedstock for production of Bio-jet are derived from renewable resources, which inherently offered advantages such as less dependence on petroleum, eco-friendly technology, sustainability, carbon dioxide recycling and renewability Bozell JJ [7]. Initially, bio-jet was derived from edible crops such as sugarcane, wheat and corn. They were the preferred source since the polysaccharides could be hydrolyzed into monosaccharaides easily, allowing for microbial fermentation Healey & Henry et al, [8]. However, they lost popularity owing to the fact that these sources are an integral part of the human food chain and would result in resource allocation issues. Following this, the attention turned to non-edible crops having a high oil content and lignocellulose biomass. This usually refers to crops such as Jatropha, Camelina, Waste animal fats and Used cooking oils.

The fatty acids contained in these sources can be converted to bio-jet my means of trans-esterification and hydroprocessing Wei H & Chen H et al. [9]. Other feedstock that can be hydrogenated to produce bio-jet are some by-products of industrial processes, such as edible oil refinery, oil sediments, crude tall oil from paper industry and acid oils Chiaramonti & Tacconi [10]. The most recent and promising addition to the list of feedstocks for bio-jet production, is algae. Algae is currently one of the most favored and researched feedstocks since requires less land for cultivation than any other feedstock while having a high oil content Zhu LD & Li ZH et al. [11]. Of these feedstocks, the ones that are most sought after for production of bio-jet are Camelina, Jatropha and Algae. As mentioned earlier, Bio-jet derived from Camelina has already received ASTM approval for use as an aviation fuel, blended up to a maximum of 50% with conventional aviation fuel. Jatropha is a strong contender for bio-jet feedstock in Asian countries where the climatic conditions suit its cultivation in abundance without competing with agrarian land for food crops Goswami & Tripathi [12].

Production Pathways for Bio-Jet

The choice of production methodology depends on the feedstock and the final fuel properties desired. The choice of methodology will also affect the cost, final composition and environmental impact. The most commonly used production pathways earmarked for bio-jet production are shown in Error! Reference source not found.

Alcohol oligomerization

Ethanol is already being considered for use in automobiles, blended with conventional petroleum-based fuels. Ethanol and Butanol are being considered as potential 'drop-in' fuels for the aviation industry, after upgrading using suitable techniques and altering the physical and chemical properties of the base alcohol. The process involves three steps, namely alcohol dehydration, oligomerization and hydrogenation WC Wang & Tao [13]. Ethanol, when subjected to the dehydration process results in Ethylene, which is converted to Olefins following Oligomerization. An intermediate distillation step is used to remove the smaller chain Olefins, which are further subjected to Oligomerization until the entire mixture contains large chain Olefins (C9-C16). The Olefins are then subjected to Hydrogenation, resulting in fuel that has properties matching aviation fuel. When using butanol, prior to hydrogenation, the smaller chain Olefins are subjected to Dimerization, resulting in a long chain hydrocarbon, which is then subjected to Hydrogenation Serrano-Ruiz & Sepúlveda Escribano [14].

The key element for a successful conversion of alcohol to bio-jet are the catalysts used. Catalysts are used during the dehydration and oligomerization processes. The choice of catalysts decides the Ethylene and Olefins yield, increasing the rate of conversion from alcohol to bio-jet. For Ethanol, some common catalysts that have been researched for dehydration include zeolite catalyst, Al_2O_3 and heteropolyacid catalysts M Zhang & Yu [15]. Of these catalysts, faujasite and H-FER give the highest Ethylene yield when the dehydration is carried out at a temperature of 573 K Phung & Busca [16].

Dehydration of butanol is typically done using mildly acidic catalysts such as γ-Al_2O_3. Over the years, with further research, other catalysts such as metal oxides, acidic resins, inorganic acids, zeolites and others have been used Taylor & Peters [17]. For the oligomerization process, either homogenous or heterogeneous catalysts can be used. For ethylene, which is the product of Ethanol dehydration, nickel-based catalysts are used during oligomerization, resulting in a highly active, selective and stable oligomerization process Andrei & Hulea [18]. Svejda & Brookhart [19]. For butanol, zeolites are preferred even though deactivation remains a problem when using them. However, in more recent times, it has been shown that using mesostructural aluminosilicates can result in conversion of 80% or more, which is better than commercially available zeolite catalysts Park & Valente JS et al, [20].

Fermentation of sugar

This process is also known as Direct Sugar to Hydrocarbons (DSHC) and involves the production of alkanetype fuels via fermentation Kandaramath Hari & Binitha [21]. This process involves bioengineering, leading to the development of micro-organisms that can metabolize sugar in a specific manner Milbrandt & Mccormick [22]. The final product after fermentation depend on the feedstock and species of micro-organism used Davis R & Jones SB et al, [23]. The process involves six major steps. The first step is pretreatment, followed by enzymatic hydrolysis. The product is then subjected to Hydrolysate clarification and fermentation using micro-organisms. The fermented products are purified prior to hydrotreatment in the presence of Hydrogen. The mixture is then subjected to fractionation, resulting in bio-jet fuel WC Wang & Tao [13]. This process does not require the use of toxic catalysts, complex operation or high temperatures and pressures. Also, the carbon footprint of this process is lower compared to all the other production pathways discussed here. However, it is difficult to engineer a microorganism that can metabolize sugar in the manner required to produce bio-jet Mawhood & Slade R et al, [24].

Hydroprocessing

This method is also termed as Hydrogenated Esters and Fatty Acids (HEFA) and the resulting fuel is commonly referred to as Hydroprocessed Renewable Jet (HRJ). In this method fats and oils extracted from plants/animals are converted to straight chain alkanes using a two-step process. The first step, catalytic hydrogenation, converts the triglycerides and unsaturated fatty acids into saturated fatty acids Morgan T & Crocker M et al, [25]. This is followed by hydrodeoxygenation and decarboxylation, resulting in the desired alkanes along with CO_2, H_2O and CO. The catalysts used in this process are transition metals or their bi-metallic composites H Wang & Simon Ng [26]. In the second step, to get the required fuel properties, the products undergo an isomerization and cracking Pearlson MN [27].

The process results in the production of clean paraffinic fuels, which can be directly used without the need for any

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additional processing. This technology has reached a relatively high maturity level compared to the other production pathways and is currently being used for commercially available bio-jet WC Wang & Tao [13]. The properties are close to that of conventional aviation fuel, making it a close competitor for being a 'drop-in' fuel. It also contains a lower aromatic content, no sulfur, a higher calorific value and lower emissions when compared with conventional aviation fuel Sundararaj & Puri SK et al, [28]. The low lubricity and aromatics content does pose a small disadvantage, which can be overcome by blending it with suitable additives. The feedstock that is most widely used for production of bio-jet using this pathway are plant oils derived from Camelina, Jatropha, algae. Animal fats and waste grease can also be converted to bio-jet using this method Hileman JI & Waitz IA et al, [29].

Catalytic hydrothermolysis (CH)

Also known as Hydrothermal Liquefaction (HL), this is another production pathway for conversion of plant/animal oils to bio-jet. This has been developed and patented for the production of "renewable, aromatic and drop-in fuels" by Applied Research Associates Inc. The final product is labeled as 'ReadiJet' and is derived from plant or algae oils Applied Research Associates Inc [30]. The process be used for wet feedstock, removing the need for drying. The conversion process requires mild temperatures ranging between 523 K and 653 K and at a pressure between 50 to 300 bar. The mild reaction conditions favor a high-energy efficiency. The process contains a series of reactions, which can be integrated into three distinct steps. The triglycerides and unsaturated fatty acids are pre-treated.

The pre-treatment process includes conjugation, cyclization and cross-linking Wei H & Chen H et al, [9]. This process improves the molecular structure prior to catalytic hydrothermolysis. Catalytic hydrothermolysis is conducted with a catalyst in the presence of water. The resulting products contains unsaturated molecules, oxygenated species and carboxylic acids, which are then further processed. In the next step, saturation and oxygen removal is carried out using catalytic decarboxylation and hydrotreating Lee IG & Park YK et al, [31]. The final treated products contain a variety of alkanes, ranging between 6 and 28 carbon numbers Li L & Walker D et al, [32]. The bio-jet derived from this source, using plant oil feedstock, meet aviation fuel standards. They also offer excellent combustion quality along with stability and cold flow properties Applied Research Associates Inc [33].

Hydroprocessed depolymerized cellulosic jet (HDCJ) (fast pyrolysis with upgrading to jet fuel).

HDCJ is a recent technology that was developed by Krior, for the purpose of converting bio-oils produced from pyrolysis into bio-jet by hydroprocessing Elgowainy A & Carter N et al, [34]. The hydroprocessing consists of two steps, the first involves hydrotreatment under mild conditions, in the presence of a catalyst. The second step involves conventional hydrogenation under high temperatures, also in the presence of a catalyst Xu & Zhang R et al, [35]. The two-step process yields hydrocarbon fuel that has fewer undesirable properties as compared to the biomass pyrolysis oil Ajam & Wang et al, [36,37]. used a three-step process, whereby the pyrolysis oil is first subjected to catalytic cracking, followed by synthesis of aromatic hydrocarbons and hydrogenation. The fuel thus produced met all required technical specifications for bio-jet.

Many commercial entities such as Ensyn, LLC, PNNL, UOP and Tesoro have also been working on similar techniques for upgrading of pyrolysis oil feedstock to usable bio-jet Abdullah Z & Wissinger RG [38,39]. The technology is still new and is being pursued by many as a suitable production pathway for alternate fuels. However, HDCJ is yet to be approved by ASTM and is still being researched upon in an effort to reduce costs and improve the fuel yield Y Zhang & Kates M [40].

Fischer–tropsch (F-T) synthesis

F-T synthesis is a combination of catalytic processes used for converting gas into hydrocarbons. The gas commonly refers to syngas (CO and H2) which can be obtained by gasification of biomass obtained from a wide variety of feedstock (SWAFEA, 2011). This process can be used for two conversion pathways, the first being biomass to liquid and the second being gas to liquid. Both the pathways yield liquid hydrocarbon fuels but differ in the fact that the former requires an intermediate gasification process to convert the biomass to syngas. When F-T is applied for converting biomass to liquid hydrocarbon fuel, the pathway consists of six steps. The first step involves preparation of the biomass by drying, to reduce the particle size Kreutz & Williams RH [41].

This step is followed by gasification, converting the biomass into syngas. Depending on the feedstock being used, a suitable gasification method and reactor design. A pressurized oxygen-blown entrained flow gasifier was identified as the optimum technology, capable of catering to a wide variety of feedstock conversion from biomass to syngas. This method has the advantage of being fuel flexible, can operate on coal, can be easily scaled and has a high efficiency Swain PK & Naik SN [42]. However, the yield and composition of syngas is dependent on other factors as well, such as temperature, heating rate, particle size, operating pressure, gasifying agent, catalyst addition and equivalence ratio Samiran & Jo Han N et al, [43]. Following gasification, the syngas is cleaned, by removal of any acid gas, such as sulfides, H2S and CO2. The clean gas is then sent to the FT reactor for FT synthesis. Prior to this, the clean gas can also be subjected to a gas conditioning system, to adjust the ratio of CO and H2 in the mixture Wei H & Chen H et al, [9]. F-T synthesis can either be done in a high temperature or low temperature mode Hamelinck C & Boerrigter H [44]. Catalysts play a significant role in the hydrogenation of carbon monoxide during F-T synthesis. Ruthenium is the most active catalyst and also the most expensive.

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Nickel, also an active catalyst, is not preferred owing to the yield containing higher quantities of methane as compared to long chain alkanes. Iron based catalysts remains the prime choice in most commercial FT synthesis plants Hall Wk & Emmett PH [45]. Using Iron as a catalyst yields a higher olefin content in the hydrocarbon distribution. The cost of procuring and using Iron as a catalyst is also low. However, it suffers from problems such as low space-time-yield, catalyst agglomeration, sintering and low product selectivity. Although cobalt is more expensive compared to Iron, it offers a higher stability, low yield of oxygenated products and a high activity. The distribution of the products in the yield, dependent on the above parameters, is given by the Schulz-Flory equation Demirbas A [46]. Fuels obtained through this process are being used as blends along with conventional fuel (SWAFEA, 2011). Similar to HRJ, the reduced aromatics content does lead to fuel leakage problems due to shrinkage of the seals. This can be overcome by the use of suitable additives Hemighaus G & Jones J et al, [47]. However, the main drawback of this production pathway is the cost incurred. While it can be used for a wide range of feedstock, it is the most expensive of the all the production pathways discussed here Roberts WL [48].

Conclusion

Numerous bio-jet production pathways exist for production of bio-jet from sustainable and renewable resources. The feedstock for these pathways offers sustainability and do not compete for resources with food crops. Many production pathways have been researched over the last few decades. Hydroprocessing is a commercially viable production pathway and has already delivered Hydroprocessed Renewable Jet (HRJ) which has been ASTM certified for use, blended with conventional aviation fuel. The properties HRJ is similar to that of conventional aviation fuel, if not better. The demerit being the reduced aromatics content, leading to fuel leakages. However, this can be addressed with the use of suitable additives. Similar to HRJ, F-T synthesis has also proven to be successful. Its capability of being used with a wide variety of feedstock makes it a lucrative production technique. However, the process is complex, heavily dependent on numerous factors and is one of the most expensive production pathways available in current times. The other production pathways, though simpler and cheaper, are limited to fewer feedstock, making them dependent on local availability.

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