A Study on Process Parameters Optimization of BD Transesterification

Seung-Hun Choi[1]

[1]Department of Automatic Mechanical Engineering, VISION University of Jeonju, Cheonjam-ro, Wansan-gu, Jeonju-si, Republic of Korea

***Abstract*:** *This paper has been considered lard oil transesterification reaction variables at different temperatures, catalyst amounts, reaction time, oil to methanol molar ratio and solvent concentration. Catalyst amount and reaction temperatures were most important reaction conditions which mostly affected lard biodiesel methyl ester yields. Based on the experimental analysis the lard biodiesel were higher at 1.5-2 wt% catalyst concentration, 6:1 methanol to molar ratio and 55-65 wt% solvent concentration. Under optimal condition lard biodiesel ester yields were 95.2±1.8% and 97.0±0.5%. The solvent blending influenced to increase biodiesel yields because of better mixing of lard free fatty acids and chemical additives. Lard biodiesel quality was evaluated through determination of several parameters according to EN 14214. Some quality parameters did not comply with the European standard limits (e.g. kinematic viscosity, cold filter plugging point). Thus, it needs to improve quality of lard biodiesel and more research activities required to develop transesterification process technology.*

Keywords: *Renewable energy, Animal fat, Biodiesel (BD), Chromatography*

1. Introduction

The search for alternative renewable fuels considering caused by the fact that the supply of fossil fuels will decrease in future as the energy demand will continue to grow rapidly, and environmental damage serious problems [Berrios et al.]. Concerning environmental damage, acid rain related to global warming transport sector, combustion toxic products of petroleum fuels has a clear responsibility. The alternative fuels must be technically acceptable, economically competitive, environmentally acceptable and easily available. Researches on biodiesel derived from vegetable oils and animal fat are being maintained to alternate this kind of fuels to petroleum based diesel fuel [Gutiérrez et al., Jike et al.]. The waste frying oils are known to be scarce but waste animal fats are more abundant [Joana et al.]. Such fats had a common application as animal feeds but this practice strongly decreased due to the possibility of severe animal disease and the consequent obligation to effectively discard or recycle the waste fats. Scientists have been looking everywhere for raw materials that will yield a new generation of renewable fuel in diesel engine. A source that is abundant enough to make a significant dent in oil market and something that doesn't divert food into energy. And researchers search for alternative feedstock to produce biodiesel, animal fat as a waste product seems to be cheapest and available at large scale. In order to run cars on biodiesel produced from animal fat also in other seasons than summer it is necessary to blend the biodiesel from animal fat with commercial diesel. A percentage of 5 to 15% biodiesel from animal fat seems to be appropriate.

Biodiesel from animal fat is less stable for oxidation, this fact being attributed to the absence of natural antioxidants as compared to biodiesel of vegetable origin. On the other hand, animal fats are highly viscous and mostly in solid form at ambient temperature because of their high content of saturated fatty acids. The high viscous fuels lead to poor atomization of the fuel and result in incomplete combustion. Generally, the use of animal fats as alternative fuels in diesel engine has not been developed in depth. And, the use of biodiesel has not expanded into developing countries, due to the higher prices of feedstock and no enough sources of feedstock which could be produce with larger scale. Also, animal fats have a significant content of saturated fatty acids and the fuel produced has higher cold filter plugging point as compared to biodiesel from vegetable oils; therefore, it might not be adequate to use it 100% pure in vehicles during cold weather. Joana M. Dias et al. consider the incorporation of pork lard in waste frying oil results in yields varying from 81.7% to 88.8 wt%.

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Minimum purity was closely obtained only when waste frying oil was used alone and when 0.2% of lard was incorporated in the raw material; however, it ranged from 93.9 to 96.3 wt% being always close to the limit. Ki-Teak Lee et al. suggested that lard was fractioned with acetone to reduce the saturated fatty acid content in the recovered fractions that were further used for cold-temperature-resistant biodiesel production with three steps reaction to maximize ester conversion. Ying et al. have produced biodiesel from three types of waste animal fats (tallow, lard and poultry fat) and quality of these biodiesel were evaluated according the EN 14214, showing that none of the biodiesel types match al the European standard limits in all the evaluated parameters. And they reported that biodiesel B100 (pure biodiesel) from these feedstocks cannot be used to the vehicle engine without further additives introduction. The present paper discussed the transesterification process of biodiesel from lard with different synthesis conditions of methanol to oil molar ratio, catalyst concentration and solvent amounts. And these parameters effects to lard BD ester yields and optimal conditions have been discovered experimentally.

2. Materials and Methods

2.1. Experimental Materials

Commercial purified lard oil was provided by Samyang (South Korea) from a local market and used without any further purification. Methanol 99.5%, potassium hydroxide powder 95% and n-hexane used for the transesterification process were purchased from Samchun pure chemical Co.,Ltd. (South Korea). Triacylglycerides (TAG) present in the lard oil were found to contain palmitic acid (23.7 wt%), oleic acid (41.4 wt%), linoleic acid (15 wt%), stearic (12.9 wt%) with traces of stearic, arachidic, miristic, palmitoleic and linolenic, which was determined by gas chromatography using standard methods [Joana et al.].

2.2. General Chemical reaction for Lard Biodiesel

Transesterification and emulsification are two main solutions that have appeared as effective methods for using animal fats in diesel engine. The transesterification with methanol is a catalyzed chemical reaction which involves vegetable oil or animal fat and methanol to yield lard BDthyl ester (ME) and glycerol as a by-product. Methanol is the most commonly used alcohol because of its low cost and its physical and chemical advantages. At industrial scale, the alkaline catalyst is the most commonly used due to its suitable operational conditions: its low cost, it is easy to install and, above all, its high reaction rate, which provides a decrease in the size of the equipment and in immobilized capital. Other researchers have noted that methanol to oil molar ratio, reaction temperature, reaction time and catalyst quantity play important role in production of biodiesel using methanolysis.

The experiments were conducted in a laboratory-scale setup, which consisted of 2000 ml flask and the reaction mixture was agitated by a magnetic stirrer at 600 rpm. The flask was kept in a water bath maintained at 57 ^{0}C, just below the boiling point of methanol. A sample of 300 g of lard was placed in a 2000 ml flat-bottom flask equipped with a magnetic stirrer-heater. The lard was heated to 55℃ slowly and blended with 0 to 200 ml solvent (n-hexane). The optimal reaction temperature for lard biodiesel production varied from 53 to 57℃. In another beaker, methanol (the methanol–lard mole ratio was selected at 6:1, 10:1 and 14:1) was mixed with 0.48 to 3.05 wt% of potassium hydroxide (1.5% by weight assuming 98% pure KOH), until all of the KOH was dissolved in methanol. This mixture was then added to the melted lard, stirred rigorously, and further heated to 60℃ close to the boiling point of methanol for 1.5 h. It was observed that the lard BD concentration was approximately constant around this time. The mixture was then transferred to a separator funnel and glycerol was allowed to separate for a minimum of 3 h. After draining off the glycerol lard BD was washed twice with 1:1 volume of water for 1.5 h to remove excess methanol. The biodiesel water content is an important parameter because it affects biodiesel oxidation stability, therefore influencing the storage life of the fuel. Lard BD was purified by distilling and drying to room temperature.

2.3. Properties of Lard BD compared to Standards

It can be clearly seen that the biodiesel obtained in the experiment mainly contained six fatty acid methyl esters. The GC/MS analysis indicated that the biodiesel contains large amount of C19 and the amount of 9, 12-octadecadienoic acid methyl ester was the highest in the biodiesel. The properties of biodiesel such as density, kinematic viscosity, saponification number, iodine value and cetane index were determined for biodiesel synthesized at optimal condition (Table 1). The properties were compared with ASTM D6751-9, EN 14214 standard and analyzed to be in good agreement. Most of the fuel properties are found to be in reasonable agreement with ASTM standard. Lard BD has lower pour point, which is about 4℃. Therefore, it can't be used as a neat diesel fuel in cold weather conditions. But lard BD can be a diesel fuel extender when blended with petroleum diesel fuel in cold weather conditions.

TABLE I: Properties of lard BD compared to standards

	Lard BD	Diesel	ASTM (D6751-09)	EN 14214
Density, (kg/m^3)	837.1	820-860	-	860-900
Kinematic viscosity, (mm^2/s)	2.49	1.3-5.5	1.9-6.0	3.5-5.0
Cetane index	57.8	30-40	>48	>51
Flash point, (^0C)	130	38-55	>93	>101
Pour point, (^0C)	4.0	-15 to 3	-15 to 10	-
Calorific value (MJ/kg)	38.79	42.7	-	-

3. Results and Discussion

3.1. Effects of Reaction Time

Temperature is the important parameter in the heterogeneous chemical reaction completely process. Higher temperatures leads to the loss of methanol and solvent from the solution through volatilization and incomplete reaction will be created. Also lower temperatures required more reaction time to extract biodiesel from animal fat oil. Fig. 1 shows the lard BD yields increase rate with various reaction temperatures and different time limits. Reaction speed was high at reaction process start period then gets slowly after 60 minutes. It is indicating that the reaction progress fast immediately after addition of the methanol/ potassium hydroxide mixture. From this figure it can be seen that lard transesterification process optimal reaction time was 90 minutes even various temperatures. It was observed that the lard BD yields was approximately constant around this time periods. Mainly, the lard BD yield was higher in the high reaction temperature conditions until 90 minutes and then tended to stabilize, indicating that the transesterification of lard was almost complete during the 1.5 h of reaction.

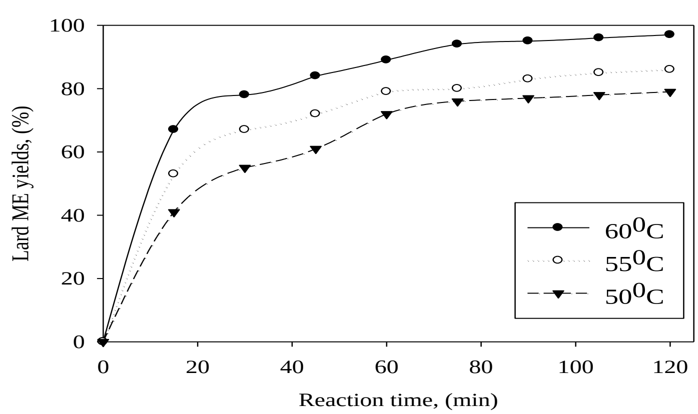

Fig. 1: Lard BD yields vs. reaction time and temperatures with solvent of 65 wt%

3.2. Effects of Solvent

In potassium hydroxide catalyzed methanolysis of lard for biodiesel production, different amounts of n-hexane were examined and it has been found that the lard BD yields increased by adding n-hexane into the reaction mixture. Fig. 2 shows the effect of solvent on the yield of lard BD. Increasing solvent percent to oil until 65 wt% the lard BD yield was increasing significantly, but further increasing tends to decrease caused by catalyst molecules effect retarded to be strongly in the reaction condition. Solvent makes the reactants oil and methanol enable to be miscible. Therefore, this homogeneous single phase reaction medium leads to a very fast reaction when compared to conventional reaction times. Using a common solvent for methanol and the oil was found to be effective by many researchers since insoluble methanol is responsible for inhibition. Boyi Fu et al. concluded that the highest yield (83.1%) was obtained with isooctane as solvent, and may be due to its unique side-chain molecular structure containing three methyl groups. This could have resulted in better mixing with triglyceride and methanol compared to linear and cyclic alkanes.

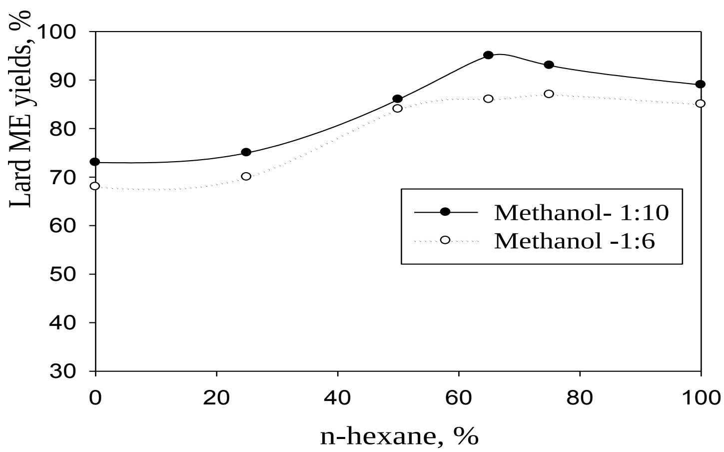

Fig. 2: Effect of solvent on the yield of BD produced from lard at 2 wt% catalyst

3.3. Effects of Methanol to Oil Molar Ratio

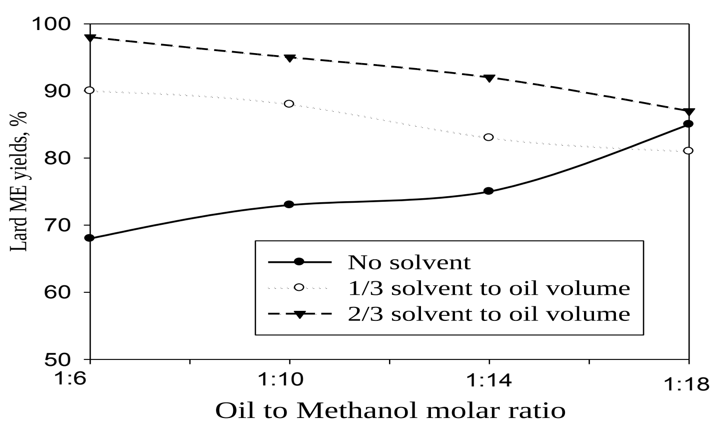

Fig. 3: Effects of methanol and solvent on the yield of BD produced from lard at 2.0 wt% catalyst

Methanol is one of the most important factor affecting quality and quantity of biodiesel production. Fig. 3 illustrates lard BD yields with various oil to methanol molar ratio between 1:6 to 1:18. From this figure the lard BD yields were very lower with no solvent mixtures. The main problem for the lower rate of reaction might be the reaction mixture is not homogeneous because the oils and alcohols are not miscible each other due to their chemical structures. This lowers the rate of collisions of molecules and so the rate of reaction causes longer reaction times, higher operating expenses. Lard BD yields were enhanced from 68.0% to 87.0% when increasing methanol to oil molar ratio from 6:1 to 18:1. For further increase of methanol amount, there was no significant difference on the lard BD yields (about 87%). The lard BD yields were increasing significantly by using solvent mixture. This figure indicates that increase lard BD yields from 83.0% to 97.0% with increase solvent amount from 30 to 65 wt% to oil volume ratio. Interestingly, we found that increasing solvent amount with methanol to oil molar ratio simultaneously the lard BD yield was decreasing because of high amount of solvent and methanol. The optimized composition of solvent and methanol was 65 wt% and 1:6 molar ratios, respectively.

3.4. Effects of Catalyst Concentration

Animal fat turns very easily into a thick glob of soap if we use just too much lye the right amount of catalyst will be crucial for the production. Fig. 4 shows the influence of catalyst concentration amount on lard BD yields after transesterification process. In the case of increasing catalyst concentration quantity from 1.0 to 2.0 wt% lard BD yield was increasing but further increase in catalyst amount resulted in decrease. Similar results also have been reported in a few studies [Ying et al., Haq et al.]. The stronger influence of catalyst amount on biodiesel yield was confirmed and high lard BD yield has obtained using 2.0 wt% catalyst. The yield of lard BD under optimal conditions was 95.2±1.8%.

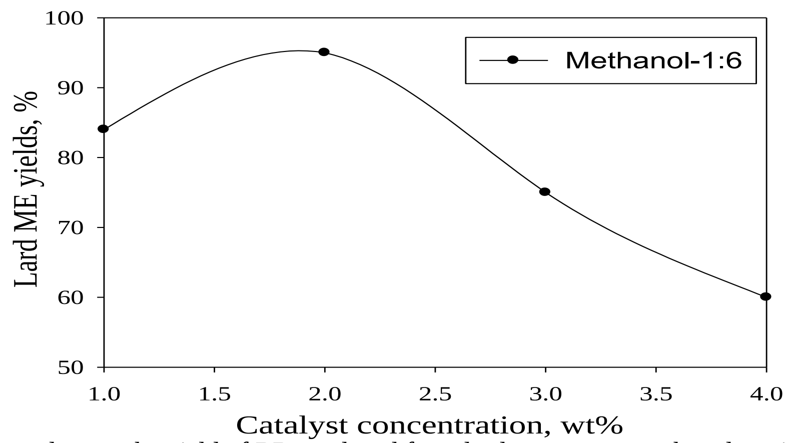

Fig. 4: Effect of catalyst on the yield of BD produced from lard at constant methanol to oil molar ratio 6:1

4. Conclusions

This work studied to obtain optimal condition of lard biodiesel producing process. The most suitable conditions to produce biodiesel from lard were: reaction temperature 57 ^{0}C, potassium hydroxide of 2 wt%, methanol to oil molar ratio 6:1 and 65 wt% solvent concentration blending. Implementation of solvent to lard biodiesel transesterification process was significant influence to increase methyl ester yields and also might improve physical properties of viscosity and cloud point. Further experimental analysis will tend to determine lard biodiesel combustion and emission characteristics. High yield of lard BD was 97.0% and lard biodiesel might be an interesting alternative to conventional diesel engine even improve some properties of the product. Also this study result indicates that the lard is quite suitable as the low-cost feedstock for biodiesel production, which not only resolved the environmental problem as global warming, acid rain but also reduced the industrial cost of biodiesel production cost competitive with conventional diesel.

5. References

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