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Optimization of biodiesel production from oils and fats with high free fatty acids

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Abstract

Biodiesel may be cost effective if produced from low cost feedstock such as animal fats, restaurant waste oil and frying oil, which contains high amount of free fatty acids (FFA). In the present work, two-stage transesterification process was used to convert a mixture of 75% restaurant waste oil and 25% pig fat oil (PFO) into restaurant waste oil pig fat methyl ester (RWOPFME). Different amounts of methanol (25, 30, 35, 40, 45 and 50% by vol.), alkaline catalyst (NaOH) concentrations (0.3, 0.5, 0.7, and 0.9% by wt.), reaction temperature (55^0C, 60^0C and 65^0C) and reaction time (90, 120 and 150 min) were selected for the transesterification process in order to optimize the experimental conditions for maximum biodiesel yield. Amount of H_2SO_4 (1.5 ml) was kept constant. Maximum yield (80% by vol.) at optimized process parameters such as methanol (40%), NaOH (0.3 g), reaction temperature (65^0C), reaction time (90 min) and H_2SO_4 (1.5 ml) was obtained.

Keywords: Biodiesel, free fatty acids, restaurant waste oil pig fat methyl ester (RWOPFME), transesterification.

Introduction

Biodiesel is gaining attention worldwide as an alternative automotive fuel due to depletion of petroleum products at faster rate and strict environment regulations. Biodiesel is an oxygenated, sulfur free, biodegradable, non-toxic, and environmentally friendly alternative automotive fuel. It can be produced from renewable sources such as vegetable oils, animal fats, restaurant waste oil and frying oil. Its use does not require any major modifications in the existing diesel engine. The major constraint in wide spread use of biodiesel is the production cost. Considerable research work has been done to reduce the cost of biodiesel by using low cost feed stocks such as animal fats, restaurant waste oil and frying oil (Laguë *et al*., 1988; Mittelbach *et al*., 1992; Cankci & VanGerpen, 1999; Cankci & VanGerpen, 2001). These low cost feedstocks are more challenging to process because they contain high amount of free fatty acids (FFA). This paper presents the use of two stage transesterification process for the conversion of a mixture of 75% restaurant waste oil and 25% pig fat into restaurant waste oil pig fat methyl ester (RWOPFME) and optimization of process parameters for maximum biodiesel yield.

Materials and methods

Two stage transesterification process used for the production of biodiesel is as shown in the Fig.1. In the first stage, concentrated H_2SO_4 (95% purity) was used as an acidic catalyst to convert high FFAs to esters and in the second stage NaOH is used as an alkaline catalyst to convert triglycerides to Biodiesel (Cankci & VanGerpen, 2001). Transesterification process is affected by parameters like amount of methanol, concentration of NaOH, amount of H_2SO_4, reaction temperature and reaction time (Freedman *et al*., 1984; Ma *et al*., 1998; Leung & Guo, 2006; Math & Irfan, 2007). One of the most important variables affecting the yield of biodiesel is the molar ratio of alcohol to vegetable oil used (Freedman *et al*., 1984). The stoichiometry of this reaction requires 3 mol of alcohol per mol of triglyceride to yield 3 mol of fatty ester and 1 mol of glycerol. Several researchers proposed a molar ratio of 5:1 for maximum biodiesel yield, hence, in order to optimize the amount of methanol, six samples were prepared by varying the amount of methanol (25, 30, 35, 40, 45 and 50% by vol) by keeping NaOH concentrations, H_2SO_4 amount, reaction temperature and reaction time were kept constant throughout the process.

In several research work (Leung & Guo, 2006), NaOH (0.1-1% by weight) has been used for biodiesel production. In the present work, to optimize the amount of NaOH, four samples were prepared by varying the amount of NaOH (0.3, 0.5, 0.7, and 0.9% by wt) by keeping all other parameters constant. Sodium methoxide solution was prepared by dissolving NaOH pellets in methanol.

Reaction temperature influences the rate of reaction and biodiesel yield. Several researchers proposed that transesterification process may be carried out at a temperature nearer to boiling point of alcohol (Ma *et al*., 1998) hence in order to optimize the reaction temperature, three samples were prepared by varying the reaction temperature (55^0C, 60^0C and 65^0C) by keeping all other parameters constant.

Several investigators have studied the effect of reaction time on biodiesel yield (Freedman *et al*., 1984). In this work experiments were carried at three reaction time (90,120 and 150 min) by keeping all other parameters constant in order to optimize the reaction time.

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Fig. 1. Process diagram

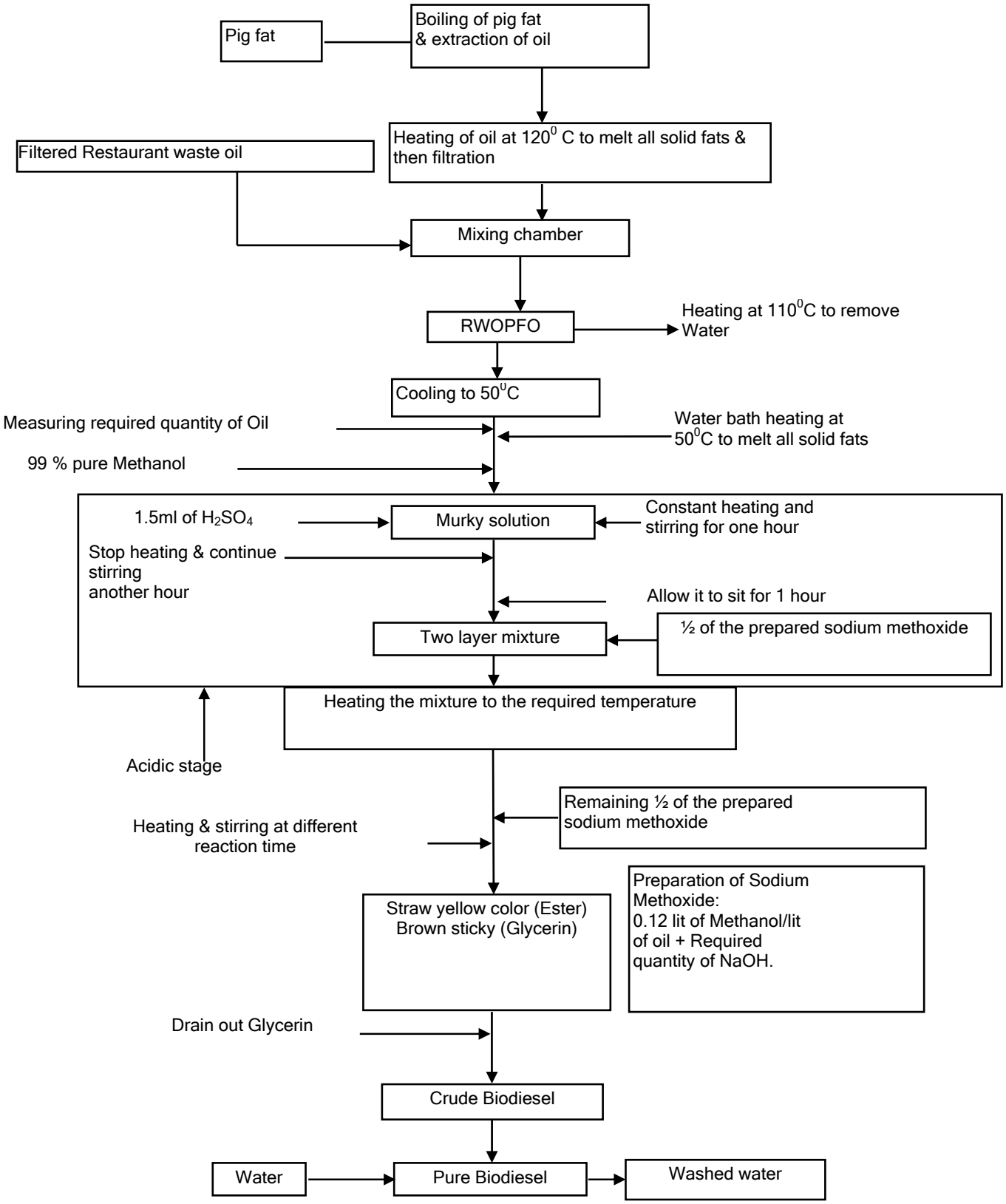

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Fig. 2a. Effect of amount of methanol

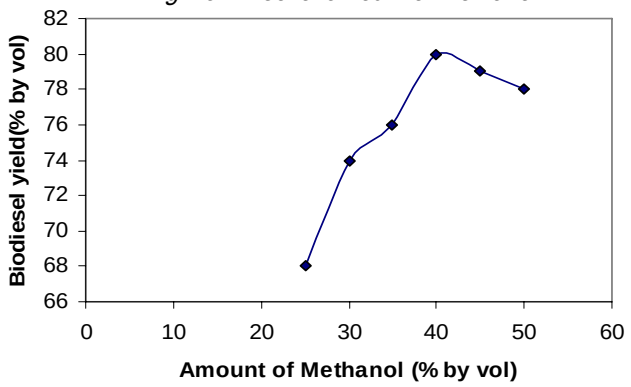


Fig. 2b. Effect of amount of NaOH

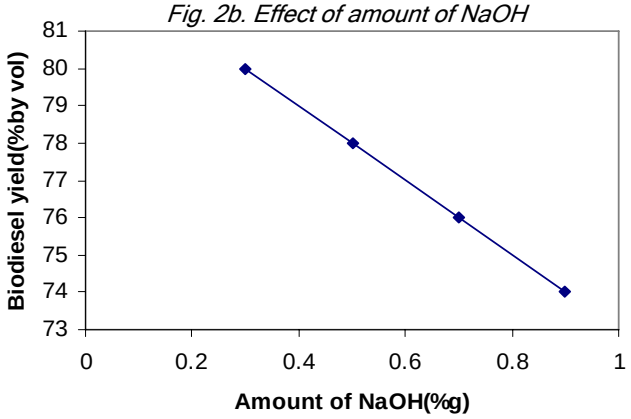


Fig. 2c. Effect of temperature

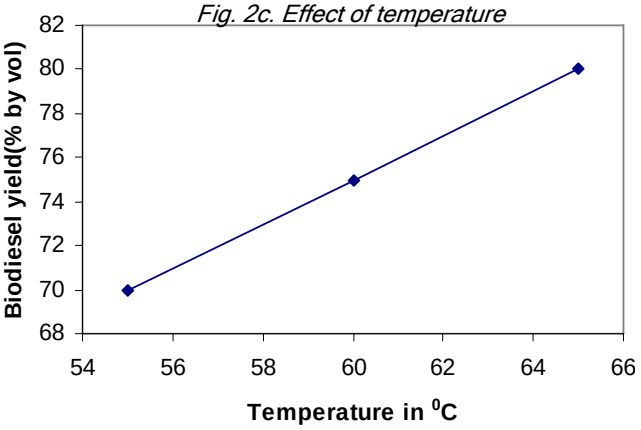
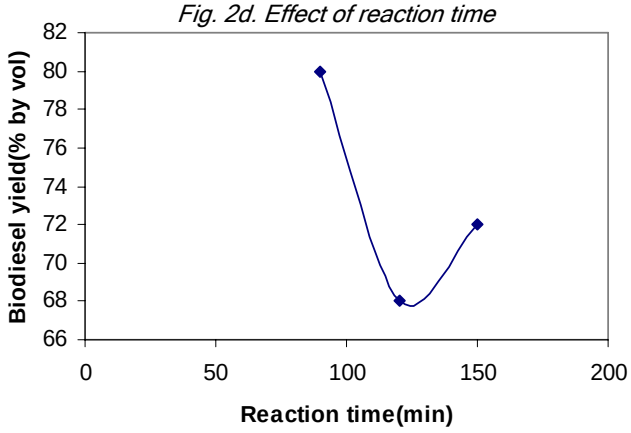


Fig. 2d. Effect of reaction time



Experimental method

Clean mixture of 75% restaurant waste oil and 25% pig fat oil (100 ml) was taken in each of six conical flasks and then heated to 120^{0}C for 15 min in order to melt all solid fats. This mixture is allowed to cool to a temperature of 50^{0}C and then required amount of methanol (99% purity) is added to the heated mixture of each flask. After stirring for 15 min, the solution became murky. To this solution, 1.5 ml of H_2SO_4 is added. Stirring continued for 1 h by maintaining temperature at 50^{0}C. After this, heating was stopped and stirring is continued for another 1 h. In the mean time, sodium methoxide solution was prepared by dissolving different amount of alkaline catalyst in 0.12 l of methanol per liter of oil. Half of the prepared sodium methoxide solution is added to this mixture and then heated to the required reaction temperature. To this mixture, remaining half of the sodium methoxide solution is added. Heating and stirring continued at different reaction time. Mixture was allowed to separate and settle overnight by gravity settling into clear, golden color liquid biodiesel at the top and light brown glycerol at the bottom. Next day, glycerol was drained off, leaving biodiesel and it was water washed two times.

Results and discussion

Effect of molar ratios

The influences of methanol/oil molar ratio on biodiesel yield are shown in Table 1 and represented in Fig. 2a. At 40% (by vol) methanol, maximum biodiesel yield (80%) was obtained. The result indicated that excess use of methanol had no significant effect on biodiesel yield and in fact complicate ester and glycerol separation.

Effect of Catalyst

Fig.2b shows the effect on amount of NaOH on biodiesel yield. The optimum catalyst amount was found to be 0.3% and yield reached 80%. The extra amount of catalyst did not contribute to an increase in biodiesel yield. This was probably because the slurry became too viscous, making it to difficult for stirring and consumes more energy.

Effect of reaction temperature

Fig. 2c shows the effect on reaction temperature on biodiesel yield. The optimum temperature was found to be 65^{0}C and yield was 80%.

Effect of reaction time

Fig. 2d shows the effect on reaction time on biodiesel yield. In this study, three reaction times were selected (90,120 and 150 min). Maximum biodiesel (80%) was obtained at 90 min reaction time. Rate of reaction increased with increase in reaction time and reached maximum at 90 min, then it remained almost constant.

Conclusions

Optimum values of methanol (40%), alkaline catalyst NaOH (0.3%), reaction temperature (65^{0}C) and reaction time (90 min) for the transesterification of mixture of 75% restaurant waste oil and 25% pig fat into restaurant waste

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Table 1. Optimized process parameters for maximum biodiesel yield

Samples	RWOPF (ml)	Methanol (ml)	Acidic catalyst (H_2SO_4) ml	Basic catalyst (NaOH) g	Reaction temp.(^{0}C)	Reaction Time (min)	RWOFPME (biodiesel) ml
S1		25					68
S2		30					74
S3		35		**0.3**			76
S4		**40**					**80**
S5		45			**65**		79
S6		50				**90**	78
S7	**100**		**1.5**	0.5			78
S8				0.7			76
S9				0.9			74
S10		40			60		75
S11				0.5	55		70
S12					60	120	68
S13						150	72

Conf. St. Josep.Mich., ASAE. 74-78.

Table 2. Comparison of parameters for the maximum biodiesel yield for different feedstock (100 ml)

Type of feedstock	Method of biodiesel production	Methanol (ml)	Acidic catalyst (H_2SO_4) ml	Basic catalyst (NaOH) g	Reaction temp. (^{0}C)	Reaction time (min)	Maximum biodiesel yield ml
Restaurant waste oil (Math & Irfan, 2007)	2-stage transesterification	35	1.0	0.3	55	90	85.50
75% restaurant waste oil + 25% pig fat		40	1.5	0.3	65	90	80.00

oil pig fat methyl esters was obtained by varying methanol amount (25-50% by vol), NaOH concentration (0.3-0.7% by wt), reaction temperature (55-65^{0}C) and reaction time (90-120 min). Maximum yield of 80% biodiesel was obtained at the optimum amount of methanol (Fig. 2a), concentration of NaOH (Fig. 2b), reaction temperature (Fig. 2c) and reaction time (Fig. 2d).

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