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Review

Investigation of Biofuel as a Potential Renewable Energy Source

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Abstract: An accelerating global energy demand, paired with the harmful environmental effects of fossil fuels, has triggered the search for alternative, renewable energy sources. Biofuels are arguably a potential renewable energy source in the transportation industry as they can be used within current infrastructures and require less technological advances than other renewable alternatives, such as electric vehicles and nuclear power. The literature suggests biofuels can negatively impact food security and production; however, this is dependent on the type of feedstock used in biofuel production. Advanced biofuels, derived from inedible biomass, are heavily favoured but require further research and development to reach their full commercial potential. Replacing fossil fuels by biofuels can substantially reduce particulate matter (PM), carbon monoxide (CO) emissions, but simultaneously increase emissions of nitrogen oxides (NO_x), acetaldehyde (CH_3CHO) and peroxyacetyl nitrate (PAN), resulting in debates concerning the way biofuels should be implemented. The potential biofuel blends (FT-SPK, HEFA-SPK, ATJ-SPK and HFS-SIP) and their use as an alternative to kerosene-type fuels in the aviation industry have also been assessed. Although these fuels are currently more costly than conventional aviation fuels, possible reduction in production costs has been reported as a potential solution. A preliminary study shows that i-butanol emissions (1.8 Tg/year) as a biofuel can increase ozone levels by up to 6% in the upper troposphere, highlighting a potential climate impact. However, a larger number of studies will be needed to assess the practicalities and associated cost of using the biofuel in existing vehicles, particularly in terms of identifying any modifications to existing engine infrastructure, the impact of biofuel emissions, and their chemistry on the climate and human health, to fully determine their suitability as a potential renewable energy source.

Keywords: biofuel; fossil fuel; climate impact; air quality; human health; aviation industry

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1. Fossil Fuel and Its Alternatives

Fossil fuel combustion started at the beginning of the industrial revolution and has since played a crucial role in supplying global energy demands. The exponential increase in industrialisation, population and urbanisation over recent years has resulted in a global energy crisis and concern regarding the dependence on non-renewable sources of energy. Fossil fuels, including petrol, diesel, coal and natural gas, supplied 84% of the global, primary energy consumption in 2019, making them the dominant source of energy worldwide (Figure 1) [1], but at current consumption rates it is predicted that gas and oil reserves will run out in ∼50 years [2].

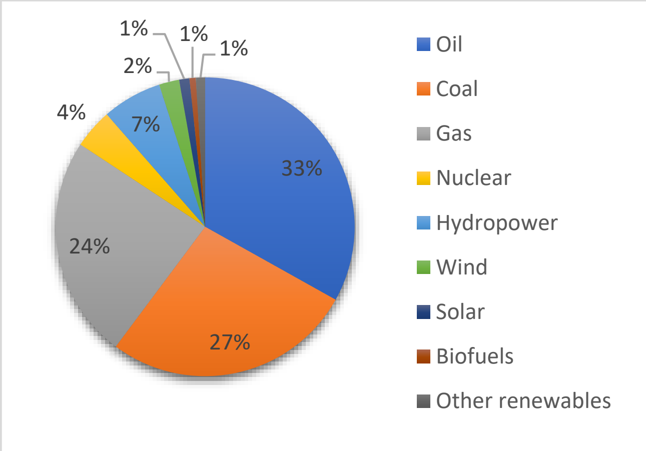


Figure 1. Global energy consumption by source in 2019. Figure was created using the data taken from BP [1].

In terms of the environment, the burning of the fossil fuels could emit gaseous pollutants (e.g., carbon dioxide (CO_2), carbon monoxide (CO), nitrogen oxides (NO_x), sulphur oxides (SO_x), volatile organic compounds (VOCs) and particulate matter (PM)), which can change the composition of the atmosphere and thus have harmful effects on climate and public health. In an effort to mitigate the damaging effects of climate change due to greenhouse gas (GHG) emissions, the Paris Agreement, introduced in 2015, set a target to "limit global temperature rise to 2 °C above pre-industrial levels, whilst pursuing efforts to limit the increase to 1.5 °C" [3].

An estimated 58% of fossil fuels are consumed by the transportation of people and goods via road, rail, air and marine travel [4]. In 2016, the transport sector alone was responsible for 16% of the total, global GHG emissions, highlighting the pressing need for green alternatives to petrol and diesel [2].

A potential solution to reduce GHG emissions, stabilise the global climate, and improve energy security is to transition away from use of conventional fossil fuels and towards greener, renewable sources of energy. Key renewable energy sources include solar, wind, hydro, geothermal and biofuel, all of which have the ability to provide energy services with reduced emissions of GHGs and air pollutants [5,6]. Sustainability Development Goal (SDG) 7, one of the 17 SDGs established by the United Nations General Assembly, aims to "ensure access to affordable, reliable, sustainable and modern energy for all" which highlights the importance of international cooperation with the increased use of renewable energy sources [7]. In addition, as countries try to reduce poverty, they in turn increase urbanisation and are becoming key contributors to the rising GHG emissions. At present, six of the top 10 emitting countries are developing countries [8]. Therefore, the research and development into renewable energy, and associated technologies, has focused on making these alternatives economically viable and sustainable for all countries.

Other efforts to reduce emissions are to increase energy efficiency and electrify sectors, for example, using electric vehicles and hybrid engines in the transport sector. Many countries have introduced policy measures to increase adoption of electric vehicles and announced electrification goals [9]. For instance, the UK plans "to end sales of new petrol and diesel cars and vans by 2030, with all vehicles required to have significant zero emission capability" [10].

2. Suitability of Biofuel as a Potential Renewable Energy Source

Considering the different renewable energies, biofuels are arguably a potential renewable energy source in the transportation industry. Almost all other renewable energies, particularly solar, wind, hydro and nuclear power sources, only generate electricity and hence cannot equally compete with oil [11]. There are multiple difficulties associated with electricity, which make these energy sources less appealing, such as transmission over long distances and conversion to different types of energy sources. In addition, biofuels can be used within current infrastructures and require less technological advances compared with other energy sources. For this reason, both developed and developing countries have focused on expanding their bioenergy market and set up intergovernmental strategies for the use of biofuels. The introduction of such policies, particularly in Europe, the US and Brazil, has caused the biofuel industry to grow in the last decade with biofuels now representing around 3% of transport fuels in use globally [12,13].

Biofuels are combustible fuels produced from organic matter such as plant material and animal waste. They can exist in solid, liquid, and gaseous forms; however, considerable research focuses on liquid biofuels as they have the greatest potential to help decarbonise the transport sector due to easier integration with existing technology [14]. Ethanol is currently the most widely used biofuel globally, accounting for approximately 80% of all liquid biofuel production [15,16]. The use of global ethanol as a biofuel (so-called, "bioethanol") production has increased significantly in recent years, with the global production predicted to be over 135 billion L by 2024 with the largest contributions from the USA (42%) and Brazil (31%) biofuel industries [17].

3. Types of Biofuels

Four categories are used to group biofuels based on the type of feedstock used to produce them, their limitations as a renewable source, and their technological progress. First generation biofuels are produced from edible feedstocks, e.g., bioethanol from corn and sugar cane and biodiesel from oil seed crops (soybean, oil palm, rapeseed ad sunflower) using well understood, economically viable technologies and processes, such as fermentation, distillation and transesterification [18,19]. First generation biofuels only provide minimum benefit over fossil fuels in terms of greenhouse gas emissions as they require a large amount of energy (from fossil fuels) to grow, collect and process.

Second generation biofuels are produced from agricultural by-products or cellulosic materials such as wood, leaves and grass and can be grown on marginal land [20–23]. They are produced by converting cellulose into sugar units, which can then be converted to ultimately produce alcohol. Cellulosic sources that grow alongside food crops could be used for biomass, but this process takes away so many nutrients from the soil and would need to be restored nutrients by applying fertilizer. This process is both costly (chemically and economically) and time-consuming, requiring sophisticated equipment and larger-scale facilities.

Third-generation biofuels are made from aquatic cultivated feedstock, i.e., algae [24,25]. Algae have been shown to have great potential as biofuel feedstocks, due to their capabilities of producing much higher yields with reduced resource inputs [26–28]. The use of algae also has other environmental advantages, as a result of their ability to fix CO_2, which has been proposed as a method for removing CO_2 from flue gases from power plants, thus reducing GHG emissions [29–31]. However, there has been little research on the economic and environmental feasibility of using algae as a biofuel feedstock, with concerns regarding its commercial-scale production. The growth of seaweed is highly seasonal, meaning that preservation methods need to be developed to allow year-round storage of the feedstock for fuel manufacturing processes [32]. The drying stage is the key part of the energy extraction method. The high water content of algae compared with terrestrial crops [33], means that this process is highly energy intensive [34]. Sun-drying has been used as a low-energy alternative method [35]. However, this has its own limitations, being highly weather dependent. These factors highlight the growing need for research into algae as biofuel feedstocks, with its future applicability being highly dependent on the development of biomass-to-fuel conversion technology which can work with wet feedstocks, or drying processes with much reduced energy requirements [32]. The fourth-generation biofuels are found from the bioengineered microorganisms, e.g., bioengineered algae, yeast, fungi and cyanobacteria [36,37]. Second, third and fourth generation biofuels are commonly referred to as 'advanced biofuels' and thought to hold many advantages over first generation fuels, but, they are still in the research and development phase and have not reached their full commercial potential.

4. Advantages and Disadvantages of Biofuel Production and Consumption

A considerable amount of research on biofuels as a renewable energy source is inconclusive and contradictory [38–41]. Reasons for these contradictions include the different generations of biofuels and geographic regions that were studied. Countries have differing economies, climates and policies, which consequently impact the production and consumption of biofuels. In 2019, the US was the largest biofuel consumer in the world, followed by Brazil, Indonesia, China and France (Figure 2), where the commercial production of first-generation feedstocks such as corn and sugar cane, is well established [42]. Global biofuel production and consumption in 2019 increased by ~3% and ~6%, respectively, as displayed in Figure 3a,b. The growth in both cases was led by Brazil and Indonesia where the majority of production and consumption involved ethanol in Brazil and biodiesel in Indonesia [1].

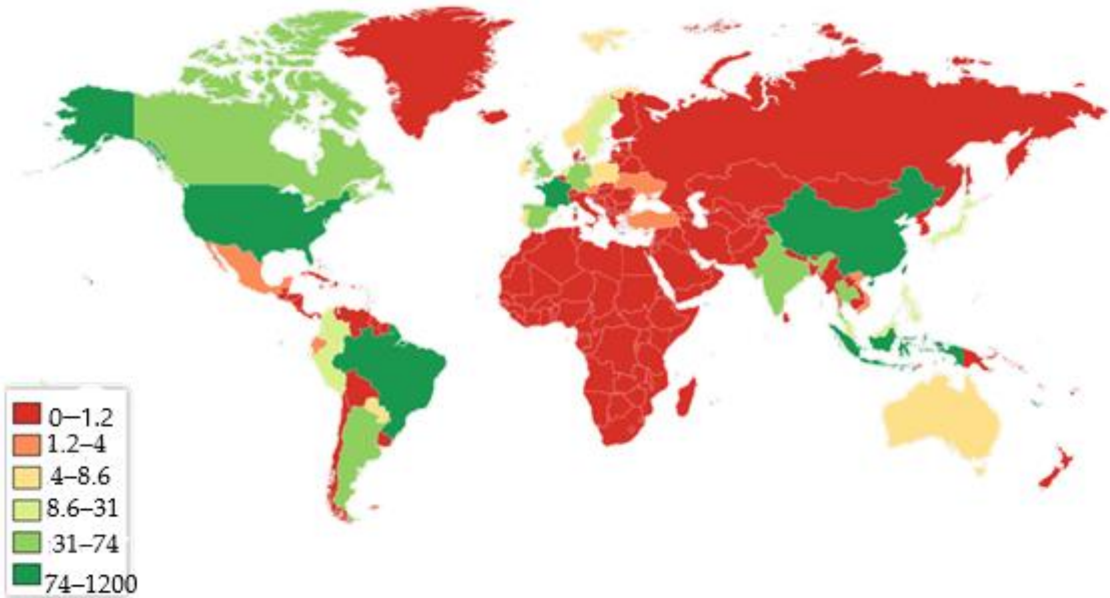
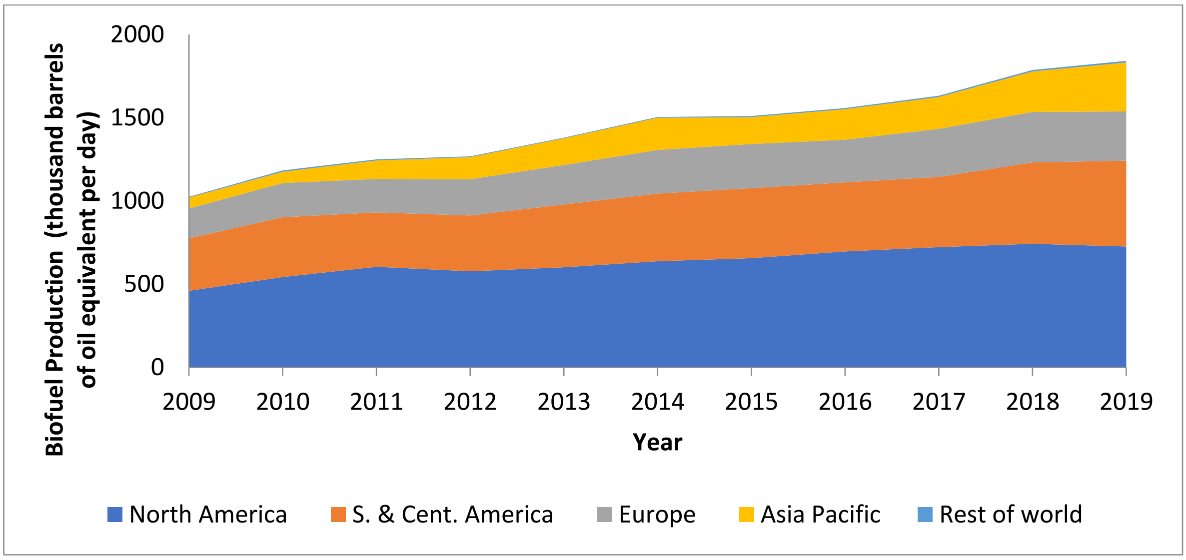


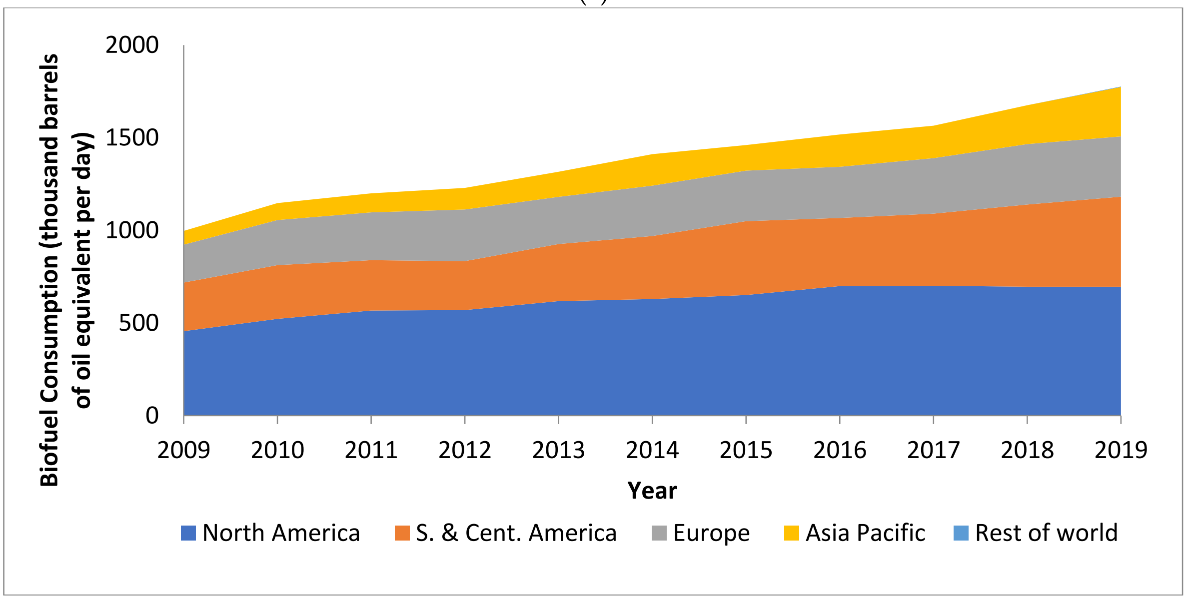
Figure 2. World map of total biofuel consumption in thousand barrels per day (Adapted from USEIA [42]). The US, Brazil, Indonesia, China and France are colored dark green as they consume between 74–1200 thousand barrels of biofuel each day.

Biofuels are often sold in the global market as blends with fossil fuels, in order to be compatible with conventional vehicle engines and reduce the need for additives [43]. Brazil has successfully implemented public policies to increase biofuel consumption and in turn improve air quality. The introduction of flex-fuel vehicles, biofuel subsidies, and government mandates have all contributed to Brazil's current ranking as one of the cleanest energy countries in the world [44]. Indonesia has the potential to become the largest biofuel manufacturer in the world [45]. Despite first generation biofuels being successfully implemented globally, recent studies highlighted negative consequences of expanding their production further and argue for a greater effort on the production of advanced biofuels [46–48].

Experts in ecology and global dynamics have long established that the removal of more than 1% of matter circulating in ecosystems leads to a violation of the stability and subsequent degradation of the biosphere. Humanity currently consumes almost 10% of the products as food, fodder and fuel from natural land ecosystem which is the main reason for the degradation of biosphere [11]. Global annual fossil fuel consumption has already exceeded 15 billion metric tonnes and continues to grow rapidly [1]. Biofuel production as an alternative of natural fossil fuel could destroy the natural ecosystem and violate the equilibrium of global biosphere processes. If we consider one percent of the annual production of dry green biomass on Earth is about 2 billion metric tonnes, which, even without taking into account the difference in specific caloric content, is almost an order of magnitude lower than the current global energy consumption [11]. However, considering the other associated energy costs for converting fuel from the green mass (e.g., costs of cultivating the land, sowing, fertilizers, harvesting, transportation, drying, chemical processing, etc.) give an accurate energy balance estimation which has high regional variability. The energy balance defined as EROEI (Energy Return On Energy Invested) for the production of bioethanol and biodiesel in the US is slightly higher than 1 [49]. Thus, in order to generate a certain amount of biofuel, it is necessary to spend almost the same amount of fossil fuel. However, EROEI for the production of ethanol from sugarcane in Brazil is 5 to 10, suggesting sugarcane ethanol production in Brazil costs less than that in US [50,51] and Brazil would benefit with using biofuel as energy source.



(**a**)



(**b**)

Figure 3. Global Biofuel (**a**) Production and (**b**) Consumption from 2009 to 2019. Figures were created using the data taken from BP [1].

Biofuels have both positive and negative effects on the economy, environment and public health [52]; many studies suggest it is crucial that governments across the globe rigorously consider these impacts prior to any future biofuel investments or implementation strategies [53,54]. Firstly, the economic security of a country can be improved with a larger biofuel industry, especially through the creation of jobs in rural and under-developed areas [55,56]. In addition, not all countries have large crude oil reserves so a shift towards biofuel production would allow countries to reduce both their dependence on fossil fuels and, consequently, their import costs. For instance, Brazilian biofuel production between 2005 and 2014 was estimated at 17.4 billion L, saving 12.9 billon US dollars in fossil fuel import costs [39]. Biodiesel also has a better lubricity and is less toxic than conventional diesel, making it safer and easier to handle [57]. In spite of these benefits, several problems stand in the way of using biofuels as a replacement to fossil fuels, for example, comparing with diesel, biodiesel has a lower calorific value, higher NO_x emissions, higher copper strip corrosion and fuel pumping difficulty [58,59]. However, the influence of the lower calorific value of biofuel on the performance of the engine is reduced by more efficient combustion due to the presence of oxygen in biodiesel and/or ethanol. Biofuels also have higher production costs in the current market due to requirement of more intensive processing procedures and, as with increased agriculture of any form, the production and end use of biofuels comes with concerns of deforestation, biodiversity loss and increased fertilizer and pesticide use [60].

The biofuel industry today consists mainly of first-generation biofuels produced from edible feedstocks, therefore, a concern which dominates the biofuel debate is that they will negatively impact food production and security [11,61]. Although biofuels are renewably sourced, the production of biofuel crops can lead to competition for natural resources, particularly land, food, and water [61,62]. Alternatively, increased biofuel consumption can cause existing food crops to move from food to biofuel markets [63]. Reduced food production is likely to trigger a subsequent rise in food prices, which could harm the economy and worsen food insecurity for those in poverty [11]. Studies in the US, Brazil, Japan and Europe suggest that the use of food crops in biofuel production has been important in explaining the steady increase in food prices since 2000 [64].

The agricultural crops (e.g., sugarcane, corn) for bioethanol production on an industrial scale led to rapid and irreversible soil degradation, water scarcity, fertilizer use and pesticide application resulting in air and water pollution, and the loss of wild and agricultural biodiversity [65]. This is one of the reasons for the transition to the production of biofuels of the subsequent generations.

The increased biofuel production can simultaneously improve food production by reducing GHG emissions which could be a current threat to food security. Reduced GHG emissions would lead to a lower global temperature, which could both increase crop yield and the quality of crops grown [56]. A greater demand for biofuels could also encourage agricultural investment which would benefit both food and biofuel production, as well as bring opportunities to under-developed areas [39]. Although debates concerning the impact of increased biofuel demand have been ongoing since the 1970s, recent policies and technological developments have given these arguments a greater significance today.

Advanced fuels share many advantages over first-generation biofuels, such as reduced land requirements and minimal fertilizer, pesticide, and fossil energy input [66]. Additional benefits have been recognized when using microalgae as a feedstock, such as faster biomass production, high oil content and a capability to grow throughout the year in both natural and artificial environments [67]. However, there are challenges to commercialize the large-scale production of these advanced biofuels as the cost of production is high and the performance of current conversion technologies requires improvement [47,68]. Additionally, despite the strong agreement across the literature that a shift to advanced biofuels is needed, the reduced application of these fuels in industry makes projections of their future environmental impact difficult. Instead of solely relying on one generation of biofuel, the best approach may be a combination of resources to manage the increasing global demand [48].

Increasing use of biofuel across the world is likely to make up a significant proportion of global trace VOCs in the near future. The large-scale use of biofuel will result in direct emissions into the atmosphere via leakage, evaporation or incomplete combustion. Therefore, we need to have a good understanding of their behaviour (e.g., chemistry, transport) under atmospheric conditions, as well as combustion conditions.

5. Environmental Impact of Biofuel Use

A key benefit associated with the replacement of fossil fuels for biofuels is the reduced air pollution from motor vehicles [11,69]. Explosions are reported with the extraction of crude oil for fossil fuels and many aquatic reserves can be polluted during extraction, posing a damaging effect to sea-life [70], thus extraction of biofuels is far less damaging to the local environment. Biofuels tend to burn cleaner, the increased use of biodiesel and ethanol blends in vehicle engines, causes a reduction in PM, CO and unburned VOC emissions than traditional fuels [53,54,71,72]. The main explanation for these reduced emissions within literature is that the higher oxygen content of ethanol and biodiesel, compared with petrol and diesel [73,74], leads to a more complete combustion and hence a decrease in particulate content and exhaust gas [11]. Although biofuels are still producing CO_2, the carbon footprint is smaller as biomass feedstocks act as a carbon sink by absorbing CO_2 for photosynthesis during crop growth [40,75]. The application of biofuels in Brazil demonstrates their potential to decrease CO_2 emissions; a recent report released by the Brazilian Department of Agriculture Livestock Supply states that by "adding up all the biodiesel consumed in Brazil since 2008, the GHG avoided emissions have already reached 21.8 million tons of CO_2, which is equivalent to nearly 158 million trees in an area corresponding to 144 thousand football fields" [39,76]. In addition, biofuels also have the potential to be 'carbon negative' through strategic choices of producers and the use of applications such as carbon capture and storage [77]. However, assuming carbon neutrality is problematic as biofuels produced in areas such as North America and Europe are often termed 'carbon positive' due to the large input of fossil fuel activities and fertilizer in their production [77]. Adoption of biodiesel as a fractional component of diesel use was investigated using a global three-dimensional chemistry transport model, STOCHEM-CRI and found an overall improvement in air quality with reductions in ozone, PM, aromatic species and peroxy acetyl nitrate (PAN) [78]. Additionally, despite the favourable reduction in PM, CO and VOC emissions, the majority of the literature demonstrates that there is an unfavourable increase in NO_x emissions when using biofuels as opposed to fossil fuels [39,53,54]. The combustion and exhaust emissions of a single cylinder diesel engine, with biodiesel blends, found that NO_x emissions were significantly higher than diesel alone [79,80]. The general consensus across the literature is that the increased NO_x emissions result from higher combustion temperatures produced by the slightly advanced injection of biofuels into the engine cycle, due to their different physical properties compared with conventional fossil fuels. An alternative theory is that the higher levels of NO_x are caused by a reduction in heat dissipation due to reduced soot production, which would also lead to increased flame temperatures [53]. The increased NO_x emissions from biofuels could lead to adverse impacts on both the environment and public health because of formation of additional ozone, which is a component of photochemical smog and powerful oxidant [81,82]. In recent decades, many epidemiological studies have investigated the link between O_3 exposure and adverse health effects. Research into the health impacts associated with O_3 exposure has continued into the 1990s and 2000s. Studies have demonstrated significant and sustained links between short-term O_3 exposure and hospital admissions [83–85], with many also reporting a strong association with mortality across the world [86–88].

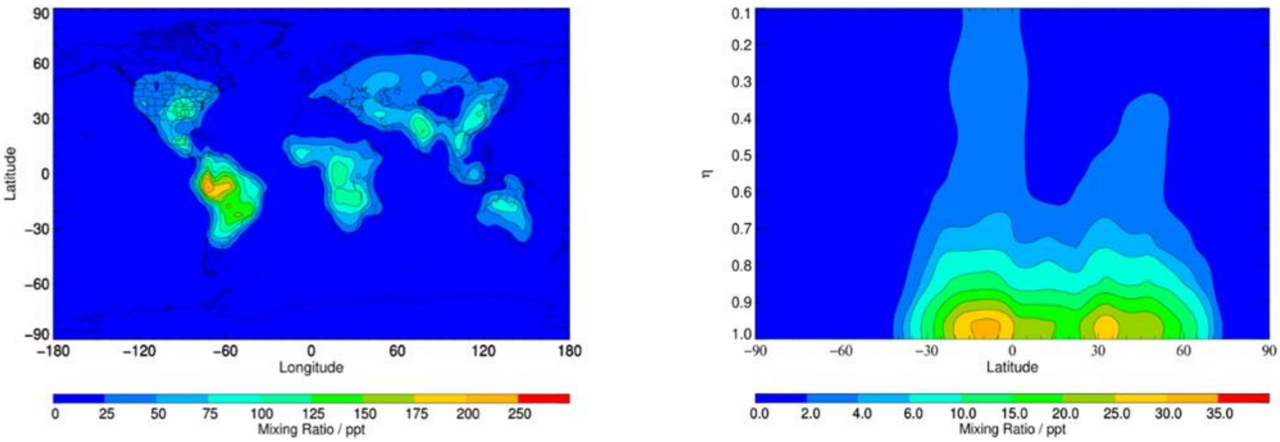
There are some cases where biofuel blends reduced NO_x and CO emissions, as a result of a greater resistance against knocking [89]. This inconsistency between literature is understandable due to the complexity of combustion and the variation between different studies such as: engine type, vehicle age, fuel injection strategy and other conditions, which influence emissions [53,90]. However, as most investigations show a beneficial reduction in PM emissions with the increased use of biofuel blends, multiple suggestions have been made on how to mitigate the associated harmful NO_x emissions. For instance, delaying fuel injection, addition of water in biofuel blends, and a medium engine speed are all potential ways to decrease NO_x pollution [53,89,91].

As well as increased NO_x emissions, the wider application of biofuels within transportation could lead to an increase in the VOCs and aerosol particles released into the atmosphere [92]. The oxidation of ethanol and biodiesel, within an internal combustion engine, can form high concentrations of aldehydes compared with fossil fuels due to the presence of the hydroxyl group [93]. Regions with high levels of bioethanol use have exhibited higher acetaldehyde concentrations, with urban levels estimated to increase by up to 650% when an 85% ethanol-petroleum blend is used [94]. Formaldehyde and acetaldehyde are the most abundant due to the use of biofuels [95], and are defined as toxic air pollutants by the US Clean Air Act as they can cause respiratory irritation and elevate ozone levels [53]. Formaldehyde in vehicle exhaust is mainly produced from the incomplete combustion of alcohols. The initial degradation of ethanol involves the direct breakage of the C-C bond forming the hydroxymethyl radical, which either reacts with oxygen or decomposes in the atmosphere, to produce formaldehyde [95]. Acetaldehyde emissions from biofuels are mainly produced from vehicle exhaust, in the post flame oxidation of unburned ethanol with a hydroxyl radical (OH) [95]. Initially, this takes place via a H-abstraction reaction which can occur at different reaction sites along ethanol [96]. Approximately 85% of the abstraction occurs at the α-site of ethanol. The resultant hydroxy-ethyl radical then reacts further with oxygen to produce acetaldehyde [97]. Once formed, acetaldehyde is rapidly removed from the atmosphere by reaction with OH and importantly photolysis that enhances HO_x levels. Reaction with OH involves H-abstraction from the carbonyl carbon to form a peroxyacetyl radical which can go on to react with NO_2 and produce PAN [98,99]. Photolysis of acetaldehyde is also an important loss process, contributing ~10% to the total loss rate for this compound [100–102]. Photolysis yields HCO and CH_3 radicals, where HCO instantly forms HO_2 radicals on reaction with O_2. Therefore, photolysis contributes to the HO_x budget and can be an important additional source of HO_x, e.g., in the upper Troposphere [103]. The reaction scheme of the degradation of ethanol and acetaldehyde can be found in the Appendix A.

Studies in Brazil and New Mexico have shown increased concentrations of acetaldehyde and PAN in the atmosphere during periods of increased biofuel use [99]. A study undertaken by Jacobson [104] also showed that such a blend causes elevations in the levels of PAN, whilst also increasing ozone-related mortality. PAN is a key contributor to photochemical smog, typically in warm summer climates, which consequently causes eye irritation and respiratory issues [53]. PAN can also transport and release NO_x to the remote troposphere which is a major concern when considering the global distribution of the two main tropospheric oxidants: ozone and OH [105]. To a lesser extent, emissions from biofuels can also occur at different stages of the supply chain such as transporting feedstock to the biorefinery, producing the liquid biofuel, and distributing biofuels to consumers [106].

In the 3-D chemical transport model, STOCHEM-CRI study [107,108], the ethanol field was generated using the emission inventory [109], the Common Representative Intermediates (CRI) mechanism for accounting chemical production and losses and physical loss processes, e.g., dry deposition and wet deposition, a level of up to 250 ppt ethanol can be seen in Brazil (see Figure 4a) where there are high vegetation emissions as well as manufacture and/or use of bioethanol [102]. Other areas of the globe with higher ethanol mixing ratios include the south-eastern U.S.A., East Asia (areas of China) and South Asia (around India). These countries produce the greatest amounts of bioethanol worldwide, because of increasing dependence on alternative fuels. The zonal plot shows the highest levels up to 35 and 30 ppt at 0–20° S and 30° N–40° N, respectively (Figure 4b).

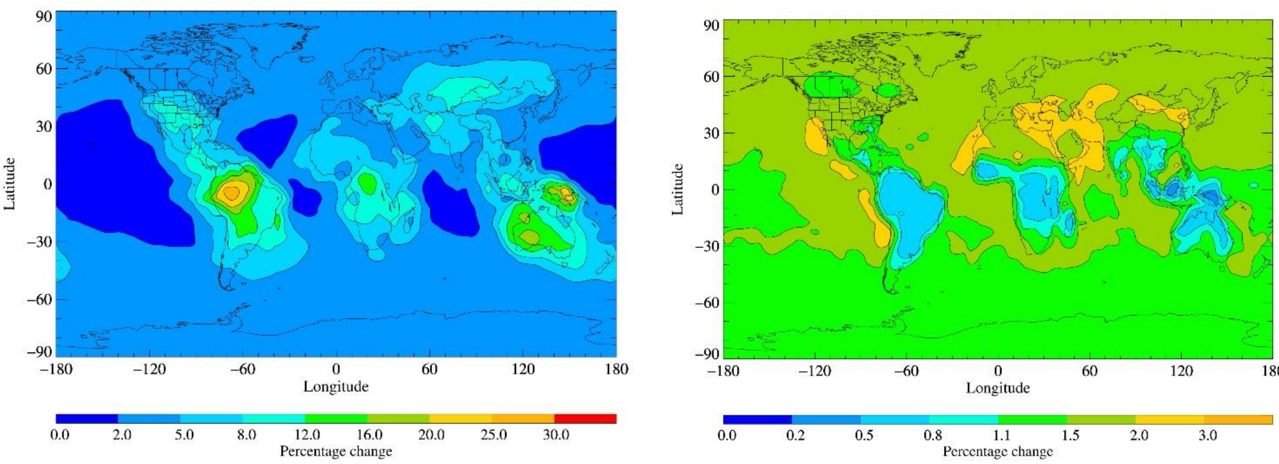
These regions encompass countries such as the USA and Brazil, which are the two greatest producers of bioethanol worldwide.



(**a**) (**b**)

Figure 4. (**a**) Surface mixing ratios of ethanol and (**b**) zonal average distribution of ethanol. The figures are adapted from Khan et al. [102].

The lifetime of ethanol is long enough (1–3 days) to be transported long distances before oxidation by OH radicals to give acetaldehyde and consequently form PAN. Khan et al. [102] showed that an increased emission flux (~11.5 Tg/year) of ethanol as a biofuel and from vegetation can cause an increment of acetaldehyde by up to 30% in areas such as Brazil, Australia and Indonesia (Figure 5a) which led to an increase in PAN (by up to 3%) over the ocean near to acetaldehyde source regions (Figure 5b).



(**a**) (**b**)

Figure 5. The annual average surface (**a**) acetaldehyde and (**b**) PAN change after adding an additional 11.5 Tg/year of ethanol as vegetation and biofuel. The figures are adapted from Khan et al. [102].

To mitigate these harmful emissions and (consequently their impact on the environment) and maximize biofuel sustainability, biofuel technology can be implemented in a different way. Some research [110,111] suggests that burning biofuels in one location, such as a power generation facility, is more efficient than burning in numerous sub-optimal vehicle engines. For example, the Drax power station in the U.K. has recently converted four of its six generating units from coal to wood pellets and operates carbon capture and storage (CCS) technologies alongside power generation [112]. Therefore, this application of biofuels is helping to remove harmful waste gases such as CO_2, whilst simultaneously producing electricity which could later be used to power battery-driven vehicles in a non-polluting way [113].

6. Gaps in the Understanding of Global Biofuel Use and Their Environmental Impact

As global demand for biofuels is projected to increase, it is essential to understand the consequences of using these fuels. Thus, it is important to examine the environmental and economic feasibility of industrial-scale production of biofuels. An example of a potential environmental barrier could be the implications of land-use changes which may be required to grow sufficient amounts of biofuel feedstock to meet the demand. Such an analysis should also include an assessment of the practicalities and associated cost of using the fuel in existing vehicles, particularly in terms of identifying any modifications to existing engine infrastructure. This could also have implications for the design of future vehicles, should any modifications be required.

A trade-off arises from the replacement of fossil fuels with biofuels and increased biofuel usage results in a reduction of harmful PM, CO and VOC emissions compared with fossil fuels, but an unfavorable rise in NO_x, aldehyde and PAN emissions. Therefore, it is important that the concentrations of these pollutants and their impact on the environment and public health, are carefully monitored before a greater application of biofuels is established worldwide. Most studies focus on the characteristics of biofuels and their advantages and disadvantages as an alternative, renewable energy source, as opposed to their atmospheric and environmental impacts throughout their lifecycle. The majority of literature surrounding biofuel emissions understandably focuses on first-generation biofuels, as they are produced with well-established technologies, and currently dominate the global biofuel market. However, as there is a strong agreement amongst scholars that a shift towards advanced biofuels is needed, it seems necessary to compare the emission properties and air quality impact of these different biofuel generations. This would determine whether a transition to advanced biofuels, whilst improving food security, would also help to decarbonise the transport sector and improve public health.

Future research is required to explicitly determine the impact that a global transition to biofuels would have on air quality and climate. Out of the few impact assessments published on the increased application of biofuels, there is no apparent evaluation of the global environmental impact as most investigations only consider one country without comparison to other regions of the world. As well as this, the transportation of biofuel emission products was not analysed, which is key to determining the impact this transition would have on global air quality and consequently, public health. These factors need to be investigated focusing on regions with a large, established biofuel market such as the US, Brazil and Indonesia. In addition, most studies concerning biofuel emissions assess multiple pollutants emitted from specific biofuel-petroleum blends, as opposed to focusing on a dominant chemical typically produced from biofuel combustion, such as acetaldehyde or ethanol. This approach could allow a more holistic method of assessing biofuel emissions to be established and enable easier comparison between countries.

7. Biofuel Use in Aviation Industry

Biofuel use in road transportation alone is unlikely to reduce GHG emissions sufficiently to achieve the Paris Agreement climate target, hence a wider application across the transport sector is necessary. The aviation industry emits approximately 700 million tonnes of CO_2eq and is accountable for almost 12% of transportation emissions worldwide [114]. It is currently estimated that the demand for conventional aviation fuels (CAF), such as Jet A and Jet A-1 (comprise of 20% naphthalene, 20% paraffins, 40% iso-paraffins and 20% aromatic compounds from the crude distillate), will continue to grow to 860 Mt/year by 2050, which is more than 4 times the demand observed in 2010 [115]. Consequently, aviation fuel consumption currently accounts for 3% of the total global fossil fuels used [116]. As environmental awareness increases, the demand for alternative fuel solutions became apparent. According to the Air Transport Action Group, a key part of the aviation sector's carbon-neutral growth strategy is the use of low-carbon, sustainable aviation fuels, which have bio-based components [117].

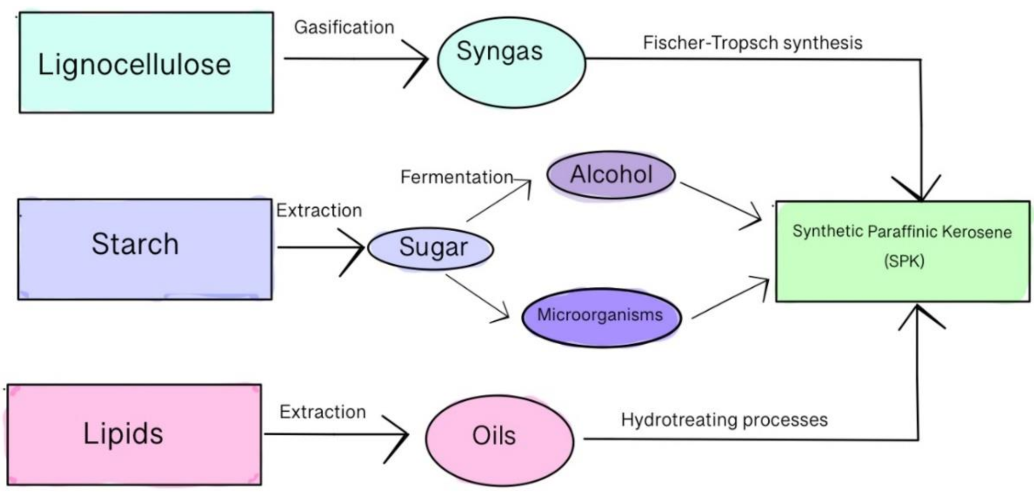
Many airlines are currently involved in research efforts to enable the implementation of these biofuels and reduce the carbon footprint of aviation [118]. The first flight to use a biofuel blend was in 2008 and since then over 150,000 flights using biofuels, have taken place. In 2018, aviation biofuel production was around 15 million L, which accounted for under 0.1% of total aviation fuel consumption [119]. Therefore, faster market development is required to increase aviation biofuel production. However, to promote the use of biofuels within aviation, production methods require technological development, fuel standards need improvement, and a strong integrated policy needs to be adopted. Research into technological advancements could have a positive environmental effect, while looking at the possibilities for fuel composition improvements could also prove promising.

Currently, there are many alternative fuels suggested that could help decarbonise the aviation industry and thus reduce the environmental impact of the sector [120]. Due to the nature of jet fuels, alternative fuels currently employed in road transportation and biodiesel cannot be used within the aviation industry. Jet fuel alternatives (e.g., fuels derived from biomass) must also be utilised at low temperatures and also display high energy density to supply the energetic demand of long-haul flights, properties which biodiesels do not display [120]. Biomass Alternative Fuels (BAF) are synthetic paraffinic kerosene's (SPK) which can be blended with CAF [121]. However, BAF must be in line with ASTM D1655 specifications to be compatible with the existing air fleets [122]. To be sustainable, BAF must be produced from sustainable feedstocks. Palm oil and many crops obtained from deforestation are not encouraged as these cause further environmental damage in different sectors [120]. Investigation into biomass feedstocks has presented issues associated with preparation, as many feedstocks are highly oxygenated, while jet fuels are required to be fully deoxygenated hydrocarbons. Biofuels must therefore involve chemical transformation to selectively remove oxygen and structural adjustments. The potential biofuels, known as Fischer-Tropsch Synthetic Paraffinic Kerosene (FT-SPK), Hydroprocessed Esters and Fatty Acids Synthetic Paraffinic Kerosene (HEFA-SPK), Alcohol To Jet Synthetic Paraffinic Kerosene (ATJ-SPK), and Hydroprocessed Fermented Sugars Synthesised Iso-Paraffins (HFS-SIP). Both FT-SPK and HEFA-SPK, have already been implemented in 50:50 blends with kerosene-type fuels and used commercially in aircraft.

7.1. FT-SPK

Production of Fischer-Tropsch Synthetic Paraffinic Kerosene (FT-SPK), displayed in Scheme 1, shows the use of syngas ($CO + H_2$) which can be converted to jet fuels [123]. The gasification process requires conversion of biomass feedstock lignocellulose into syngas under high-temperature conditions while controlling the oxidant species present [120]. Although this technique is well-developed, the specific composition of the gas stream is hard to control as impurities may be present in the feedstock, these include N_2, chlorine (Cl) and tar. Before the Fischer-Tropsch synthesis, the syngas must be purified and adjusted to ensure the syngas ratios of CO and H_2 are appropriate for FT. Many of these impurities would be destructive for FT catalysts. This increases the cost and time of this process, which poses a problem for commercial-scale implementation [120].

The FT reaction has been extensively studied, and it has been shown FT-SPK produced contains a high concentration of long chain paraffins, both branched and unbranched, which are produced from syngas in the presence of iron or cobalt catalysts. Once synthesised, the crude product is processed, which involving both cracking and separation techniques [123]. Reports have shown that use of FT-SPK displayed emissions which contained negligible quantities of sulphur, soot and aromatic content [124]. Unfortunately, FT-SPK fuels are required to be blended with traditional kerosene fuels (50%) before use in aircraft to meet standard aviation fuel specifications [122]. Development of a biomass feedstock that is suitable for this process still poses a problem [123].

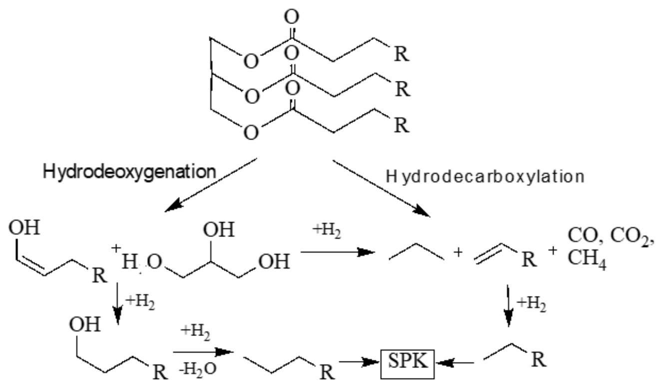


Scheme 1. Main methods available for converting biomass feedstock into Synthetic Paraffinic Kerosene (SPK). The main intermediates involved in the conversion processes are displayed. Figure has been adapted from Díaz-Pérez and Serrano-Ruiz [120].

7.2. HEFA-SPK

In 2011, ASTM D7566 approved Hydroprocessed Esters and Fatty acids (HEFA) as an alternative biofuel suitable for blending with CAF, following the approval of the FT-SPK:CAF blend [123]. Vegetable oils are comprised of triglycerides typically possessing a carbon length between 14–22, which is outside the range used within the aviation industry. Triglycerides must initially be hydrotreated to isolate the free fatty acid chains [125]. Hydrotreating involves the triglycerides reacting with hydrogen over a solid catalyst at high pressure and temperature. This reaction results in the extraction of three fatty acid chains, and also releases a propane molecule as the backbone of the triglyceride [126].

These free fatty acid chains must be catalytically deoxygenated through hydrodeoxygenation reactions or decarboxylation reactions resulting in long linear alkanes, as seen in Scheme 2 [127]. Due to the length of these chains hydrocracking must occur to reduce the carbon length to be compatible with the length traditionally seen in CAF [122]. Linear alkanes (analogous to paraffins) display excellent high-density properties which, due to increased combustion performance is a vital jet fuel property [120]. The carboxylation process removes oxygen as either CO or CO_2, thus a carbon is lost in this process [126]. The catalyst required for deoxygenation processes was Pd/SiO_2 with the presence of H_2 free-flowing during the reaction [128].



Scheme 2. Proposed mechanism for conversion of vegetable oils into fuels via hydrotreating, figure adapted from work completed by Melero et al. [127].

The formation of aromatic paraffins is important for use in jet fuels as they contribute to ensuring valves in engine systems are sealed properly by promoting swelling of the valve [120]. Takemura et al. [129] reported Ni and Pd catalysts with aluminium supports were useful for forming aromatic paraffins, particularly through decarboxylation of benzoic acid in a batch autoclave. This occurred in the presence of either N_2 or H_2 providing less stringent reactive components with a greater extent of carboxylation under N_2 atmosphere. Snåre et al. [130] further investigated this catalytic reactivity, identifying a greater variety of catalysts that could be used for deoxygenation processes, including Pd/C. The abundance of catalysts available for this process give the potential for mass implementation of these routes within the biofuel aviation industry.

Research conducted by Wang et al. [131] reported an efficient 4-step conversion method for synthesising HEFA-SPK. These steps include enzyme transesterification, catalytic transfer hydrogenation, alkene cross-metathesis and catalytic hydrodeoxygenation. This employed the use of Grubb's catalyst for the alkene cross-metathesis and Pt/ZSM-22 catalyst for hydrodeoxygenation. This method was highly efficient and provided a more economically feasible solution compared with previously reported hydrotreatment processes.

Furthermore, a wide range of vegetable oil feedstocks have been reported, these include camelina, canola rapeseed, soybean and jatropha oils, although production of jet fuels utilising these oils is controversial as the production is not entirely sustainable [120]. As a non-edible crop, camelina possesses a high oil content, but, growing this crop purely for oil uses poses a question regarding feedstock availability and land use concerns [120]. Although often camelina crops are grown in rotation with wheat crops, where land would otherwise be left to refresh itself, this still presents a problem as the feedstock would only be available seasonally [132].

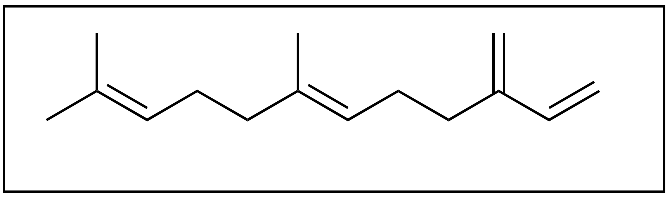
As environmental conscience has increased, several reports have detailed the potential use of waste cooking oils in the formation of alternative jet fuels. Utilisation of waste cooking oils removes the concern over growing crops just for oil usage as these oils have already been used in another sector and are thus multi-purpose [133]. However, issues have been reported with using waste oils. Low-grade waste oils cannot be used as the concentration of free fatty acids is too high to produce biofuels [134]. Furthermore, waste oils possess a higher abundance of impurities which could interact with catalysts present and disrupt hydroprocessing [120]. Further research has been conducted recently in processing fatty acids into aromatics and cycloalkanes, components also present in CAF. The use of non-edible jatropha oil coupled with Ni catalysts at high temperatures led to a production of 8% aromatic content. Development into these conditions could increase the number of aromatic components produced this way [135].

The literature has reported promising results from the vegetable oils processed into jet fuels, with many reports indicating these fuels have been already blended with CAF to power commercial jets [120]. Additionally, reports have recommended that the cost of production could be reduced if propane, produced during the hydroprocessing stage, was sold back to for use in industry [136]. Alternatively, triglycerides extracted from algae oil could prove promising in the future. As algae are known to have a high yield production and function at low water and fertilizer concentrations, this could be a cost-effective solution [137].

7.3. HFS-SIP

Sugar molecules have also been reported as potential feedstocks for production of alternative fuels. Typically, highly oxygenated sugar molecules, containing OH, CO and COOH groups, have a carbon number of 6. To effectively convert these to jet fuels many steps are required involving oxygen removal and C-C coupling reactions to increase the carbon length to 9–16 in line with kerosene fuels [120]. However, direct conversion of sugar to hydrocarbon molecules has been reported which avoids complexity issues with a number of synthetic steps involved. Microorganisms has been reported to be extremely effective in creating alternative aviation blending fuels. Genetically engineered yeast has been utilised as it consumes sugars and excretes long chain alkenes, predominantly β-farnesene [138].

The structure of β-farnesene and is displayed in Scheme 3 and typically is produced from sugarcane and lignocellulosic biomass. Hydrogenation of β-farnesene produces farnesane which is an alkane which has displayed potential as a high energy density alternative fuel option [139]. HFS-SIP fuels, produced via hydroprocessing processes of β-farnesene, have been certified to be blended in 10 vol% with kerosene and used as aviation fuel [122].

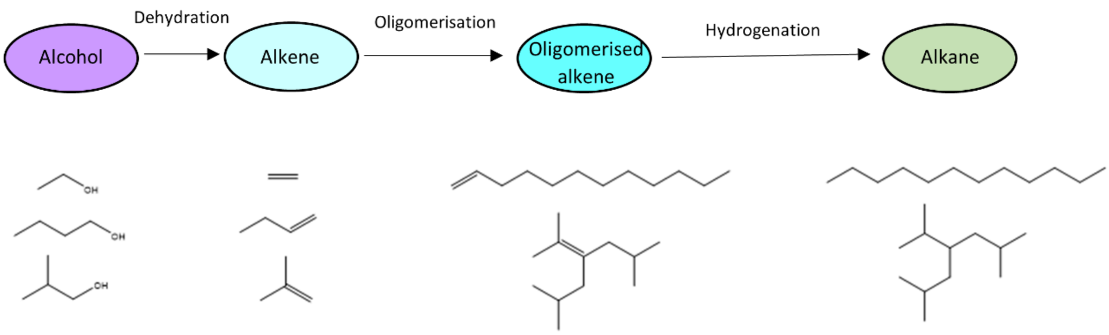


Scheme 3. Structure of β-farnesene, excreted by genetically engineered yeast, which can be hydroprocessed to produce HFS-SIP.

Nevertheless, this process uses an expensive feedstock and the production of the fuel is a high energy process, implantation of HFS-SIP fuels on a commercial scale would be extremely costly [138].

7.4. ATJ-SPK

Conversion of alcohol to jet synthetic paraffinic kerosene involves three key steps involving dehydration to remove heteroatom oxygen to produce alkenes, oligomerisation to increase the carbon chain length of the alkenes and finally hydrogenation to produce the unsaturated long chain alkanes [125]. This is displayed in Scheme 4.



Scheme 4. Conversion process of alcohol to SPK employing dehydration, oligomerisation and hydrogenation steps. Example structures also present in the diagram. Scheme adapted from Díaz-Pérez and Serrano-Ruiz [120].

Currently, only iso-butanol and ethanol are used in ATJ-SPK processes, but, future development hopes to incorporate all C_2-C_5 alcohols in the production process [122]. Both ethanol and iso-butanol are easily dehydrated in the presence of acid catalysts such as silica-alumina and at moderate temperatures, e.g., 250 °C and 325 °C, respectively [140]. If similar methods could be employed when dehydrating C_3 and C_5 alcohols variability would be increased, thus, decreasing high demand for land for specific C_2 and C_4 crops. It is difficult to identify a microorganism suitable to produce C_5 and other C_4 substituted alcohols from sugar glucose while minimising the steps in the process and making it cost effective [141].

Presently, the iso-butanol/ethanol feedstock is generally obtained through sugar microbial fermentation commonly employed in both wine and beer production processes [120]. However, the method of extracting sugars initially provides some difficulty. With edible feedstocks, sugar cane and corn, extraction of sugar is relatively simple and requires only hot water treatment. Extraction of sugars from non-edible feedstocks, namely lignocellulose, require several stages of processing and poses a problem as the structure of the lignin surrounding the cellulose must be weakened before extraction which is a costly process [125]. Unfortunately, ATJ-SPK would also be required to be blended with kerosene (approx. 15 vol%) to be used as aviation fuel [120]. Ethanol, in particular, cannot be used directly in aircraft engines due to its high volatility, high water absorption and a much lower energy density than CAF, but iso-butanol has a lower water absorption and higher energy density than ethanol, however, it is still much lower than CAF [142].

Although the implementation of iso-butanol would be promising, this ATJ-SPK could only be employed within short-haul flights as the energy density of the fuel would decrease the aircraft flight range if employing this fuel [120]. The implementation of ATJ-SPK is at the beginning stage of development, particularly focusing on iso-butanol, as it can also be employed to produce aromatic paraffins which are also a required component of jet fuel. This presents an advantage over FT-SPK, as this process only produces saturated linear hydrocarbons [120].

i-Butanol have gained a lot of interest in the aviation fuel, having many preferential physical and chemical properties compared with ethanol. The energy density and chemical structure of butanol is much closer to gasoline, thus overcoming miscibility issues associated with bioethanol. It also burns more cleanly (containing around 22% oxygen) and is far less corrosive than ethanol, meaning that it can be shipped and distributed through existing infrastructure.

The relatively short lifetime of i-butanol (a few days) [143] mean that its emission and its oxidation products are likely to impact local and regional air quality. However, the larger-scale, global implications should also be considered in order to fully assess their environmental impacts. Once released into the atmosphere, the photo-oxidation products of i-butanol can influence tropospheric ozone, as well as other secondary pollutants such as secondary organic aerosols (SOA) and PANs. Once emitted, i-butanol is predominantly removed from the atmosphere via reaction with the OH radical, which is a highly site-specific process. There are a number of competing pathways by which this reaction can proceed, thus leading to the formation of different stable end product(s) (see Figure 6) and potentially, different impacts on atmospheric composition. Laboratory studies by McGillen et al. [143,144] investigated the removal of the i-butanol isomers under atmospheric conditions, deducing the branching ratios and dominant reaction pathways associated with the OH radical initiated degradation. Thus, the use of i-butanol as a global biofuel will result in significant emissions into the atmosphere, with its subsequent transport and degradation likely to impact atmospheric composition.

The incorporation of 1.8 Tg/year of i-butanol emissions and associated oxidation products in the model, STOCHEM-CRI increase the level of ozone and PAN by up to 6 and 4.5%, respectively, in the upper troposphere (see Figure 7). PAN enables the long-range transport of NO_x, away from primary sources and then thermally decomposes to release NO_x into the remote troposphere. This NO_x and RO_2 radicals formed over the course of the multi-generation oxidation of i-butanol resulted in the catalysis of ozone formation, as they promote the production of NO_2 in a closely coupled photochemical reaction cycle. The effects are significant in the upper troposphere, with sufficient timescales allowing the transport of RO_2 and hence effects on ozone to be seen at these higher altitudes.

The increase in ozone in the upper troposphere could have implications for the global climate. Numerous studies have reported its potency as a greenhouse gas at these altitudes, due to its ability to absorb IR, UV and visible radiation [146–149]. This had led to growing concerns around anthropogenic sources of upper tropospheric ozone and their role in global climate change [150], with this study finding that anthropogenic emissions from biofuel usage could be a significant part of this.

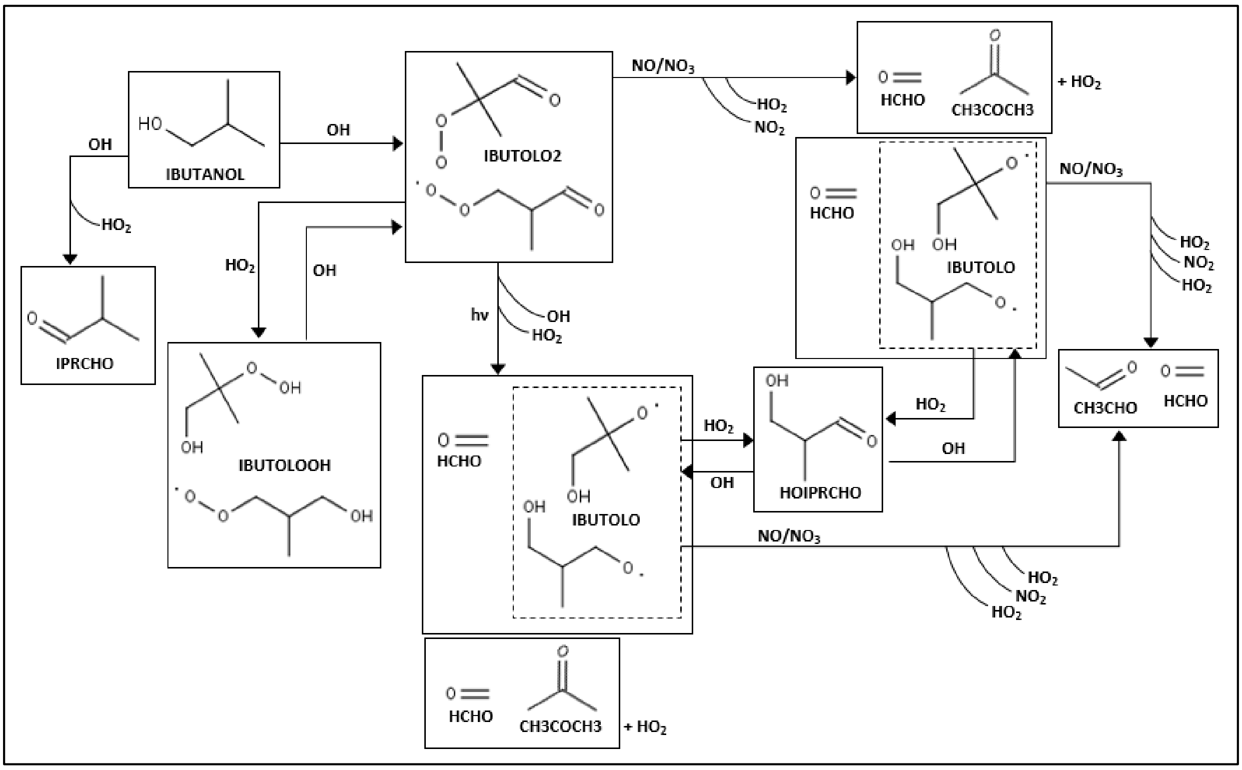


Figure 6. The possible degradation mechanism of i-butanol oxidation by OH. The reactions are taken from Master Chemical Mechanism (MCM) and then simplified for using in model, STOCHEM-CRI.

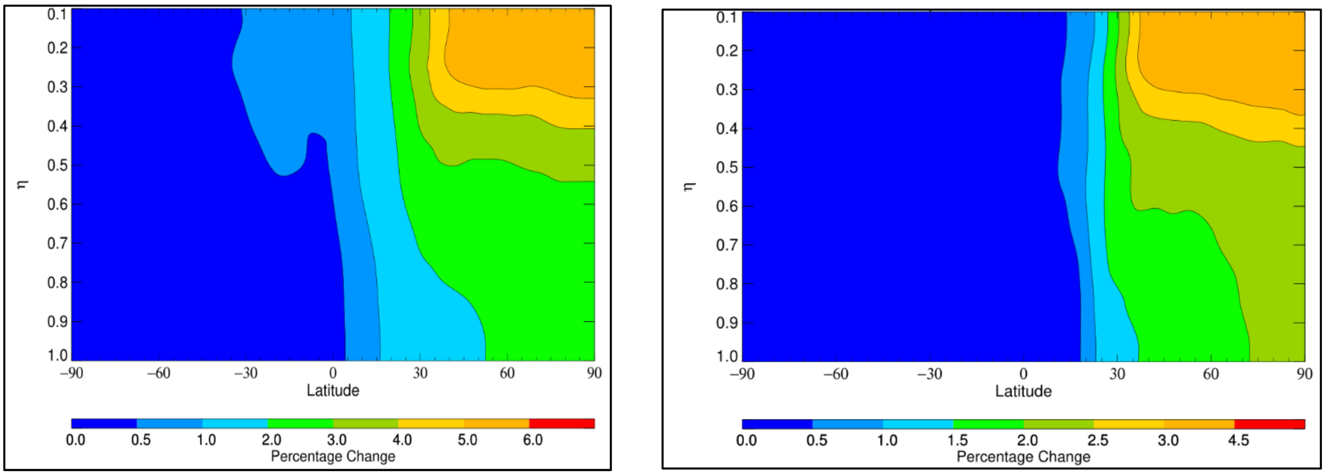


Figure 7. The annual average zonal (**a**) ozone and (**b**) PAN change after adding 1.8 Tg/year of i-butanol as biofuel. Note: η is the hybrid height coordinate, the relationship of η with the altitude levels can be found in Collins et al. [145].

8. Problems with Biofuels in the Aviation Sector

When considering the application of biofuels within aviation, most studies examine the consequence this has on GHG emissions. For example, research by Kousoulidou et al. [117] and Mohsin et al. [118] showed that a significant reduction in GHG emissions can be achieved by replacing aviation fossil fuels with biofuels. However, the impact of aviation biofuels on other environmental factors, such as biodiversity and air quality remains uncertain and requires further investigation.

There are many other challenges for the implementation of sustainable biofuels in aviation industry. First, there is still a significant price difference between BAF and CAF. Many processes discussed also require catalysts, the design and selection of catalysts to improve cost-effectiveness is in itself a costly process. Decarbonisation of the aviation industry relies heavily on biofuels; however, this increase in demand could lead to deforestation which affects soil fertility and can decrease biodiversity in forested regions [146].

Algae feedstocks provide a cost-effective solution to biofuel growth, due to minimal water and fertilizer requirements, but, problems emerge with producing the feedstock on a commercial scale [151]. Additionally, stringent temperature requirements are needed for algae growth which presents a problem. It is also important to consider the overall carbon footprint of the biofuel produced. Furthermore, fuel efficiencies of alternative fuels are still largely undefined, improving and optimising fuel efficiencies of BAF would reduce the emissions released into the atmosphere. It is vital to determine which alternative fuel would be the most efficient when combusted. Finally, BAF must be compatible with CAF as they are currently blended when used in aircraft. However, advancements in bio-fuel implementation are promising, with clear emission reduction in CO_2, CO, SO_x and NO_x, particularly when blending FT fuels [124]. Alas, these alterations in fuel composition could have a significant impact on atmospheric chemistry. Currently, there have been limited studies investigating the impact of biofuel emissions on altering O_3 and SOA formation [152]. Future investigations into these factors must be considered.

9. Conclusions

As global energy demand increases exponentially and fossil fuels continue to harm the environment, it is imperative to find an alternative, renewable energy source to supply the world's growing population and help countries to meet strict emission targets. The transportation sector is a major contributor to GHG emissions and urgently needs a replacement for petroleum and diesel fuels. Consequently, in recent years there has been a growing interest in biofuels, as they are a strong replacement for transportation fuels in comparison to other renewable energies. It is largely accepted that biofuels have a great potential to help decarbonise the transport sector, but there is significant controversy surrounding how sustainable they are.

The future of biofuels requires a shift from first-generation biofuels produced from food crops, to second and third generation biofuels derived from cellulosic material and algae, respectively. This is particularly important in developing countries as first-generation biofuels raise issues of food security and production which can increase poverty levels and harm the economy. However, there are current challenges with commercialisation of advanced biofuels as their production costs are very high and conversion technologies need improvement. Therefore, governments should promote future development of these biofuels in an effort to improve global acceptance and increase production feasibility. Advanced biofuels, particularly those derived from algae, have a strong capability to replace fossil fuels without giving rise to negative effects such as food insecurity and biodiversity loss. A greater production of these fuels is likely to have a positive impact on the global economy and help to mitigate climate change. However, more research is required to assess the impact that these fuels will have on global air quality and public health in order to make an accurate evaluation as to whether they are a sustainable alternative to fossil fuels.

In general, PM, CO and VOC emissions from biofuels were lower than that of petrol and diesel, with the higher oxygen content of biofuels being the main reason for this finding. However, unfavourable increases in NO_x, aldehyde and PAN emissions were also seen when using biofuel. This demonstrates that the wider application of biofuels presents a trade-off between a reduction in PM pollution or an increase in harmful NO_x and PAN emissions.

The use of biofuels with analysis of potential fuel compositional changes in aviation industry has been discussed. FT-SPK alternatives are a promising alternative to reduce emissions, although developments of suitable cost-effective methods for purifying syngas are still up for debate. HEFA-SPK fuels also provide an effective solution and, like FT-SPK, fuels are compatible with current air fleets if blended with current kerosene fuels. Mass production of HEFA-SPK with algae oil proposes a solution to reduce current production costs due to the high yield production of these microorganisms. ATJ-SPK fuels are promising as the conversion processes are already well-known and executed within the fuel industry. Future developments are required to produce longer carbon chain lengths to reduce processing steps. Although, ATJ-SPK and HEFA-SPK fuels do provide a synthetic method for producing aromatic hydrocarbons, whereas other fuel alternatives mentioned currently cannot. HFS-SIP fuels provide a simple direct sugar-to-hydrocarbon process employing microorganisms and avoiding multi-step processing. However, this provides a costly route to producing biofuels and commercial implementation would come at a higher cost than continuing with CAF. Furthermore, all of these alternative fuels also have to be blended with CAF to be compatible with current air fleets. Although the solutions reduce emissions, they do not completely prevent them.

A variety of factors can determine the success of biofuels as a renewable energy source, such as the geographical region and climate, economic infrastructure and the feedstock used in biofuel production. Therefore, countries should cultivate oil producing crops which are suitable to their climate and establish incentives which would be easily adopted in their current infrastructure. In addition, a stronger focus should be placed on the implementation of biofuels across different sectors, like aviation, to maximise the probability of achieving the global climate change target established in the Paris Agreement. It is particularly important to determine how the transition from fossil fuels to biofuels could in turn influence climate and human health. Further methodologies should be investigated to predict emission levels and atmospheric chemistry impacts when using biofuels.

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Appendix A

Degradation of ethanol and acetaldehyde

$$CH_3CH_2OH \rightarrow CH_3 + CH_2OH \quad (A1)$$

$$CH_2OH + O_2 \rightarrow HCHO + HO_2 \quad (A2)$$

$$CH_2OH + M \rightarrow HCHO + H + M \quad (A3)$$

$$CH_3CH_2OH + OH \rightarrow CH_3CHOH + H_2O \quad (A4)$$

$$CH_3CH_2OH + OH \rightarrow CH_2CH_2OH + H_2O \quad (A5)$$

$$CH_3CH_2OH + OH \rightarrow CH_3CH_2O + H_2O \quad (A6)$$

$$CH_3CHOH + O_2 \rightarrow CH_3CHO + HO_2 \quad (A7)$$

$$CH_3CHO + OH \rightarrow CH_3CO + H_2O \quad (A8)$$

$$CH_3CO + O_2 \rightarrow CH_3CO_3 \quad (A9)$$

$$CH_3CO_3 + NO_2 \leftrightarrows CH_3CO_3NO_2 \text{ (PAN)} \quad (A10)$$

$$CH_3CHO + h\nu + 2O_2 \rightarrow CH_3O_2 + HO_2 + CO \quad (A11)$$

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