

# Biodiesel development from rice bran oil: Transesterification process optimization and fuel characterization

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## Abstract

Increased environmental awareness and depletion of resources are driving industry to develop viable alternative fuels from renewable resources that are environmentally more acceptable. Vegetable oil is a potential alternative fuel. The most detrimental properties of vegetable oils are its high viscosity and low volatility, and these cause several problems during their long duration usage in compression ignition (CI) engines. The most commonly used method to make vegetable oil suitable for use in CI engines is to convert it into biodiesel, i.e. vegetable oil esters using process of transesterification.

Rice bran oil is an underutilized non-edible vegetable oil, which is available in large quantities in rice cultivating countries, and very little research has been done to utilize this oil as a replacement for mineral Diesel. In the present work, the transesterification process for production of rice bran oil methyl ester has been investigated. The various process variables like temperature, catalyst concentration, amount of methanol and reaction time were optimized with the objective of producing high quality rice bran oil biodiesel with maximum yield. The optimum conditions for transesterification of rice bran oil with methanol and NaOH as catalyst were found to be 55 °C reaction temperature, 1 h reaction time, 9:1 molar ratio of rice bran oil to methanol and 0.75% catalyst (w/w). Rice bran oil methyl ester thus produced was characterized to find its suitability to be used as a fuel in engines. Results showed that biodiesel obtained under the optimum conditions has comparable properties to substitute mineral Diesel, hence, rice bran oil methyl ester biodiesel could be recommended as a mineral Diesel fuel substitute for compression ignition (CI) engines in transportation as well as in the agriculture sector. © 2007 Elsevier Ltd. All rights reserved.

**Keywords:** Rice bran oil; Biodiesel; Transesterification; Kinetics; Fuel characterization; Process optimization

## 1. Introduction

Diesel fuels have an important role in the industrial economy of any country. The high energy demand in the industrialized world and widespread use of fossil fuels is leading to fast depletion of fossil fuel resources as well as environmental degradation. The world petroleum reserves are so unevenly distributed that many regions have to depend on others for their fuel requirements. The degrading air quality due to emissions is the main adverse effect of petroleum based fuels. All these factors necessitate con-

tinued search and sustainable development of renewable energy sources that are environmentally friendly. Biomass sources, particularly vegetable oils, have attracted much attention as an alternative energy source. They are renewable, non-toxic and can be produced locally from agriculture and plant resources. Their utilization is not associated with adverse effects on the environment because they emit less harmful emissions and green house gases.

Vegetable oils have long been promoted as possible alternatives for mineral Diesel. In fact, Rudolph Diesel, the inventor of the Diesel engine, used peanut oil as the fuel for its demonstration at the 1900 world exhibition in Paris and said, “The use of vegetable oils for engine fuels may seem insignificant today, but such oils may become, in the course of time, as important as petroleum and the coal

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tar products of the present time” [1]. However, it is only in recent years that systematic efforts have been made to utilize vegetable oil as fuels in the engines. The mineral Diesel fuel is a complex mixture with carbon atoms ranging between 12 and 18, whereas vegetable oils are a mixture of organic compounds ranging from simple straight chain compounds to complex structures of proteins and fat soluble vitamins and are commonly referred to as triglycerides [2–5]. Vegetable oils are usually triglycerides, generally with a number of branched chains of different lengths and different degrees of saturation. Vegetable oils have about 10% lower heating value than mineral Diesel due to the oxygen present in their molecules. The viscosity of vegetable oil is several times higher than that of mineral Diesel due to their large molecular mass and chemical structure. The cloud point and pour point are higher, and the cetane number is comparable to that of mineral Diesel [2,4,5]. The high viscosity of vegetable oils (30–200 cSt) as compared to mineral Diesel oil (4 cSt) at 40 °C leads to unfavorable pumping and spray characteristics. The inefficient mixing of fuel with air contributes to incomplete combustion. The high flash point and lower volatility characteristics result in increased carbon deposit formation, injector coking, lubricating oil dilution and degradation. With vegetable oil as a fuel, short term engine performance results are comparable to those with mineral Diesel, but long term results with vegetable oil or blends with mineral Diesel lead to severe engine deposits, piston ring sticking, injector coking and thickening of the lube oil [5–7]. Vellguth [6] performed tests with heated vegetable oils and found that the deposits were even more than those of unheated vegetable oil. He tested vegetable oils on direct injection (DI) as well as indirect injection (IDI) engines and found that the problem in DI engines was more severe than that in IDI engines. High viscosity, low volatility and a tendency to polymerize within the cylinder are the root of many problems associated with direct use of vegetable oils as fuel [4,7]. Because of these problems, vegetable oils need to be modified to bring their combustion related properties closer to those of mineral Diesel. The fuel modification is mainly aimed at reducing the viscosity and increasing the volatility. Considerable efforts have been made to develop vegetable oil derivatives that approximate the properties and performance of the hydrocarbon fuels. The methods employed include pre-heating the oil, pyrolysis, microemulsion, blending and transesterification [2,3,6]. From various studies [8–14], it is found that the best way to make vegetable oil compatible with existing engines is to convert it into ester (biodiesel). In comparison to mineral Diesel, biodiesel has a more favorable combustion and emission profile. Emissions of CO and particulate matter decrease by 45%, hydrocarbon (HC) emissions decrease by nearly 70% but NOx emissions increase by 10% with 100% biodiesel (B100) as a fuel [15]. The carbon cycle time for fixation of CO<sub>2</sub> from biodiesel is quite small compared to mineral Diesel. It means that biodiesel usage reduces greenhouse gas emissions compared to mineral Diesel [16–19]. Biodiesel has a relatively high flash

point, which makes it safer to handle. Agarwal et al. [20,21] found that biodiesel provides good lubricating properties that can reduce component wear and enhance engine life. The physical wear of various vital parts and carbon deposits were found to be substantially lower in the case of 20% biodiesel fuelled engine. Hence, vegetable oil is a potential alternative for mineral Diesel if it is converted to biodiesel. Biodiesel usage not only improves emissions but also improves engine life.

Several experimental researches have shown that the fuel properties of vegetable oils can be improved by transesterification, and this is the method of choice in the current study. Transesterification is a most common and well established chemical reaction in which alcohol reacts with the triglycerides of fatty acids (vegetable oil) in presence of a catalyst. It is a reversible reaction of fat or oil (triglyceride) with a primary alcohol to form esters and glycerol. The alcohol combines with the triglycerides to form glycerol and esters. The reaction is shown in Fig. 1. The stoichiometry for the reaction is 3:1 molar ratio of alcohol to oil, however, since the reaction is reversible, in practice, excess alcohol (6:1) is required to shift the equilibrium to the products side to raise the product yield [2,3,8,9]. Methanol and ethanol are used most frequently, especially methanol because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol). It can quickly react with triglycerides, and NaOH gets easily dissolved in it.

The transesterification reaction can be catalyzed by both homogeneous and heterogeneous catalysts. Homogeneous catalysts include alkalis and acids. The most commonly used alkali catalysts are NaOH, KOH, carbonates and the corresponding sodium and potassium alkoxides such as sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide [3–5,22–27]. Freedman et al. [23] investigated the effect of various parameters on the purity of biodiesel produced. Sulfuric acid, sulfonic acid and hydrochloric acid are usually used as catalysts in the acid catalyzed reaction. Vicente et al. [22] found more conversion with methoxide catalyst, but these catalysts are very expensive and hygroscopic. They transesterified sunflower oil using different catalysts and found that the purity of biodiesel with methoxide and KOH and NaOH was similar (near 100%), but the yield with KOH and NaOH

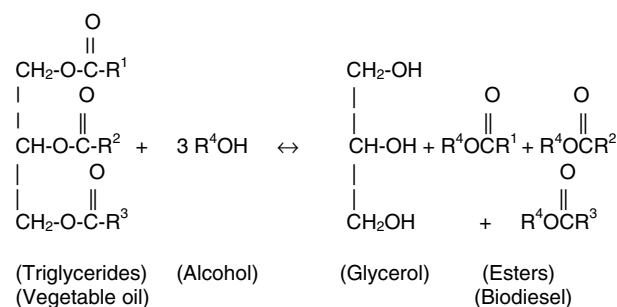


Fig. 1. Transesterification reaction.

was 91.67 and 85.9 wt%, respectively, which could be improved by optimizing the reaction parameters. For an alkali catalyzed transesterification, the triglycerides should have lower free fatty acid (FFA) content, and the alcohol must be substantially anhydrous because water makes the reaction partially change to saponification, which produces soap. Soap formation lowers the yield of esters and renders the separation of esters and glycerol as well as water washing of esters difficult [3,5,23,25]. Up to about 5% FFA, the reaction can be catalyzed using an alkali catalyst [18]. Acid catalysts (HCL, H<sub>2</sub>SO<sub>4</sub>) are advantageous for oil having high FFA content, as acids catalyze the FFA esterification to produce fatty acid methyl ester, increasing the biodiesel yield, but the reaction time and alcohol requirement is very high [12,28]. Boocock et al. [29] proposed the addition of a co-solvent (tetrahydrofuran and methyl tertiary butyl ether) to create a single phase, and this accelerates the reaction so that it reaches substantial completion in a few minutes. The primary concerns with this method are the additional complexity of recovering and recycling the co-solvent and the hazard level associated with the proposed co-solvents.

Several researchers [30–32] tried transesterification without using any catalyst in supercritical methanol, which eliminates the need for the water washing. Saka and Kusdiana [31,32], found that in supercritical methanol, the reaction requires only four minutes, and also, the presence of water did not effect the yield of ester, but very high pressure (45–65 bar), temperature (350 °C) and very high molar ratio of alcohol to oil (42:1) was required. Enzymes like lipases can also be used as biocatalysts for transesterification, but the cost is the main hurdle in commercializing enzymes as catalysts [3,33,34]. Marchetti et al. [34] compared the different technologies given in Table 1.

More recently, there has been an increase in the development of heterogeneous catalysts (enzymes and solid catalysts) because their utilization in the transesterification reaction greatly simplifies and economizes the post-treatment (separation and purification) of the products. The use of heterogeneous catalysts does not produce soaps through fatty acid neutralization and triglyceride saponification. However, heterogeneous catalyzed reaction also requires extreme reaction conditions, while the methyl ester yield and the reaction time are still unfavorable compared to the alkali catalysts [22,35].

In summary, base catalysts are most common, since the process is faster and reaction conditions are moderate. Although it is a well-known process, the proportions of reagents affect the process in terms of conversion efficiency, and this factor differs according to the vegetable oil type. Several researchers have identified the most important variables that influence the reaction, namely, reaction temperature, type and amount of catalyst, quantity of alcohol, stirring rate and reaction time [3,23,36–38]. Depending upon the climate and soil conditions, different nations are looking into different vegetable oils as potential Diesel fuel replacement. Most of the western countries use soybean, sunflower, saffola, rapeseed, palm oil, etc. for production of biodiesel and investigations on engines [39–41]. These oils are edible in nature and developing countries like India cannot afford edible oils as a fuel substitute. Use of such edible oil to produce biodiesel in India is not feasible in view of a big gap in the demand and supply of such oils in the country for dietary consumption. Increased pressure to augment the production of edible oils has also put limitations on the use of these oils for production of biodiesel. To extend the use of biodiesel, the main concern is economic viability of producing biodiesel. The price of feedstock (vegetable oil) is one of the most significant factors, which consists of approximately 75–88% of the total biodiesel production cost [40–42]. Obviously, developing nations have to focus their attention on oils of non-edible nature, which are cheaper. In India, a variety of non-edible oils like linseed, mahua, karanja, rice bran and jatropha are available in surplus quantities. The production of oil seeds, percentage oil recovery and their cost are given in Table 2 [4].

India is the second largest producer of rice in the world, next to China, with the potential to produce about 1 million tonnes of rice bran oil per annum. Rice bran is a low value co-product of rice milling, which contains approximately 15–23% oil. Currently, the industry is processing about 3.5 million tonnes of rice bran, leading to a production of about 0.65 million tonnes of oil, and an additional 0.33 million tonnes could be produced through modernizing the huller rice mills and installation of rice bran oil refineries. This non-edible oil remains mostly under utilized. A huge quantity of rice bran is produced (approximately 8% w/w of paddy), which is an agricultural waste. It has significant potential as an alternative low cost feedstock for biodiesel production. Therefore, in this study, the use of rice bran

Table 1  
Comparison of different technologies to produce biodiesel [34]

Variable	Alkali catalysis	Lipase catalysis	Supercritical alcohol	Acid catalysis
Reaction temperature (°C)	60–70	30–40	239–385	55–80
FFA in raw material	Saponified products	Methyl esters	Esters	Esters
Water in raw material	Interference with reaction	No influence	–	Interference with reaction
Yield of methyl esters	Normal	Higher	Good	Normal
Recovery of glycerol	Difficult	Easy	–	Difficult
Purification	Repeated washing	None	–	Repeated washing
Production cost of catalyst	Cheap	Expensive	Medium	Cheap

Table 2  
Production of oil seeds in 2002–2003 in the world and India [4]

Oilseed	Production (million tonnes)		Total oil availability (million tonnes)	% Recovery	Oil cost (Rs. per quintal)
	World	India			
Soya bean	123.2	4.3	0.63	17	4300
Cottonseed	34.3	4.6	0.39	11	3200
Groundnut	19.3	4.6	0.73	40	6200
Sunflower	25.2	1.32	0.46	35	5360
Rapeseed	34.7	4.3	1.37	33	5167
Sesame	2.5	0.62	–	–	6800
Palm kernels	4.8	–	–	–	–
Coconut	4.9	0.65	0.42	65	3035
Linseed	2.6	0.2	0.09	43	–
Castor	1.3	0.51	0.21	42	–
Niger	0.8	0.08	0.02	30	–
Rice bran	–	–	0.6	15	2000
Total	253.6	21.18	4.92	–	–

oil is investigated for the production of biodiesel. Zullaikah et al. [43] investigated two step acid catalyzed methanolysis for rice bran oil of high FFA content. They achieved 96% conversion into methyl ester in 8 h of reaction time. Very little literature is available for the transesterification of rice bran oil, and no systematic scientific study on the effect of the different process parameters on the reaction yield and characterization of the rice bran methyl ester is available in the open literature. The present research is conducted to optimize the base catalyzed transesterification process parameters for rice bran oil, which is a relatively rapid transesterification process with moderate reaction conditions. Characterization of biodiesel for utilization as a replacement of mineral Diesel in CI engines has also been done in the present investigation.

## 2. Experimental procedures

Vegetable oils primarily contain triglycerides, and their chemical structure is significantly different from that of mineral Diesel. Transesterification is an efficient method to convert high viscosity vegetable oil into a fuel with chemical properties similar to those of mineral Diesel. Non-edible rice bran oil was procured for the present investigation and characterization was done as per ASTM procedures. Specific gravity was measured by a density meter of accuracy of  $\pm 0.1\%$  (Model: DA-130N; Make: Kyoto Electronics, Japan). A small volume of liquid sample is introduced into an oscillating sample tube, and the change in the oscillating frequency caused by the change in the mass of the tube is used in conjunction with calibration data to determine the density of the sample (ASTM D 4052). Kinematic viscosity was measured using a kinematic viscosimeter (Model: Setavis 83541-3, Make: Stanhope-seta, UK), (ASTM D455). Kinematic viscosity can be determined by measuring the time required for a specified volume of liquid to flow through a calibrated glass capillary tube. The kinematic viscosity is the product of the measured flow time and calibration constant for that particular viscosimeter capillary tube. Time is measured by a

digital timer with an accuracy of  $\pm 0.01$  s, which makes it possible to measure the viscosity with an accuracy of  $\pm 0.01$  cSt. The calorific value and flash point were measured using a bomb calorimeter (ASTM D240) and Pensky Marten's closed cup tester (ASTM D93), respectively. CHNOS analysis was performed at the Central Drugs and Research Institute, Lucknow, India using an elemental analyzer (Model: Vario EL III-1108; Make: Carlo Erba, Italy). Determinations of the cloud point (ASTM D 2500), pour point, ash content, Conradson carbon residue (ASTM D 189) were also done. The cloud point and pour point were measured with a thermometer having a least count of  $1^\circ\text{C}$ . For weight measurement, an analytical weighing balance (Make: Mettler, USA) with an accuracy of  $\pm 0.1$  mg was used.

In the present research, base catalyzed transesterification (catalyst: KOH, NaOH) is used to prepare biodiesel from rice bran oil. Methyl alcohol (Merck) of 99.5% purity (Density: 0.791–0.792 kg/l) was used. Washing of the biodiesel thus produced is essential for removal of the impurities and the residual catalyst, which may be harmful for combustion engines. In the experiment, transesterification and washing of biodiesel were thoroughly studied.

For transesterification, 1 l of rice bran oil was heated to  $65^\circ\text{C}$  in a round bottom flask (Fig. 2). Catalyst (KOH/NaOH-0.5% w/w<sub>oil</sub>) was dissolved in methyl alcohol (270 ml), and this was poured into the round bottom flask containing the heated rice bran oil while stirring the mixture continuously. A platinum RTD temperature sensor, (Pt-100) with an accuracy of  $[\pm 0.3 + (0.005 \times \text{temperature})]$  was placed in the reacting mixture, for measurement of reaction temperature, and connected to a digital temperature indicator. A temperature of  $55 \pm 1^\circ\text{C}$  was maintained for 1 h, and the reaction products were allowed to settle under gravity for 6 h in a separating funnel. The products of the transesterification process, i.e. rice bran oil methyl ester (biodiesel) and glycerol form the upper and lower layers, respectively. The bottom layer of glycerol was removed, and the upper layer of biodiesel was mixed with warm distilled water (10% v/v) in order to remove the

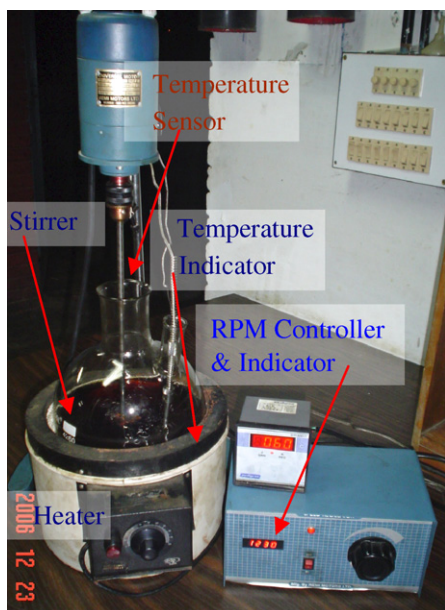


Fig. 2. Experimental set up.

Table 3

Chemical and physical properties of rice bran oil

Fatty acids (%) <sup>a</sup>	
Palmitic C16:0	18.8
Stearic C18:0	2.4
Oleic C18:1	43.1
Linoleic 18:2	33.2
Linolenic 18:3	0.6
Arachidic C20:0	0.7
Free fatty acids (%)	2.8
Density (kg/m <sup>3</sup> )	922
Kinematic viscosity@40 °C (cSt)	43.52
Kinematic viscosity @100 °C (cSt)	9.21
Flash point/fire point (°C)	316/337
Cloud point/pour point (°C)	13/01

<sup>a</sup> Source: Srivastava and Prasad [2].

the literature, while most of the others were determined in the laboratory. Fatty acid composition of the oil is essential for determining the quantity of reactants and the catalyst. FFA can be determined from the acid value. Many researchers have reported that the acid value of the vegetable oil should be less than one for a base catalyzed transesterification process. Dorodo et al. [38] reported that transesterification would not occur if the oils have a FFA content more than 3%, while Van Gerpan [18] reported that the reaction can be catalyzed with an alkali catalyst up to about 5% FFA content of the vegetable oil. In this study, the FFA content of the oil was found to be 2.8% which is within the acceptable limit (3–5%) for base catalyzed transesterification. The kinematic viscosity of the rice bran oil was significantly high. Because of the high viscosity and flash point, rice bran oil demonstrates poor atomization and volatility characteristics, and may not be suitable as a fuel for unmodified Diesel engines.

### 3.2. Transesterification and catalyst removal process

In starting, for transesterification of rice bran oil, 6:1 molar ratio of alcohol, 0.5% (w/w<sub>oil</sub>) catalyst, 1 h reaction time and 55 °C reaction temperature were selected. The reaction was conducted under atmospheric pressure. Two basic catalysts KOH and NaOH were used under identical conditions. After gravity separation of the glycerol, water washing of biodiesel is performed in order to remove the impurities present in the product. If they are not removed, they may cause problems during storage and can damage the fuel system and other components of the engine. For catalyst removal, one liter of ester was mixed with warm (70 °C) distilled water (10% v/v) and allowed to settle under gravity in the separating funnel. Two layers were formed, the upper layer was of biodiesel, and the lower layer comprised of water and impurities. This process was repeated until the lower layer had a pH similar to the pH of distilled water, indicating that the biodiesel is free of catalyst. It was found that during the process of catalyst removal, some ester was also lost due to emulsion formation. In the present research, washing was done in

impurities like unreacted methanol, unreacted oil and catalyst. The mixture was again allowed to settle under gravity for 6 h, and the lower layer of water containing impurities was drained out. The washing process was investigated for both catalysts with different rates of agitation.

Process yield investigations were conducted with NaOH as a catalyst to study the effect of different parameters like reaction temperature, reaction time, molar ratio of alcohol to oil and amount of catalyst on the ester yield as well as the extent of conversion (represented by the viscosity of the ester). The stirring speed was kept constant at 1100 rpm for every experimental run. The reaction temperature was varied from 50 °C to 65 °C in steps of 5 °C. The molar ratio of alcohol was varied from 6:1 to 15:1 in steps of 3:1, process time was varied from 45 min to 105 min in steps of 15 min and the catalyst amount was varied from 0.5% to 1.5% (w/w<sub>oil</sub>) in steps of 0.25%. Experiments for each set of variables were repeated twice to reduce experimental errors. The effect of each variable on the ester yield and viscosity of the ester was recorded while keeping other factors constant. Ester yield (%w/w) results were related to the weight of rice bran oil at the beginning of the reaction. These four parameters were optimized for the transesterification of rice bran oil.

After optimization of the process parameters for rice bran oil transesterification, characterization of the rice bran methyl ester (ROME) was done along with the base line data of mineral Diesel.

## 3. Results and discussion

### 3.1. Oil characterization

Various chemical and physical properties of the oil are given in Table 3. Some of these properties are taken from



Fig. 3. Gentle washing.



Fig. 4. Rigorous washing.

two ways (1) gentle washing and (2) rigorous agitation, (Figs. 3 and 4). It was observed that during rigorous agitation, fewer number of washings was required, but more ester was lost because of emulsion formation. It was also found that the loss of ester with KOH was more than that with NaOH. With rigorous agitation, catalyst removal was achieved in one washing, but the ester loss due to emulsion was as high as 22% and 15% for KOH and NaOH, respectively. In the case of gentle washing, three to four washings were required to achieve a pH value similar to that of distilled water, but less emulsion was formed. The loss of ester in case of gentle washing with KOH and NaOH was 10% and 5%, respectively. So, it was observed that a lower loss of ester during washing takes place when NaOH is used as catalyst. The mixing of ester with water should be gentle to reduce the loss of ester due to formation of the emulsion. After washing, the product is kept for settling under gravity for 10–12 days or it is filtered (Fig. 5), to get the final product, i.e. biodiesel to be used as a fuel.

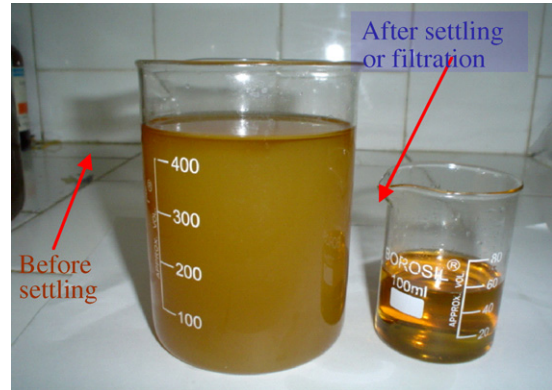


Fig. 5. Settling or filtration after washing.

### 3.3. Transesterification parameters optimization

NaOH was selected as catalyst for the base catalyzed transesterification of rice bran oil for further investigation.

### 3.4. Effect of molar ratio

One of the most important parameters affecting the yield of ester is the molar ratio of alcohol to vegetable oil. The stoichiometry of the transesterification reaction requires 3:1 molar ratio to yield 3 mol of ester and 1 mol of glycerol, but most researchers found that excess alcohol was required to drive the reaction close to completion. In the present research, methanol was used. The effect of methanol in the range of 6:1 to 15:1 (molar ratio) was investigated, keeping other process parameters fixed. The reaction temperature was kept constant at  $55 \pm 1$  °C, and reaction was performed for 1 h. The reaction was performed with different concentrations of NaOH. The results are shown in Fig. 6.

It was found that the ester yield increases with increase in molar ratio of methanol to vegetable oil, and for low values of molar ratio, the ester yield was sensitive to the concentration of NaOH. The incremental gain in ester yield

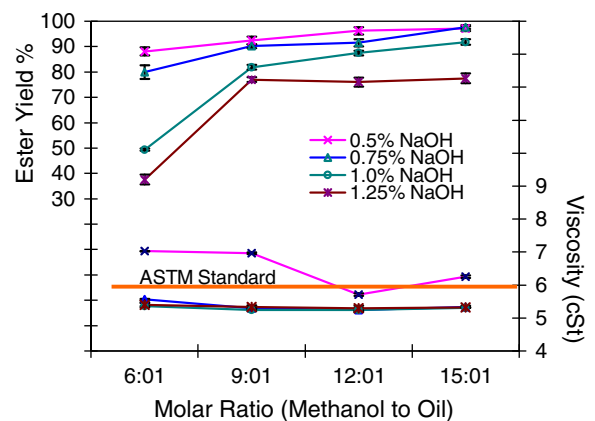


Fig. 6. Effect of molar ratio (methanol to oil) on ester yield and viscosity at different NaOH concentration.

decreases with increase in the molar ratio. Similar results was reported by earlier researchers for other vegetable oils [23,37,38]. The viscosity of the ester does not vary significantly with methanol to oil molar ratio (Fig. 6), but for 0.5% NaOH, the viscosity of the ester produced was found to be higher than the ASTM limit for the viscosity of biodiesel (6 cSt) (ASTM D6751).

### 3.5. Effect of catalyst concentration

The effect of NaOH concentration was studied in the range of 0.5–1.5% (weight of NaOH/weight of oil). The reaction temperature and time were kept constant at 55 °C and 1 h, respectively. The results for different molar ratios of methanol to oil are shown in Fig. 7. It was found that the ester yield decreases as the amount of catalyst increased from 0.5% to 1.5%. Ester yield decreases drastically as the NaOH concentration increases above 1% and reduces to almost 50% for 1.5% NaOH concentration. This lesser yield at high NaOH concentration may possibly be due to high soap formation. Fig. 7 also shows that for higher molar ratio of alcohol to oil, higher amount of NaOH can be used. The viscosity first decreases up to 0.75% NaOH concentration, and after that, it is almost constant. Hence, for 0.75% NaOH concentration, the viscosity of the rice bran oil biodiesel is found to be within the ASTM limits. Excess NaOH reduces the yield and also leads to undesirable extra processing cost because it is necessary to remove it from the reaction products at the end.

Similar results were reported by Encinar et al. [37] for used frying olive oil and sunflower oil mixture and Dorado et al. [36] for brassica carinata oil with KOH catalyst.

### 3.6. Effect of reaction temperature

For studying the effect of temperature on the transesterification reaction, the reaction temperature was varied as 50, 55, 60 and 65 °C, while the other parameters such as molar ratio of methanol to oil (9:1), reaction time (1 h)

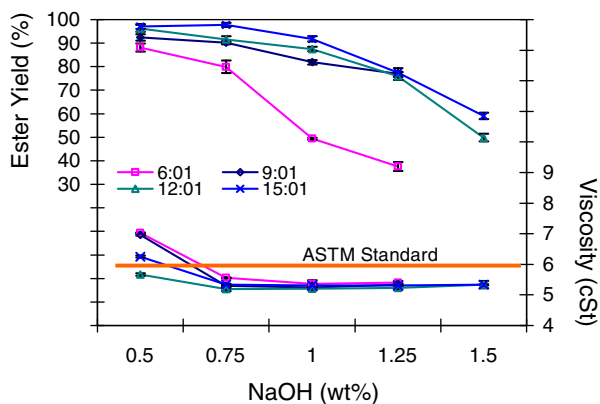


Fig. 7. Effect of NaOH concentration on ester yield and viscosity for different molar ratio of alcohol to oil.

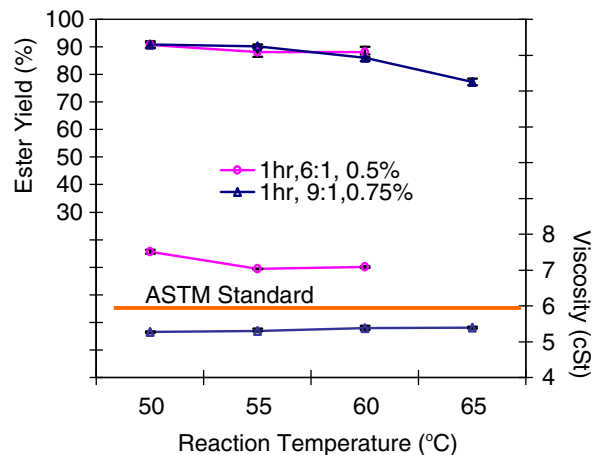


Fig. 8. Effect of reaction temperature on ester yield and viscosity.

and NaOH (0.75% w/w<sub>oil</sub>) were kept constant. The effect of reaction temperature on the ester yield and the viscosity of the ester are shown in Fig. 8. It is found that ester yield decreases as the reaction temperature increases above 50 °C. An insignificant increase in the ester viscosity with reaction temperature is observed in Fig. 8.

Several researchers found that the temperature increase influences the reaction in a positive manner [2,3,23,28,37]. Dorado et al. [36] found that the ester yield slightly decreases above 50 °C reaction temperature. It may probably be due to a negative interaction between the temperature and catalyst concentration due to the side reaction of saponification. High process temperature tends to accelerate the saponification of the triglycerides by the alkaline catalyst before completion of the transesterification.

### 3.7. Effect of reaction time

Several investigators found that the reaction starts very fast and almost 80% of the conversion takes place in first 5 min, and after 1 h, almost 93–98% conversion of the triglycerides into ester takes place [2,3,23,27,37]. In the present work, the effect of reaction time from 45 min to 105 min on the reaction yield and viscosity is investigated. It was found that as the reaction time was increased beyond 1 h, the ester yield decreased slightly, but there was no significant effect on the viscosity of the ester (Fig. 9).

### 3.8. Process parameter selection

The combined effect of catalyst concentration and molar ratio of methanol to oil can be summarized in Figs. 6 and 7. Based on Figs. 8 and 9, the optimum reaction time and reaction temperature were selected as 1 h and 55 °C. It is clear that as the catalyst concentration is increased, the ester yield decreases for all molar ratios of methanol to oil. Ester yield is found to be a maximum for 15:1 molar ratio of methanol to oil and 0.75% catalyst. At the same time, the viscosity (Figs. 6 and 7) does not vary signifi-

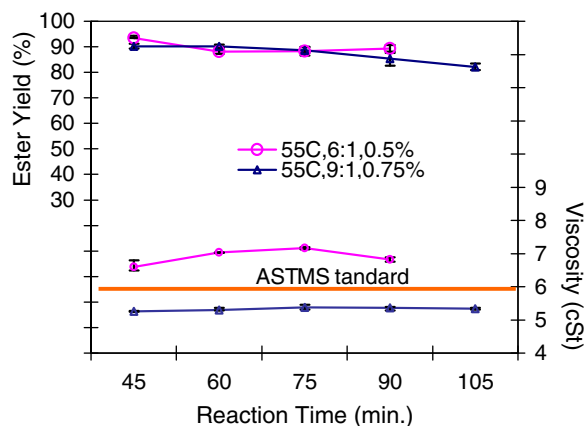


Fig. 9. Effect of reaction time on ester yield and viscosity.

cantly for catalyst amounts of 0.75% and 1.0% for the molar ratio of alcohol to oil from 9:1 to 15:1, which shows that the reaction was completed to the fullest extent at 9:1 molar ratio, and the gain in yield with 15:1 molar ratio was

not enough to justify the increase in the quantity of the additional alcohol used in the reaction. So, the optimum value of the molar ratio of methanol to oil was selected as 9:1 for rice bran oil, in contrast, other researchers have found it to be 6:1 or less for other edible oils, [9,13,22,23,36,37]. The viscosity of the ester is within the limit as per ASTM norms except when the catalyst amount is 0.5%. Hence, catalyst higher than 0.5% was required. However, as the catalyst amount increases, the ester yield decreases. Different researchers [9,13,23,26,27,36–38] found the amount of catalyst ranging from 0.28% to 1.5% for different oils. In the present investigation, 0.75% (w/w) NaOH was found to be optimum so as to give the ester with viscosity in an acceptable range along with high ester yield.

In summary, for the transesterification of rice bran oil, optimum reaction conditions were found to be 55 °C reaction temperature, 9:1 molar ratio of methanol to oil, 0.75% catalyst (w/w<sub>oil</sub>) and 1 h reaction time. These conditions gave an ester (rice bran oil methyl ester) yield of 90.18% by weight, and the ester viscosity was found to be 5.3 cSt.

Table 4  
Fuel specifications of rice bran oil, rice bran oil methyl ester and mineral Diesel

Property	Test procedures	Diesel	Rice bran oil	Rice bran oil methyl ester
Specific gravity @ 30 °C		0.839	0.920	0.877
Kinematic Viscosity @ 40 °C (cSt)	ASTM D445	3.18	43.52	5.29
Cetane Number	ASTM D613	51	50.1	63.8
Cloud Point (°C)	ASTM D2500	6	13	9
Pour Point (°C)		−7	1	−2
Flash Point (°C)	ASTM D93	68	316	183
Fire Point (°C)		103	337	196
Conradson Carbon Residue (% w/w)	ASTM D 189	0.1	0.6	0.35
Calorific Value (MJ/kg)	ASTM D 240	44.8	41.1	42.2
Elemental analysis (% w/w)	C	83	74.13	72.96
	H	13	11.0	12.73
	N	1.76	1.34	0.94
	O	0.19	12.25	11.59
	S	0.25	ND	ND

ND = Not detected.

Table 5  
Comparison of properties of different biodiesels

Property	Sunflower methyl ester <sup>c</sup>	Soybean methyl ester <sup>c</sup>	Peanut methyl ester <sup>a</sup>	Rape methyl ester <sup>c</sup>	Palm methyl ester <sup>a</sup>	Mahua methyl ester <sup>b</sup>	Jatropha methyl ester <sup>b</sup>	Karanja methyl ester <sup>b</sup>	Present research ROME
Density, kg/m <sup>3</sup>	0.880	0.884	0.883	0.893	0.880	0.880	0.880	0.876	0.877
Viscosity, cSt (40 °C)	4.2	4.08	4.9 <sup>A</sup>	4.8	5.7 <sup>A</sup>	3.98	4.84	9.6	5.29
Calorific value (MJ/kg)	40.1	39.8	33.6	40.0	33.5	37	37.2	36.12	42.2
Flash point (°C)	164	141	176	153	164	208	192	187	183
Fire point (°C)	183	171	–	–	–	–	–	–	196
Cloud point (°C)	−3	2	5	−3	13	–	–	–	9
Pour point (°C)	−6	−2	–	–	–	6	6	7	−2
Cetane no.	49	47	54	–	62	–	–	–	63.8
Carbon residue (wt%)	0.05	0.3	–	–	–	0.2	0.025	0.24	0.35

<sup>A</sup> At 37.8 °C.

<sup>a</sup> Srivastava et al. [2].

<sup>b</sup> Ghadge and Rehman [44].

<sup>c</sup> Encinar et al. [37].



### 3.9. Biodiesel characterization

The fuel properties of the biodiesel (rice bran oil methyl ester) and mineral Diesel were determined using standard test procedures (Table 4).

The calorific value and cetane number tests were conducted at the Indian Oil Corporation's R&D centre, Faridabad, India. Calorific value is a measure of the energy content of the fuel and is a very important property of biodiesel, which determines its suitability as an alternative to mineral Diesel. The calorific value of ROME and rice bran oil is 42.2 and 41.1 MJ/kg, which is almost 94% and 91% of the calorific value of diesel (44.8 MJ/kg), respectively. The lower calorific value of ROME is because of the presence of oxygen in the molecular structure, which is confirmed by elemental analysis also. The cetane number of ROME is found to be higher than that of mineral Diesel, which suggests better combustion properties of biodiesel.

The flash point and fire point were tested with a closed cup Pensky Marten's apparatus. The flash point is the measure of the tendency of a substance to form flammable mixtures when exposed to air. This parameter is considered in the handling, storage and safety of fuels. The high value of flash point and fire point in the case of ROME represents it is a safer fuel to handle.

The fuel properties of rice bran oil biodiesel obtained, produced in this investigation, compared with the biodiesel produced by other researchers [2,37,44] are shown in Table 5. The properties of ROME are almost similar to other biodiesel except that ROME has a higher calorific value and cetane number.

## 4. Conclusions

Base catalyzed transesterification was studied with KOH and NaOH as catalyst for biodiesel production from rice bran oil. Biodiesel can be made successfully using both catalysts. During this investigation, transesterification as well as catalyst removal from biodiesel has been studied in detail. Transesterification reaction parameters control the yield of the ester, whilst catalyst removal is required for purification of the ester to make it suitable fuel for Diesel engines. It was found that the ester has a tendency to form emulsion when it comes in contact with water during catalyst removal. Loss of biodiesel due to formation of emulsion was found to be less in case of NaOH catalyst. Emulsion formation also depends on the level of agitation during mixing of water with the ester. Care must be taken to maintain a low level of agitation during catalyst removal, however, this may require a number of washing steps before getting the desired quality of biodiesel. In the reaction stage, factors that greatly influenced the yield and quality were the molar ratio of methanol to oil and catalyst concentration.

The effects of the parameters, namely process temperature, reaction time, molar ratio of alcohol to oil and catalyst concentration on the ester (biodiesel) yield and the

viscosity were investigated. The combination giving optimum biodiesel yield was found to be 9:1 molar ratio of methanol to oil, 0.75% (w/w<sub>oil</sub>) NaOH, 55 °C reaction temperature and 1 h reaction time, followed by 3–4 times gentle washing of the biodiesel with 70 °C distilled water (10% v/v).

The viscosity of rice bran oil reduces substantially after transesterification and becomes comparable to that of Diesel. The density, flash point and cloud and pour points for ROME were higher than those of the mineral Diesel. Comparatively, the higher flash point of ROME makes it a safer fuel to handle. The calorific value of ROME was slightly lower than that of Diesel. All these tests for the characterization of ROME demonstrated that almost all characteristics of ROME are comparable to those of Diesel, and this makes it a potential substitute for Diesel fuel in compression ignition engines.

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