

In Situ Transesterification of Mahogany Seed Oil (*Swietenia Macrophylla King*) Become of Methyl Ester with Co-solvent N-hexane

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Abstract: The purpose of this research was to assess the effectiveness of the use of co-solvent n-hexane for in situ transesterification reaction mahogany seed oil as a biodiesel. Variables and operating conditions include catalyst KOH 0.075 mol/L, stirring speed of 600 rpm, 40°C the reaction temperature, % FFA oil is 1,42%, moisture content seed of 0.8%, reaction time is 2, 4, 6, 8 and 10 hours and the mass ratio of seed:methanol:n-hexane is 1:3:2, 1:3:3 and 1:3:4. Mahogany seeds that have been dried and pulverized size +20/-30 mesh as much as 50 grams included in the three-neck flask equipped condenser and added methanol, n-hexane and catalyst KOH and the reaction carried out in accordance with the variables and operating conditions. After the reaction is complete, the filtrate and cake was separated. To stopped the reaction with neutralized the KOH catalyst with added HCl 1 mol/L to pH 4. The filtrate distilled at a temperature of 70°C and the residue distilled included in the separating funnel and allowed to stand for 12 hours in order to form two layers. From the research data obtained the best results at a mass ratio of seed:methanol:n-hexane is 1:3:4 and reaction time 4 hours with yield methyl esters of 88.18%. Methyl ester density 0.8791 g/cm³ meet SNI 04-7182-2006 from 0.85 to 0.89 g/cm³.

Keywords : biodiesel, co-solvent, in situ transesterification, mahogany seed oil.

Introduction

The world needs more fuel will increase every year and as long as this can only be met by fossil fuels. On the other side of fossil fuel reserves are already very thin out and eventually will run out too. The use of renewable energy sources is the right choice to replace fossil fuels. Selection of renewable energy sources is based on the advantages compared to fossil fuels that is due to its eco-friendly raw material available continuously. One source of renewable energy is an environmentally friendly biodiesel, which in some countries has been used.

Mahogany (*Swietenia Macrophylla King*) is a plant that is commonly grown as a street tree. The wood from this plant is commonly used for furniture because of its harsh, resin can be used for adhesive, while the seeds can be used as a remedy for various ailments. In addition to the efficacious as a remedy, in the seeds of mahogany also contained oil. The oil contained in the seeds of mahogany very potentially for utilization and development of biodiesel.

The seeds of mahogany type *Khaya Senegalensis* contain oil about 52.5%, mahogany seed oil does not contain essential fatty acids that do not have values for the nutrients and is non-edible oil^{1,2}. Mahogany seeds content oil greater than castor bean are about 30-50%³. The fatty acid composition of mahogany seed oil was

palmitic acid (12.50%), stearic acid (16.42%), oleic acid (25.30%), linoleic acid (33.87%) and linolenic acid (11.32%)⁴.

Some research on making biodiesel from mahogany seed oil with the process of transesterification has done. Transesterification *neem* oil get yield 83% at a temperature reaction of 50°C, reaction time of 90 minutes, catalyst NaOH 1.5% weight and volume of methanol 180 mL⁵. Biodiesel produced from *neem* oil which is non-edible oil can be used as diesel fuel and environment-friendly raw material does not compete with foods⁶. Transesterification of *Neem* seed oil (*Azadirachta indica*), namely the family *Meliaceae* mahogany trees that grow in India with NaOH catalyst, get methyl ester yield of 83% at a temperature reaction of 55°C, ratio mole of oil: methanol = 1:12 and reaction time of 2 hours⁷. Biodiesel from seed oil of *Azadirachta indica* regards with European EN 14214 and US ASTM D 6751 02⁸.

In situ transesterification can be one alternative to get a more efficient process. In situ transesterification process of combining the two processes should be done separately, namely the process of oil extraction and transesterification reaction, so that the time processing, cost, and the amount of solvent needed could be saved⁹. Triglyceride used on in situ transesterification process is triglycerides derived from raw material sources and not from oil extraction and purification¹⁰. The mechanism of in situ transesterification process is the direct contact between the oil resources of raw materials with alcohol and acid or base catalyst. The function of acid or base catalyst is to help destroy the cell walls containing oil, so the alcohol can dissolve the oil¹¹. On in situ transesterification, alcohol has two functions as a solvent in the process of oil extraction and as a reactant in the transesterification process.

Research in situ transesterification process in the manufacture of biodiesel has been widely performed. On in situ transesterification of cotton seed oil getting conversion oil into biodiesel of 98% with the concentration of NaOH 0.1 mol/L, a molar ratio of reactant (methanol/oil) 135:1, seed moisture content < 2%, particle size of 0.3-0.335 mm, temperature and reaction time are 40°C and 3 hours¹². On in situ transesterification of soybean seed oil with an alkaline (NaOH) catalyst, generating the highest yield on temperature reaction of 60°C with a molar ratio of methanol/NaOH/triglyceride of 226:1:1.6 and reaction time of 8 hours¹³. Obtained methyl ester yield of 88.8% and methyl ester concentration of 90.3% on in situ transesterification of rapeseed oil with reaction temperatures of 60°C, reaction time of 1 hour, a molar ratio of methanol:oil = 475:1, size seeds of 300–500 µm, mass material of 25 g and concentration of catalyst NaOH 0,1 mol¹⁴.

If seen from the above research in situ transesterification, the shortcomings of the in situ transesterification method was required relative reaction temperature is still high (40-60°C), reaction time is relatively long (60 minutes to 8 hours), stirring is relatively fast (600-800 rpm) and the ratio molar of material:methanol is high. This is because the solubility of triglycerides in alcohol is low. Catalyst in methanol phase where the reaction occurs at this phase giving rise to mass transfer limitations that cause lag time on transesterification with metanol¹⁵. One way to overcome the limitations of mass transfer and speeding up reaction time with the addition of an inert material that acts as co-solvent. Co-solvent will change the reaction system from two phases into one phase, because co-solvent capable of dissolving alcohol and triglycerides.

Research on the use of co-solvent on in situ transesterification has also already done. Get FAME yield of 99.8% with the size of the castor bean seed < 0,355 mm, co-solvent n-hexane 10% vol. methanol, reaction temperature of 60°C, reaction time of 24 hours, ratio methanol:seed is 7,5 ml/gr and catalyst H₂SO₄ 15%⁹. Get the biodiesel yield of 89% with ratio methanol:castor seed is 6:1, 0.075 mol/L KOH in methanol, the ratio of n-hexane methanol:seeds = 3: 3: 1, the stirring speed 600 rpm, the reaction temperature of 40°C and reaction time of 6 hours¹⁶. On the transesterification of castor seed oil getting to ethyl ester yield of 65.6% on reaction time of 2 hours, stirring speed 300 rpm, a mass of castor seed 20 grams, catalyst KOH of 1%, ratio molar of ethanol:oil is 60:1, ratio volume of ethanol:n-hexane = 20% volume of oil¹⁷. On in situ transesterification copra using a mixture of methanol and THF, get the highest yield of 96.7% at a temperature reaction of 60°C, reaction time of 20 hours, the ratio of methanol/copra = 200 mL/100 g, the ratio volume of THF: methanol = 0.4, ratio molar of methanol:oil = 60: 1 and catalyst H₂SO₄ 15 mL¹⁸.

This research is expected to optimize the utilization of mahogany seed waste as feedstock for biodiesel through the in situ transesterification process using a co-solvent n-hexane so that it brings a more efficient process and produces a high yield of methyl ester.

Materials and Methods

The primary research material namely seeds of mahogany obtained from Blitar area. The reagents used in the study include methanol (MERCK, 99.9%) of n-hexane (MERCK, 99.8%) and KOH pellets (Riedel-de Haen, 99%). The reaction was carried out on a laboratory scale using a three-necked flask fitted with condenser, thermometer and magnetic stirrer. The reaction temperature was maintained at a temperature of 40°C using atmospheric pressure and the water bath.

Mahogany grains that have been drained and mashed the size + 20/-30 mesh, analyzed the levels of the water and % FFA. Constructing the reactors as a reaction place consisting of three neck flask and condenser and strengthening the position with a statif. Then put the reactor on a hot plate magnetic stirrer. Enter 50 grams mahogany seeds dried, n-hexane, methanol and catalyst KOH of 0.075 mol/L into the reactor and do the reaction at a temperature of 40°C and arrange buttons round magnetic stirrer at a speed of 600 rpm¹⁶. The reaction temperature control was performed by looking at the temperature of the thermometer mounted on the reactor and the evaporation of methanol and n-hexane prevented by condenser. Variations in the ratio weight of oil:methanol:n-hexane was used 1:3:2, 1:3:3 and 1:3:4 and the reaction time of 2, 4, 6, 8 and 10 hours. To stop the reaction KOH catalyst was neutralized with added 1 mol/L HCl to pH 4¹⁹. Results of the reaction and mahogany seed cake then separated with filter paper. The filtrate results reaction was distilled at a temperature of 70°C until no dripping distillate. Separation of spent methanol and co-solvent n-hexane can be done easily because the boiling point closed²⁰. Distillate was spent methanol and co-solvent, while the residue was a mixture of methyl ester, oil, glycerol and catalyst. Residues were incorporated in funnel separator for 12 hours to form 2 layers were then separated. The lower layer was lightly browned was glycerol and catalyst KOH, while the top layer of yellow was a methyl ester and a mahogany seed oil did not react. The top layer as heavily weighted of methyl esters.

Results and Discussion

Raw material mahogany seed after the dried and crushed, analyzed the water levels and water levels obtained by 0.8%. Mahogany seed powder was extracted of oil with solvent methanol and n-hexane with a mass ratio of material:methanol:n-hexane = 1:3:4 for 10 hours. From the results obtained by extraction of 18 grams of seed oil of 50 gram dried mahogany seeds. Oil extraction results was analyzed % FFA and % FFA of 1.4034% so that it can be directly carried out in situ transesterification reactions. Yield methyl ester was calculated using the following equation:

Yield (%) =	Weight of methyl ester	X 100
	Weight of initial mahogany seed oil	

The Influence of Ratio Weight of Seed:Methanol:N-hexane and Reaction Time Against the Weight of The Methyl Ester

The residue distillation results after separated was then weighted weight of methyl esters. Weighing was carried out for each of the variables ratio weight of seed:methanol:n-hexane at different reaction time. From Table 1 it can be seen that the ratio weight of seed: methanol:n-hexane and reaction time give effect on the weight of the methyl esters obtained. The greater the ratio weight of seed:methanol:n-hexane and the longer reaction time, then the weight of the methyl ester was got bigger.

Table 1. Weight of Methyl Esters on Different Variable Ratio Weight of Seed: Methanol:N-hexane and Reaction Time

Ratio Weight of Seed:Methanol:N-hexane	Reaction Time (hour)	Weight of Methyl Ester (gram)
1:3:2	2	7,3695
	4	8,4223
	6	10,5278
	8	12,6334
	10	13,6862

1:3:3	2	9,8223
	4	12,2778
	6	13,5056
	8	14,7334
	10	15,4350
1:3:4	2	15,4306
	4	15,8715
	6	15,7112
	8	15,5509
	10	15,2703

On reaction time of 10 hours for ratio weight of seed:methanol:n-hexane 1:3:2 and 1: 3:3 was obtained by weight of methyl ester 13,6862 grams and 15,4350 grams. On the ratio weight of seed:methanol:n-hexane 1:3:4 for reaction time of 4 hour was obtained by weight methyl ester 15,8715 grams and this result was the optimum conditions. From these results it can be said that the ratio weight of seed:methanol:n-hexane was the most influential variables on the increased weight of the methyl ester.

The Influence of Ratio Weight of Seed:Methanol:N-hexane to % FFA and The Density of Biodiesel

Ratio weight of seed:methanol:n-hexane effect on % FFA and the density of biodiesel were produced. Analysis of the % FFA and the density of biodiesel were done on each of the variables ratio weight of seed:methanol:n-hexane for the best conditions. From Table 2 to see that the higher ratio weight of seed:methanol:n-hexane, then the lower the % FFA methyl ester. This was because with the growing number of oil into methyl ester reacting, then the less residual oils that didn't reacted that was the source of the causes of high FFA. The smaller the % FFA then the better quality of the methyl ester was generated, because the % FFA-related damage to components of the compiler of the methyl ester. The best result obtained of % FFA in the ratio weight of seed: methanol: n-hexane = 1:3:4 of 0.5439%.

All density of methyl ester produced regards the specifications of the SNI 04-7182-2006 of 0.85-0.89 g/cm³. On the ratio of weight of seeds:methanol:n-hexane = 1:3:4 was the best conditions available density of methyl ester of 0.8785 g/cm³.

Table 2. The Influence of Ratio Weight of Seed:Methanol:N-hexane to % FFA and The Density of Methyl Ester

Ratio Weight of seed:methanol:n-hexane	% FFA	Density (g/cm ³)
1:3:2	0.5790	0.8649
1:3:3	0.5614	0.8751
1:3:4	0.5439	0.8785

The Influence of Ratio Weight of Seed:Methanol:N-hexane and Reaction Time to Yield Methyl Ester

Ratio weight of seed:methanol:n-hexane and reaction time was affected to yield methyl ester. From Figure 3 it can be seen that with the increasing ratio weight of the addition of co-solvent n-hexane and the longer reaction time, methyl esters yield obtained will be higher. This is because with the longer reaction time then the more methyl esters obtained. The longer the solvent and co-solvent to extract mahogany seed oil, it will produce more oil which was a reactant in the form of methyl ester in the process of in situ transesterification. Can be seen that the addition of co-solvent n-hexane can improve the methyl ester results. This was because in addition n-hexane as a solvent to speed up reactions also help extract oil from the seeds of mahogany. The more n-hexane was added, the solubility of triglycerides of methanol is getting bigger and faster running and reaction of methyl ester produced more and more.

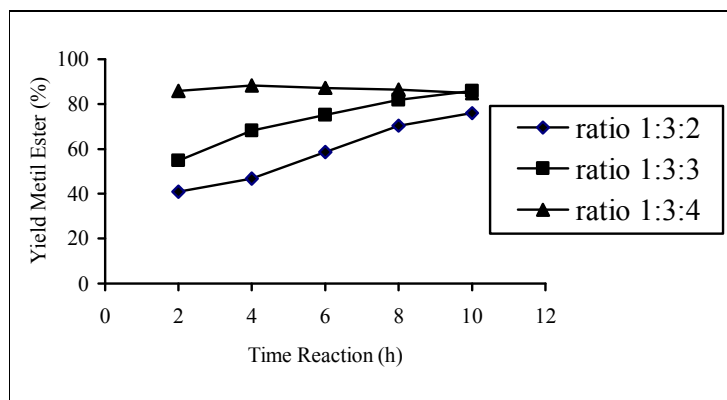


Figure 1. Influence of Reaction Time (h) and Ratio Weight of Seed:Methanol:N-hexane to yield methyl ester (%) on In Situ Transesterification of Mahogany Seed Oil.

The addition of co-solvent n-hexane and reaction time effect on acquisition to yield methyl ester. Can be seen from Figure 1, the best condition on ratio weight of seed:methanol: n-hexane 1:3:2 with a reaction time of 10 hours obtained yield methyl ester of 76.03%, whereas the ratio of the weight of seed:methanol:n-hexane 1:3:3 with a reaction time of 10 hours obtained yield methyl ester of 85.75%. Optimum condition on this research in ratio weight of seed:methanol:n-hexane 1:3:4 with a reaction time of 4 hours, obtained yield methyl ester of 88.18%.

Neem oil transesterification get yield of 83% at a temperature reaction of 50°C, reaction time of 90 minutes, catalyst NaOH of 1.5% weight and volume of methanol 180 mL⁵. On a conventional transesterification seed oil of *Neem (Azadirachta indica)* without co-solvent obtained yield of 83% at a temperature reaction of 55°C, mole ratio of oil:methanol = 1: 12 and reaction time of 2 h⁷.

When compared to the results of research on the mahogany seed oil transesterification, then research results was relatively better because the highest yield methyl 88.18% was obtained at a temperature reaction of 40°C. On conventional transesterification mole ratio of oil:methanol was used smaller when compared to the ratio of moles of oil:methanol on in situ transesterification with co-solvent. This is because the methanol as the solvent in the in situ transesterification in addition reactions, the reactants/help also to extract oil from the seeds of different to conventional transesterification of oil already available as reactants.

Obtained yield methyl ester of 99.8% with solvent n-hexane 10% vol. of methanol, a temperature reaction of 60°C, reaction time of 24 h and the ratio of methanol:seed 7,5 ml/gr⁹. Obtained yield biodiesel of 89% on the ratio of methanol:castor bean seeds 6:1, the ratio of n-hexane: methanol: ingredient 3: 3: 1, the stirring speed of 600 rpm, the reaction temperature of 40°C and reaction time of 6 h¹⁶. The results of this research were relatively better because the highest yield methyl of 88.18% was obtained on the reaction time of 4 h and the reaction temperature of 40°C.

Got to yield methyl ester of 65.6% on reaction time of 2 h, the ratio of the volume of ethanol:n-hexane = 20% of the volume of oil¹⁷. The highest yield was obtained by 96.7% at a temperature reaction of 60°C, reaction time of 20 h, the ratio of methanol/copra = 200 mL/100 g, the ratio of the volume of THF:methanol = 0.4 and catalyst H₂SO₄ of 15 mL¹⁸. The results of this research were relatively better because the highest yield methyl of 88.18% was obtained on the reaction time of 4 h and the reaction temperature of 40°C.

Conclusions

The highest yield methyl ester was obtained of 88.18% in reaction time of 4 h, the reaction temperature of 40°C, stirring speed of 600 rpm, and the ratio weight of seed: methanol:n-hexane = 1:3:4. This was because the longer the reaction time and the greater the ratio weigh of seed:methanol:n-hexane then yield methyl ester was got bigger. Yield methyl ester produced on in situ transesterification mahogany seed oil with solvent was higher when compared to the process conventional transesterification of mahogany seed oil with the same reaction time. The use of alkaline catalysts will generate yield methyl esters was higher in a relatively short time compared to the acid catalyst.

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