



METHANOLYSIS REACTION FOR PRODUCTION OF BIODIESEL FROM PALM-OIL

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ABSTRACT

Clean and effective Biodiesel was produced using perfect methodology, the produced biodiesel has the following properties which is in agreement with the standard of the ASTM. The properties are as follows; Flash point was found to be 150°C, Moisture content was found to be 0.12%, Cloud point was 10.5°C, Pour point was found to be 4°C, Viscosity was found to be 3.90mm²/s and Cetane number was found to be 60. All the values are in agreement with the standard of the ASTM. The average yield was found to be 91.71% and the highest yield was found to be 99.87%.

INTRODUCTION

Biodiesel production is performed through several chemical engineering processes but the most commonly employed is the process of transesterification, in which animal fat or vegetable oil is combined with a low molecular weight alcohol such as methanol and ethanol and a catalyst to produce an alkyl ester (biodiesel, B100) and glycerol (Afshar Ghotli, *et al.*, 2015; I. M. Atadashi, *et al.*, 2015). It has a reducing characteristic for greenhouse gas emissions, helps in reducing a country's dependence on crude oil importations, it aids agricultural activities by providing a new market for domestic crop-plants, it has high lubricating properties that eradicate the need for any lubricating additives and it has broad acceptance by vehicle manufacturers (Calero, *et al.*, 2014; Talebian-Kiakalaieh, Amin, & Mazaheri, 2013).

Energy from renewable sources, that use indigenous resources have the potential to offer energy services with zero or almost zero emissions of both

greenhouse gases and air pollutants. Renewable energy technologies create marketable energy by converting natural materials into useful forms of energy (Singh, *et al.*, 2014). Currently, energy from renewable sources supply 14% of the total world energy demand (Sharma, *et al.*, 2008). Large-scale hydropower supplies 20% of global electricity. Energy from renewable sources are derived from those natural, mechanical, thermal, and growth processes that repeat themselves within our lifetime and may be relied upon to produce predictable quantities of energy when required. Renewable technologies like hydro and wind power probably would not have provided the same fast increase in industrial productivity as fossil fuels (Chongkhong, Tongurai, & Chetpattananondh, 2009). Thus the share of Energy from renewable sources is expected to increase very significantly (30 to 80% in 2100). Biomass, wind, and geothermal energy are commercially competitive and are making relatively fast progress (Ayhan Demirbas, 2008).

SUCCINCT HISTORY OF BIODIESEL

Biodiesel was first utilized by German scientist, Rudolph Diesel, the inventor of compression ignition (CI) diesel engine in 1900. Because of the availability of crude oil in large reserves and its easy refining process and use on diesel engines, the direct use of peanut oil as a fuel to run the diesel engine was not broadly put in to practice. Hence, both animal fats and vegetable oils were neglected as sources of fuel. But, recently, because of the realization that crude oil is no more abundantly available, and poses threat to the wellbeing of mankind due to emissions of carbon-dioxide gases, vegetable oil especially has been used for its efficiency as fuel in CI diesel engines (B.H. Hameed, L.F. Lai, & Chin, 2009; Murzin & Simakova, 2013). On the other hand, because of low volatility and high viscosity, its long-term use posed diverse difficulties such as ring sticking, deposition, and injector choking in engine. For this reason, augmentation in the vegetable oil was seen to improve the fuel quality. Thus, to reduce the viscosity of vegetable oils and animal fats; thermal and chemical processes were tried to make fats and oils compatible with CI diesel engines (Muralidhar, Chirumamila, Marchant, & Nigam, 2001). The well-known thermal process pyrolysis, resulted in the production of low value materials and sometimes resulted in the production of more gasoline instead of diesel fuel (A. Demirbas, 2003). Other processes such as blending and micro-emulsification of vegetable oils also reduce the viscosity although still posed a small number of problems. These problems were namely lubricating oil contamination and carbon deposition. Hence, transesterification reaction is the most suitable process for plummeting the viscosities of vegetable oils (Balat & Balat, 2008; Huang & James I. C., 2010; Montgomery, 1997).

RENEWABLE ENERGY USE AND INTEREST

The bio-energy commercialization has offered an efficient way to decrease the difficulty of petroleum shortage and the influence on environment. In this circumstance, substantial quantities of researches were performed over the past three decades, to increase this new sustainable and renewable energy resource that might function as an alternate for petroleum. In comparison to diesel, biodiesel is said to be carbon neutral, as biodiesel yielding plants take in more carbon-dioxide than that added to the atmosphere when used as fuel (Gerpen, 2008.; Hass, McAloon, Yee, & Foglia, 2006). Further, biodiesel is exceedingly biodegradable in soil as well as in fresh water. In addition, under aerobic or anaerobic conditions, the best part of biodiesel (90–98%) is mineralized in 21–28 days. Also, the use of biodiesel in diesel engines

significantly reduces the emissions of carbon monoxide, hydrocarbons, particulate matter and Sulphur dioxide and leads to minimization of the intensity of greenhouse effects. Additionally, biodiesel is better than diesel fuel in terms of combustion efficiency, aromatic content, flash point, and cetane number. Only nitrogen oxides emission increases; this behavior is because of the oxygen content of biodiesel fuel (Harding, Dennis, von Blottnitz, & Harrison, 2008; Hayyan *et al.*, 2011).

MARKET PENETRATION OF BIODIESEL FUEL

The global biodiesel production has grown from approximately 5 million gallons in 2001 to 250 million gallons in 2006 (Nakpong, 2010; Rashid, Anwar, Moser, & Ashraf, 2008). Although high oil prices have lately tended to reduce production of biodiesel, several forces may contribute to long-term expansion in the biodiesel industry (Rashid, *et al.*, 2008): High petroleum prices are raising diesel prices and the likely increasing costs of future oil production; Depletable resources follow Hotelling's prices in the long run and tend to increase over time, as petroleum is depleted; Government mandates, such as the provisions of the Energy Independence and Security Act of 2007 that includes mandates of up to 36 million gallons of biofuels; the public and government's concern over global warming may provide a value for biodiesels carbon-dioxide (CO₂) recycling characteristics (Sharma, *et al.*, 2008).

Germany, Belgium, and France are the top countries, ranked by their potential biodiesel volumes. In one hand, this was not unexpected as they are among the top palm and soybean growers; the two are the most widespread oil-seed crops in the world (According to United States Department of Agriculture USDA). Together, they constitute over 70% of the total biodiesel volume potential (Casas, Fernández, Ramos, Pérez, & Rodríguez, 2010; Ramadhas, Muraleedharan, & Jayaraj, 2005). Conversely, countries from West that have limited land area for oil-seed cultivation use animal fats as feed stocks. Processed animal fats are a by-product of the animal slaughter industry, with few competing commercial applications can contribute to low-cost biodiesel production. Besides the feed stocks, the final cost is depended also on the purification technologies in addition to the production technologies (Casas, *et al.*, 2010; Chongkhong, *et al.*, 2009).

PRODUCTION TECHNOLOGIES

There are four primary technologies used for making biodiesel from animal fats and vegetable oils which include; direct/blends, microemulsion, pyrolysis and transesterification (Hayyan, *et al.*, 2011; Leung, *et al.*, 2010).

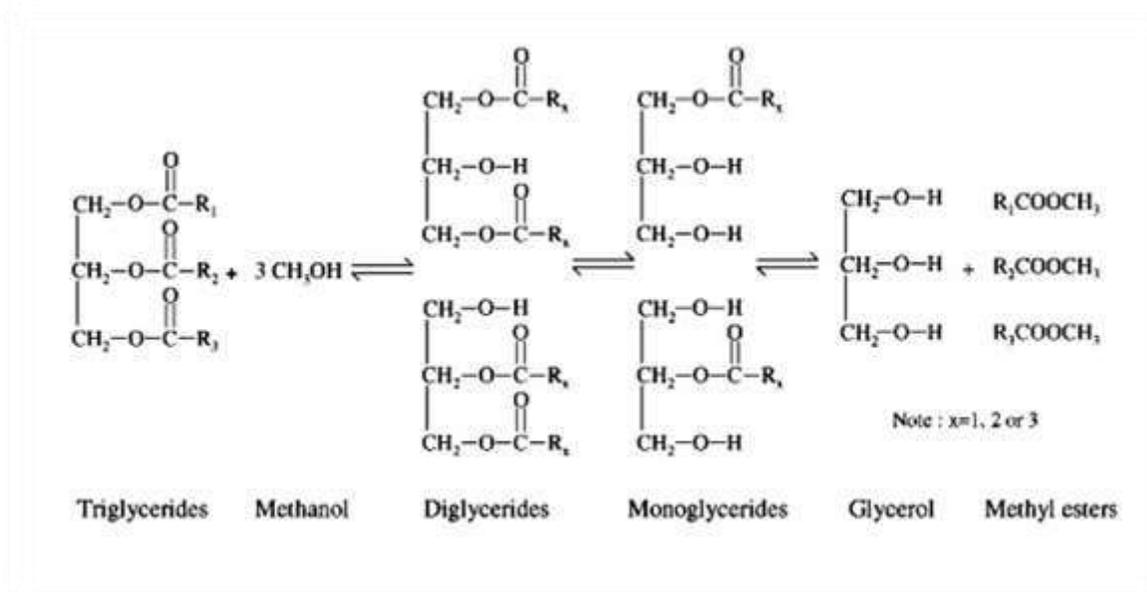


Figure 1: Reactions in the transesterification of a triglyceride (24. A.Z. Abdullah, (2007)).

Mechanism for the production of Biodiesel.

The mechanism of the acid-catalyzed transesterification of vegetable oils is shown in Figure 2. It can be extended to di- and triglycerides. The

protonation of carbonyl group of the ester leads to the carbocation, which after a nucleophilic attack of the alcohol produces a tetrahedral intermediate. This intermediate eliminates glycerol to form a new ester and to regenerate the catalyst (A. Demirbas, 2009).

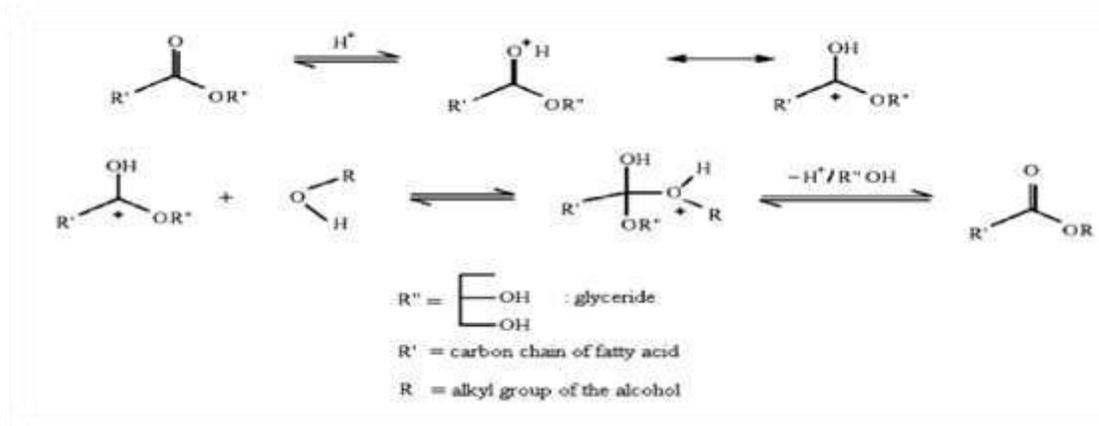


Figure 2: Mechanism of the acid-catalyzed transesterification (A. Demirbas, 2009)

MATERIALS AND METHODS

Methanol, sulphuric acid, potassium hydroxide, crude palm-oil, sodium sulphate, transesterification reactor, water bath, beakers, separating funnel, evaporation apparatus, thermometer and conical flasks.

Two-Step Alkali-catalyzed Transesterification Reaction

In the acid-catalyzed esterification process, the following conditions were adopted; oil to alcohol molar ratio, 10:1, time of reaction, 90min., temperature, 60°C, and 3% of H₂SO₄. The reaction mixture was then poured into a separating funnel to remove excess alcohol, sulfuric acid and impurities.

The sample produced having free fatty acid of 0.185% was used for the alkali-catalyzed transesterification reaction. The crude palm oil has an initial free fatty acid value of 3.451%. The experimental set-up for alkali-catalyzed transesterification was the same as the

one used for acid-catalyzed pretreatment process. It is worthy to mention that the experimental conditions presented in **Table 1** were adopted for the two-step experimental process.

Table 1: Yields of Biodiesel (Two-step transesterification)

Run	Factor 1 A:Temp.°C	Factor 2 B: Time-min.	Factor 3 C: Cat. Conc %	Response 1 R1 % (Yield)
1	63.00	90.00	1.50	89.85
2	63.00	90.00	0.50	94.01
3	59.00	45.00	1.00	99.66
4	55.00	67.50	1.00	98.92
5	59.00	67.50	1.00	97.15
6	55.00	90.00	1.00	98.97
7	59.00	67.50	1.00	99.13
8	63.00	67.50	1.00	96.45
9	63.00	45.00	0.50	83.54
10	59.00	67.50	1.50	99.87

ANALYSIS OF BIODIESEL

The yields of biodiesel samples were analyzed by a HP 6890 Gas Chromatogram (GC) equipped with a Flame Ionization Detector (FID) and capillary column DB23 (60-m×0.25-m×0.15-µm) according to a methodology proposed by Agilent. Normal hexane solutions of the biodiesel samples with a concentration of 100 mg/ml were injected by an auto injector at an

oven temperature of 50 °C, which was then heated up to 230 °C. The injector temperature and the detector temperature were 250°C and 280 °C, respectively; helium was used as the carrier gas (S.Baroutian, *et al.*, 2011). Besides, other physical properties such as density, viscosity, cetane number, pour Point, moisture water content, cloud Point and flash point were determined using ASTM D6751 and EN 14214.

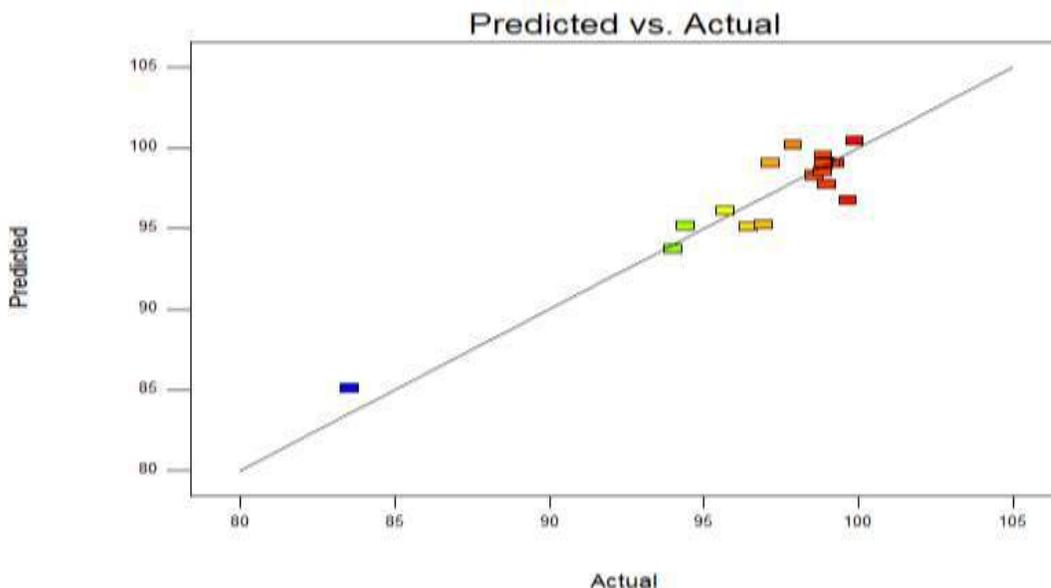


Figure 3: Correlation between predicted and actual

Table 2: Overall optimization results and model evaluation

Temp (°C)	Time (Min)	Cat. Conc (%)	%R (Yield)	
			Predicted	Experimental
50	67.50	1	97.20	97.50

The Figure 3 for the two-step alkali-catalyzed transesterification reaction showed that the model was able to successfully and adequately capture the correlation between the process parameters and the response (%R).

Physical Properties of Biodiesel Produced

The properties of the biodiesel produced from crude palm oil were determined at optimum conditions. The fuel properties of biodiesel are given in Table 3.

Table 3: Comparison of physical properties of biodiesel produced

Properties	Test method	Unit	ASTM Standard	Biodiesel
Flash point	ASTM D93-07	°C	130 min	150
Viscosity	ASTM D445-06	mm ² /s	1.9–6.0	3.90
Density	ASTM D4052-96	kg/m ³	-	868
Cloud point	ASTM D2500	°C	Report	10.5
Pour point	ASTM D97-93	°C	-	4
Moisture content	KARL FISHER	%	<0.10	0.12
Cetane Number	ASTM D 613		47 min	60

CONCLUSION

Sulfuric acid with concentration of 3% is effective for reducing FFA level of the feedstock.

The FFA level of the feedstock amounting 3.451 % FFA was reduced to 0.18%.

High biodiesel yield was obtained after transesterification reaction with KOH. The methyl ester yield was 97.534%. This value is far above the value stipulated by EN14214 (96.5%).

The measured fuel properties of the biodiesel properties were almost or just the same with a result which was reported by (Edmond, 2018) and are all well within ASTM D6751 and EN 14214 biodiesel standards.

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