PROCESS OPTIMIZATION FOR BIODIESEL PRODUCTION FROM SISSOO SEED OIL

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Abstract - *In this study,* ***Sissoo seed*** *oil was used to produce its* ***methyl esters****. The acid value of this oil was determined by* ***titration*** *and was found to be* ***1.2 mg KOH/g*** *for Sissoo seed oil. Biodiesel production process consists of one-step:* ***transesterification*** *process. This process was used to convert its methyl ester. The parameters affecting the transesterification process for this oil was optimized in order to achieve maximum ester yield. This process gives yields of about 89.21% using* ***sodium methoxide*** *as a catalyst. Density, viscosity, flash point, fire point, acid value and calorific value of the produced methyl esters were determined and found to be within the limits of ASTM D6751 and IS 15607 specifications.*

1. INTRODUCTION

Petroleum fuels play an important role in the development of industrial growth, transportation, agricultural sector and to meet many other basic human needs. These fuels are limited and depleting day by day as the consumption is increasing rapidly. India is importing more than 80% of its fuel demand and spending a huge amount of foreign currency on fuel. Among the other options, biodiesel is one of the best available sources to fulfill the energy demand of the world (Basha, Gopal, and Jebaraj 2009).

Biodiesel is an alternative fuel, contains no petroleum products, which has a correlation with sustainable development, energy conservation, management, efficiency and environmental preservation (Agarwal 2007). Biodiesel may be used in compression ignition engine with little or no modification in the engine hardware. (Tsolakis and Megaritis 2004). Amarnath and Prbharakaran (2012) used karanja biodiesel as an alternative fuel in existing diesel engine without any major modifications. The engine was found to operate smoother, with less noise and vibrations, at higher compression ratios. The advantages of using biodiesel compared with diesel fuel include reduced exhaust emissions, improved biodegradability, reduced toxicity and improved lubricity, higher flash point, and lower vapor pressure (Margaroni 1998; Knothe and Steidley 2005). The amount of carbon monoxide and hydrocarbon emissions in heavy-duty engines are less compared with small engines (Godiganur, Murthy, and Reddy 2009).

Several methods exist for making vegetable oils usable in diesel engines. The most significant is the transesterification method (Yamane, Ueta, and Shimamoto 2001). The purpose of transesterification process is to lower the viscosity of the oil. The main drawback of vegetable oil is their high viscosity and low volatility, which causes poor combustion in diesel engines. The transesterification is the process of removing the glycerides and combining oil esters of vegetable oil with alcohol. This process reduces the viscosity to a value comparable to that of diesel and hence improves combustion (Basha et al. 2009).

Free Fatty Acid and moisture contents in triglycerides have significant effects on transesterification process (Goodrum 2002). For alkaline transesterification process, the triglycerides should have an acid value less than 1 mg KOH/g and all materials should be substantially anhydrous (moisture content less than 0.5%) (Ma and Hanna 1999). According to Ramadhas, Jeyaraj, and Muraleedharan (2005); Van Gerpen and Canakci (2001), biodiesel production from high free fatty acid oil needs a two-step transesterification. i.e., acid esterification followed by transesterification to get high biodiesel yield. Dalvi and Mohite (2012) studied biodiesel production from Thespesia populnea L. oil. They developed a two-step transesterification process to convert the high free tatty acid oil to mono-ester. The major factors affect the conversion efficiency of the process such as molar ratio, amount of catalyst, reaction temperature and reaction duration was analyzed. Saravanan et al. (2010) discussed the production of biodiesel using mahua (Madhuca Indica) oil. The effect of three alcohols namely methanol, ethanol and 1-butanol on the yield of acid-catalyzed production of biodiesel had been studied at boiling temperature of alcohol. Morshed et al. (2011) presented a three-step method to convert rubber seed oil to biodiesel. Rashid, Anwar, and Knothe (2009) reported detailed transesterification procedures for methyl esters of cottonseed oil using sodium methoxide, potassium methoxide, sodium hydroxide and potassium hydroxide as catalysts. Use of sodium methoxide catalyst exhibited the best efficiency than the other catalysts tested. A

As the demand of edible oil is higher than its production, it is not possible to use edible oils for vehicular applications. India being a tropical country is rich in forest resources having a wide range of trees, which yield a significant quantity of oilseeds (Ma et al. 1999). Few non-edible oils available in India are as follows: Simarouba, Mahua, Karanja, Jatropha, Neem and Castor.

1.1 Pretreatment process*:*

The Sissoo oil will be first converted to esters in the pretreatment process using sulfuric acid as a catalyst. The experiments will be conducted in a laboratory scale apparatus at 60◦C. Just below the boiling point of methanol. Each reaction will be allowed some time . Experimental setup consists of reaction flask equipped with reflux condenser, magnetic stirrer and thermometer. The Sissoo oil will be added into the reaction flask, and heated up to 60◦C. Then a fixed amount of alcohol and catalyst mixture will be added to Sissoo oil, and stirred. The progress of the reaction was monitored by measuring acid value of Sissoo oil. On completion of this reaction, the reaction mixture was then poured into a separating funnel to remove excess alcohol, sulfuric acid and impurities. The product having acid value less than 2 mg KOH/g using lowest methanol and catalyst amount in the pretreatment process was used for the alkaline transesterification reaction.

1.2 Transesterification process:

The treated Sissoo oils will be transesterified using alkaline catalyst. The process parameters such as alcohol to Sissoo oil molar ratio, catalyst amount, reaction temperature, and reaction time will be analyzed. The transesterification process and laboratory apparatus must be same as those of pretreatment experiments except catalyst. After the transesterification reaction, the glycerin layer will be separated in a separating funnel and the ester layer will be washed with warm water. After washing, the methyl ester will be heated up to certain temperature to remove excess alcohol and water. At the end of process optimization, the process will be repeated for three times to check the repeatability. The final product will be tested and compared with diesel and recommended standards of biodiesel.

2. OPTIMIZATION PROCESS OF BIO DIESEL

2.1 Factors affecting the acid value of sissoo oil:

2.1.1 Effects of molar ratio:

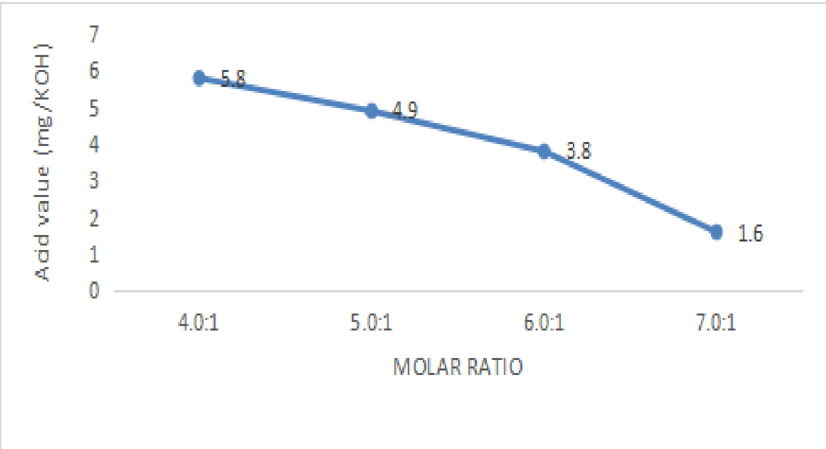

Fig 2.1.1: Effect of Methanol to oil molar ratio on acid value

An increase in the molar ratio of methanol to oil ratio from 4:1 up to the level of 7:1 exhibited encouraging effects on the acid value of esters. The reaction was incomplete for a molar ratio less than 4:1. The ester acid value decreases with increasing in methanol to oil molar ratio. The minimum acid value for sissoo seed oil was obtained at the methanol to oil molar ratio of 7:1. With further increase in molar ratio (beyond 7:1) there is no improvement in the yield considerably.

2.2.2 Effect of catalyst concentration

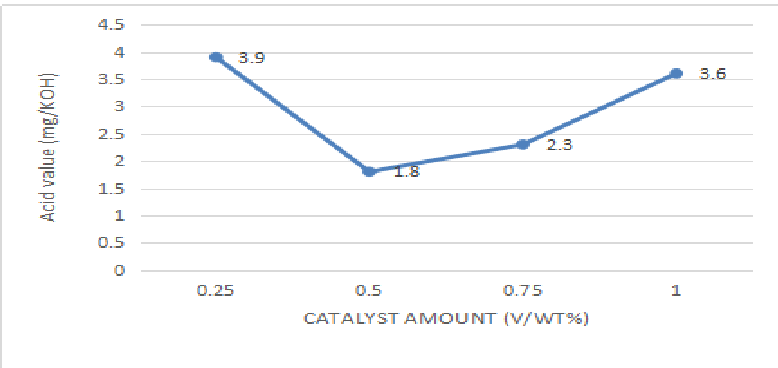

Fig 2.1.2: Effect of acid catalyst amount on acid value

The alkaline catalyst was studied in the range of 0.25-1% for sissoo seed oil. For each case, the reaction continued for 30 minutes at 60^{0}C. The effect of catalyst amount on acid value is shown in Figure 3.1.2. It can be seen from figure that the acid value is more at lower catalyst concentration due to incomplete reaction. The excess addition of catalyst decreased the acid value. The optimal catalyst concentration for sissoo seed oil was found to be at 0.5%. Further increase of catalyst amount (beyond 0.5%) leads to increase in acid value. This increase in acid value might be attributed to formation of an emulsion, which has increased the viscosity.

3.2 TRANSESTRIFICATION

3.2.1 Effects of molar ratio:

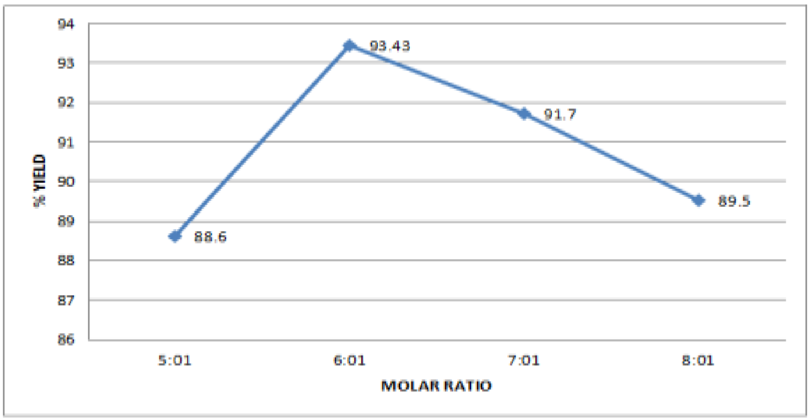

Fig.3.1: Effect of alcohol to oil molar ratio on yield.

An increase in the molar ratio of methanol to oil ratio from 5:1 up to the level of 6:1 exhibited encouraging effects on the yield of esters. The reaction was incomplete for a molar ratio less than 6:1. The ester yield percentage increases with increasing in methanol to oil molar ratio. The maximum yield for sissoo seed oil was obtained at the methanol to oil molar ratio of 6:1. With further increase in molar ratio (beyond 6:1) there is no improvement in the yield considerably. The other researchers (Rashid et al. 2009; Sivakumar, Anbarasu, and Renganathan 2011) observed the maximum yield at 100% excess alcohol (6:1, alcohol to oil molar ratio) while using cotton seed oil and dairy waste scum, respectively.

3.2.2 Effect of catalyst concentration

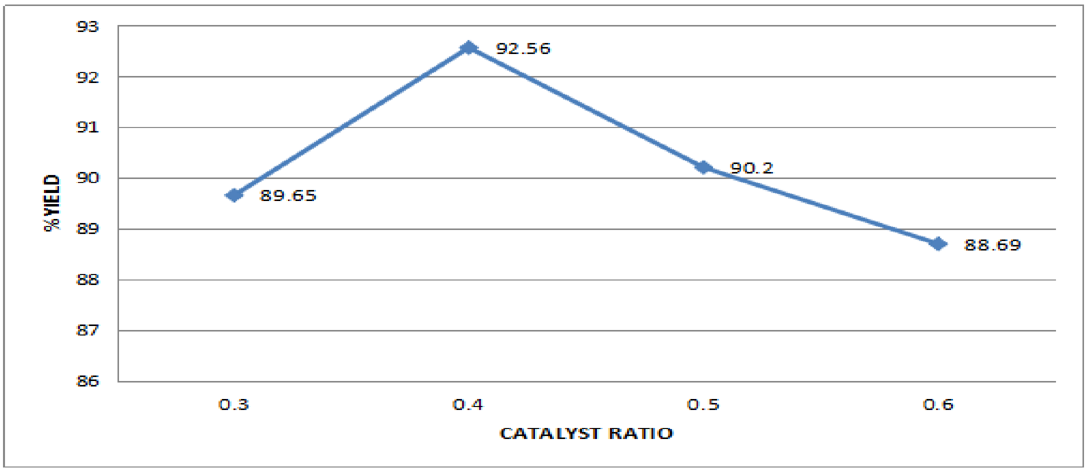

Fig.3.2: Effect of alkaline catalyst on yield.

The alkaline catalyst was studied in the range of 0.3-0.6% for sissoo seed oil. For each case, the reaction continued for 30 minutes at 60^{0}C. The effect of catalyst amount on yield is shown in Figure 3.2. It can be seen from figure that the yield is less at lower catalyst concentration due to incomplete reaction. The excess addition of catalyst increased the yield. The optimal yield for sissoo seed oil was found to be at 0.4%. Further increase of catalyst amount (beyond 0.4%) leads to lower yield. This decline in ester yield might be attributed to formation of an emulsion, which has increased the viscosity. Das and Sahoo (2009) achieved better results at 1.1%, 1% and 0.9% (weight of KOH/volume of oil) of potassium hydroxide for Jatropha, Karanja and Polanga oil respectively.

3.2.3 Effect of Reaction Temperature

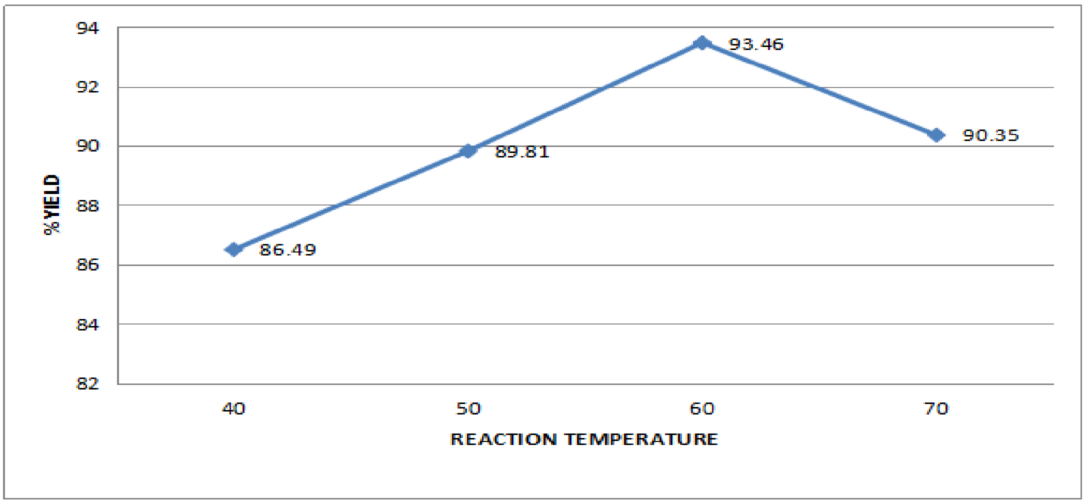

Fig.3.3: Effect of temperature on yield

The effect of reaction temperature on the yield is studied in the temperature range of 30-60˚C. The maximum yield was obtained at 60˚C for Sissoo seed oil. An increase in the yield was observed when the reaction temperature went beyond 40˚C for Sissoo seed oil. This could be due to gel formation at high temperatures. Therefore, these conditions should be avoided. Other researchers (Ramadhas et al. 2005; Yuan et al. 2008; Rashid et al. 2009) achieved better results at 45˚C, 48.2˚C, and 65˚C while using rubber seed oil, waste rapeseed oil and cotton seed oil, respectively.

3.2.4 Effect of Reaction Time

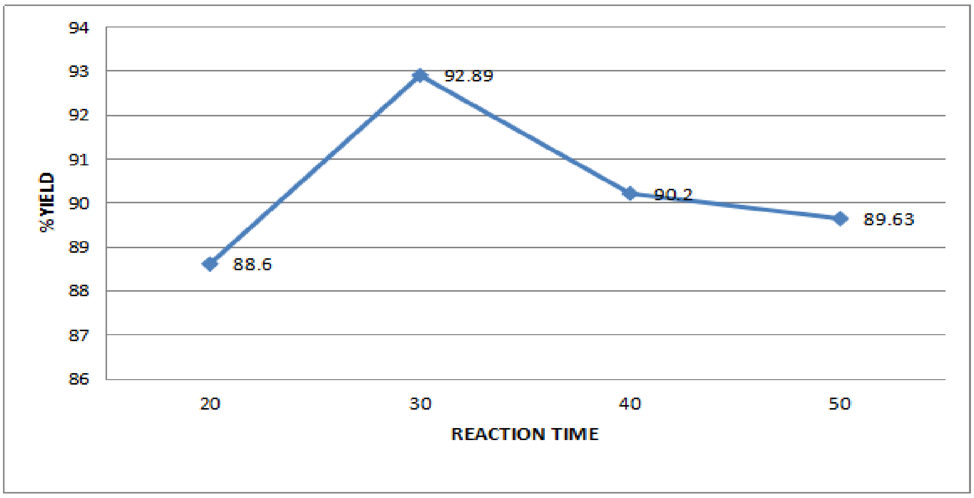

Fig.3.4: Effect of reaction time on yield

In this study, the reaction time was investigated using the optimal parameters obtained in the previous sections. The experiments were carried out for various periods of times between 30 and 60 min (Figure 6). It was observed that the yield was more for shorter duration and it decreased as the time increased to 45 min. Further increase of reaction beyond 60 min no noticeable change in the yield was observed, the yield changed slightly. According to Ma et al. (1999) and Srivastava and Prasad (2000), transesterification reaction starts very fast and almost 80% of the conversion takes place in the first 30 min and 93-98% conversion of the triglycerides into esters takes place after 30 min.

Properties	Biodiesel from sissoo oil	Final biodiesel	Diesel
Flash point(°C)	110	126	45-60
Fire point(°C)	119	134	78
Viscosity(cSt)	4.67	4.26	4-8
Density(kg/m^3)	880	875	820
Calorific value(kJ/kg)	-	39057.6	43500

3. CONCLUSIONS

The following conclusions are drawn from the biodiesel production study.

- Bio-diesel production process consists of one-step: transesterification (Step-1), a single-step was adapted to convert the oil to its ester.
- The sissoo seed oil was transesterified using sodium methoxide as alkaline catalyst. The parameters affecting the transesterification process were analyzed. The maximum yield (89.21%) for sissoo seed oil methyl ester was obtained at 0.4% sodium methoxide, 6:1 methanol to oil molar ratio at 65 ^{0}C after 60 min of reaction. The properties of biodiesel produced from sissoo seed oil were comparable to those of the ASTM D6751 and IS 15607 biodiesel standards.

ACKNOWLEDGEMENT

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