

An alkali catalyzed transesterification of rice bran, cottonseed and waste cooking oil

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Abstract

The biodiesel production by trans-esterification of three raw materials including virgin and used edible-oil and non-edible oil has been presented in this paper. A two step method following acidic and alkali catalyst was used for non-edible oil due to the unsuitability of using the straight alkaline-catalyzed trans-esterification of high FFA present in rice bran oil. The acid value after processing of rice bran, cottonseed and waste cooking oil was found to be 0.95, 0.12 and 0.87, respectively. The influence of three variables on percentage yield was studied at this stage, *i.e.*, methanol to oil molar ratio, reaction temperature and reaction time. The cottonseed oil, waste cooking oil and rice bran oil showed a maximum yield of 91.7, 84.1 and 87.1% under optimum conditions. The fuel properties of those three biodiesels have met standard biodiesel fuel results.

Keywords: biodiesel, rice bran oil, cottonseed oil, waste cooking oil.

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Besides coal and natural gas, with the exception of hydroelectricity and nuclear energy, the petroleum resources have been supplying the world energy needs. However, the rising concerns on depleting reserves of these natural resources, which are predicted to be consumed by the end of the next century and environmental problems that arise from the use of fossil fuel, have led the worldwide economy to endorse both the academic and industrial researchers to explore new sources of fuel [1]. One of the feasible sources, which is able to perform as well as the fossil fuel and also considered as environment-friendly is biodiesel, as a result of trans-esterification reaction. The straight vegetable oils have been used in the past; however,

due to the issues of high viscosity, deposit formation in the injection system and poor cold start, it is extremely important to reduce the viscosity of oil [2]. There are various techniques that could be used to reduce the viscosity of vegetable oils, especially pyrolysis, micro-emulsion and trans-esterification [3].

Trans-esterification is a chemical reaction that occurs between triglycerides and alcohol in the presence of a catalyst with glycerol as a major by-product [4] as shown in Figure 1.

The advantage of transesterification is that it decreases the viscosity of the vegetable oils and improves the fuel properties of fatty acid esters. This is due to the fact that viscosity of vegetable oils is much higher

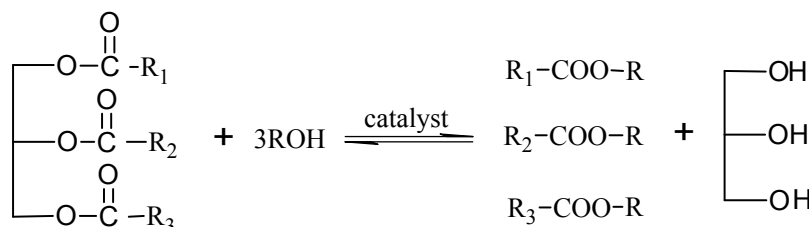


Figure 1. Trans-esterification reaction of triglycerides with alcohol.

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than in diesel; there would have been several problems if these vegetable oils were directly used in diesel engine as a fuel [5].

Global energy scenario

Today, in the modern age, with the increase in demand of fossil fuels, the reservoirs of fossil fuels are decreasing day by day due to its increasing demand in this era. According to an estimate, the reserves will last for 218 years for coal, 41 years for oil and 63 years for natural gas [6–8]. The economic growth during industrial revolution in the late 18th and 19th century has created serious problems for energy shortage. The world primary energy production is almost the same since those years, but consumption is rapidly increasing and creating an unbalance between demand and supply. It is believed that 50% more energy will be required round the world till 2030 [9,10] as shown in Figure 2.

The major part in this energy consumption is industry and transportation sector. Transportation is the second largest energy consuming sector. The most of the fossil fuel consumption for transportation sector is oil consumption, which is around 97.6%. The major oil demand is expected to be raised for transportation sector [11]. Although the major source of energy is oil and it is expected to be the largest source of energy, but dependence on oil share for energy is expected to decrease by 5% from current till 2035 [11].

Global environment issues

The climate change is believed to be the current most important global issue. The temperature of the Earth is rapidly increasing with the passage of time. If this may be allowed to rise at a rate of 2 degrees per year, there would be a drastic effect for human beings

and as a result thousands of people may lose their lives just because of this issue [12]. The CO₂ levels in the atmosphere have increased from 280 to 350 ppm from the pre-industrial era till now. This increase in the CO₂ levels is mainly due to the aggressive use of fossil fuels [13]. Approximately, 8.6 billion metric tons (BMT) of carbon dioxide is expected to be released into the atmosphere from 2020 to 2035 [11,14]. Figure 3 shows the expected increase in CO₂ emissions till 2035 [11].

Most of the countries have started working towards the renewable energy sources and almost all countries are seriously working on the reduction of the emissions. For this purpose, they have set standards and targets to their greenhouse gas (GHG) emissions to certain levels. Europe aims to reduce GHG emissions by one fifth till 2020. US president has announced to reduce GHG emissions by 28% till 2020. China has planned to control GHG emissions till 45% as from 2005. Japan has planned to cut GHG emissions to a target of 60–80% by 2050 from their emissions in current level [15]. Similarly India, Germany, Brazil, Pakistan and some other countries have made their targets to reduce GHG emissions as shown in Table 1.

The alternative renewable fuels therefore have received increasing attention for future utilization. In this respect the fermentation, transesterification, pyrolysis of biomass, industrial and domestic wastes have been proposed as alternative solutions. Among these different approaches, the trans-esterification seems to be a simple and an efficient method for fuel production [16].

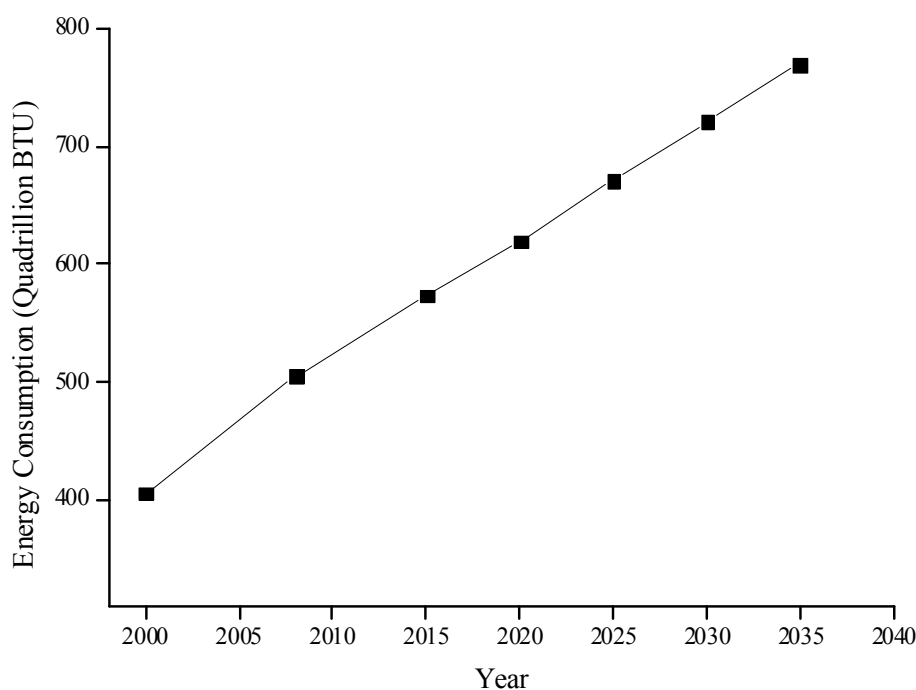


Figure 2. World energy consumption from 2000–2035.

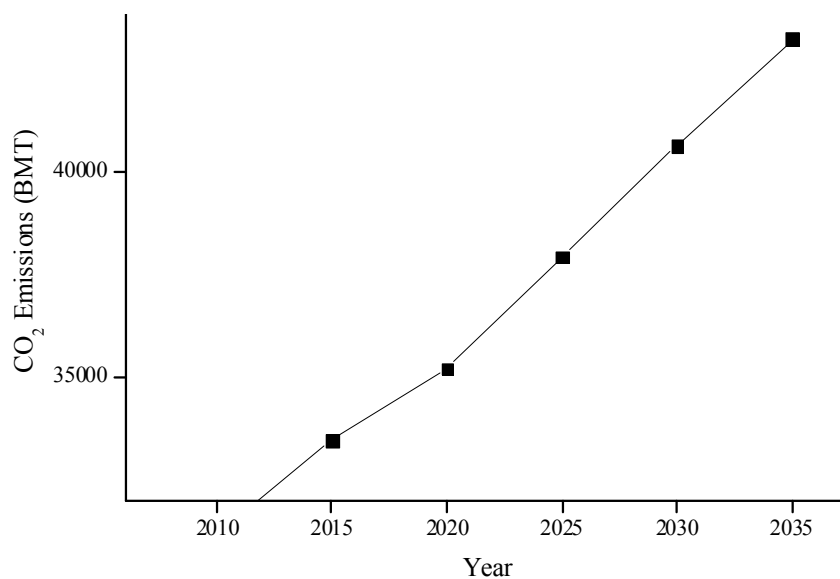


Figure 3. World CO₂ emissions.

The cost of biodiesel is higher than the conventional fossil fuel, but it can be controlled by using waste vegetable oil instead of fresh oil that has major contribution towards the increase in the price of biodiesel. For the maximum projection of biodiesel, the cost of biodiesel should be less as compared to fossil fuels, so that it can attract people towards this new change [17].

Technologies for biodiesel production

There are different technologies that can be used for the trans-esterification processes. This depends upon the amount of free fatty acids and the water content present in the feedstock. The alkali catalytic process is more effective when the FFA level is less than 1%. When the FFA contents of the raw material are greater than 1% then acid catalyzed process is preferred. Anyhow, this process requires higher catalyst concentration and high molar ratio that results in corrosion issues [18]. A brief description of the process used for trans-esterification reaction is presented in Figure 4.

The current research work investigates the optimal reaction conditions of biodiesel production from cottonseed oil, waste cooking oil and rice bran oil. It has been explored that the three oils used in this study

could be viable for biodiesel production. Hence, it can contribute to the development of renewable energy resource.

MATERIALS AND METHODS

Crude rice bran oil (RBO) and cottonseed oil (CSO) were obtained from the local market while the waste cooking oil (WCO) was taken from the local fast food corner. Methanol (99.8%) and potassium hydroxide were purchased from Merck Chemicals.

Oil characterization

All three oils were analyzed for different properties which are listed in Table 2.

Experimental set-up

A lab scale experimental setup was developed for the transesterification reaction of biodiesel production. This was comprised of reaction flask, water bath, condenser and magnetic stirrer. The glass reactor was 1000 ml capacity having 3 necks, one for condenser and others for temperature detection and inlet of reactants. The temperature indicator was used to measure the reaction temperature.

Table 1. World energy targets

Country	Target
World	5.2% GHG emissions reduction till 2012 on 1990 levels
Germany	10% target of biodiesel
China	15% biodiesel share till 2020
UK	Renewable transport fuels accounting 10% till 2015
USA	4% soya biodiesel in 2016
India	10% renewable energy share till 2012
Pakistan	10% biodiesel share by volume till 2025

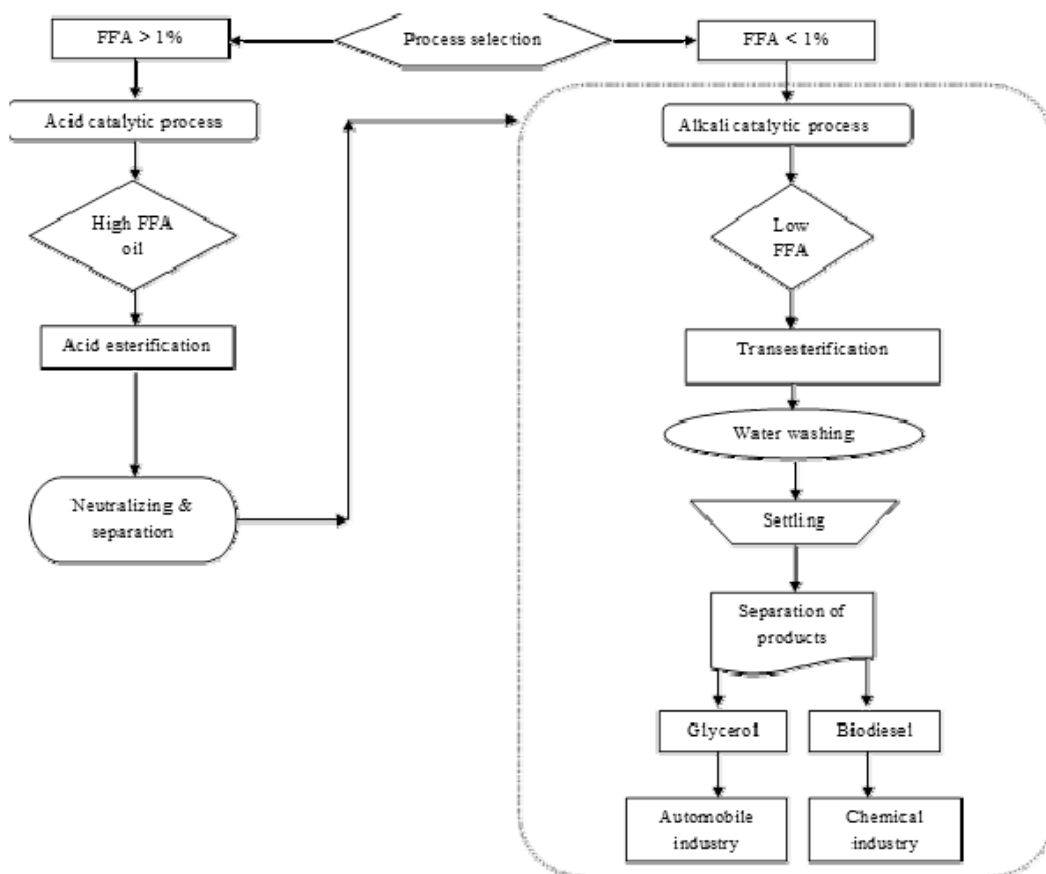


Figure 4. Steps for biodiesel production.

RESULTS AND DISCUSSION

Pretreatment and acid value determination

The three oil samples of cottonseed, rice bran and waste cooking oil were heated up to 40 °C to reduce the viscosity and then they were filtered to make them free of any unwanted suspended particles. Water is not required in the oil samples since it inhibits the process due to the saponification of the samples instead of trans-esterification. Therefore filtered oil samples were heated up to 105 °C to remove traces of water.

The acid value is the number of milligrams of potassium hydroxide necessary to neutralize the free acids in

1 g of sample. The acid value of the three samples was measured using the Eq. (1):

$$\text{Acid value} = \frac{(A - B) M \times 56.1}{W} \tag{1}$$

where *A* = KOH required for titration of sample, mL, *B* = KOH required for blank titration, mL, *M* = molarity of the KOH solution and *W* = sample used, g.

The acidity can either be measured as acid value or as free fatty acids (FFA) present [19]. Free fatty acids are the saturated or unsaturated monocarboxylic acids which are present in nature in fats, oils and greases but are not attached to glycerol backbones [20]. Higher amount of free fatty acids results in higher acid value.

Table 2. Physical and chemical properties of rice bran, cottonseed and waste cooking oil

Property	RBO	WCO	CSO
Palmitic acid C16:0	18.8	16.3	20.6±1.2
Stearic acid C18:0	2.4	5.63	4.6±0.31
Oleic acid C18:1	43.1	32.23	19.54±0.43
Linoleic acid C18:2	33.2	39.47	52.5±1.44
Linolenic acid C18:3	0.6	0	0.23±0.05
Arachidic acid C20:0	0.7	0.12	0.31±0.11
Kinematic viscosity at 40 °C, cSt	42.15	54.3	35.7
Acid value, mg KOH/g	38	0.87	0.12

For alkaline trans-esterification the free fatty acids value should be in the desired limits otherwise either the yield will be very low or reaction will not take place. Most researchers have different opinion about the level of FFA, but usually it is ranging from 0.5 to 3% for alkaline trans-esterification [21–24].

The acid value for cottonseed oil and waste cooking oil was found to be 0.12 and 0.87, respectively, but for the rice bran oil it was 38 and a two step acid catalyzed reaction was carried out to reduce it to the desired limit. In each step effect of molar ratio (methanol/oil) and the reaction time (45, 60, 75 and 90min) on acid value of the crude rice bran oil was studied. A 500 ml sample of rice bran oil was heated by placing it in the water bath. The sulfuric acid methanol solution was added in the reaction flask along with preheated oil sample. This was stirred for some time to make the solution homogeneous. The reaction mixture was poured into a separating funnel after the completion of this reaction. The impurities present were removed along with excess methanol and sulfuric acid. The acid value of the product was measured at the predefined intervals [4]. For the first step, the Acid Value of 3.6 mg KOH/g was selected, which consumed 75 min and molar ratio of 1:7 given in Figure 5.

This was used as a raw material for second step and the same experiment was repeated. The acid value 0.95 KOH/g was selected using minimum amount of alcohol and minimum time required, as shown in Figure 6. The final reaction mixture was separated using a separating funnel, washed, centrifuged and was used for further analysis.

Transesterification reaction

The experimental setup was established for trans-esterification process. All three oils were preheated before starting the reaction to avert moisture absorbance. A fresh prepared KOH-methanol solution was used in order to uphold the catalytic activity. The methanolic solution was added to all three reaction flasks. At proper intervals of time, the samples were withdrawn from reaction mixture and analyzed. The constant speed of 400 rpm was used throughout the reaction.

The product mixture from three reaction flasks was poured into separating funnel. The esters were separated from the lower aqueous glycerol layer under gravity and then were washed with distilled water. The washed esters were dried under vacuum and used for subsequent analysis.

Effect of methanol to oil molar ratio

The molar ratio of methanol to oil is very important factor as it affects the yield and also the cost of overall reaction. Higher molar ratio generates more esters than lower ratios in lesser time. The vegetable oils can be converted to biodiesel using 6:1 to 40:1 oil/alcohol molar ratio [25]. According to stoichiometric ratio, 3 mol of alcohol and 1 mol of triglyceride produce 3 mol of ester and 1 mol of glycerol for the trans-esterification reaction to occur. However, as trans-esterification is an equilibrium reaction, in practice, excess alcohol is required to move the reaction to forward direction. In this study, effect of methanol in the range

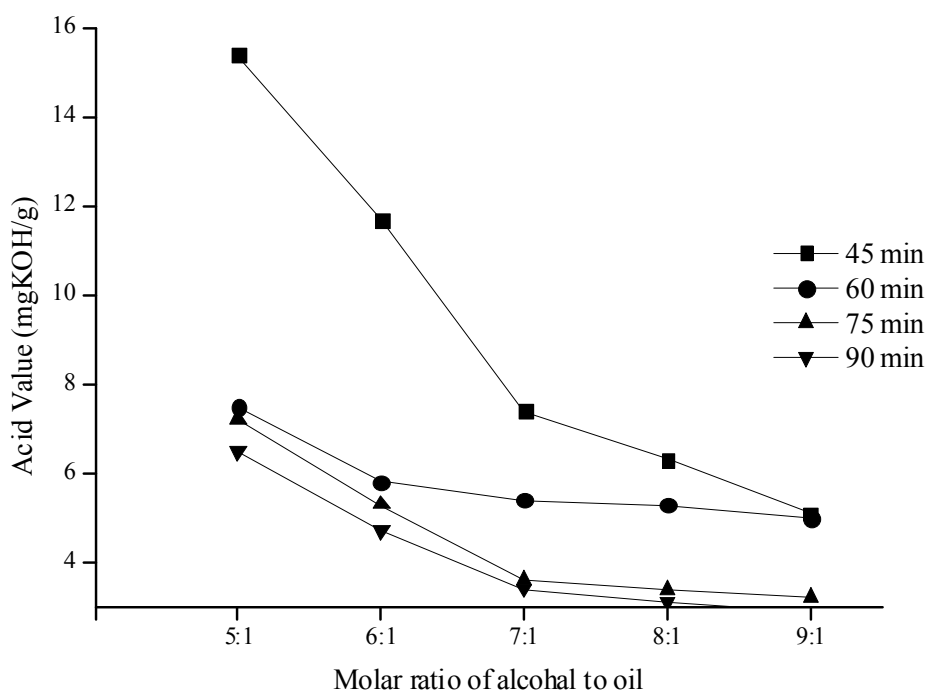


Figure 5. First step: acid value reduction.

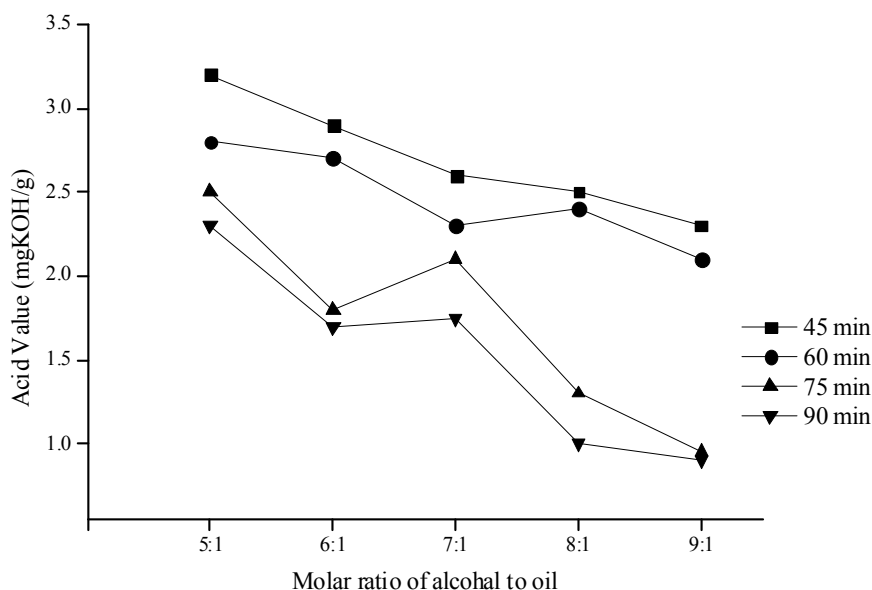


Figure 6. Second step: acid value reduction.

of 3:1 to 12:1 was investigated, keeping other process parameters fixed. The reaction temperature was kept constant at 55 ± 1 °C, and reaction was carried out for 1 h at 400 rpm. The results are shown in Figure 7. Rice bran oil yield was found to be maximal at 6:1 molar ratio. However, after the molar ratio of 6:1, the conversion remained less. Waste cooking oil showed two different layers at a molar ratio of 3:1 due to the presence of un-reacted triglycerides. This showed that methanol delivered was not enough to perform the complete reaction. At a molar ratio of 6:1, a maximum yield of 86% was achieved. At molar ratio of 9:1; the yield was 87.3%. For cottonseed oil, the reaction was incomplete for a molar ratio less than 6:1 and no separation was observed during the separation process. It is observed that beyond molar ratio of 6:1 further addition of methanol had very little effect on % yield of biodiesel. With further increase it remained nearly constant. In addition, the higher molar ratio of alcohol to oil makes the solubility higher, which as a result inhibits the separation of glycerin. This presence of glycerin drives the equilibrium to backward direction and results in lower yield of esters [27].

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Effect of reaction temperature

Reaction rate is strongly influenced by the reaction temperature. The trans-esterification reaction can even occur at room temperature provided sufficient time is

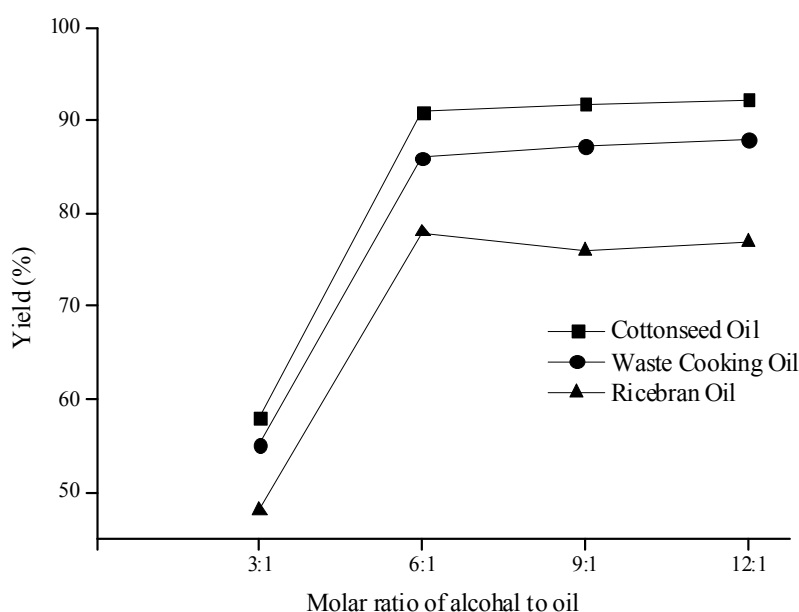


Figure 7. Effect of methanol to oil ratio on methyl ester yield.

given for the reaction to occur. The effect of reaction temperature in this study was investigated using the optimal parameters achieved in previous sections. Several investigators found that although the reaction is usually carried out at nearly boiling point of alcohol, the maximum yield has been reported at a temperature range of 60–80 °C at a molar ratio of 6:1 [23,27,28].

The effect of reaction temperature on the production of biodiesel is shown in the Figure 8. Temperature was changed in the intervals of 5 °C. It was found that biodiesel produced from cottonseed oil, waste cooking oil showed maximum yields at 60 °C and

from rice bran oil at 55 °C. Since boiling point of methanol is 64.7 °C, at near temperatures, the methanol starts boiling and this affects the yield. The ester conversion is decreased when the temperature is higher than 60 °C although a reflux condenser was used to avoid methanol losses in this experiment.

Effect of reaction time

The influence of esterification reaction time on percent yield is shown in Figure 9. The percent yield increases with the reaction time. In reality most of the reaction is completed in the first few minutes. Most of the investigators found that 80% of reaction takes

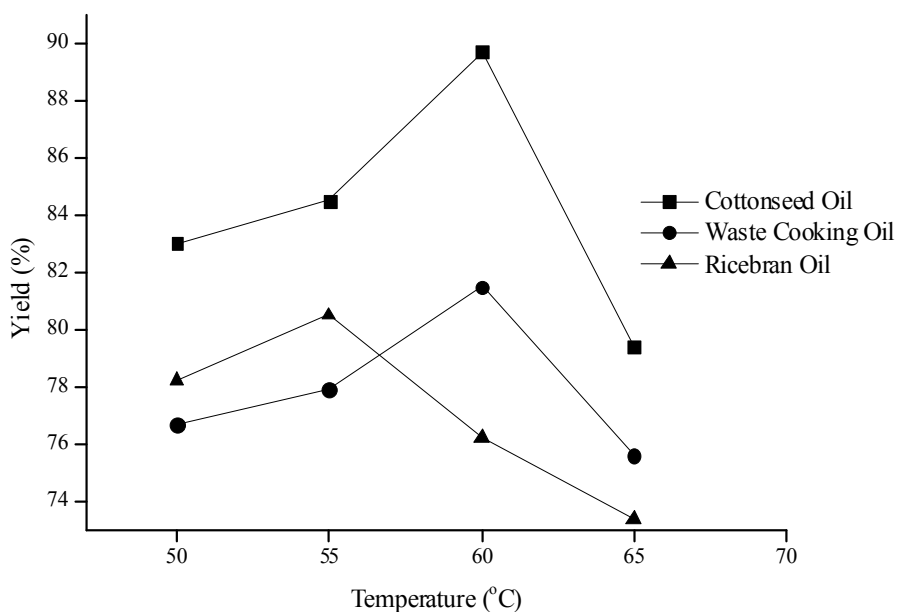


Figure 8. Effect of reaction temperature on % yield.

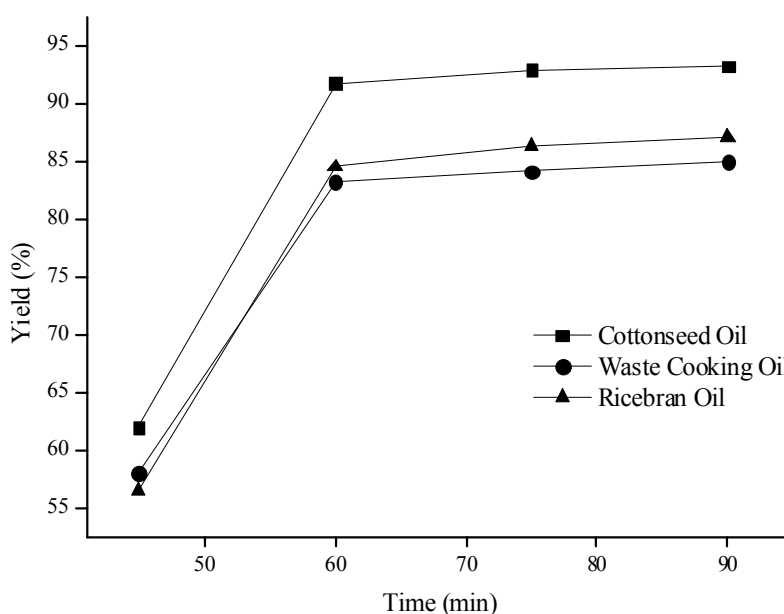


Figure 9. Effect of reaction time of % yield.

place in the first 5 min and the rest of conversion may take almost 1 h, in order to have 93–98% conversion of triglycerides [20, 27]. In this study time was changed from 45 to 90 min with interval of 15 min and effect on percent yield was studied. It was found that conversion increased very quickly with the reaction time between 30 and 60 min. It was observed that there was no noticeable change in the yield by increasing the reaction time for more than 60 min.

Effect of parameters

After the production of biodiesel, it was tested for different properties of the diesel such as specific gravity, kinematic viscosity, cetane no, cloud point and pour point. These were determined by using the ASTM D6751. The results are given in Table 3.

Table 3. Fuel parameters of methyl esters as compared to ASTM biodiesel

Property	Biodiesel D 6751-02	CSO Ester	RBO Ester	WCO Ester
Specific gravity	0.86–0.90	0.84	0.86	0.87
Kinematic viscosity, cSt	1.9–6.0	4.81	4.38	4.58
Cetane No, min	47–70	58	59.5	55.8
Cloud point, °C	No est. limit	6	8	4
Pour point, °C	–	3	-3	1
Flash point, °C	122–185	172	185	188

CONCLUSION

Three different vegetable oils, cottonseed, waste cooking and rice bran, were explored for their potential use as an alternative source for biodiesel production. It was observed that cottonseed oil showed a maximum yield of 91.7% at 60 °C, 6:1 molar ratio and consuming 60 min. However, rice bran oil gave a yield of 87% at 55 °C, 6:1 molar ratio, and 90 min, while waste cooking oil showed a maximum yield of 84% under optimum conditions of 60 °C temperature, molar ratio of 9:1 and consuming 75 min. This catalysis provides a simple and economic alternative method for biodiesel production. In addition, the separation of glycerol and soap (created by KOH) in this process could be easily isolated from the rich ester layer.

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IZVOD

BAZNO-KATALIZOVANA REAKCIJA TRANSESTERIFIKACIJE PIRINČANIH MEKINJA, SEMENA PAMUKA I OTPADNOG JESTIVOG ULJA

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(Naučni rad)

U ovom istraživačkom radu opisana je proizvodnja biodizela reakcijom transesterifikacije iz tri vrste sirovina, uključujući devičansko, korišćeno jestivo i nejestivo ulje. Zbog visokog sadržaja slobodnih masnih kiselina u pirinčanim mekinjama, proporcionalna bazno-katalizovana transesterifikacija je nepodobna, te je na nejestivo ulje primenjena dvostepena, kiselinsko i bazno katalizovana reakcija transesterifikacije. Vrednosti kiselinskog broja nakon tretmana pirinčanih mekinja, semena pamuka i otpadnog jestivog ulja bile su: 0,95, 0,12 i 0,87, redom. Uticaji tri promenljive na procenat prinosa (na primer molarni odnos metanola i ulja), temperaturu i vreme reakcije su ispitivani na ovom nivou istraživanja. Pri optimalnim uslovima, ulje iz semena pamuka, jestivog otpadnog ulja i ulja iz pirinčanih mekinja dalo je maksimalni prinos od: 91,7, 84,1 i 87,1%. Karakteristike dobijenog biodizela iz tri različite sirovine zadovoljavaju standarde propisane za biodizel kao gorivo.

Ključne reči: Biodizel • Ulje semena pamuka • Ulje pirinčanih mekinja • Otpadno jestivo ulje