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Biodiesel production from waste cooking oil: A brief review

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ABSTRACT

Biodiesel is a source of new renewable energies and a substitute fuel with much potential in the future for petroleum-derived diesel. According to BP Statistical Review of World Energy, total global consumption of diesel from petroleum increasing in one decade which is 3.5 million tonnes in 2010 and 3.9 million tonnes in 2019. Despite reducing the dependence on fossil fuel, the question of how waste cooking oil (WCO) disposal and related environmental damage issues might be solved by biodiesel production. In Malaysia, an estimated 540 000 tonnes of WCO from vegetable and animal fats are discarded each year without being treated as wastes. WCO recognize as a raw material for biodiesel process and have a great potential. Biodiesel is made through a reaction between triglyceride and alcohol, with triglyceride being a raw material found primarily in plants and animals. Transesterification is the popular process of biodiesel production with low cost and mild reactions conditions. Some studies have done on the variable of transesterification process with the optimum condition of biodiesel production from WCO. This study examines WCO as a raw material for biodiesel production, including the various variables of transesterification process and a comparison of WCO biodiesel and petroleum diesel.

1. Introduction

The rapid growth of the world's population has resulted in an increase in the use of limited fossil resources. This scenario is a great way to promote the research and formation of a new renewable fuel, such as biodiesel [1]. Furthermore, rising petroleum prices, environmental concerns about car exhausts, local changes in the atmosphere, and an increasing proportion in the usage of diesel engines, which have greater performance than gasoline engines, have all led to the growing of biodiesel as an substitute fuel [2].

The use of fossil fuels or petroleum products is becoming more prevalent. According to [3], total global consumption of diesel from petroleum increasing in one decade which is 3.5 million tonnes in 2010 and 3.9 million tonnes in 2019. In region of Asia pacific including country like China, Japan and Malaysia, diesel consumed in 2010 is 1.1 million tonnes and in 2019 is 1.4 million tonnes [3]. This is reason why the alternative for diesel is needed to cover up the consumption for worldwide.

Biodiesel is the best option for dealing with this problem because biodiesel is derived from sources other than fossil fuels. Many researchers have investigated the possibility of biodiesel as alternative sources energy beside petroleum diesel. According to the studies, biodiesel appears to be a very excellent possibility for a variety of reasons, including its high biodegradability and low toxicity. Furthermore, it also better than petroleum diesel in terms of fewer combustion emissions, and it is closed carbon cycle means it does not contribute to global warming. Most fascinating is that biodiesel may be utilised in existing diesel engines with little or no modification and just a minor performance loss [4]. The presence of sufficient oxygen in biodiesel has been found in most studies to result in significant reductions in exhaust emissions when compared to diesel fuel in terms of CO, CO_2, SO_2, hydrocarbons, particulate matters, and smoke. This can be attributed complete combustion and lower emissions due the presence of sufficient oxygen in biodiesel [5].

Biodiesel is made through a reaction between triglyceride and alcohol, with triglyceride being a raw material found primarily in

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plants and animals. Generally, the plants are divided into two categories which are edible oil namely coconut oil, soybean, peanut, palm and rapeseed, and nonedible, namely algae, Karanja, seamangoes, jatropha and halophytes, as a raw material in biodiesel production. However, their use faces a lot of difficulties, including a food versus fuel crises, as well as substantial environmental issues such as substantial soil resource loss, deforestation, and the utilisation of much of the available arable land [6]. Some may not be able to meet world energy demand sufficiently, and they operate poorly in cold conditions. Animals sources is mainly from tallow, yellow grease, chicken fat and by-products from fish oil, but for many types of animal fats it is challenging since they include significant quantities of fatty acids saturated [6].

In order to produce better and relatively high biodiesel, a study and development for raw materials used in biodiesel manufacturing was done in response to some of these issues. Based on study, WCO is believing as an alternative to replace palm oil in biodiesel production. WCO which is much less expensive than pure vegetable oil shares some qualities and value with palm oil in terms of biodiesel production. Transesterification process is the common method use to produce biodiesel from WCO. However, several factors need to be study in the process such as the temperature, time reaction, alcohol to oil molar ratio and the catalyst. The study from [7], obtained 89.8% of biodiesel yield at optimum condition of methanol to oil molar ratio 9:1, 1.0 wt% sodium hydroxide, temperature of 50 °C and 90 min. The study from [8] was conducted with a methanol to oil molar ratio of 6:1, 1.5 wt% CaO, a temperature of 60 °C, and a time of 60 min, yielding 93 percent biodiesel. This paper provides a review of WCO as a raw material in biodiesel production, including the different process involve of biodiesel production from WCO and the comparison of biodiesel produce from WCO and petroleum diesel.

2. Waste cooking oil as raw materials for biodiesel

WCO remains of frying food composed of plant or animal fats with cooking oil. Cooking oil is a glycerol ester composed of different essential fatty acids that can only be dissolved in organic solvents [9]. It is harmful to the environment and to consumer's health when cooking oil waste is consumed. When fried meals are utilised, it is believed that the poisonous substances generated when the oil is oxidised would cause cancer [10]. WCO is widely available, although it is often abandoned after usage, particularly after frying. Table 1 illustrates the estimated amounts of WCO produced in Asia's countries, as well as the source of the oil. According to [11], in Malaysia, an estimated 540 000 tonnes of WCO from vegetable and animal fats are discarded each year without being treated as wastes [12] supports this by stating that the majority of spent cooking oil from houses is disposed of in the drainage and soil. Thus, one recommendation to overcome these issues is to utilise the WCO as raw materials for biodiesel which is more economical and environment friendly. It is also having potential to be a feedstock for biodiesel production as the amount of WCO produce will become larger.

The chemical reactions that occur during the frying process which are oxidation, hydrolysis, polymerization, and material transfer between the food and the oil, cause the properties of WCO to differ from fresh oil [17]. However, WCO have identical properties to produce biodiesel in terms of density, kinematic viscosity, acid value and iodine value and meet the quality requirement [18]. WCO contains a higher concentration of free fatty acids (FFA) than vegetable oil, which is significant when selecting a catalyst for use in the manufacturing process [19]. In situations when the concentration of FFA is high, large-scale biodiesel production is restricted, while soap manufacturing is favoured [20]. Based on study, the value of kinematic viscosity, saponification, flash point, moisture content and free fatty acids in WCO are very high [9]. These chemical properties will influence the quality and amount production of biodiesel. Furthermore, it is difficult to inject fuel from fuel tank to engine if the concentration or viscosity of oil is high and will causes atomization to occur [9]. Table 2 shows the percentage of free fatty acid in waste cooking oil collected by [21] and [22], respectively. Table 3 shows physical and chemical properties of waste cooking oil collected by [232425].

WCO is 2 to 3 times cheaper than fresh vegetable oil, resulting in a significant reduction in total processing costs [26]. The retail price of biodiesel is significantly influenced by the cost of raw material as up to 75–90% of the entire biodiesel production cost is spent on procuring the necessary raw materials alone [27]. The uses of WCO as raw materials are out from any crisis or issues such as debate on Food vs Fuel, environmental issue.

3. Process of biodiesel production from WCO

There are several processes can be used to produce biodiesel from refined oil or waste cooking such as pyrolysis, micro emulsification, and transesterification. The main process, advantages and disadvantages was summaries and tabulated in Table 4. Transesterification is a popular and common method used in biodiesel production. When an oil and an alcohol are mixed with a catalyst, a transesterification process takes place, resulting in the production of alkyl ester and glycerol as by-products. A three-step process starts with triglyceride to diglyceride conversion, diglyceride to monoglyceride conversion, and monoglyceride to glycerol production. The reaction generates three ester molecules from each glyceride molecule as a result of each reaction step [28]. This is shows in Fig. 1.

4. Kinetics study of transesterification process

There are two types of transesterifications which are transesterification with presence of alkali catalyst and transesterification with presence of acid catalyst. In the past, transesterification processes that use acid and alkali have proved to be faster and less costly. A catalysts function to improve the reaction rate and yield. In addition its function to splits oil molecules and an alcohol combines with a separate ester to produce alkyl ester [33]. However, the use of alkali catalysts is quite challenging when the FFA content

Table 1
Amount of WCO generated in Asia Countries.

Country	Quantity (million tonnes/ year)	References
China	5	[13]
Malaysia	0.54	[14]
Taiwan	0.05–0.03	[15]
Indonesia	0.9	[16]

Table 2
Percentage of free fatty acid in waste cooking oil collected.

Type of Free Fatty Acid	Value Content (%)	
	[21]	[22]
Oleic acid	43.67	41.04
Palmitic acid	38.35	31.88
Linoleic acid	11.39	17.98
Stearic acid	4.33	6.45
Myristic acid	1.03	0.77
Linolenic acid	0.37	0.43
Others	0.86	1.45
TOTAL	100	100

Table 3
Physical and chemical properties of waste cooking oil collected.

Properties	Waste Cooking Oil Values		
	[23]	[24]	[25]
Acid value (mg KOH/gm)	28.5	1.86	35.4
Saponification value (mg.KOH/gm)	175.87	181.25	234.71
Viscosity (mm^2/s)	46.97	42.01	–
Density (kg/m^3)	908	–	916
Free fatty acid (%)	14.25	–	18
Flash point (^oC)	223	234	–
Moisture content (%)	–	0.1	0.136

Table 4
Main process, advantages, and disadvantages of biodiesel production process.

Process	Main Process	Advantages	Disadvantages
Pyrolysis	The oil is preheated and decompose at certain temperature (generally high) with or without catalyst. The analysis is based on their boiling temperature of different products, such as gas and liquids [29].	The process is effective, simple, and free pollution and waste [30].	It is necessary to use expensive and high-temperature equipment. Produce biodiesel with a low purity level [30].
Transesterification	The oils are reacting with present of alcohol as solvent and catalyst. The biodiesel obtain with glycerol will be separate and purify before further usage [31].	High conversion with low cost, mild reaction conditions, the biodiesel obtain closer to the petroleum diesel and applicable for industrial production [31].	Require low amount of free fatty acid and water content in the raw materials, extensive separation and purification steps and generate large amount of wastewater [31].
Micro emulsification	The oils were solubilized in a solvent and surfactant until the require viscosity is obtained [29].	Easy process and pollution free [32].	High viscosity, low stability and could lead to sticking, incomplete combustion and carbon deposition [29].

is high, even though it is produce high biodiesel yield and the high purity of the products [34]. A two-step transesterification procedure is used to deal with excessive FFA levels. During the first stage of this approach, an acid-catalysed reaction is used to esterify the FFA into fatty acids methyl esters (FAME), which is then followed by an alkali-catalysed transesterification reaction [20]. The FFA concentration in the raw materials must be between 0.5% and 3% for the necessary conversion rate to be achieved by using an alkali-catalysed transesterification.[35].

As the transesterification process is the popular method and will be use in this study, the influence kinetics or parameter of this process have been investigated. The critical variables impacting the transesterification reaction, according to several researchers, are the reaction temperature, reaction time, catalyst concentration and molar ratio of oil and alcohol.

4.1. Effect of reaction temperature

The transesterification process is an endothermic reaction and temperature affects the amount of biodiesel generated in a transesterification process [36]. Generally, the biodiesel production will be increase as the reaction temperature increase, this resulting decreases of the viscosity value of oil. This is because the oil's viscosity remains high at low temperatures, and the absence of a reaction temperature resulted in insufficient mixing of the reactants [37]. However, increased reaction temperature above the optimal temperature reduces biodiesel synthesis by evaporating the alcohol. Evaporation of the transesterification alcohol caused by a reaction temperature greater than the alcohol's boiling point reduced its availability, lowering the alcohol-oil contact duration, and decreasing the total biodiesel output [38]. Based on research by [8], the optimum temperature for WCO in transesterification process was 60^{o}C. The research with high free fatty acid of WCO done by [24], the optimum temperature for WCO in transesterification process was 75^{o}C. The research with low free fatty acid of WCO done by [25], the optimum temperature for WCO in transesterification process was 65^{o}C.

4.2. Effect of reaction time

In general, the output of biodiesel increases as the reaction time increases. The ideal transesterification reaction period, on the other hand, is depends on the feedstock, catalyst, and concentration. When compared to acid catalyst, base catalyst produced the most biodiesel at a rate of 4000 times faster. This is one of the reasons why acid catalyst is commonly adopted as a pretreatment before transesterification process [39]. The shortage of reaction time will cause the raw material and alcohol did not mixing and disperse appropriately. The biodiesel yield is minimal at the start of the process. The feedstock has been changed throughout time to two main triglycerides, monoglyceride and diglyceride, facilitating the synthesis of biodiesel. The production reaction took off with a sufficient amount of mono and diglycerides and reached equilibrium at the optimum reaction time [40]. However, the reaction was forced to preserve equilibrium when the reaction time was too long. The ester was hydrolysed and then saponified. These two situations led to low biodiesel yields in the end [41]. Research from [8], the optimum reaction time for transesterification process of waste cooking oil was 60 min. The research with high free fatty acid of WCO done by [24], the optimum reaction time for transesterification process of waste cooking oil was 5 h of reaction. The research with low free fatty acid of WCO done by [25], the

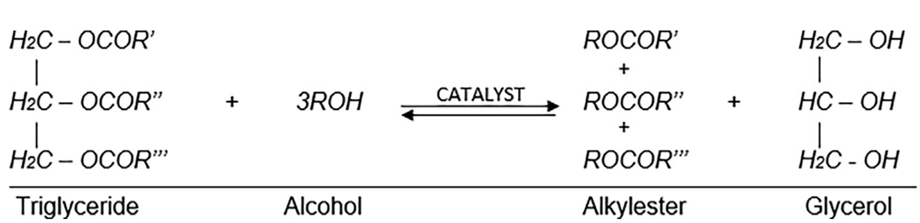

Fig. 1. Reaction mechanism structure of transesterification process.

optimum reaction time for transesterification process of waste cooking oil was 4 h.

4.3. Effect of catalyst

The type of catalyst and its concentration are essential in transesterification. Acid catalyst is better for feedstocks with a high FFA level, while base catalyst is better for feedstocks with a low FFA level. A catalyst, regardless of its type, accelerates a reaction by reducing the activation energy of the reaction [42]. Catalyst concentration is one of the most important factors affecting biodiesel yield. Lower catalyst concentrations usually result in less biodiesel being produced. The reasons for the poor yield is that there is less catalyst present, which implies that there is less catalytic surface available for the transesterification process to take place [43]. As the catalyst concentration increased, yields often peaked and subsequently dropped. Increased catalyst concentration reduced biodiesel yield by forming slurry, increasing viscosity, and then increasing soap formation [43]. As the soap formation increase, the biodiesel production will be decrease. Therefore, when it came to biodiesel production by transesterification, the optimal amount of catalyst was typically investigated. Table 5 shows catalyst were used for biodiesel production from waste cooking oil via transesterification process with their percentage of yield.

4.4. Effect of alcohol to oil ratio

The alcohol to oil molar ratio is one of the most important transesterification variables. Various types of alcohol may be used to make biodiesel, such methanol, ethanol, isopropyl alcohol, propanol, pentanol, and butanol [42]. Based on study, methanol is widely favoured for producing biodiesel because its commercial significance is smaller than that of other longer chain alcohols. As a result, it is a less expensive choice for biodiesel transesterification. There is no azeotrope with water also in methanol. It may thus be recycled easily for the manufacture of biodiesel [46]. In transesterification, the catalyst type influences the oil to methanol ratio. Acid catalyst, in contrast to base catalyst, necessitates a greater oil to methanol ratio. For acid catalyzed transesterification, a 1:15 oil to methanol ratio is required, whereas for base catalyzed transesterification, a 1:6 oil to methanol ratio is probably preferable [47]. Insufficient or excessive methanol resulted in a poor biodiesel output. If the ratio of oil to methanol is too low, the reaction will not proceed to product production. Instead of making biodiesel, the transesterification reaction will reverse towards the reactants. This is due to the fact that the trans esterification process is reversible [48]. Optimum molar ratio of methanol to oil for production of biodiesel from WCO via transesterification process was 1:6 [8]. The research with high free fatty acid of WCO done by [24], molar ratio of ethanol to oil for production of biodiesel from WCO via transesterification process was 10:1. The research with low free fatty acid of WCO done by [25], molar ratio of methanol to oil for production of biodiesel from WCO via transesterification process was 15:1.

Table 5
Catalyst use for biodiesel production from waste cooking oil with percentage of yield.

Catalyst	Yield (%)	Ref.
NaOH	89.8	[7]
H_2SO_4	95	[44]
KOH	97.5	[44]
CaO	93	[8]
$SrO–ZnO/Al_2O_3$	95.7	[24]
CaO/Al_2O_3	30.91	[45]

5. Comparison of Biodiesel, diesel and Gasoline.

Biodiesel made from natural and renewable resources has been proven to be a superior alternative to present diesel, particularly for transportation. Table 6 shows the comparison of biodiesel, diesel and gasoline properties based on the ASTM standard. Biodiesel have a better advantage compared to diesel and gasoline. In term of emission when comparing biodiesel and others, the majority of studies have reported significant decreases in exhaust emissions. The existence of sufficient oxygen in biodiesel is one of the more widely acknowledged reasons for the reduction of emissions, including CO, CO_2, hydrocarbons, SO_2, particles, and smoke. Biodiesel contains 10% oxygen, whereas diesel contains no oxygen [49]. As stated in Table 5, biodiesel surpasses diesel and gasoline in a number of categories, including higher cetane number, low ash content, and low carbon residue, while the other attributes can be enhanced through blending [33]. High cetane value will reduce the ignition value for better performance of engine and emission [22].

Biodiesels contain high number of viscosities compared to diesel. Viscosity influences fuel injection systems performance, especially when fuel fluidity is affected by an increase in viscosity at low temperatures. High viscosity causes low fuel spray atomisation and less precise operation of fuel injectors. As the lower the viscosity of the biodiesel, the easier it is to pump and atomize and achieve finer droplets [33]. The most significant advantage of biodiesel over petroleum diesel is its environmental friendliness. Portability, easy availability, renewability, better combustion efficiency, and lower sulphur and aromatic content are all benefits of biodiesel as a diesel fuel [18]. The biodegradability of biodiesel has been offered as a waste solution. Biodiesels have a growing number of possible applications and are environmentally friendly.

6. Conclusion

In terms of biodiesel generation from waste cooking oil (WCO), the following significant factors were emphasized. Biodiesel has been proven to be the most effective alternative to fossil fuels. Because it is renewable, biodegradable, and non-toxic, it outperforms petroleum-based fuels. WCO has a lot of potential as a biodiesel source material because of how much waste cooking oil is created around the world. WCO is more likely than other raw materials to play a larger part in future biodiesel manufacturing due to its lower cost. WCO, on the other hand, necessitates a number of pretreatment steps in order to remove solid impurities and reduce FFA and water content. The transesterification process is used in biodiesel synthesis under the influence of many parame-

Table 6
Comparison between biodiesel, diesel and gasoline.

Properties	Biodiesel [50]	Diesel [50]	Gasoline [5152]
Flash point (°C)	130 minimum	60–80	−13
Pour Point (°C)	−15 - −16	−35 - −15	–
Kinematic viscosity at 40°C (mm^2/s)	1.9 – 6.0	2.0–4.5	1.0–1.68
Density at 15°C (kg/m^3)	880	820–860	750–765
Cetane number	47 minimum	46	13–17
Ash content (%)	–	100 maximum	–
Carbon residue (%)	0.05 maximum	0.2 maximum	85.5
Sulphur content (%)	0.002 maximum	–	–
Water content (%)	0.005 vol% maximum	0.05 maximum	–
Higher heating value (MJ/kg)	42.65	46.48	47.3

ters such as temperature, reaction time, catalyst concentration, and oil molar ratio to alcohol. Biodiesel has a number of advantages over diesel, including a higher cetane number, lower ash percentage, and lower carbon residue. It also features improved engine ignition and emission performance.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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