TRANSESTERIFICATION OF MAHOGANY (*Swietenia macrophylla*) SEED OIL USING ALKALI CATALYSTS FOR BIODIESEL PRODUCTION

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1. Introduction

Due to industrialization and modern civilization, the majority energy demand depends on coal, natural gas and petroleum [1]. Fossil fuels produce greenhouse gases such as carbon dioxide when they burned, and this effect causes global warming.

The reliance on conventional energy sources can be reduced by adapting alternative source of energy. Since 2020, the investment on clean energy has risen by 40%.

Biofuels are considered as green fuel as produce fewer particulate matters and carbon dioxide cause of having more oxygen molecules in its structure [2]. Compared with fossil fuel, biodiesel is a safe, cleaner and more environmentally friendly fuel. Traditional fuel sources are limited and decreasing day by day. Biodiesel can be produced from a large variety of feedstock such as animal fats, edible seed oils, non-edible seed oils and even from waste cooking oils [3]. Production of biodiesel from edible oil can create imbalance in food supply chain. There are many non-edible seed oil which can be used to produce biodiesel such as rubber seed oil, cotton seed oil, jatropha seed oil etc. Biodiesel is produced by a reaction called transesterification reaction in which triglycerides react with lower carbon alcohol such MeOH or EtOH and produce a multiple single chain methyl ester. Another important factor of this reaction is the presence of catalysts. Acid and base catalysts are of two types depending on the phase such as homogeneous and heterogeneous catalysts. Homogeneous catalysts such as NaOH, KOH, $NaOCH_3$ etc dissolves in the reaction mixture or remains in the same phase [4]. On the other hand, heterogeneous catalysts such as CaO, MgO, ZnO etc does not dissolve in the reaction mixture, only the surface particles can participate in the reaction.

Biodiesel can be produced from a non-edible oil produced from Mahogany (Swietenia macrophylla) seed oil. Rana *et al.* [5] investigated about the biodiesel production and oxidation stability of the biodiesel from Mahogany seed oil. They used acid catalyzed esterification followed by transesterification of the oil using homogeneous basic catalyst NaOH. The molar ratio of oil and methanol and oil and catalyst were variable with a constant temperature and time of 60 and 120 min respectively with highest biodiesel yield was 97.34%. Moreover, another researcher Arazo *et al.* [6] researched about the extraction of Mahogany oil and used this oil production of biodiesel. KOH was used as the catalyst in this study for the transesterification reaction with variable amount. They concluded that one ton of Mahogany seeds might produce 352 L of biodiesel and 420 L of bio-oil.

The objective of this study was the application of Mahogany seed oil (MSO) to a raw material for biodiesel production. The model feed oil (MFO) and MSO were characterized, pretreated, i.e., deacidified, and transesterified by homogeneous and heterogeneous catalysts (NaOH and CaO) to study the effects of difference between catalysts, the concentration of free fatty acid in the feed oil, and so on.

2. Experimental

2.1. Materials

All chemicals used in the experiments were analytical chemical grade. Mahogany seed oil (MSO) was collected from the seed of Mahogany tree (Swietenia macrophylla) which is indigenous to Bangladesh.

2.2. Analysis

For the model feed oil, triolein was analyzed which was used as model feed oil for transesterification reaction. Oleic acid was analyzed as it can be found in the plant oil. Methyl ester and glycerol were also analyzed by GC. In GC, for detection of these chemical components, a characteristic peak appears in a specific time after that component passes through a chromatograph column. This specific time period is known as retention time.

MSO was analyzed to identify what types of triglycerides and FFA it contains. For this reason, the MSO reacted with MeOH in presence of NaOH to convert all the triglycerides into methyl ester. So all the fatty acid functional groups can be identified and each component can be detected by GC. The total reaction time was for 6 h. The conditions of the reaction have given in Table 1.

Table 1 Experimental conditions for MSO analysis

Molar ratio of MeOH to MSO	[-]	24
Molar ratio of NaOH to MSO	[-]	0.02
Reaction temperature	[K]	333
Reaction time	[h]	6

To determine acid value of the oils, 1g (M_{oil}) of oil was taken in a conical flask and 0.1M KOH (C_{KOH}) was taken in the burette. The titration was carried out using alcohol

medium and hexane was used for the dilution of the mixture. After that, 2-3 drops of Phenolphthalein indicator were added to the oil mixture to identify the end point of titration. KOH was added in the mixture until the color the mixture turned to pale pink. Using the volume and molar mass of KOH, the acid value was calculated. Using the volume of KOH (V_{KOH}) and molar mass of oleic acid (mm) free fatty acid was calculated. The equation of acid value and x_{FFA} are as follows

$$AV = V_{KOH}\, C_{KOH}\, 56.1 / M_{oil} \quad (1)$$

$$x_{FFA} = (C_{KOH}\, mm\, 10 / M_{oil})\, 100 \quad (2)$$

2.3. Deacidification

After determining the acid value of MSO, deacidification of the MSO were done as the acid value was higher. The MSO was first heated to 80 ℃ and then 9.5 wt% of aqueous solution of NaOH was added to the oil. The mixture was stirred for 5 mins to complete and then kept it overnight for settling. After pouring the mixture into separating funnel, two layers were obtained. The lower layer of the separating funnel was deacidified oil. The upper layer was soap mixed with alkali salts which was discarded. This process is also known as alkali neutralization. The conditions of deacidification process are given in Table 2.

Table 2 Deacidification reaction conditions

Molar ratio of NaOH to FFA	[-]	1.15
Reaction time	[h]	0.083
Reaction temperature	[K]	353

2.4. Transesterification

Transesterification reaction of both model feed oil and untreated MSO were done by using homogeneous (NaOH) and heterogeneous (CaO) catalysts. Methyl ester and glycerol are the main product results from the transesterification reaction. At first, the oil was taken into a three neck round bottom flask. The flask was equipped with a thermocouple, a reflux condenser and another neck were used for adding methanol and catalyst. The oil was first heated to 60 ℃ and then the catalyst and methanol were added. Upon completing the reaction, the reaction mixture subjected to ice bath to conclude the reaction. The mixture was then poured into a separating funnel with a filter paper and kept for overnight to settle the mixture. The conditions of the reaction are given in Table 3.
The procedure and conditions were same for both model feed oil and MSO.

Table 3 Transesterification reaction conditions

Molar ratio of MeOH to MSO	[-]	12
Molar ratio of NaOH to MSO	[-]	0.01
Molar ratio of CaO to MSO	[-]	4
Reaction time	[h]	4
Reaction temperature	[K]	333

3. Results & Discussions

3.1. Characterization of feed oils

Similar to other plant oils, the composition of MSO is a mixture of several triglycerides, fatty acids and other components.

MSO has given peaks in the similar retention time as the triglycerides, oleic acid and methyl ester. Nevertheless, the conversion of triglycerides was not completed. Due to this reason, most of the fatty acid functional groups had remained unidentified. Only one kind of triglyceride; triolein can be identified in this process. In Table 4 the mass fraction data proves the presence of methyl ester which is considered as biodiesel.

Table 4 Mass fractions of triolein, oleic acid, and methyl ester present in MSO

Catalyst	Time [h]	Components	Mass fraction [–]	
			BD phase	MeOH phase
NaOH	6	Triolein	0.35944	-
		Oleic acid	0.01987	0.004278
		Methyl ester	0.03130	0.00435

3.2. Deacidification

MSO had the acid value of almost 5.32 mg KOH/g and the x_{FFA} value was higher than 1%. To reduce the FFA content in the MSO, deacidification by alkali neutralization was done. Deacidification by neutralization can only be applied to the plant oil with relatively low FFA content [7]. Removal of FFA was done before proceeding to transesterification reaction. In this procedure, the FFAs are neutralized with alkali and removed as salts. The alkali NaOH amount in the reaction was high and emulsification of the system occurred. Thus, the operation was stopped. After deacidification, the oil showed an acid value of 2.39 mg KOH/g which is lower than the initial value of MSO. The free fatty acid value was then become 1.19% which is still above the satisfactory limit required for transesterification reaction. Acid values of the model feed oil and MSO before and after deacidification are given in Table 5

Table 5 Acid values of model feed oil and MSO before and after deacidification

	Acid value [mg-KOH/g]	
	Before deacidification	After deacidification
Triolein	0.96	-
MSO	5.32	2.39

3.3. Transesterification

In the model feed oil, after completing the transesterification reaction, two phases were obtained. The upper aqueous layer or MeOH phase contained MeOH, glycerol and Methyl ester. On the other hand, the

lower level is assumed to be the organic layer or biodiesel (BD) phase containing unreacted triglycerides, FFAs and methyl ester. For the confirmation of the components, both MeOH and BD layer was subjected to the GC. After analyzing the layers, presence of triolein which worked as triglycerides, methyl ester, glycerol and MeOH was confirmed according to the previously determined calibration of these components. In **Table 6**, the mass fractions of the triglycerides and methyl ester have shown for both MeOH and BD phase of the transesterification reaction by both catalysts.

For NaOH, there was no trace of triolein in the MeOH phase. Moreover, the mass fraction of triolein was decreased from the initial mass fraction of 0.65.

On the other hand, for CaO, a low concentration of triglycerides can be observed in the MeOH phase. But in the BD phase, the mass fraction is very high indicating large quantity of unreacted triglycerides. Clearly for CaO, the mass fraction of triglycerides did not decrease as expected in the 4h reaction showing by the values of **Table 6**. The reason behind this might be that the surface particles of CaO did not participate in the reaction and the triglycerides mass fraction did not reduce. CaO catalysts need more time to complete the reaction. So, Unlike NaOH catalysts, CaO catalysts did not perform well in a certain period of time.

For the case of NaOH, the mass fraction of methyl ester was higher than CaO. On the other hand, for CaO, the mass fraction of methyl ester in 4h was obtained although the amount of methyl ester was lower than the NaOH catalyzed reaction. Both the reactions did not reach to equilibrium after 4h.

Table 6 Mass fractions of triolein and methyl ester in model feed oil transesterification reaction

Catalyst	Time [h]	Component	Mass fraction [–]	
			BD phase	MeOH phase
NaOH	4	Triolein	0.27264	-
		Methyl ester	0.23595	0.02159
CaO	4	Triolein	0.34157	0.09462
		Methyl ester	0.12630	0.00268

For MSO, the time for transesterification reaction was 4h similar to the the model feed oil reaction, using both catalysts.

The mass fractions of unreacted triglycerides and produced methyl esters were calculated. As MSO has chemical structure with several triglycerides and most of the triglycerides could not be determined, only one kind of triglyceride such as triolein was considered. The reason behind this was, as the retention time of triolein was detected beforehand, the presence of triolein in the MSO can be confirmed. Beside triolein, there was also methyl ester present in the MSO. In **Table 7**, the mass fraction of triolein and methyl ester is showed for both NaOH and CaO catalysts.

Table 7 shows, there was no mass fraction of triolein detected in the MeOH phase of both NaOH and CaO catalyzed reactions. Moreover, the amount of unreacted triolein is much higher in the BD phase of NaOH catalyzed reaction than the CaO catalyzed one.

Table 7 Mass fractions of triolein and methyl ester after transesterification

Catalyst	Time [h]	Component	Mass fraction [–]	
			BD phase	MeOH phase
NaOH	4	Triolein	0.04778	-
		Methyl ester	0.00207	-
CaO	4	Triolein	0.00994	-
		Methyl ester	0.00950	0.00771

For the case of CaO, the amount of mass fraction of methyl ester in both BD and MeOH phase is much higher than that of NaOH catalyzed transesterification reaction. The MSO had a higher value of x_{FFA} which interferes with the methyl ester conversion in NaOH catalyzed reaction. On the other hand, the effect of FFA does not affect much in the case of CaO. The mass fraction of methyl ester proves that, or heterogeneous catalyst has less effect of FFA than homogeneous catalyst.

Methyl ester conversion

In **Table 8** the total amount of converted methyl ester and the total amount of unreacted triolein was showed. From the table, it can be observed that for both NaOH and CaO catalyst, the amount of unreacted triolein is almost same at 4h time of the reaction. However, the opposite result was seen for the conversion of methyl ester.

Table 8 Conversion of methyl ester and unreacted triglycerides in model feed oil for both catalysts.

Catalyst	Time [h]	Component	Conversion [–]
NaOH	4	Triolein	0.438048171
		Methyl ester	0.387675653
CaO	4	Triolein	0.423858171
		Methyl ester	0.147472945

For NaOH catalyzed reaction, the conversion of methyl ester was highest of 38% at 4h reaction time. The reason might be, as NaOH can be dissolved in the reaction mixture, the rate of the reaction increased and continue

increasing with time. The total conversion of methyl ester was lower because of the impurity present in the triolein. On the other hand, the reverse was observed in the case of CaO. For CaO, the highest conversion of methyl ester which was only 14% for the 4h reaction time when using CaO. As for CaO catalysts, only surface particles take participation in the reaction, so it takes longer time to initiate the reaction.

MSO was reacted with both NaOH and CaO catalysts for 4h. The conversion of the methyl ester and the quantity of unreacted triglycerides were calculated. In **Table 9**, the methyl ester conversion and quantity of unreacted triglycerides are shown for MSO transesterification reaction with both NaOH and CaO. From the **Table 9,** the unreacted triolein quantity for NaOH catalyzed reaction was higher than the CaO catalyzed reaction. The highest methyl ester conversion of transesterification of MSO is 0.75% resulted with CaO catalyst. For NaOH, the amount of methyl ester conversion is 0.20%. When calculating the methyl ester for the transesterification reaction, only one type of methyl ester was calculated which was oleic acid methyl ester so the conversion cannot be calculated accurately.

From the table, it can be observed that the methyl ester conversion is higher for the CaO catalyzed transesterification reaction than that of NaOH catalyzed reaction.

Table 9 Conversion of methyl ester and unreacted triglycerides in MSO for both catalysts

Catalysts	Time [h]	Component	Conversion [–]
NaOH	4	Triolein	0.045994496
		Methyl ester	0.001977341
CaO	4	Triolein	0.006000827
		Methyl ester	0.007497433

The reason behind the low conversion resulted from NaOH catalyst reaction is the interference of x_{FFA} existing in the MSO feed oil.

From the results of the reactions, shows that the free fatty acids have more effect on the homogeneously catalyzed reactions than the heterogeneously ones. The MSO had a higher value of FFA which interferes with the methyl ester conversion in NaOH catalyzed reaction. On the other hand, the effect of FFA does not affect much in the case of CaO.

4. Conclusion

It was difficult to determine the composition of Mahogany seed oil (MSO) in detail, since MSO could not be converted sufficiently for analysis. In some runs with larger amount of sodium hydroxide, MSO phase was emulsified and the deacidification was impossible.

The transesterification rate of the model feed oil with the catalyst of sodium hydroxide, homogeneous catalyst, was higher than that with calcium oxide, heterogeneous catalyst, because the content of free fatty acid was low in the model feed oil. On the contrary, the transesterification of MSO with calcium oxide was faster than that with sodium hydroxide, where MSO contained high amount of free fatty acid.

These results are helpful to design the system of biodiesel production from Mahogany seed oil.

5. References

[1] Fact Sheet | Climate, Environmental, and Health Impacts of Fossil Fuels (2021) | White Papers | EESI, 2021. [Online]

[2] Sahar, Sadaf, S., Javed, I., and Inam, U., Biodiesel production from waste cooking oil: An efficient technique to convert waste into biodiesel, Pakistan, 2018, pp. 220–226.

[3] Gebremariam S. N., and Marchetti J. M., Economics of biodiesel production: Review, Norway, vol. 168, 2018, pp. 74–84.

[4] Thangaraj, B., Solomon, P. R., Muniyandi, B., Ranganathan, S., and Lin, L., Catalysis in biodiesel production—a review, China, vol. 3, no.1, 2019, pp. 2–23.

[5] Rana, S., Haque, M., Poddar, S., Sujan, S., Hossain, M., and Jamal, M., Biodiesel production from non-edible Mahogany seed oil by dual step process and study of its oxidation stability, Bangladesh, vol. 50, no. 2, 2015, pp. 77–86.

[6] Arazo, R. O., Abonitalla, M. R., Gomez, J. M. O., Quimada, N. E., Yamuta, K. M. D., and Mugot, D. A., Biodiesel production from Mahogany seed oil, Philippines, vol. 1, no. 2, 2016, pp. 8-18.

[7] Habaki, H., Hayashi, T., and Egashira, R., Deacidification process of crude inedible plant oil by esterification for biodiesel production, Japan, vol. 6, no. 2, 2018, pp. 3054–3060.