

Review Article

A Review of Biofuels and Their Positive Impacts on Health and the Environment

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Abstract: Indonesia's high population and rapid economic growth are driving a major transformation in the transportation sector, which is in line with the high increase in fuel demand. The need for biofuel as a substitute for conventional fuel is increasingly being prioritized by considering sustainable development goals (SDGs). Biofuel has safer health and environmental impacts than conventional fuel but still has fuel performance that meets fuel standards and engine performance. Biofuels can be derived from a variety of more sustainable and abundant raw materials, such as biomass and vegetable oils. In this review biodiesel, hydrogenated vegetable oil (HVO), and direct vegetable oil (SVO) are discussed in depth regarding the transformation of their production processes and their impacts on health and the environment. Biodiesel is one of the most widely developed and implemented compared to HVO and SVO to encourage the use of renewable energy in various aspects of people's lives in Indonesia. These three biofuels have different fuel characteristics and performance but can continue to be developed in the future to increase the implementation of renewable energy more massively.

Keywords: biodiesel; biofuel; transesterification; vegetable oil

1. Introduction

Biofuel is a type of renewable fuel derived from renewable resources based on vegetable biomass, animal by-products, or microorganisms. Peanut oil was the first biomass used as a raw material for biodiesel about a century ago (Roberts and Patterson, 2014) and now vegetable oil is the largest biomass used for biofuel production in Indonesia (EBTKE, 2014). To be used properly in existing engines, vegetable biomass-based fuels known as biofuels must be compatible with conventional petroleum fuels and engine performance requirements. Therefore, there needs to be similarities between the characteristics of conventional fuel and biofuel. Biofuels can be generally classified into the following categories: (1) biofuels produced through the fermentation of biomass into alcohol,

(2) biofuels produced from vegetable oil that is reacted with short-chain alcohol to form hydrocarbons or fatty acid methyl esters (FAME), (3) biofuels produced from hydrogenated vegetable oil to produce hydrocarbons with carbon chain lengths close to conventional petroleum fuels, and (4) biofuels produced by diluting vegetable oil using a solvent/co-solvent.

Currently, biofuel production is an innovative field that is developing rapidly in Indonesia, especially those that have a hydrocarbon structure similar to conventional fuel. This review focuses on biodiesel, hydrogenated vegetable oil (HVO), and straight vegetable oil (SVO) which are quite widely used today and/or are under interesting development in the coming years. In this review, the physicochemical properties and toxicity of

biofuels are also discussed to provide insight into their effects on health and environmental aspects.

2. Biodiesel

The imbalance between the availability and demand for fossil fuels as well as the increasing costs of processing fossil fuels creates an urgency to look for other fuel substitutes that can be produced from renewable resources and makes biodiesel an alternative fuel option. Biodiesel is a biofuel composed of monoalkyl esters of long-chain fatty acids derived from renewable vegetable oils (food and non-food) or animal fats and derived through (1) the transesterification process of vegetable oils or (2) the esterification process of vegetable oils with high free fatty acid content and short-chain monohydric alcohols (Roberts and Patterson, 2014). This reaction involves triacylglycerol and free fatty acids that react with alcohol in the presence of a suitable catalyst, such as an alkali, acid, or enzyme, at high temperatures to form fatty acid alkyl esters (FAAE) and glycerol (Moser, 2009). The alcohols generally used are methanol and ethanol because they are cheap and widely available.

Biodiesel was first introduced in 1912 by Rudolph Diesel and was called the future of using vegetable oils (Mishra and Goswami, 2018). Various agricultural commodities are then used as a source of biodiesel production. In Western countries, soybean oil and canola oil are the agricultural products most commonly used to mass produce biodiesel (Hanson, 2019; Nickel et al., 2021), while in tropical countries, including Indonesia, the most common biodiesel is made from palm oil (OECD/FAO, 2021). Indonesia itself is known as the largest palm oil producer in the world with palm oil production reaching 48.3 million tons in 2020 (Statista, 2024).

Currently, biodiesel development has been carried out extensively because of its environmentally friendly characteristics, such as low carbon monoxide and particulate emissions, renewable, easily decomposed, low toxicity, and does not release hydrocarbons (Mishra and Goswami, 2018). Compared to diesel fuel, biodiesel does not produce sulfur and produces

less carbon dioxide. Biodiesel also contains more oxygen, thus producing enough free oxygen to induce complete combustion and reduce emissions (Atabani et al., 2012; Fazal et al., 2011; Silitonga et al., 2011). Biodiesel has lubricating properties and a cetane number equivalent to low-sulfur diesel fuel. The calorific value of biodiesel is generally around 37.27 MJ/kg which is 9% lower than Petrodiesel No. 2 with sulfur levels below 15 ppm. Variations in the energy density of biodiesel depend on the type of raw material used (Mishra and Goswami, 2018). There are more than 350 vegetable oil-producing plants that have been identified and can be a source for biodiesel production (Atabani et al., 2012). Table 1 summarizes various vegetable oil-based biodiesels along with their operating conditions, yield, and purity.

Biodiesel itself has high compatibility with most diesel engines and can be used without requiring changes to the engine system because the combustion characteristics and physicochemical properties are similar between biodiesel and diesel (Table 2). Therefore, various countries, such as Indonesia, Brazil, Malaysia, the United States, France, Germany, and other European countries (Atabani et al., 2012), have mass-produced and used biodiesel. Globally, annual biodiesel production is increasing up to 15 thousand barrels per day in 2000 and 289 thousand barrels per day in 2008 (Atabani et al., 2012; Silitonga et al., 2011).

In biodiesel production, raw materials and catalysts are two important factors that need to be considered, especially from an economic perspective, because these two components determine the number of steps in the process and the synthesis route (Konwar et al., 2014). The choice of raw materials in biodiesel production will affect the carbon content of biodiesel. For example, soybean oil which has a carbon chain of C16:0 palmitic acid, C18:0 stearic acid, C18:1 oleic acid, C18:2 linoleic acid, and C18:3 linolenic acid and reacted with methanol as an alcohol source will produce methyl esters with the same carbon length of fatty acids as the raw material, such as methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, and methyl linolenate.

Table 1. Biodiesel production method from vegetable oil

Method	Raw materials	Catalysts	Alcohols	Operating conditions (T = temperature, P = pressure, r = alcohol-to-oil ratio, t = time, c = catalyst amount)	Yields	Ref.
Trans-esterification	Soybean oil	-	Supercritical methanol	$T = 280^{\circ}\text{C}$ $r = 24:1$	98%	(Han et al., 2005)

				$t = 10-30 \text{ min}$		
without a catalyst	Sunflower oil	-	Supercritical methanol and ethanol	$T = 200-400^\circ\text{C}$ $P = 200 \text{ bar}$ $r = 40:1$ $t = 40 \text{ min}$	78-96%	(Madras et al., 2004)
	Kapok seed oil	-	Supercritical methanol	$T = 322^\circ\text{C}$ $P = 16.7 \text{ MPa}$ $r = 30:1$ $t = 476 \text{ s}$	95.5%	(Ong et al., 2013)
Trans-esterification with homogeneous catalysts	Madhuca indica	H_2SO_4 and KOH	Methanol	$T = 60^\circ\text{C}$ $r = 0.30-0.35 \text{ (v/v)}$ $t = 60 \text{ min}$ $c = 1\% \text{ (v/v) acid and } 0.7\% \text{ (w/v) base}$	98%	(Ghadge and Raheman, 2005)
	Castor oil	H_2SO_4 and NaOH	Methanol	$T = 50^\circ\text{C}$ $r = 5:1 \text{ (v/v)}$ $t = 2 \text{ hours}$ $c = 0.008 \text{ (v/v) acid and } 8 \text{ g/L base}$	-	(Dubey and Gupta, 2017)
	Canola oil	NaOH	Methanol	$T = 45^\circ\text{C}$ $r = 6:1$ $t = 60 \text{ min}$ $c = 1\% \text{ (w/w)}$	98%	(Leung and Guo, 2006)
	Rice bran oil	H_2SO_4	Methanol	$T = 60^\circ\text{C}$ $r = 10:1$ $t = 8 \text{ hours}$ $c = 2\% \text{ (w/w)}$	<96%	(Zullaikah et al., 2005)
	Palm oil	KOH	Methanol	$T = 60^\circ\text{C}$ $r = 1:4 \text{ (v/v)}$ $t = 2 \text{ hours}$ $c = 1\% \text{ (w/w)}$	-	(Fattah et al., 2014)
Trans-esterification with heterogeneous catalysts	Canola oil	KOH/ $\text{Fe}_3\text{O}_4@$ Al_2O_3	Methanol	$T = 65^\circ\text{C}$ $r = 12:1$ $t = 6 \text{ hours}$ $c = 4\% \text{ (w/w)}$	98.8%	(Kazemifard et al., 2018)
	Sunflower oil	MgO/ MgFe_2O_4	Methanol	$T = 110^\circ\text{C}$ $r = 12:1$ $t = 4 \text{ hours}$ $c = 4\% \text{ (w/w)}$	91.2%	(Alaei et al., 2018)
		MgO/ MgAl_2O_4	Methanol	$T = 65^\circ\text{C}$ $r = 12:1$ $t = 3 \text{ hours}$ $c = 3\% \text{ (w/w)}$	95.7-96.5%	(Vahid et al., 2017)
	Palm oil	$\text{NaAlO}_2/$ $\gamma\text{-Al}_2\text{O}_3$	Methanol	$T = 64.72^\circ\text{C}$ $r = 20.79:1$ $t = 3 \text{ hours}$ $c = 10.89\% \text{ (w/w)}$	97.65%	(Zhang et al., 2020)
		$\gamma\text{-Al}_2\text{O}_3/$ KI	Methanol	$T = 60^\circ\text{C}$ $r = 14:1$ $t = 4 \text{ hours}$ $c = 4\% \text{ (w/w)}$	98%	(Islam et al., 2015)
	Fe/DS- HMS-NH ₂	Methanol	$T = 60^\circ\text{C}$ $r = 6:1 \text{ (w/w)}$ $t = 4.5 \text{ hours}$ $c = 6\% \text{ (w/w)}$	85.36%	(Suryajaya et al., 2021)	
	Corn oil	Ca/ $\gamma\text{-Al}_2\text{O}_3$	Methanol	$T = 65^\circ\text{C}$ $r = 12:1$ $t = 5 \text{ hours}$ $c = 6\% \text{ (w/w)}$	87.89%	(Moradi et al., 2015)
Trans-esterification with a biocatalyst	Castor oil	Immobilized <i>Burkholde</i>	Ethanol	$r = 10:1$ $t = 24 \text{ hours}$ $c = 5.25 \text{ mg}$	78%	(Abdulla and Ravindra, 2013)

	<i>ria cepacian Pseudomonas cepacia</i>	Ethanol	$T = 40^{\circ}\text{C}$ $r = 4:1$ $t = 24$ hours $c = 5-8\%$ (w/w)	98%	(Shah and Gupta, 2007)
	Lipozyme <i>Thermomyces lanuginosus</i> e IM.	Methanol	$T = 45^{\circ}\text{C}$ $r = 3:1$ $t = 24$ hours $c = 15\%$ (w/w)	67.58%	(Maleki et al., 2013)
Corn oil	Lipozyme <i>Thermomyces lanuginosus</i> e IM.	Ethanol	$T = 35^{\circ}\text{C}$ $r = 6:1$ $t = 12$ hours $c = 2.8\%$ (w/w)	69.2%	(Bardone et al., 2012)

Table 2. Physicochemical properties of biodiesel and diesel based on ASTM D6751 and ASTM D975

Parameters	Units	Test methods	ASTM D6751 (Biodiesel)	ASTM D975 (Diesel)
Kinematic viscosity (at 40°C)	mm ² /s	ASTM D445	1.9 to 6.0	2.0 to 4.5
Density (at 15°C)	kg/m ³	ASTM D1298	880	820 to 860
Flash point	°C	ASTM D93	130 min	60 to 80
Cloud point	°C	ASTM D2500	-12 to -3	-15 to -5
Pour point	°C	ASTM D97	-16 to -15	-35 to -15
Cetane number	-	ASTM D613	47 min	46
Acid number	mg KOH/g	ASTM D664	0.5 max	-
Copper corrosion	-	ASTM D130	No. 3 max	Class 1 max
Water and sediment	%vol.	ASTM D2709	0.005 max	0.05 max
Free glycerine	%wt.	ASTM D6584	0.02 max	-
Total glycerine	%wt.	ASTM D6548	0.24	-
Sulphur (S 10 grade)	ppm	ASTM D5453	-	10 max
Sulphur (S 15 grade)	ppm	ASTM D5453	150 max	-
Sulphur (S 50 grade)	ppm	ASTM D5453	-	50 max
Sulphur (S 500 grade)	ppm	ASTM D5453	500 max	500 max
Phosphorus	ppm	ASTM D4951	0.001 max	-
Carbon residue	%wt.	ASTM D4530	0.05 max	0.2 max
Oxidation stability	mg/L	ASTM D2274	-	25 max
Distillation temperature	°C	ASTM D1160	360	370 max

During use, biodiesel can migrate into soil, water, and sediment whereas biodiesel with shorter chains is more easily mobile and biodegrades in soil and water systems. Based on laboratory tests, generally, more than 80% of biodiesel will be degraded within 28 days. With a faster biodegradation rate than diesel, biodiesel migrates less and is deposited in the environment than diesel. On the other hand, the presence of biodiesel in soil and water systems can slow down the biodegradation of petroleum hydrocarbons, such as benzene and toluene. Biodiesel also has low volatility although evaporation of its components can still occur (Roberts and Patterson, 2014). This makes biodiesel safer and does not require complex control units during storage and transportation. In addition, biodiesel is predicted not to cause bioaccumulation because FAAE can be easily metabolized into fatty acids and alcohol and then excreted if absorbed by living creatures. Some fatty acids

will also be further oxidized to form carbon dioxide and water through breaking down into 2-carbon fragments which are used by the body for energy and incorporation into tissue. Biodiesel has low toxicity and the data show that exposure to biodiesel is not harmful. Soybean, sunflower, and canola-based FAAEs are classified as non-hazardous materials for oral exposure with an acute oral LD50 >5 g/kg. Similarly, dermal and inhalation exposure to FAAE also show low toxicity. The results of irritation tests on human eyes and skin also show that biodiesel with carbon chain lengths C8-C10, C12-C14, and C16-C18 is not an irritant. Exhaust emissions from engines using FAAE did not produce systemic toxicity in F344 mice exposed for 13 weeks with exposure levels of approximately 0.04, 0.2, and 0.5 mg of particulates per cubic meter. This research was conducted as part of the Tier 2 testing program under the Clean Air Act program. Significant biological effects occurred in

highly exposed female mice indicated by the presence of proinflammatory cytokines, increased lung weight, and increased alveolar macrophage content but this was considered a normal response to repeated inhalation of particulate matter. There are no chronic effects of biodiesel on humans and animals; nearly all alkyl esters of biodiesel (myristate (C14:0), palmitate (C16:0), stearate (C18:0), oleate (C18:1), linoleate (C18:2)) are accepted by the US Food and Drug Administration (US FDA) as a source of added fat in animal feed under the rule of 21CFR573.640. Biodiesel is also reported to have no toxicity on reproduction and organ development, non-carcinogenic, and non-mutagenic. Biodiesel produces similar environmental effects to diesel where it can cause oxygen depletion and food-chain disruption. However, biodiesel does not show toxicity to aquatic species, such as microbes, invertebrates, and fish, with LC50 and EC50 values >1000 mg/l. Meanwhile, toxicity studies with organisms that grow in soil and sediment have never been carried out and are only predicted based on their partitioning into soil/sediment (Roberts and Patterson, 2014).

3. Hydrotreated vegetable oil (HVO)

3.1. Bioaviation fuel (BAF)

Bioaviation fuel (BAF) known as biojet fuel is a type of biofuel specifically used for aircraft and can be classified as sustainable aviation fuel (SAF). With the growing role of the aviation industry in the global economy, the Air Transport Action Group (ATAG) predicts that 7.2 billion passengers will be served by the aviation industry through the world's main airports in 2035 with the projected total greenhouse gases produced reaching 3.1 billion tons in 2050 (4 times greater from 780 million tons in 2015) (Doliente et al., 2020). Therefore, the development of aviation technology and operations, as well as the search for alternative biofuels to replace aviation fuel are the focus of the aviation industry to reduce greenhouse gas emissions. Bauen et al., 2009 reported that the use of BAF can reduce carbon dioxide emissions by 20-98% compared to conventional aviation fuel. International Air Transport Association (IATA) calls BAF as one of the key elements for reducing the carbon footprint in the environmental impact of aviation. BAF can help reduce the rate of fuel carbonization in medium and long-distance air travel which generally produces large amounts of emissions, thereby extending the life of aircraft by lowering their carbon footprint (IATA, 2019). Flight tests using a mixture of BAF and aviation

fuel began in 2008 and then mixed fuels with 50% BAF were permitted in commercial flights in 2011. In 2019, IATA's ambition was to increase BAF production penetration to 2% by 2025. However, the International Energy Agency (IEA) Bioenergy reported that BAF production will only be around 0.1% of the world's total aviation fuel demand until 2021 (van Dyk and Saddler, 2021).

BAF is synthetic kerosene (synthesized paraffinic kerosene, SPK) which is derived from biomass (Yang et al., 2019). BAF can be produced from various sources, such as *Jatropha* plants, algae, waste-based fats and oils, and palm oil, via (1) hydroprocessed esters and fatty acids (HEFA) technology combined with hydrogenation-deoxygenation (HC-HEFA) and (2) catalytic hydrothermolysis (CH). Solid biomass can also be converted into biojet fuel and BAF through gasification and pyrolysis processes using the Fischer-Tropsch process. Alcohols produced from the fermentation of waste or lignocellulose, such as ethanol and isobutanol, can be used as raw materials for BAF using the alcohol-to-jet (ATJ) process or by biological synthesis using solar reactors (Seber et al., 2014). In this subchapter, the discussion is limited to the conversion of vegetable oil into BAF via the two routes above, namely HC-HEFA and CH.

In general, BAF raw materials via the HC-HEFA method include animal fats, vegetable oils, and algae oils (Seber et al., 2014). Palm oil has been widely used in the BAF production process via the HC-HEFA method which is the only renewable jet fuel technology applied industrially (Roth et al., 2017). Bosch et al., 2017 reported that raw material costs constitute a significant part of total production costs. As the lowest-cost vegetable oil, palm oil can potentially offset the high cost of hydrogen in the HC-HEFA procedure. Apart from that, Indonesia is currently one of the largest palm oil producers in the world. Together with Malaysia, these two countries supply more than 80% of global demand (Schoneveld, 2010). Therefore, the market is seeing an increase in interest in using palm oil raw materials in BAF fuel production (Ernsting, 2017; Schoneveld, 2010).

The HC-HEFA process involves four main steps, namely (1) extraction and purification, (2) deoxygenation and hydrogenation, (3) cracking and isomerization, and (4) distillation (Richter et al., 2018). Various extraction processes can be used to obtain vegetable oils, such as centrifugation, filtration, and mechanical pressing. Depending on the purity of the oil required, various refining and processing processes can be selected, such as steam injection, neutralization, vacuum evaporation, and filtration (De Araújo et al., 2013). The choice

of method at this stage will be greatly influenced by the quality and type of raw materials used as well as the availability of costs.

Figure 1 summarizes the reaction mechanism of this HEFA process. The reaction starts from the hydrogenation of double bonds in the fatty acid carbon chain of triglycerides into single bonds through a reaction with hydrogen. This reaction continues with the breakdown of saturated triglycerides into three fatty acid chains. The reaction process continues to a cracking reaction where the long hydrocarbon chain in the fatty acid is reduced to a carbon chain length that is in the range of aviation fuel carbon chain lengths. Then, the next process involves deoxygenation of the fatty acid chain [44] where three routes occur simultaneously, namely (a) hydrodeoxygenation of free fatty acids which produces water molecules, (b) decarboxylation of free fatty acids which produces carbon dioxide, and (c) decarbonylation of free fatty acids producing carbon monoxide and water

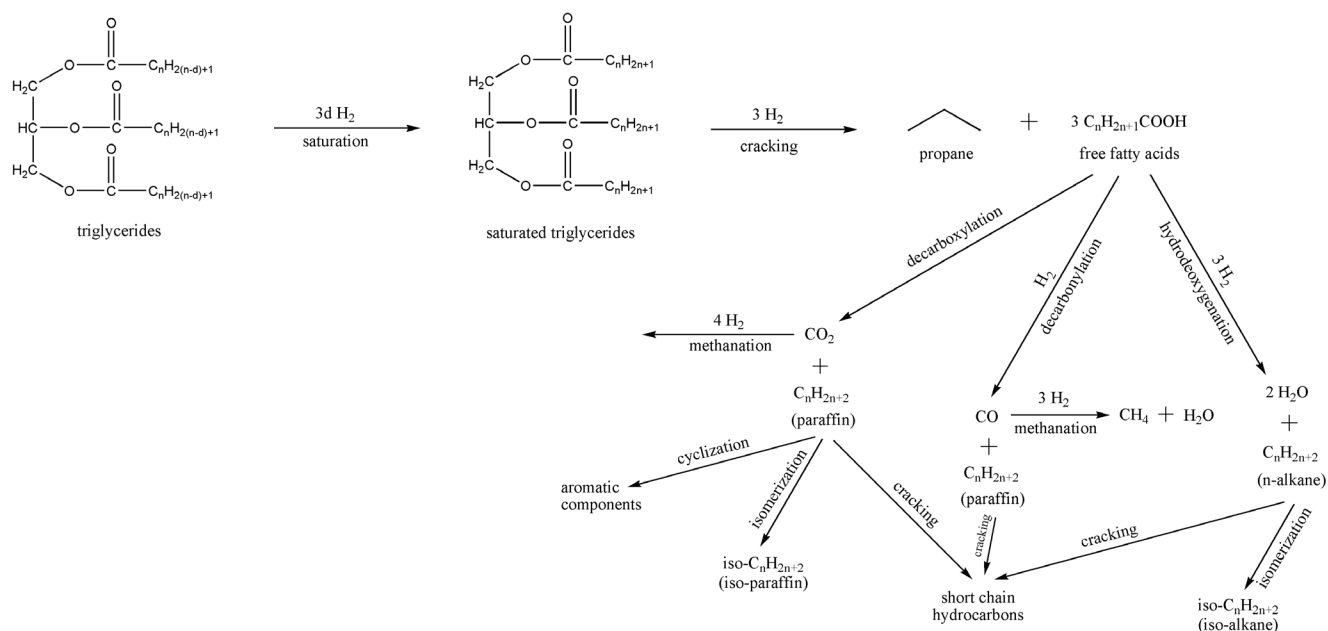


Figure 1. Scheme of the mechanism of the BAF manufacturing process via the HC-HEFA method

In improving the combustion properties of the product, the reaction process continues with isomerization, cracking, and cyclization to obtain iso-alkanes, short-chain hydrocarbons, and aromatic hydrocarbons, respectively. This isomerization reaction is aimed at changing linear hydrocarbon chains into branched hydrocarbons with the same number of carbons which can increase the freezing point of BAF (Gutiérrez-Antonio et al., 2013). The HC-HEFA process ends with distillation which is used to separate BAF from other products. The main advantage of HC-HEFA is the exothermic nature of the first reaction which reduces energy costs

(Boichenko et al., 2013). This deoxygenation reaction produces linear hydrocarbon chains (paraffins) by removing oxygen atoms from the molecules.

Important factors in these three reaction stages include (a) the amount of hydrogen used to saturate the fatty acid chains and separate free fatty acids from glycerol, and (b) the choice of catalyst to increase the yield. These reactions generally occur at 250-400°C and 10-18 bar with the catalyst choices being NiMo/ γ -Al₂O₃ and CoMo/ γ -Al₂O₃ (Popov and Kumar, 2013). Modified NiMoW/ γ -Al₂O₃ was also reported by Kovács et al., 2010 in the conversion of sunflower oil to BAF which has a high iso-paraffin content (23-29%), good cold flow properties (CFPP = 9-13°C), and a high cetane number (71-76) compared with conventional aviation fuel. Eller et al., 2016 added that sulfidation agents can be added to increase the yield and maintain catalyst activity.

for the entire process and has positive economic and environmental implications (Gutiérrez-Antonio et al., 2013). The quality of BAF using the HC-HEFA method is also not affected by the raw materials used. BAF from the HC-HEFA process even has better physicochemical characteristics than conventional aviation fuel: (1) BAF has a higher heating value (44 MJ/kg) and faster ignition than Jet A (a common type of aviation fuel used in commercial aviation), (2) BAF is also not susceptible to oxidation which makes it suitable for use as an aviation fuel (Crown Oil UK, 2019), and (3) a blend of Jet A-1 (an aviation fuel similar to Jet A with a lower freezing point) with

35% BAF synthesized using the HC-HEFA method only produces a small amount of reactive soot when the aircraft is on the ground and taking off (Liati et al., 2019). This is an important factor for aviation fuel because these three things affect the air quality around the airport.

Although the HC-HEFA method of BAF production is technically and commercially feasible, it is limited by the availability of raw materials where oil-rich crops and waste oil are currently insufficient to meet projected industrial demand (Bosch et al., 2017). The shorter chain length of BAF compared to the chain length of most triglycerides from plants (C14-C20) means that the BAF production process from vegetable oil requires a hydrogenation and deoxygenation process before HEFA. This additional process requires quite high amounts of hydrogen (around 10-15 moles per mole of triglyceride) (Huber et al., 2007). This limitation makes some parties argue that biofuel production using the HEFA method is more suitable for green diesel production than aviation fuel.

Judging from the perspective of hydrogen use, BAF obtained from the HC-HEFA process also harms the availability of fossil fuels indirectly. Currently, the most commonly used methods in hydrogen production are steam reforming of natural gas and fossil fuels (van Dyk and Saddler, 2021). With the widespread use of hydrogen in BAF production via HC-HEFA, of course, there will be an increase in the demand for natural gas and fossil fuels. As a result, meeting the need for alternative fuels is also covered by fossil fuels where this is certainly not desirable.

Catalytic hydrothermolysis is one of the BAF production routes that has been certified under ASTM D7566. This process was developed by Applied Research Associates (ARA) in collaboration with Chevron Lummus Global (CLG) and is called the Biofuels Iso-conversion (BIC) process (van Dyk and Saddler, 2021). The BIC method also uses lipids as raw materials, including fats, oils, and greases. Raw materials and water are mixed with a ratio of 3:1 and reacted at 200-250 bar and 500-600°C (supercritical conditions) (Kaltschmitt and Neuling, 2017). This stage is then continued with hydrotreatment and fractionation to produce LPG, naphtha, kerosene, and diesel. The BAF fraction produced was around 33% yield.

One of the advantages of catalytic hydrothermolysis compared to HC-HEFA is its 25% lower hydrogen consumption (Kaltschmitt and Neuling, 2017). Unlike HC-HEFA, where most of the molecules have straight or unbranched chains (paraffins), catalytic hydrothermolysis also produces cyclo-alkanes

and aromatic compounds similar to conventional aviation fuels. According to ASTM D7566, BAF produced via the CH route can contain 8–20% aromatic content. However, a maximum blend level of 50% with aviation fuel can still be used. ARA also added a pre-treatment process, Hydrothermal Cleanup (HCU), as an integrated part of the CH technology where HCU is aimed at removing heavy metals and other contaminants from raw materials before the production of BAF products (McGarvey and Tyner, 2018).

3.2. Green diesel

Green diesel (GD) is a second-generation alternative energy product from biofuel. GD has a molecular structure similar to petroleum-based diesel but has better characteristics. Unlike biodiesel, GD has chemically identical characteristics to petroleum-based diesel and can be used as a drop-in replacement in diesel-engine vehicles without modification. Some of the advantages and benefits of using GD can be seen in the points below (Honeywell UOP, 2021):

- Pure GD can be mixed with conventional diesel in varying compositions;
- GD has a high cetane number and low density so it can improve the performance characteristics of diesel engines;
- The use of GD does not require changes to the fuel composition or vehicle technology;
- Greenhouse gas emissions produced by GD are lower (up to 85%) compared to conventional diesel, low NO_x emissions and very low sulfur emissions;
- GD has extraordinary performance, both at high and low temperatures;
- The characteristics of GD are very stable and are not easily oxygenated.

Various feedstocks can be used to produce GD, such as biomass rich in oils and fats (palm oil, corn oil, animal fats, and others), lignocellulosic biomass (crop residues, wood, and sawdust), and switchgrass (Kittisupakorn et al., 2016). Mangindaan et al., 2022 reported the potential of insects, such as black soldier fly larvae (*Hermetia illucens*), as a feedstock for GD production. Instead of using acid or alkaline catalyst, GB productions with enzymes or without any catalyst become a breakthrough to provide a green process. However, development opportunities are still wide open because there are still shortcomings in terms of energy consumption, biodiesel yield and costs.

Similar to BAF synthesis, GD production routes can be divided into several thermochemical methods, such as HC-HEFA for oil and fat biomass, gasification, and pyrolysis via the Fischer–Tropsch process for lignocellulosic

biomass. In making GD via HC-HEFA, the process mechanism is divided into 4 main reactions: (1) hydrogenation to break the double carbon bond and release fatty acids from their glycerol groups, (2) deoxygenation (DO), (3) decarboxylation (DCO₂), and (4) decarbonylation (DCO) (Faungnawakij and Suriye, 2013; Kubička and Kaluža, 2010) which aim to remove oxygen, carbon dioxide, carbon monoxide, and water respectively (Gong et al., 2012; Snåre et al., 2006). In contrast to BAF, there is no cracking and isomerization process in the GD synthesis process. The hydrogenation process in making GD is also only used to break double carbon bonds and release fatty acid chains but not to break long carbon chains into short carbon chains so the amount of hydrogen used in this process is lower when compared to BAF production (Doliente et al., 2020).

3.3. HVO impacts

HVO which has a short carbon chain length, such as pentane or isopentane, is very volatile and is predicted to be partitioned into the atmosphere. Meanwhile, HVO with medium carbon chain length and low density generally partitions into water bodies and forms a sheen on the water surface before evaporating and/or being degraded by water microorganisms. HVO which has a simple structure (hydrocarbons with short straight chains or single branches) can be easily and quickly biodegraded by soil microorganisms. Some HVOs, especially those with long chains and/or having cyclic and aromatic structures, can be absorbed into the soil system and transported quite far from the initial partition location. Complete microbial degradation of HVO results in the production of methane or carbon dioxide.

Although in general HVO has advantages in terms of biodegradability, several consequences have the potential to be dangerous for the environment, namely benzene and toluene. Both content in HVO can be degraded more quickly than conventional fuel. However, benzene and toluene have a fairly long shelf life compared to straight-chain or single-branched hydrocarbons in the environment so aerobic metabolism to degrade these two components requires quite a lot of oxygen. This of course depletes the oxygen content in water bodies which is needed for biosystems and indirectly reduces the natural ecological diversity in water. Due to its high resistance, benzene and toluene that are partitioned into the soil can be transported quite far from the pollution site. This will cause the formation of methane and carbon dioxide which is not properly controlled.

Exposure to HVO can occur through inhalation and dermal penetration by users. Roberts and Patterson, 2014 reported that skin penetration of individual constituents in HVO is quite low. Meanwhile, inhalation of BAF showed deposition of components in the bronchioles. Metabolic tests on aviation engineering workers showed the presence of alcohol and ketone metabolites in the liver, urine, and feces. Therefore, although biomonitoring standards for HVO exposure do not yet exist, monitoring potential HVO exposure can generally be done by measuring alcohol and ketone metabolites in urine.

When compared to conventional fuels, HVO causes only mild irritation upon contact via inhalation and dermal routes. The LC₅₀ of HVO has a very high value, namely >2000 mg/m³, indicating that acute inhalation caused by HVO is very rare. However, low-viscosity HVO can pose a risk to the lungs if swallowed and can cause pneumonia which can be fatal. Repeated inhalation exposure to HVO for 2 weeks, up to exceeding the maximum exposure limit (>2000 mg/m³) can cause olfactory degeneration and hyperplasia in the nasal area, as well as inflammatory cell infiltration in the bronchioles (Roberts and Patterson, 2014).

Symptoms of central nervous system depression, such as dizziness, headache, drowsiness, or loss of consciousness and lack of coordination, may most likely occur due to high inhalation exposure to the volatile hydrocarbons in HVO dissolved in water. The specific mechanism of toxicity is still unknown, but hydrocarbons that have short to medium carbon chain lengths have quite high neurotoxicity upon repeated exposure.

HVO toxicity studies on reproductive performance have never been conducted. HVO is also reported to have no genetic toxicity (non-mutagenic). Based on comparative toxicity studies carried out on HVO and its constituent single hydrocarbons, HVO is considered to have varying ecotoxicity to aquatic systems depending on its composition and carbon range. Short-chain alkanes such as heptane and octane are highly toxic to aquatic organisms, while long-chain hydrocarbons such as dodecane and hexadecane are non-toxic. The use and transportation of HVO need to be controlled because it is flammable and tends to accumulate static charges if not grounded properly (Roberts and Patterson, 2014).

4. Straight vegetable oil (SVO)

Vegetable oil or straight vegetable oil (SVO) can be used directly as an alternative fuel in diesel engines and heaters, whether modified or not. However, Babu and Devaradjane, 2003 and Sidibé et al., 2010 also stated that the use of SVO can reduce engine life due to long-term deposition of carbon caused by its high viscosity and boiling point. This causes SVO to need to be modified for use by mixing it with a solvent to ensure that the viscosity is low enough to allow good fuel atomization. This low viscosity characteristic helps prevent incomplete combustion, which would damage the engine due to carbonization and carbon buildup. SVO can also be blended with conventional diesel fuel for use in a wider range of conditions. Most diesel engines in cars are suitable for use with SVO which has modified viscosity and surface tension. In addition to diluting it using solvents and/or conventional fuels, one common solution is by adding (1) a heat exchanger and (2) an additional fuel tank for switching petrodiesel or biodiesel to SVO just after heating and vice versa just before cooling. In colder climates, heating the SVO lines and fuel tank is necessary to prevent the SVO from hardening and clogging the lines during use. The single-tank conversion was developed in Germany and is now used throughout Europe. This tank modification is intended so that rapeseed oil can be used as engine fuel, where this change helps combustion during the start-up phase and engine warm-up phase (Zoynal Abedin et al., 2011).

As one of the most important parameters in the fuel flow rate in an engine, the kinematic viscosity of SVO is considered high enough to work well so it must be reduced to be compatible with conventional compression engines. As previously mentioned, mixing SVO with low molecular weight cosolvents is the easiest technology to implement because it requires low costs (Dunn, 2002). Co-solvents that can be used include (1) a mixture of alcohol (methanol, ethanol, propanol, and butanol) and amphiphilic solvents, where the second component functions to help homogenize SVO and alcohol, (2) diesel fuel, (3) kerosene, and (4) gasoline; however, various arguments and failures in use have been reported, especially with fuel pumps and pistons (Cloin, 2007). Apart from being a transportation fuel, SVO can also be used for heating and driving turbines in residential areas; generally referred to as bioliquid. Bioliquid has been used for years to provide heat on a small scale, but now major energy providers are looking at its use on a larger scale. A controversial plant in Bristol, England, was granted permission to operate a bioliquid-

based plant with enough power capacity for 25,000 homes, despite receiving several hundred complaints (BBC, 2011).

Bioliquids have several key advantages over other renewable energy sources (Seljak et al., 2020):

- Bioliquid has a high energy density;
- Bioliquid technology has been used for many years;
- Bioliquid can be used on demand and reacts quickly to power change requests;
- Similar to other renewable energy sources, bioliquids can help reduce dependence on foreign oil and reduce greenhouse gas emissions.

Apart from its advantages, bioliquid also triggers competition for the use of SVO in food, soap, and fuel, causing fluctuating fuel prices. Other disadvantages of using bioliquids are (1) the raw material supply chain is still quite new and (2) the government seems to still have doubts about the sustainability of using bioliquids to meet energy needs (McDermott et al., 2011).

In countries such as the UK, Canada, and the United States, the main raw material for SVO that is generally used is rapeseed oil which has a freezing point of -10°C . To increase the use of SVO in cold weather, sunflower oil which forms a solid at lower temperatures (-12°C) (Gregg and Goodwin, 2013) is being studied and developed. However, oils with lower freezing points tend to have quite a lot of unsaturated carbon chains (high iodine numbers) and polymerize more easily in the presence of oxygen in the atmosphere. This polymerization is often associated with component damage such as injection pump shaft damage and injector tip damage which result in component damage to the combustion tank (Gregg and Goodwin, 2013; Srivastava and Prasad, 2000). This causes the use of SVO to be very limited.

5. Conclusion

Biodiesel, HVO, and SVO are three of the biofuels that are being massively developed to make greater use of renewable energy in various fields while encouraging efforts to achieve sustainable development goals (SDGs). These biofuels are used because they have good fuel performance and meet current fuel standards according to engine needs. In addition, the superior characteristics of these biofuels are offset by much lower health and environmental impacts compared to conventional fuels. In the future, the development and implementation of renewable energy, including biofuels, needs to be

balanced with advances in engine technology that have performance in line with various current renewable energies. In that way, biofuels can be used more massively and the use of conventional fuels can be further reduced so that environmental sustainability and human civilization can be further maintained.

Author contributions

Conceptualization – M.Y., S.I., F.E.S; data analysis – M.Y., C.J., J.L., N.P.; resources – M.Y., S.B.H., W.I., S.L.; writing original draft – M.Y., C.J.

Conflict of interest

The authors declare no conflict of interest.

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