Extraction of Crude Rubber Oil from Rubber Seed and Production of Biodiesel

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ABSTRACT

Biodiesel is a mono alkyl ester of long chain fatty acids derived from renewable feed stocks, such as vegetable oils or animal fats, for using in compression ignition engine. Studies were carried out to extract non-edible crude rubber oil from rubber seed and to produce potential biodiesel from it. Crude rubber oil was extracted by Soxhlet extraction process with n-hexane solvent and also mechanically extracted by using continuous screw expeller. Due to its high free fatty acid (3.89% FFA) content, the crude rubber oil was processed in two steps. The acid-catalyzed esterification and followed by the base catalyzed transesterification. The acid-catalyzed esterification reaction was carried out with concentrated H_2SO_4 acid and ethanol-to-oil ratio. The production of biodiesel involved the transesterification of treated rubber oil with ethanol in the presence of a base catalyst (KOH) to yield ethyl ester as a product and glycerine as a by-product. The first step reduces the FFA level from 3.89% to 1.1% in one hour at 50°C for 40% w/w ethanol-to-oil ratio with 1% w/w H_2SO_4 . After the reaction the mixture was stagnated for an hour and ethanol-water upper layer was discarded. The second step convert the product into biodiesel and glycerol through transesterification using 30% w/w ethanol-to-oil and 0.8% w/w KOH to oil at 65°C. The maximum biodiesel yield achieved at rate of 89.36% within one hour and the glycerol concentration in the by-product (glycerol layer) obtained after duel step transesterification was found 18.82%.

Keywords: Biodiesel, Rubber seed, Extraction, Free fatty acid, Acid Value

1. INTRODUCTION

Biodiesel is an efficient, clear, non-toxic, biodegradable, 100% natural energy alternative to petroleum fuels. It is safe for using in all conventional diesel engines offering the same performance and engine durability as petroleum diesel fuel. Compared with petroleum diesel in diesel engine, it reduces the emission of visible smoke, noxious fuels, carbon monoxide (CO), sulphur hydrocarbons and particle matters during the combustion process. Furthermore, burning biodiesel has no net addition to atmospheric carbon dioxide (CO₂) level because it is made from agricultural material produced via photosynthesis carbon fixation. Non-edible oil such as rubber oil would be potential biodiesel sources for most of the developing countries[1]. In recent years, researchers have been directed to explore plantbase fuels because it is renewable and environment friendly. Biodiesel can be produced by the transesterification of C14-C20 fatty acid triglycerides with short-chain alcohol such as methanol or ethanol in the presence of a catalyst such as NaOH, KOH, etc.[2]. The high cost of biodiesel is mainly due to the cost of virgin vegetable oil. Therefore, it is not surprising that the biodiesel produced from edible vegetable oil (for example, pure soybean oil) costs much more than petroleum-based diesel[3–4]. However, non-edible vegetable oil can reduce the production cost of biodiesel. Therefore, it is necessary to explore ways to reduce production costs of biodiesel. In this sense, methods that permit to minimize the costs of the raw material are of special interest. The use of non-edible rubber crude oil, instead of edible oil to produce biodiesel is an effective way to reduce the raw material cost because non-edible rubber seed oil is estimated to be about one third of the price of other vegetable oils [4–5]. Several processes have been developed for biodiesel fuel production. Biodiesel is recently gaining prominence as a substitute for petroleum-based diesel due to environmental considerations and depletion of vital resources like petroleum and coal. The possible use of renewable resources as fuels and as a major feedstock for the chemical industry is currently gaining acceptance. Further as petroleum is a fast depleting natural resource, an alternative renewable route to petroleum is a deemed necessity. Now serious efforts are being made on the production and utilization of biodiesel in Bangladesh. Methyl and ethyl esters are clean burning fuel with no sulfur emission. Despite having slightly lower heat of combustion than that of the petro-diesel, no engine modification is required to achieve comparable efficiency[6]. Chemically, biodiesel is a mono alkyl esters of long chain fatty acids derived from different kinds of edible oils, non-edible oils and fats. The process of transesterification is affected by the mode of reaction condition, molar ratio of alcohol to oil, types of alcohol, types and amount of catalyst, reaction time, temperature and purity of reactants[7]. By-product glycerin can be used in various industrial purposes. Rubber seed oils are easily available in many parts of the world including Bangladesh and are very economical compared to other sources. It is a waste product and available in Bangladesh. In our country, there is no reserve/source of petroleum-based diesel. So, it is necessary to find out a potential alternative source. Co-ignition of biodiesel (rubber oil diesel) with commercial diesel will reduce the demand of fossil diesel. The ultimate objectives of this study are production and optimization of biodiesel characteristics from rubber seed oil, to reduce the pollution of the environment and to evaluate the co-ignition characteristics of biodiesel with commercial diesel.

2. MATERIALS AND METHOD

2.1. Materials

Rubber (*Hevea brasiliensis*) seed was used as a raw material to produce biodiesel which was collected from rubber garden under the control of Bangladesh Forest Industries Development Corporation (BFIDC). The rubber seed oil was extracted chemically by soxhlet solvent extraction process in Institute of Fuel Research & Development, BCSIR. The rubber seed oil was also extracted mechanically in the expeller. n-hexane, ethanol, catalyst (H_2SO_4 , KOH), etc. were used as a chemical which were analytical grade.

2.2. Methodology

2.2.1. Pretreatment of Rubber Seed

For extracting rubber seed oil, the rubber seeds were cleaned and dried well, and then crushing was carried out to remove the hard heavy husk from the kernel. The rubber husk was also dried and grind into powder by using mortar.

Rubber seed kernel was dried well to remove moisture and grind well into powder and weight loss percentage of moisture was calculated by the following way:

% weight loss =
$$\frac{A-B}{A}$$
 x 100

Where, A= weight of sample before heating; B = weight of sample after heating.

For 100 gm kernel, the weight loss percentage of moisture was calculated =1.813%

2.3. Extraction of Crude Rubber Oil

2.3.1. Solvent Extraction Process

In this process, organic solvents are used to extract oil particles. These solvent dissolve the oil particle into the solvent and thus extraction is carried out. Some organic solvents are benzene, toluene, n-hexane. Crude rubber seed oil was extracted by using soxhlet extraction process. In this process n-hexane was carried as a solvent to extract oil from powder. Several experiments were done to extract the highest percentage of oil and the solvent was recovered or recycled by distillation process.

2.3.2. Mechanically Expeller Process

This indigenous expeller process was employed to extract oil in large quantity. And the oil extracted by this process was used in experiment. For this type of extraction, the husk was removed from the kernel[8].

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Distillation

It is a separation technique where two liquids are separated according to their boiling point on heat treatment. The low boiling point component vaporizes first and higher boiling point one later. Then it condenses and collected in different chambers. The oil-solvent mixture was distilled at the boiling point of n-hexane. Then the solvent was recycled and the rubber oil was collected. The complete distillation time is around one hour. Overview of the rubber seed oil production process is shown in Figure 1.



Figure 1: Flow diagram of crude rubber oil production

2.4. Acid Value Estimation

Acid value is defined as 'The number of milligram of potassium hydroxide required to neutralize the 1 gm of oil or fat'. In the first stage, the acid value of the reaction mixture was determined by a standard acid base titration method (ASTM 2003) where a standard solution of one mol KOH solution was used. 100 ml solution of mixture (toluene + isopropyl alcohol + H_2O) was added to 0.5044 gm of sample in the presence of 2/3 drops of phenolphthalein indicator. Titration was done between 0.1 M KOH and solution mixture.

$$AN = (V_{eq} - b_{eq}) N 56.1/W_{oil}$$

2.5. Synthesis of Biodiesel

2.5.1. Acid Catalyzed Esterification (Pretreatment of Rubber Oil)

The amount of moisture and percentage of FFA of the oil are determined. If the FFA level or moisture level is too high it may cause problems in the form of soap formation (saponification) and the separation of the glycerin by-product downstream. Esterification process carried out due to high FFA contain of rubber seed oil. Catalyst H_2SO_4 is dissolved in the alcohol using a standard agitator or mixer. The alcohol/catalyst mix is then charged into a closed reaction vessel and rubber seed oil was added. The system was totally closed to the atmosphere to prevent the loss of alcohol. In this process, oil was treated with acid catalyst (1.0% H_2SO_4 based on the oil weight) and different

ethanol-to-oil ratio (10 to 50 % w/w) to investigate their influence on the acid value as well as FFA of rubber seed oil. Reaction conditions set for this experiment were 50°C temperature, 400 rpm agitation rate and time of one hour. After one hour of reaction, the mixture was allowed to settle for one hour and the ethanol–water fraction at the top layer was removed. The optimum condition having the lowest acid value was used for the main transesterification reaction[9].

2.5.2. Base-Catalyzed Transesterification

The reaction mixture is kept just above the boiling point of the alcohol (around 70° C, 158° F) to speed up the reaction though some systems recommend the reaction take place anywhere from room temperature to 55° C (131° F) for safety reasons. Recommended reaction time varies from 1 to 2 hours, under normal conditions the reaction rate will double with every 10° C increase in reaction temperature. Excess alcohol is normally used to ensure total conversion of the fat or oil to its esters. The glycerin phase is much denser than biodiesel phase and the two can be gravity separated with glycerin simply drawn off the bottom of the settling vessel. In some cases, a centrifuge is used to separate the two materials faster.

2.5.3. Separation and Purification of Biodiesel

After completion of reaction, ethyl ester was separated from mixture of ethyl ester and glycerin. Ethyl ester was separated by separating funnel after establishment of the layer for 16 hours[10]. After separation, the properties of the produced biodiesel were determined by the laboratory method.

3. RESULTS AND DISCUSSION

3.1. Rubber Seed Oil Extraction

The oil was extracted chemically by using n-hexane solvent in the soxhlet extractor and also mechanically in the expeller. The oil extraction (production) rate by solvent extraction process was 44.5% and the extraction rate by mechanical process from pure kernel was 14.5% for a single stage (time) operation of expeller. The crude rubber oil was allowed to settle to remove mud sediment. The used solvent was recovered to use it again. The solvent recovery rate was determined as 85.5%

3.2. Determination of Acid Value and FFA in Rubber Seed Oil

The acid value of rubber seed oil was determined as 7.78 and then the free FFA (%) was determined as 3.89 %

3.3. Variation of Acid Value and FFA (%) with wt % of Ethanol-to-Oil

In every case, 2 gm of oil sample with catalyst (H_2SO_4) , 1% w/w to oil were taken for the determination of acid value and FFA (%).

From Figure 2, it was observed that the acid value and FFA (%) decreases with increased amount of ethanol (wt. %). When the number of ethanol molecule is insufficient then the more number of acid molecules remains unesterified. So when the percentage of ethanol molecule increases, then the acid value and FFA decrease. The optimum acid value and FFA (%) were found 2.2(%) and 1.1 (%), respectively at 40% ethanol to oil ratio. Due to the high cost of ethanol, 40% ethanol for esterification reaction was selected.

3.4. Effect of Change of Molar Ratio of Limiting Reactants (Ethanol)

Esterification was carried out in small scale with the help of 10 ml measured test tube with stirrer. Here, the amount of catalyst (H_2SO_4) was kept fixed.

It was observed from Table 1 that the maximum yield (%) 77.23% was found at 5:10 molar ratio of ethanol to oil. Increasing molar ratio of ethanol oil slightly increase the yield.



Figure 2: The change of acid value and FFA (%) with the change of ethanol-to-oil ratio

Expt. No.	wt. % of ethanol	wt. of rubber	wt.of	w/w % of	Ethanol to	Yield
•	to oil (mg)	seed oil (mg)	catalyst %	ethanol to oil	oil ratio	%
Expt. No. 1	10% w/w to oil	2	1	10%	1:10	71.15
Expt. No. 2	20% w/w to oil	2	1	20%	2:10	73.49
Expt. No. 3	30% w/w to oil	2	1	30%	3:10	75.36
Expt. No. 4	40% w/w to oil	2	1	40%	4:10	76.92
Expt. No. 5	50% w/w to oil	2	1	50%	5:10	77.23

Table 1. The effect of variation of ethanol to oil ratio on product (treated oil) vield

Table 2: The properties of rubber seed oil which are used as a ra	aw material for biodiesel production
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Name of the analysis	Method	Result	
Density at 15°C, g/cc	IP-160/57	0.8748	
Kinematic viscosity, 40°C,cSt	ASTM-D 445-65	66.4045	
Kinematic viscosity, 100°C cSt	ASTM-D 445-65	38.99	
Pour point, °C	ASTM-D 97-57	-10°C	
Flash point, °C	ASTM-D 93-62	86	
Acid value, mg KOH/g	IP-1/58	7.78	
Sulfur content, %mass	ASTM-D 129-64	0.426	
Cetane number	ASTM-D 613-86	51	
Water content, %	IP-74/57	0 %	
Carbon residue, %	ASTM-D 189-65	2.4350	
Ash content, %	ASTM-D 482-63	0.01904	
Calorific value, Kcal/kg	-	9765.58	
Specific gravity	-	0.8989	

3.5. Base Catalyst (KOH) Optimization

Transesterification was carried out in small scale with the help of two necks round bottom flux with stirrer. From Table 3, it was found that the maximum yield (%) 89.36% at 0.8%w/w of KOH to rubber oil at 30% ethanol. With the increasing wt% of KOH to rubber oil at 30% fixed ethanol the yield of biodiesel increased and glycerin production decreased up to 0.8%w/w of KOH.

No. of observation	W/w % of catalyst (KOH) to oil	wt. of treated rubber seed oil (gm)	w/w % of ethanol to oil	Yield % (Biodiesel)	Yield % (glycerin)
Expt. No -1	0	20	30%	0% (No conversion)	0% (No conversion)
Expt. No -2	0.2	20		84.89	15.12
Expt. No -3	0.4	20		86.02	13.98
Expt. No -4	0.6	20		87.69	12.31
Expt. No -5	0.8	20		89.36	10.64
Expt. No -6	1.0	12.6		80.95	19.05
Expt. No -7	1.2	10		79.76	20.24
Expt. No -8	1.5	10		79.15	20.85
Expt. No -9	2.0	10		77.46	22.53

Table 3: The optimization of catalyst to fixed amount of ethanol (30% ethanol) to oil ratio on product yield

Then with the increase of KOH % the biodiesel production rapidly decreased. At 0.2%, 0.4%, 0.6 % w/w of KOH to oil there were a soap and foam layer between the biodiesel and glycerin layer observed. Ethanol was kept fixed at 30% of rubber seed oil for above experiment which was shown in Figure 3.



Figure 3: Variation of yield of biodiesel with different amount of catalyst

It was observed from Figure 3 that the maximum yield was found at 0.8% w/w of KOH to oil at 30% fixed ethanol. At first yield of biodiesel increases with increasing amount of KOH. However, after 0.80% KOH the biodiesel yield was decreased successively. This is due to fact that the ethoxy group is produce by using KOH. If the % of KOH is more than some of catalyst remains unreacted. The unreacted catalyst reacted with glycerin molecule (HOR) produce starting ester because the reaction is reversible. So the production increase in certain level then decreases if the catalyst remains unreacted.

Name of the analysis	Method	Result		
Density at 15°C	IP-160/57	0.8868		
Kinematic viscosity, 40°C, cSt	ASTM D 445-65	29.5858		
Kinematic viscosity, 100°C, cSt	ASTM D 445-65	18.2972		
Pour point, °C	ASTM D 97-57	-12		
Flash point, °C	ASTM D 93-62	48		
Burn point, °C	ASTM D 93-62	50		
Acid value, mg KOH/g	IP-1/58	0.052		
Sulfur content, % mass	D 129-64	0.22		
Cetane no.	ASTM D 613-86	49		
Water content, %	IP-74/57	Nil		
Carbon residue, %	ASTM D 189-65	1.71		
Ash content, %	D 482-63	0.06		

Table 4: Physical and chemical properties of rubber seed oil biodiesel

3.6. Cetane Number Determination

Cetane number of produced biodiesel from rubber seed oil was determined from density of biodiesel and the boiling range of the biodiesel[11]. The temperature when 10%, 50% and 96% of the biodiesel was transferred from round bottom flux was marked. Then the cetane number was calculated and it was 49.

4. CONCLUSION

Crude rubber seed oil contains more than 3.89% FFA. It is difficult to produce biodiesel if the selected oil contains more than 2% FFA. So two step processes were followed. Firstly, acid catalyzed esterification to reduce acid value as well as free FFA (%) and finally, base catalyzed transesterification were carried out for production of biodiesel. Two different types of reactions were carried out to optimize the process condition. The maximum yield of biodiesel was obtained 89.36%. The cetane number of biodiesel was determined to be 49. The properties of crude rubber seed oil as well as biodiesel produced from it were determined with the help of different ISO standard method which were satisfied the range of ISO standard biodiesel properties. The properties of the produced biodiesel from rubber seed oil have been studied and compared with commercial diesel and found that the properties of produced biodiesel to save foreign exchange and to help in controlling environmental pollution to a great extent.

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