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Esterification and Purification of Rubber Seed Oil for Biodiesel Synthesis

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Abstract: Rubber seed oil (RSO) is extracted from rubber seed kernel by using screw press and used as a feed stock for biodiesel synthesis via acid treatment. The yield of RSO from rubber seed kernel is about 36 % and free fatty acids (FFA) content of this oil is 9.288%. Due to high acid value of RSO, acid treatment of RSO has been carried out to reduce FFA and purification process is followed to synthesize biodiesel. Acid treatments (esterifications) of RSO are carried out to study the influence of: including molar ratios of methanol to RSO, quantity of sulfuric acid catalysts, reaction temperatures and reaction times. The best condition of acid treatment is molar ratio of methanol to RSO 6:1, 1% (vol. %) of sulfuric acid, temperature 50ºC, reaction time of 30 minutes and the yield of esterified rubber seed oil (ERSO) about 95%. The amount of FFA is reduced from 9.288% to less than 2% at the end of the acid treatment. ERSO obtained from the acid treatment is purified by using sodium hydroxide and methanol solution to synthesize biodiesel. The best yield of biodiesel about 89% is obtained when the operating condition of the purification process (neutralization and transesterification) is 9:1 molar ratio of methanol to ERSO, 0.5 wt. % of sodium hydroxide, temperature of 50ºC, reaction time of 30 minutes and stirring rate of 750 rpm. The prepared biodiesel from this study is analyzed and found that its properties meet within the limits of ASTM specifications of biodiesel.

Keywords: biodiesel, RSO, methanol, sulfuric acid, esterification, sodium hydroxide, transesterification

1. INTRODUCTION

Worldwide increasing oil crisis and reducing fossil fuel reserve act as a driving force behind the search of alternative fuels. The major portion of the total energy consumed worldwide is now coming from fossil fuel sources. Fossil fuel sources are non-renewable, and will be exhausted by near future. Biodiesel can be a wonderful replacement to conventional petro-diesel fuel, which can be produced from a renewable domestic resource [1].

Biodiesel derived from renewable plant sources is monoalkyl esters of long chain fatty acid which fall in the carbon range C_{12}-C_{22}. It has similar properties as mineral diesel. Various processes exist to convert vegetable oils (mainly triglycerides) into biodiesel. Transesterification of vegetable oils using alcohol in a catalytic environment is most commonly used method for producing biodiesel. The equilibrium conversions of Triglycerides (TG) is affected by various factors, namely, type of alcohol used, molar ratio of alcohol to TG, type of catalyst, amount of catalyst, reaction temperature, reaction time and feedstock quality (like free fatty acid content, water content etc.) [2].Biodiesel, however, is made from renewable resources, is biodegradable and nontoxic, and has a higher flash point than normal diesel. In addition, biodiesel increases lubricity, which prolongs engine life. Another significant advantage of biodiesel is its low emission profile and its oxygen content of 10-11%. In other words, biodiesel does not contribute to global warming. Many researchers reviewed and investigated the methods for the synthesis of biodiesel. Currently, most biodiesel is prepared using alkaline catalysts. Even though transesterification is feasible using base catalysts, the overall base – catalyzed process suffers from serious limitations that translate into high production costs for biodiesel. In particular, the total free fatty acids (FFA) content associated with the lipid feedstock must not exceed 0.5wt%. FFA which acts as a potential contaminant reacts with alkaline catalyst to form soap. Soap can cause glycerol separation problem [3]. The demanding feedstock specifications for base catalyzed reactions have led researchers to seek catalytic and processing alternatives that could ease this difficulty and lower production costs. Methodologies based on acid-catalyzed reactions have the potential to achieve this fact. The production of biodiesel from high FFA containing feedstock needs a treatment to convert the FFAs to ester. This treatment process is known as esterification. Numerous different vegetable oils (soybean oil, coconut oil or palm oil, etc.) have been tested as biodiesel in our country. In the present study, rubber seed oil, typical non-edible high FFA oil is considered as a potential feedstock for biodiesel production [4].

The annual rubber seed production potential in Myanmar is about 21,600 tons and from this tonnage of seed about 3,700 tons of oil could be obtained. At present rubber seed oil does not find any major applications. The purpose of the present study is to develop a method for the acid treatment of high FFA rubber seed oil to synthesize biodiesel. Thus, rubber seed oil is considered as a potential feedstock for biodiesel production in this study.

2. EXPERIMENTAL PROCEDURE

In this work, the following steps were contained.

(1) Preparation of the raw materials, rubber seeds
(2) Extraction of the rubber seed oil
(3) Analysis of the extracted rubber seed oil

(4) Acid treatment (esterification) of the rubber seed oil (RSO)
(5) Preparation of Base-Catalyst solution for esterified rubber seed oil (ERSO)
(6) Purification process of the ERSO to biodiesel synthesis
(7) Determination of the properties of the prepared biodiesel

2.1. Preparation of Raw Materials

Rubber seeds were discarded the damaged and discolored wet kernels and crushed the fresh kernels. The rubber seeds usually ripen during July, August, September and collection has to be well organized during this period. The seeds should be collected as fresh as possible, not allowing them to be on the ground for more than three days.

For this study, matured rubber seeds from Mayantaung Village in Kyaikto Township are purchased in July. These matured rubber seeds are partially sun dried and decorticated manually. The moisture contents of the shell and fresh/wet kernels are determined and their weights are measured to estimate the average composition of the fresh rubber seed. These wet kernels are not suitable for the extraction of oil. The kernels are sun dried for several hours and heated for about 30 minutes in oven to reduce the moisture content.

2.2. Extraction of the Rubber Seed Oil

Rubber seed oil (RSO) is obtained from the dried kernels by the method of mechanical extraction using a screw press. In carrying out the first pressing, no oil can be extracted. After the second run, the oil content obtained is not preferrable and so the operation is recycled until no more oil can be extracted.The extracted RSO and residual press cake are weighed and determined the moisture contents of them to estimate the composition of the dried kernels.

The residual cake, by-product of this process, can be used as an animal feed for its high nutritive value or as a fertilizer for containg nitrogen and potash.

2.3. Analysis of the Rubber Seed Oil

In this study, rubber seed oil was used as triglyceride source and methanol was used as alcohol source. The free fatty acid, acid value, moisture content, saponification value, peroxide value, iodine value, specific gravity, cloud point of rubber seed oil were analyzed and the result data are shown in Table 1.

Table 1. Characteristics of Rubber Seed Oil

Item	Result
Moisture content (vol%)	0.1779
Free Fatty Acid (as oleic acid %)	9.288
Acid Value	18.58
Saponification Value (g/100g sample)	184.253
Iodine Value (g/100g sample)	121.46
Peroxide Value (meq/kg)	0.6767
Specific gravity	0.92
Cloud point	4.5

2.4. Esterification of the Rubber Seed Oil

The acid-catalyzed esterification reaction of rubber seed oil are added into a 1 liter flat bottom flask and placed over a magnetic stirrer. The catalyst and methanol was added and stirred the mixture with stirring rate 750rpm. The reaction time is 30 min. After 30 min the mixture is poured into the separating funnel to remove the excess alcohol. In the excess alcohol, sulfuric acid and other impurities are included and then these are moved into the upper layer. Then the lower layer (ERSO) is separated to neutralize and transesterification.

Process Condition for preparation of Esterified rubber seed oil is shown in Table 2.

Table 2. Process Condition for Esterification Process

Alcohol to oil molar ratio	4:1,5:1,6:1,7:1,8:1
Acid catalyst (%)	0.3, 0.4, 0.5, 0.6, 0.7
Reaction temperature(˚C)	40, 45, 50, 55, 60
Reaction time, min	20, 30, 45, 60, 120
Stirring rate, rpm	750

2.5. Preparation of Base-Catalyst Solution

The catalyst Sodium hydroxide, 0.5wt% of the oil was first weighed and dissolved in methanol with the stoichiometric amount required for the reaction. It looks more than 15 min to form homogeneous solution.

2.6. Purification Process for Biodiesel

The base-catalyzed transesterification reaction of esterified rubber seed oil are preheated to the required reaction temperature of 45± 2˚C in the 1 liter flat bottom flask and placed over a magnetic stirrer. Meanwhile, catalyst dissolving methanol is added and stirred for 30 min with stirring rate 750 rpm. The reaction is stopped, and the products are allowed to separate into two layers. The lower layer, which contained impurities and glycerol, is drawn off. The ester remains in the upper layer. Methyl ester is washed by distilled water to remove the entrained impurities and glycerol. Lower layer is discarded and yellow color layer (known as biodiesel) is separate. The biodiesel layer is then heated to remove all the solvent and water. Table 3 shows the process conditions for biodiesel synthesis.

Table 3. Process condition for the preparation of Biodiesel

Alcohol to oil molar ratio	6:1, 7:1, 8:1, 9:1, 10:1, 11:1
Base to oil ratio (wt. %)	0.3, 0.4, 0.5, 0.6, 0.7
Reaction temperature(˚C)	40, 45, 50, 55, 60
Reaction time (min)	20, 30, 60, 120
Stirring rate (rpm)	400, 750, 800

3. RESULTS AND DISCUSSION

3.1. Effect of Molar Ratio to Acid Esterification

The results of yield percentage of esterified oil layer and FFA values are shown in Table 4. From Figure 3.1 for constant temperature (50˚C), constant time (30min), constant acid catalyst (0.5%) and stirring rate 750 rpm. In Figure 3.1, the

good conversion and yield of oil layer is achieved vary close to the molar ratio 6:1. With further increase in molar ratio there is only improvement in the conversion efficiency but not in yield of oil layer. The esterification process reduces the viscosity of the oil. Also it has been found that the reduction in viscosity increases with increase in molar ratio.

Table 4. Yield% of RSO with different molar ratio

Expt.	MeOH:Oil	FFA (%)	Conversion (%)	Yield (%)
Expt.1	4:1	2.9	69	90
Expt.2	5:1	2.7	71	91
Expt.3	6:1	1.4	85	95
Expt.4	7:1	1.9	80	93
Expt.5	8:1	1.5	84	94

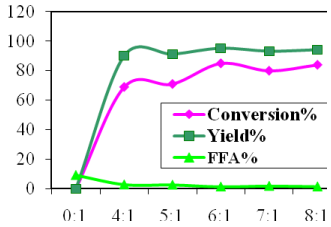

Figure 3.1. Conversion%, Yield% & FFA% of ERSO

3.2. Effect of Reaction Temperature

Four different variation of temperature are shown in Figure 3.3 and it has been found that 50˚C is the best and appropriate temperature at constant time (30min), constant catalyst (0.5%) and constant molar ratio (6:1). With increase in temperature the conversion percent gradually increase. High reaction temperature increase in darkness of the product esterified rubber seed oil (ERSO) and also increase the production cost of biodiesel. The maximum yield of ERSO is obtained at 50˚C. And then high reaction temperature effect the production cost. Table 5 shows the effect of reaction temperature on FFA and yield percent of ERSO.

Table 5. Effect of reaction temperature on Yield% of RSO

Expt.	Temp (˚C)	FFA (%)	Conversion (%)	Yield (%)
Expt.6	40	2.5	74	87
Expt.3	50	1.4	85	95
Expt.7	60	1.9	79	90
Expt.8	70	1.7	82	89

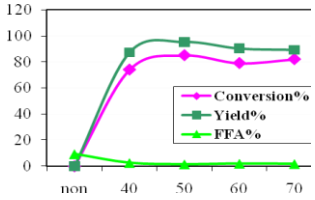

Figure 3.2. Conversion%, Yield% and FFA% of ERSO at different reaction temperature

3.3. Effect of reaction time to Esterification

The results of yield percentage of are shown in Table 6 and conversion percent and FFA are shown in Figure 3.3. From Figure 3.3, it has been found that the yield slightly decrease with increase in reaction duration after 30 min. Therefore, prolong reaction time is not suitable for ERSO preparation process. Therefore, prolong reaction time is not suitable for ERSO preparation process. Therefore, reaction time 30 min is the best to prepare ERSO.

Table 6. Yield% of RSO with different reaction time

Expt.	Time (min)	FFA (%)	Conversion (%)	Yield (%)
Expt.9	20	3.8	59	70
Expt.3	30	1.4	85	95
Expt.10	45	2.0	78	85
Expt.11	60	2.7	71	84
Expt.12	120	2.8	70	82

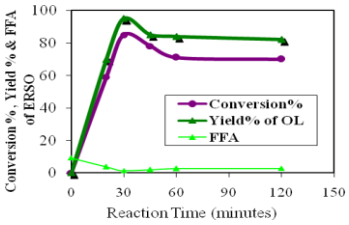

Figure 3.3. Conversion%, Yield% & FFA% of ERSO with different reaction time

3.4. Effect of Acid Catalyst Amount

The amount of acid catalyst used in the process also affects FFA and the conversion efficiency of the process. The catalyst amount is varied in the range of (0.25, 0.5, 0.75, 1 and 1.25% of sulfuric acid) are shown in Table 7. These percentages are volume fractions of the oil supplied for this reaction. The maximum yield of oil layer was achieved if the added catalyst amount was 1%. Increasing the catalyst amount can give the gradually increase conversion percent but be darken the color of ERSO. So, the appropriate catalyst amount for this process was 1% H_2SO_4.

Table 7. Yield% of RSO with different acid catalyst amount

Expt.	H_2SO_4	FFA (%)	Conversion (%)	Yield (%)
Expt.13	0.25	3.5	62	75
Expt.3	0.5	1.4	85	95
Expt.14	0.75	1.6	83	89
Expt.15	1.00	1.1	88	95
Expt.16	1.25	1.4	85	94

3.5. Effect of Molar Ratio to Purification

The effect of molar ratio on biodiesel yield was studied. The results of yield percentage of biodiesel are shown in Table 8. In this Table, six different variation of molar ratio at constant sodium hydroxide catalyst 0.5%, reaction temperature 50˚C, reaction time 30min and stirring rate 750 rpm. Molar ratio 9:1

gives the highest yield percent of biodiesel. The more methanol is added, the lower yield percent of biodiesel can give. In Figure 3.5, it shows that the maximum yield percent is obtained for the molar ratio 9:1. Therefore, the best and the appropriate molar ratio of the purification process is chosen as 9:1.

Table 8. Yield% of Biodiesel with different molar ratio

Expt.	Molar Ratio (MeOH:ERSO)	Yield% (Biodiesel)
Expt.15-1	6:1	70
Expt.15-2	7:1	73
Expt.15-3	8:1	85
Expt.15-4	9:1	89
Expt.15-5	10:1	80
Expt.15-6	11:1	58

3.6. Effect of Alkaline Catalyst Amount to Purification Process

The effect of catalyst percent on biodiesel yield was studied. Table 9 shows that, different variations of catalyst (0.3, 0.4, 0.5, 0.6 and 0.7%) at constant reaction temperature 50˚C reaction time 30min and stirring rate 750 rpm. The value of catalyst percent reached 0.5%, yield percent of biodiesel was 89%. Beyond the catalyst percent at 0.55, the yield percent of the biodiesel was decreased. It was due to the trace amount of soap formation in the reaction mixture. Moreover, the increase amount of catalyst was also resulted in higher salt and water concentration in the crude glycerin.

Table 9. Yield% of Biodiesel with different amount of alkaline catalyst

Expt.	NaOH (wt%)	Yield% (Biodiesel)
Expt.15-7	0.3	55
Expt.15-8	0.4	75
Expt.15-4	0.5	89
Expt.15-9	0.6	82
Expt.15-10	0.7	81

3.7. Effect of reaction temperature to Purification Process

The effect of reaction temperature on biodiesel yield is studied. According to the Figure 3.4 the reaction temperature was increased, the yield percent of biodiesel is decreased. If the lower the reaction temperature (below 50˚C), the yield percent of biodiesel will be decreased. Different kinds of temperature are shown in Table 10. Reaction temperature 50˚C is the best to give the highest yield of biodiesel.

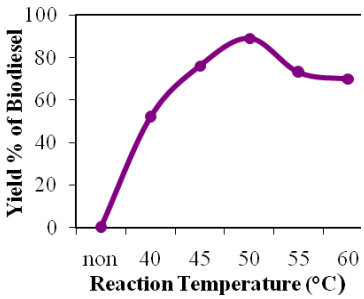

Figure 3.4. Yield% of Biodiesel with different reaction temperature

Table 10. Yield% of Biodiesel with different reaction temperature

Expt.	Temperature (˚C)	Yield% (Biodiesel)
Expt.15-11	40	52
Expt.15-12	45	76
Expt.15-4	50	89
Expt.15-13	55	73
Expt.15-14	60	70

3.8. Effect of reaction time on Purification process

In order to achieve perfect yield percentage of biodiesel, they must be needed to sufficient reaction time. Table11 shows different variation of reaction time studied. Reaction time 30min gives the highest yield percent of biodiesel 89%. If the reaction time is increased, the yield percent of biodiesel will be slightly decreased as shown in Figure 3.5.

Table 11. Yield% of Biodiesel with different reaction time

Expt.	Time (minutes)	Yield% (Biodiesel)
Expt.15-15	20	70
Expt.15-4	30	89
Expt.15-16	60	77
Expt.15-17	120	79

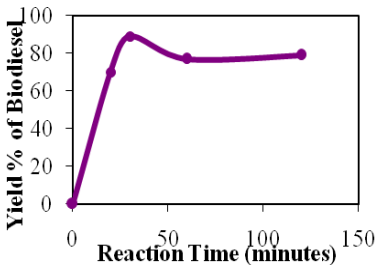

Figure 3.8. Yield% of Biodiesel with different reaction time

3.9. Effect of stirring rate on Purification Process

Mixing by stirring is very important for transesterification reaction, as oils or fats are immiscible with sodium hydroxide-methanol solution. The reaction can become diffusion

controlled or poor diffusion between the phases results in a slow rate. Table 12 shows the different stirring rate was studied. Among them 750 rpm gives the highest yield percent of biodiesel.

Table 12. Yield% of Biodiesel with different stirring rate

Expt.	Stirring rate (rpm)	Yield% (Biodiesel)
Expt.15-18	400	80
Expt.15-4	750	89
Expt.15-19	800	62

3.10. Properties of Biodiesel from RSO Compared with ASTM Standards

The results of total, free and combined glycerol content and fuel properties of prepared biodiesel are shown in Table 13.

According to the Table 13 , carbon residue is higher than the specification. If the proper separation is conducted, the carbon residue value will be within the specification. From the color test, biodiesel is not being colorless. This color may be due to the color of the rubber seed oil. But its color does not predict fuel quality.

Table 13. The Properties of Crude Biodiesel Compared with ASTM Standard

Properties	ASTM D_{6751}	Biodiesel
Total glycerol %	0.24%	0.045
Free glycerol %	0.02%	0.006
Combined glycerol %	0.22%	0.089
Kinematic viscosity	1.9-6.0 cSt	4.56
Specific gravity	0.88	0.88
Flash point	100-170	100
Pour point	-15to 10 ˚C	+9
Carbon Residue	0.01wt%	0.048wt%
Total acid number	0.8	0.6
Free Fatty acid	-	0.0908
Cetane index	48.65	47.27
Copper strip corrosion	3Max:	1(a)
Initial boiling point	-	312 ˚C
Colour	-	L1.0

4. CONCLUSION

In this study, the production of fuel-quality biodiesel from rubber seed oil is investigated. Rubber seed oil's stir rate of 750 rpm is carried out. Initial free fatty acid and moisture content of rubber seed oil are 9.288% and 0.1779% respectively. In the esterification process, initial FFA content of the oil is reduced to less than 2%. In this process, different variations of methanol to oil molar ratio (4:1, 5:1, 6:1, 7:1, 8:1), acid catalyst (0.25%, 0.5%, 0.75%, 1%, 1.25%), reaction temperature (40˚C, 50˚C, 60˚C, 70˚C) and reaction time (20, 30, 45, 60, 120 min) are analyzed in order to obtain which one is the best. Excess addition of sulfuric acid gives darkens color of the esterify rubber seed oil. In this process, it has been also found that molar ratio 6:1, acid catalyst 1%, reaction temperature 50˚C and reaction time 30 min is the best. We were obtained the esterify rubber seed oil (ERSO) and it was included a few amount of acid catalyst. So, these ERSO is needed to neutralize. In this steps, neutralization and transesterification reaction was occurred simultaneously to form the best biodiesel. Different variation of methanol to oil molar ratio (6:1, 7:1, 8:1, 9:1, 10:1, 11:1), base to oil ratio (wt%) (0.3%, 0.4%, 0.5%, 0.6%, 0.7%), reaction temperature (40˚C, 45˚C, 50˚C, 55˚C, 60˚C), reaction time(20, 30, 60, 120min) and stirring rate (400,750, 800rpm) has been adopted in order to obtain the experimental conditions for the highest biodiesel yield of 89% is obtained by using methanol to oil 9:1, base to oil ratio ratio 0.5%, reaction temperature 50˚C, reaction time 30min and stirring rate 750rpm. Estimation of percent reaction completion gives 99.56%.

Most of the physical properties of biodiesel from rubber seed oil are found to be within the specified limits. The specific gravity, flash point, pour point, total acid number, kinematic viscosity, initial boiling point, cetane index and copper corrosion of product biodiesel meet the ASTM specifications (D_{6751}). Although the value of carbon residue is 0.048wt%, the result of free glycerol, total glycerol and combined glycerol are close to the ASTM specified limits.

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