A comparative review of some physicochemical properties of biodiesels synthesized from different generations of vegetative oils

Fozy Binhweel 1,2, Murad Bahadi 3, Hassan Pyar 2, Alyaa Alsaedi 1, Md. Sohrab Hossain 1 and Mardiana Idayu Ahmad 1*  

1 Environmental Technology Division, School of Industrial Technology, Universiti Sains Malaysia, 11800 Penang, Malaysia  
2 College of Environmental Science and Marine Biology, Hadhramout University, Hadhramout, Yemen.  
3 College of Education, Hadhramout University, Hadhramout, Yemen  
* Corresponding author: mardianaidayu@usm.my

Abstract. Physicochemical properties of different biodiesel generations synthesized from 11 vegetative oils have been reviewed in purpose of comparing the values of biodiesel physicochemical properties and determination the required feedstock for preferable biodiesel. According to the review, two main factors are affecting the physicochemical properties of yielded biodiesel; the first factor is the raw material of vegetative oil that leads to inherent properties like the energy content, cloud, pour, flash points, kinematic viscosity, cetane and iodine numbers. The other factor is synthesis method and handling procedures of biodiesel production which results in properties such as alcohol and glycerin content, suspended solids, and acid value. This review focuses on 9 important physicochemical properties; Density at 15°C, kinematic viscosity at 40°C, cloud, pour, and flash points, heating value, acid value, Cetane number, and iodine number. The standards of ASTM D6751, EN 14214, IS 15607, and MS 2008:2008 are provided to check matching with the physiochemical properties of reviewed biodiesels.

1. Introduction
The global demand of fossil oils as a source of non-renewable energy is growing fast. Based on International Energy Agency, the increasing energy consumption will reach 30% in 2040 [1]. Unfortunately, most of the provided energy sources are non-renewable, which is considered unsustainable due to sharp depletion of resources and degradation of the environment [2]. We, as a human race, will reach a point zero in terms of energy resources if our consumption stays unsustainable. Therefore, researchers of sustainable and clean energy resources had triggered this critical issue long time ago. [3].

Biodiesel is one of those promising substitutes that can achieve sustainability and eco-friendliness [4]. Some researches defined biodiesel as the alkyl esters from vegetative and animal oils. However, others said that the blended mixture of diesel and vegetative origin oil is still considered biodiesel. [5].
The definition of the American Society for Testing and Materials (ASTM) for biodiesel is “monoalkyl esters of long-chain fatty acids resulting from edible oils, non-edible oils, and waste oils” [6]. In technical terms, it is the alkyl esters of fatty acids produced through transesterification of vegetative or animal oils with alcohols promoted by acid or base catalyst in specific reaction temperature [5].

Based on feedstock sources, biodiesels are classified into four generations. The first generation is synthesized from edible oils. Biodiesels produced from vegetative oils of soybean, canola, rapeseed, and palm plants are considered the first biodiesel generation. Nonedible oils are second generation such as biodiesel produced from *jatropha curcas*, *madhuca indica*, and *pongamia pinnata* in India [7]. The third generation is waste oil used in fry and other purposes. Some researchers classify biodiesel produced from microalgae as the third generation. The fourth generation includes synthetic biology technology which is considered infancy in terms of conducted researches [4], [8].

Transesterification is the process to produce biodiesel. It is a reversible chemical reaction between oil and alcohol in presence of catalysis. During transesterification, the alkyl group of the oil ester is exchanged by another alkyl group in alcohol [9]. Short chains of alcohols like methanol, ethanol, propanol, and butanol are appropriate for this process. However, methanol and ethanol are commonly used for their affordability and physical and chemical characteristics. [10]. Transesterification can be catalyzed by acid, base, or enzymatic catalysts [11]. Biodiesel is synthesized by transesterification of triglycerides with methanol. The acidic or alkaline catalyst is preferable to fasten the reaction. This process will yield methyl esters and glycerol as a by-product that can be used in detergent industry.

Biodiesels, or what we can call it chemically Fatty Acid Methyl Esters (FAME), possess different physicochemical properties based on feedstock and synthesis method. Properties like high heating value, cetane number, fast biodegradable ingredients, and less carbon monoxide emissions are preferable as a fuel for diesel engines and surrounding environment [4].

In this review, physicochemical properties of biodiesels synthesized from fatty acids of 11 vegetative oils were studied. The review collected information regarding biodiesel production and physicochemical properties from different references. Descriptive analysis has been conducted to provide comparative information that will help researchers who are interested. Moreover, standards of biodiesel have been provided from ASTM D6751, EN 14214, IS 15607, and MS 2008:2008 to match reviewed values.

### 2. Biodiesel Chemistry

The vegetative source of oil determines the chemical composition of biodiesel. Saturation, unsaturation degree, and carbon chain length are affected by the fatty acids within the oil [12]. The vegetative oils are classified by chemical composition of fatty acids. Therefore, analytical chromatography is usually conducted to identify fatty acids content of the oil [13]. Fatty acids, which are dominant in vegetative oils, are monounsaturated such as oleic acid (C18:1; 6.2 – 71.1%), saturated such as palmitic acid (C16:0; 4.6 – 20.0%), and polyunsaturated fatty acids like linoleic acid (C18:2; 1.6 – 79%) [14]. To produce biodiesel, 1 mole of the oil triglycerides reacts with 3 moles of alcohol. The output will be 3 moles of methyl esters plus 1 mole of glycerol as in the reaction equation below as shown in Figure 1 [15].

Characteristics of vegetative oil fatty acids and how they affect the biodiesel production process were studied [16]. The findings showed that low cetane numbers are related to more highly unsaturated fatty acids. High cetane number enhances ignition properties. It ensures active cold start properties and reduces the white smoke emissions. Iodine number can be a measurement indicator for the unsaturation condition of oil. Higher iodine number means higher unsaturated fatty acids within oil. Even though, biodiesel production process has no great influence on iodine number, that is why it seems identical for biodiesel and its vegetative roots. [17]. Going to the stability of oxidation, it is observed that oxidation stability goes down if the polyunsaturated fatty acids were high. Furthermore, fatty compounds Stability can be affected by variables like atmosphere, extremely high temperatures, presence of metals, peroxides, radiation, or double bonds within internal compounds structure [16], [18].
Figure 1. Transesterification reaction of triacylglycerol (Vegetable oil).

3. Biodiesel Standards

International bodies specified standards sets for synthesizing biodiesel. In United States, ASTM developed ASTM D6751 standards for biodiesel. In European Union, European Committee for Standardizations CEN developed biodiesel standards EN 14, 214 [4], [17]. In India, The National Standards Body of India developed IS 15607 for biodiesel production. MS 2008:2008 was developed in Malaysia as Malaysian standards of biodiesel. Table 1 shows Comparison of four standards sets for biodiesel. The standards are guidelines to check physicochemical properties of the synthesized biodiesel from different vegetative oil sources. Biodiesel must fulfill these physicochemical standards specifications to be used in the assigned area.

| No | Physicochemical properties | Units | ASTM D6751 | EN 14214 | IS 15607 | MS 2008:2008 |
|----|---------------------------|-------|------------|-----------|-----------|---------------|
| 1  | Density at 15 °C          | Kg/m³ | 880        | 860 – 900 | 860 – 900 | 860 – 900     |
| 2  | Kinematic viscosity at 40°C | mm²/s | 1.9 – 6.0  | 3.5 – 5.0 | 2.5 – 6.0 | 3.5 – 5.0     |
| 3  | Cloud point °C            |       | -3 to -12  | -         | -         | -             |
| 4  | Pour point °C             |       | -15 to -16 | -         | -         | -             |
| 5  | Flash point °C (Minimum)  |       | 130        | 101       | 120       | 120           |
| 6  | Acid number (mg KOH/g)    |       | 0.5        | 0.5       | 0.5       | 0.5           |
| 7  | Boiling point °C          |       | 100 - 615  | -         | -         | -             |
| 8  | Cetane number (Minimum)   |       | 47         | 51        | 51        | 51            |
| 9  | Iodine number (g I₂/100 g) |       | -         | 120       | -         | 110           |
| 10 | Carbon residue (% m/m)    |       | 0.05       | 0.3       | 0.05      | -             |
| 11 | Sulphur Content ppm       |       | -         | -         | -         | 10.0          |
| 12 | Carbon wt %               |       | 77        | -         | -         | -             |
| 13 | Oxygen wt %               |       | 11        | -         | -         | -             |
| 14 | Hydrogen wt %             |       | 12        | -         | -         | -             |
| 15 | Phosphorus Content % mass |       | 0.001     | 0.001     | 0.001     | 0.001         |
| 16 | Monoglycerides % mass     |       | -         | 0.8       | -         | 0.8           |
| 17 | Diglycerides % mass       |       | -         | 0.2       | -         | 0.2           |
No | Physicochemical properties | Units | ASTM D6751 | EN 14214 | IS 15607 | MS 2008: 2008 |
--- | --- | --- | --- | --- | --- | --- |
18 | Triglycerides | % mass (Maximum) | - | 0.2 | - | 0.2 |
19 | Free glycerine | % mass (Maximum) | 0.02 | 0.02 | 0.02 | 0.02 |
20 | Total glycerine | % mass (Maximum) | 0.24 | 0.25 | 0.25 | 0.25 Max |
21 | Water and sediment | Vol% or mg/kg (Maximum) | 0.005 vol% | 500 mg/kg | 0.005 vol% | - |
22 | Cold Filter Plugging Point (CFPP) | °C (Maximum) | +5 | - | - | - |
23 | Saponification value | mg KOH/g (Minimum) | 370 | - | - | - |
24 | Lubricity (HFRR) | % mass (Maximum) | 0.002 | 0.02 | 0.002 | 0.02 |
25 | Distillation temperature | °C | 520 Max. | - | - | - |
26 | Oxidation stability | Time: hour (Minimum) | - | 3 | 6 | 6 |
27 | Sulphated ash content | % mass (Maximum) | 24 | 24 | 24 | 24 |
28 | Total contamination | mg/kg (Maximum) | 0.2 | 0.2 | - | 0.2 |
29 | Methanol Content | mg/kg (Maximum) | 500 | 500 | - | 500 |
30 | Water Content | mg/kg (Maximum) | - | - | - | - |

4. Biodiesel physicochemical properties

Biodiesel produced from vegetative oil has inherent physicochemical properties derived from vegetative raw oil properties. It was reported that the synthesized biodiesel takes most of its physicochemical properties from its raw material [4].

Other biodiesel physiochemical properties resulted from handling procedures and synthesizing method of the production. The synthesized-related physicochemical properties influence biodiesel fuel performance. Examples of such physicochemical properties are alcohol and glycerin content, suspended solids, and acid value [24]. Here in this comparative review, 9 physicochemical properties were chosen to be elaborated. Values of biodiesel generations synthesized from 11 different vegetative oils were listed. Table 2 was collected according to the reviewed literatures. It shows values of the 9 most important physiochemical properties for the 11 biodiesel generations to be compared and determined the preferable and unfavorable biodiesel for the engine performance and the environmental impact.

Table 2. Comparison of physiochemical properties of biodiesels from 11 different vegetative oil sources.

| Biodiesel Sources | Density at 15°C (Kg/m³) | Kinematic Viscosity at 40°C (mm²/s) | Cloud Point (°C) | Pour Point (°C) | Flash Point (°C) | Heating Value (MJ/Kg) | Acid Value (mgKOH/g) | Cetane Number | Iodine Number (g I/100g) | References |
|---|---|---|---|---|---|---|---|---|---|---|
| Soybean | 882 | 4.15 | 0.4 | 3 | 160 | 39.76 | 0.18 | 58.1 | 11.7 | [4], [25], [28] |
| Coconut | 867 | 3.1435 | -1.6 | -8.3 | 118.5 | 38.2 | 0.18 | 64.65 | N/A | [4], [29], [30] |
| Mustard | 888.9 | 5.53 | 16 | -18 | 169.16 | 41.91 | 0.2 | 56 | 128 | [4], [31], [33] |
| Sunflower | 869 | 4.10 | 1 | -2 | 183 | 40.6 | 0.357 | 49 | 128.7 | [4], [12], [25], [34], [35] |
| Palm | 880 | 4.52 | 14.25 | 14.33 | 175 | 34.41 | 0.25 | 54.6 | 50.5 | [4], [25], [36], [38] |
| Sesame | 867 | 4.580 | -1.5 | -9 | 180 | 40.1 | 0.32 | 56.32 | 80.32 | [39], [41] |
| Camelia | 885 | 4.53 | 2.5 | -6.3 | 150 | 52.2 | 0.36 | 52.8 | 146.5 | [4], [42], [43] |
| Jatropha | 880 | 4.80 | 4 | 2 | 175.5 | 40.79 | 0.48 | 57.1 | 95.75 | [4], [25], [44] |
4.1. Density at 15°C
Density of biodiesel is biodiesel’s mass divided by its volume. The measurement of biodiesel density should be conducted at 15°C as a standard [51]. Density is used to determine the amount of biodiesel pumped by injection batches for fuel combustion [22]. It is influenced by unsaturation degree of fatty acid methyl esters. Biodiesel is always denser if we compare it with conventional diesel. In case of blended fuel, petroleum diesel will decrease the density of the mixed blended fuel [4]. Figure 2 shows comparison of density at 15°C for different generations of biodiesels. It ranges from 888.9 kg/m³, for mustard biodiesel, to 867 kg/m³, for sesame and coconut biodiesel.

4.2. Kinematic viscosity at 40°C
Liquid resisting to be flowed is what we call it kinematic viscosity [51]. Comparing with petroleum diesel, biodiesel possesses higher kinematic viscosity value as a result of heavier molecular mass within biodiesel [8]. An inadequate fuel atomization happens as a result of high kinematic viscosity which leads to inefficient thermal combustion and deposition of dirt and debris. In contrast, low kinematic viscosity creates small size of fuel droplets that facilitate fuel transfer for combustion which increases thermal efficiency [4]. Kinematic viscosity is measured at 40°C as a standard. According to figure 3, the kinematic viscosity of pond algae biodiesel 5.82 mm²/s is the highest, and the kinematic viscosity of coconut biodiesel 3.1435 mm²/s is the lowest.
Figure 3. Comparison of kinematic viscosity at 40°C for biodiesels synthesized from different vegetative oils.

4.3. Cloud point
It is the temperature point when biodiesel starts forming cloud or crystal particles. In general, cloud point is used to fix control of fuel at the low temperature. The high values of cloud point are considered not good property for biodiesel because crystals can be formed in the ordinary weather. Such fuel crystals generate engine-related problems [52]. In the given table 2 and figure 4, the highest cloud point 16°C and 14.25°C for mustard and palm biodiesels respectively are unpreferable, particularly in cold weather areas, whereas the lowest cloud point in negative temperature values -5°C, -3.3, and -1.6 for sesame, canola, and coconut biodiesels respectively are most preferable.

Figure 4. Comparison of cloud point for biodiesels synthesized from different vegetative oils.

4.4. Pour point
It is the temperature point when biodiesel cannot be poured anymore as a result of forming gel-like material. [52]. Pour point is an important characteristic for cold flow process because fuel is adequate if it is above pour point. Biodiesel always has pour point higher than conventional diesel [4]. Lower values under zero temperature are most desirable in the fuel because it can be flowed even in cold weather. Otherwise, the high values of biodiesel pour point will cause several troubles in engine walls.
and pipes like slowing, or even stopping, pumping fuel to the engine and clogging filters [52]. Most of the provided biodiesel pour points in figure 5 are low negative values. The lowest values are -18°C and -16°C go for mustard and pond algae biodiesel respectively. The highest pour point is 14.33°C, which is unpreferable, goes for palm biodiesel.

![Figure 5. Comparison of pour point for biodiesels synthesized from different vegetative oils.](image1)

### 4.5. Flash point

It is the least temperature point in standard atmospheric conditions, at which biodiesel fuel specimen ignites [53]. Flash point value of biodiesel is always above flash point value of fossil fuel diesel. Conventional diesel has flash point value between 55 – 65°C. The reason behind the higher values of biodiesel flash point is that the low volatility within biodiesel. That’s why biodiesel is considering safer in transit and storage cases [54]. In this review, flash point values of different biodiesel sources range between 118.5°C to 183°C for coconut and rubber biodiesel respectively.

![Figure 6. Comparison of flash point for biodiesels synthesized from different vegetative oils.](image2)
4.6. Heating value

It is the biodiesel thermal content within unit quantity getting freed by combustion if biodiesel fuel was totally burned in controlled and calculated conditions [53]. Therefore, heating value is another expression for the energy content of biodiesel. Unsaturated situation level of biodiesel influences heating value because unsaturated esters possess high volumetric energy and low mass energy [55]. Compared with fossil fuel diesel, biodiesel is 10% less in terms of energy content or heating value [4]. Figure 7 shows that the highest heating values 52.2, 42.372, 41.91, 40.8, 40.79, and 40.6 MJ/kg are for camelina, rubber, mustard, pond algae, Jatropha curcas L, and Sunflower biodiesels, whereas the lowest heating value is 34.41 MJ/kg for palm biodiesel.

![Figure 7. Comparison of heating value for biodiesels synthesized from different vegetative oils.](image1)

4.7. Acid value

It is the free fatty acids present in the fuel sample [4]. Acid value is measured by the amount of potassium hydroxide in milligrams needed for neutralizing the content of organic acids in one gram of fuel [56]. Acid value is one of those physiochemical properties inherited from the raw oil used in transesterification to synthesize biodiesel. High acid value means high free fatty acids that result in corrosion in fuel delivery channels and pipes [20], [22]. The provided acid values in table 2 range from 0.12 mg/g for rubber biodiesel, to 0.48 mg/g for canola and jatropha curcas L biodiesel as it is shown in figure 8.

![Figure 8. Comparison of acid value for biodiesels synthesized from different vegetative oils.](image2)
4.8. Cetane Number
It is defined as the ordinary cetane percentage by volume if biodiesel fuel combustion is conducted in a standard engine under specified burning and operating conditions [53]. High cetane number means that the biodiesel would ignite fast in the engine within the combustion chamber. Otherwise, low value of cetane number is a sign for incomplete combustion that would lead to more exhausted emissions [19], [57]. As a comparative in figure 9, the highest cetane number is 64.65 that goes for coconut biodiesel and the lowest is 49 that goes for sunflower biodiesel. The other biodiesels have cetane number values within 50s.

![Figure 9. Comparison of cetane number for biodiesels synthesized from different vegetative oils.](image)

4.9. Iodine Number
Biodiesel unsaturated condition is known as iodine number [58]. Iodine number refers to the amount of absorbed iodine molecules by double bond of fatty acid methyl esters molecules. Even though, it doesn’t give a significant importance for double bonds positions which are there for oxidation. Iodine number is influenced by a couple of biodiesel characteristics like cetane number, CFPP, and kinematic viscosity [19]. In figure 10, we can notice high range of iodine number values from the lowest value 11.7 g I₂/100g which belongs to soybean biodiesel to the highest value 146.5 I₂/100g which belongs to camelia biodiesel.

![Figure 10. Comparison of iodine number for biodiesels synthesized from different vegetative oils.](image)
5. Conclusion

Based on the reviewed data, it is inferred that the physicochemical properties of biodiesel fuel are dependent on the chemical composition of the raw vegetative oil and the synthesizing procedures. There is a wide spectrum of vegetative oils to be extracted from different biomass feedstocks that can be sources for biodiesel production. However, determination of the proper biomass feedstock depends on availability, affordability, and economical feasibility of feedstock itself. Each feedstock produces biodiesel with own physicochemical properties values depending on the inherited characteristic of the raw oil. For good biodiesel quality, less polyunsaturated and more saturated fatty acids are crucial components. The recommended oil feedstocks for biodiesel synthesis are non-edible and discarded oils since they do not cost much. Plus, avoiding edible oils is an ethical initiative to make food needs out of the competition with energy resources. Overall, the physicochemical properties of any biodiesel should meet biodiesel standards issued by ASTM D6751 in US, EN 14214 in EU, IS 15607 in India, and MS 2008:2008 in Malaysia.

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