

Transesterification of Palm Oil for the Production of Biodiesel

¹Khalizani Khalid and ²Khalisanni Khalid

¹Department of Human Resource Management, Faculty of Business Administration,
University Technology MARA, Kampus Seri Iskandar,
32610 Bandar Baru Seri Iskandar, Perak, Malaysia

²Department of Applied Chemistry, Faculty of Applied Sciences,
University Technology MARA, 40450 Shah Alam, Selangor, Malaysia

Abstract: Problem statement: Palm oil is known as an important source of edible oil with significant values of renewable energy. Depletion of petroleum had captured much attention on producing biodiesel from the palm oil. **Approach:** The most concerning methods for the production of biodiesel were discussed, namely transesterification (alkali and acid), enzymatic approach and supercritical alcohol. **Results:** The results showed the vis-à-vis of the methods for possible consideration of research. **Conclusion:** Concerning the importance of this vegetable oil, the contribution of palm oil towards diminution of fossil fuel, possible methods for the production of biodiesel and the opportunity for the futures is very much important.

Key words: Supercritical alcohol, significant values, possible methods, vegetable oils, catalytic process, fossil fuel, hectare per, low volatility, potential vegetable

INTRODUCTION

One of the most promising alternative fuels is vegetable oils and their derivatives such as biodiesel (Zubir and Chin, 2010). Vegetable oils including palm oil have been used directly as diesel fuel substitutes. Biodiesel can be made either from vegetable oil (palm oil, coconut oil, castor oil, silk cotton seed oil, jathropa oil) or animal fat. Based on few criteria, palm oil (*Elais Guineensis*) is the most potential vegetable oil which can be used as raw material to manufacture biodiesel and on the other hand the usage of crude palm oil is also meant to anticipate oversupply (Jayed *et al.*, 2009). These efforts have shown that all the vegetable oils tested can be used as fuel with some reservations. The most detrimental properties of these oils are their high viscosity, low volatility, poor atomization and auto-oxidation (Paul *et al.*, 2009).

The golden crop of Malaysia, oil palm, is regarded as the most cost effective vegetable oil crop with average yields of 3.5-5.0 tonnes of palm oil per hectare per year. Thus, it offers a potential environmental friendly alternative fuel source. As biodiesel is gaining considerable global attention and market, standards are vital for its commercialization and market introduction. It is necessary for the authorities to evaluate the safety risk and environmental impact, while giving quality assurance to the users. There is an increasing campaign for cleaner burning fuel in order to safeguard the

environment and protect man from the inhalation of genotoxic substances. The exhaust from petroleum products, especially diesel is known to be toxic and carcinogenous in nature, since they contain polycyclic aromatic hydrocarbons. Apart from these reasons, there has also been a surge in the prices of petroleum products worldwide and it is doubtful if these prices would ever again down-plunge since their rising trend has been consistent since late 2004 (Aqeel *et al.*, 2011).

Biodiesel, meanwhile, is an alternative or additive to standard diesel fuel that is made from biological ingredients instead of petroleum. Biodiesel is usually made of bio oils through a series of chemical reactions but is non-toxic and renewable. There are a few different ways to make biodiesel, but most manufacturing facilities in the world produce industrial biodiesel through a process called transesterification, because it is easier and saving. In this process, the fat or oil is first purified and then reacted with an alcohol, usually methanol (CH₃OH) or ethanol (CH₃CH₂OH), in the presence of a catalyst such as potassium hydroxide (KOH) or sodium hydroxide (NaOH). When this happens, the triacylglycerol (oil or fat) is transformed to form esters and glycerol. The esters that remain are called biodiesel (Ghanei *et al.*, 2011; Sylvain *et al.*, 2009; Mário and José, 2011).

Biodiesel blend is the blend of petroleum diesel and biodiesel (methyl ester). A blend of 5% biodiesel

Corresponding Author: Khalizani Khalid, Faculty of Business Administration, University Technology MARA, Kampus Seri Iskandar, 32610 Bandar Baru Seri Iskandar, Perak, Malaysia

and 95% regular diesel is called a B5 blend. Biodiesel has similar physical characteristic as diesel oil and in addition it is a renewable energy and safe for the environment. Biodiesel can be used easily because it can be mixed at any proportion with diesel oil, hence enabling us to apply it immediately for diesel engines that are available without much modification; easy biodegradability; 10 times less poisonous compared to the ordinary diesel oil, the waste product is not black, less sulphur and other aromatic contents, hence the combustion emission produced is safe for environment and perform less accumulation of carbon dioxide gas in atmosphere thus lessen furthermore global heating effect (Abdullah *et al.*, 2009; Christian *et al.*, 2009; Sérgio and Graciela, 2006; Lilian *et al.*, 2008; Haseeb *et al.*, 2011; Cumali *et al.*, 2011).

MATERIALS AND METHODS

Transesterification process are divided as follows; alkali/ base catalyst, acid catalyst, enzymatic (lipase) and supercritical alcohol process. In all cases, the triglycerides (palm oil) is used as raw materials for the production of biodiesel.

RESULTS

For a basic catalyst, either sodium hydroxide (NaOH) or potassium hydroxide (KOH) should be used with methanol or ethanol as well as any kind of oils, refined, crude or frying (Rajesh and Jeffrey, 2011; Kai *et al.*, 2010; Khalisanni *et al.*, 2008). In this process it is better to produce the alkoxy before the reaction to obtain a better global efficiency (Fig. 1).

Acid catalyst transesterification is the second conventional way of making the biodiesel. The idea is to use the triglycerides with alcohol and instead of a base to use an acid; the most commonly used is sulfuric acid, sulfonic acid or solid acid catalyst (Shigeki *et al.*, 2011; Siddharth and Sharma, 2010). This type of catalyst gives very high yield in esters but the reaction is very slow, requiring almost always more than one day finishing (Fig. 2).

In the presence of enzyme catalyst, the triglycerides will be converted to methyl ester. The lipase can be secreted from *Candida* spp. or readily available in the market.

Supercritical alcohols method (>200°C) has several advantages over that of catalytic process, including high production efficiency and environmental friendliness. Supercritical fluid transesterification does not require catalysts, therefore, the neutralization, washing and drying steps can be omitted from the process in comparing with conventional biodiesel production process (Fig. 3).

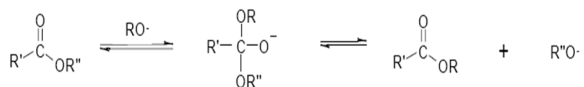


Fig. 1: Mechanism of alkali alcoholysis

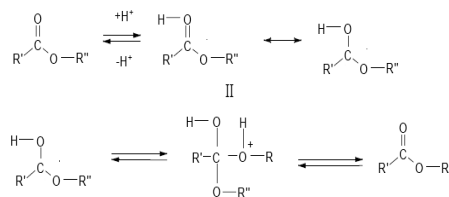


Fig. 2: Mechanism of acid alcoholysis

DISCUSSION

For basic catalyst, the alcohol-oil molar ratio that should be used varies from N=1:1-6:1. However N=6:1 is the most used ratio giving an important conversion for the alkali catalyst without using a great amount of alcohol. The types of alcohol are usually methanol and ethanol. The last one has fewer safety problems because it is less toxic. The oils used could come from any vegetable, e.g., corn, canola, peanut, sunflower, soybean, olive, palm, palm kernel. As you may see there are quite a few sources that can be used as raw material and all of them are equally relevant only consideration is in the choice is which has lower price on the market. The amount of catalyst that should be added to the reactor varies from 0.5-1% w/w, but some authors prefer advice any values between 0.005-0.35% w/w should be used. The last but not least important variable is the reaction temperature. The standard value for the reaction to take place is 60°C, but depending on the type of catalyst different temperatures will give different degrees of conversion and for that reason the temperature range should be from 25-120°C. The reason why there is a great interest in the alkali process is it is more efficient and less corrosive than the acid process, making it a preferred catalyst to be used in industries (Zahir *et al.*, 2011; Oguzhan, 2011; Siddharth *et al.*, 2011; Ruzaimah *et al.*, 2011; Mi *et al.*, 2011).

The limits of this technology are due to the sensitivity that this process has to purity of reactants, to the fatty acid, as well as to the water concentration of the sample. If too much water, it increases the risk of making some soap instead of the desired product. If soap is the end product, a consumption of the reactive will take place and the formation of an emulsion, which makes downstream recovery and purification very difficult and expensive. A normal amount of free fatty acid on the waste cooking oils is about 2% w/w. If the

amount is big, it is recommend a pretreatment via esterification with alcohol and sulfuric acid. After this, the normal alkali process should be continued (Ritesh *et al.*, 2011; Romain *et al.*, 2011; Sivakumar *et al.*, 2011).

Acid-catalyzed transesterification is more suitable for waste or unrefined oil. The process has not gained as much attention as the base-catalyzed transesterification because of the slower reaction rate and the very high methanol to oil molar ratio requirements. The two-step biodiesel process addressed this issue by using an acid catalyst followed by a normal base-catalyzed transesterification. Compared with homogeneous catalysts such as NaOH, the conditions of acid catalyzed transesterification also make the process impractical and uneconomical. Therefore, a process for the conversion of fatty acids and triglycerides to the corresponding ester in a manner that is mild, fast, convenient and universally applicable is required (Habib *et al.*, 2008; Hyunjoon *et al.*, 2003; Dennis *et al.*, 2010; Dora *et al.*, 2007; Xiaoling *et al.*, 2009). Lipases are enzymes used to catalyze some reaction such as hydrolysis of glycerol, alcoholysis and acidolysis, but it has been discovered that they can be used as catalyst for transesterification and esterification reactions too.

Biocompatibility, biodegradability and environmental acceptability of the biotechnical procedure are the desired properties in agricultural and medical applications. The extra cellular and the intracellular lipases are also able to catalyze the transesterification of triglycerides effectively (Andreina *et al.*, 2011; Giovana *et al.*, 2011; Ríos *et al.*, 2011; Junmin *et al.*, 2011; Shiva and Patrick, 2011).

Advantages of using lipases:

- Possibility of regeneration and reuse of the immobilized residue, because it can be left in the reactor with the ingredients flowing continuously
- Use of high concentration of enzyme prolongs the activation of the lipases
- A bigger thermal stability of the enzyme due to the native state
- Immobilization of lipase could protect it from the solvent that could be used in the reaction and that will prevent all the enzyme particles getting together
- Separation of product will be easier using this catalyst

Disadvantages of using lipases:

- Lost of some initial activity due to volume of the oil molecule

- Number of support enzyme is not uniform
- Biocatalyst is more expensive than the natural enzyme

In supercritical alcohol method, large energy consumed to perform the transesterification process with supercritical alcohols is compensated by more high reaction rate and no requirement of additional clean stages. Finally, this has led to general reduction of production prime cost by 10-15% in comparing with catalytic method. The advantage of this method is that FFA present in the oil could be simultaneously esterified in supercritical methanol. These methods allow reaching the conversion value up to 100%, however this caused the increasing of the cost of electrical energy and capital cost (increasing the size of the reactor). Therefore, the method of solubility increasing of the oil in methanol without using the catalytic is needed (Ayhan, 2009; Masafumi *et al.*, 2010; Alessandro *et al.*, 2011).

The properties of biodiesel depend very much on the nature of its raw material as well as the technology or process used for its production. In this respect, the aforementioned standards have specified relevant parameters to govern the quality of biodiesel. Inherent properties from vegetable oils or animal fats that have an effect on the performance of biodiesel as diesel substitute, such as Iodine Value (IV), density, viscosity, cetane number, copper strip corrosion, linolenic acid methyl esters content, polyunsaturated (more or having four double bonds) methyl esters content and phosphorus content, have been included. On the other hand, the properties of biodiesel related to the production technology are, namely, the contents of ester, sulphated ash, water, partial glycerides (mono-, di- and tri-glycerides), alkali, free and total glycerol, flash point and the acid value (Karl *et al.*, 2007; Scott *et al.*, 2010).

CONCLUSION

Exhaust of biofuel gas emission of the engines much cleaner with reduction CO, CO₂, NO_x, SO₂ and so the opacity, therefore it is more environmentally friendly. The commercial production of biodiesel is still at its primary stage. Brief comparison between several potential methods for the production of methyl ester gives significance to cut cost of production and lowering risk of procedure deficiencies. Transesterification process by using alkali catalyst was believed the most promising and productive methyl ester production method for current period.

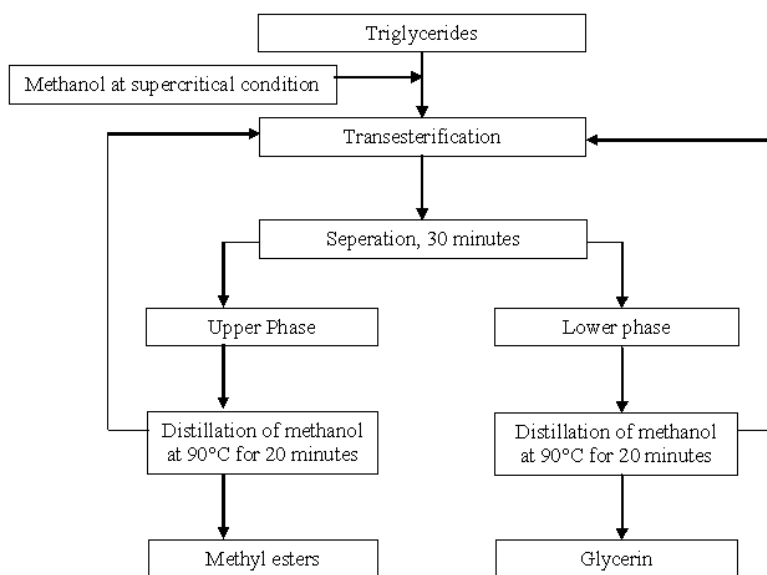


Fig. 3: Process flow diagram for biodiesel production using supercritical methanol

Regardless the production of saponified compound as by products, this method is reliable because the retention of methyl ester stability compared to supercritical alcohol process. At 400°C, methyl ester which produced from palm oil will loss stability, because palm oil rich with palmitic and oleic fatty acids which the boiling point of this compounds is about 400°C. Acid catalyst are also potential to be used for methyl ester production process in industries but the process produced more water than alkali catalyst while the use of lipase enzyme for fatty acids esterification is very relatively costly.

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