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RESEARCH ARTICLE

OPTIMISATION OF METHYL ESTER OF NEEM OIL

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ABSTRACT

Cost of biodiesel can be reduced if produced from high free fatty acid non edible oils such as neem oil, jatropha etc. In the present study, two stage transesterification processes has been used to convert high free fatty acid neem oil into neem oil methyl ester. In this stage, experiments have conducted by varying methanol quantity (5, 10 and 15 % v / v of oil and reaction time (45 min, 60 min and 75 min) by keeping acid catalyst concentration (H_2SO_4, 1 % v / v) and reaction temperature (55^0C to 60^0C) constant. FFA level of neem oil has reduced to 0.8% by acid esterification at the optimized molar ratio of 3 (methanol quantity of 15 % v / v of oil) and reaction time (60 minutes). In the second stage, different concentration of methanol (20% to 45%, by vol), NaOH (0.3% to1.5%, by wt), reaction temperature (30^0C to 55^0C) and reaction time (60 min to 120 min) were selected in order to optimize the neem oil methyl ester yield. Maximum yield (85.50%) has obtained at optimum amount of methanol (35%), catalyst NaOH concentration (0.3%), temperature (55^0C) and reaction time (90 minutes).

INTRODUCTION

Limited non-renewable energy sources, depleting reserves of fossil fuels, increasing demand for diesel oil, and uncertainty in their availability and increasing stringent environmental regulations has motivated an intense search for an alternative transportation fuel over the last three decades. Highly fluctuating international prices of crude oil have a negative impact on the economy of oil importing nations, posing severe strain on their foreign exchange. The diesel oil demand has expected to grow steadily to keep pace with industrialization and development of the economy. Non-renewable fossil fuels have contributed nearly 90% of the fuel consumed for power generation and transportation (Ma and Hanna, 1999). To meet the future energy demand of the transportation sector, all over the world, lot of research work has conducted to find a suitable alternative to diesel fuel.

Transesterified vegetable oil (biodiesel) is one of the most attractive alternative automotive fuels among several other alternative. It is one of the present favourites to be the next generation diesel fuel. Biodiesel has recently been attracted attention as an alternative fuel for diesel engines because of its renewability, better combustion, better gas emission, and its biodegradability. Biodiesel can be defined as an oxygenated, sulphur free, biodegradable, nontoxic and eco-friendly alternative diesel oil (Krawezyk, 1996; Kerutzer, 1984; Schwab *et al*., 1987). Chemically, it can be defined as a fuel composed of mono-alkyl esters of long chain fatty acids derived from renewable sources (Mohibbe Azam *et al*., 2005; Van Gerpen, 2005), such as vegetable oil, animal fat, and used cooking oil (Canakci, 2007; Connemann and Fischer, 1998). In this work, one – factor – at – a –time (OFAT) method has used for the optimization of experimental parameters such as catalyst concentration, amount of methanol, reaction temperature, and reaction time on transesterification for the production of neem oil methyl ester. Selection of process parameters and their values has done on the basis of trial experiments conducted in the laboratory and from the literature review on the optimization of process parameters for biodiesel production (Antolin *et al*., 2002; Sahoo *et al*., 2009).

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MATERIALS AND METHODS

Two-stage transesterification process has used for production of methyl ester from neem oil as its free fatty acid level (12%) is more than 1%. Methanol has chosen as an alcohol for transesterification process. In the first stage, sulphuric acid (H_2SO_4) is used as an acidic catalyst to convert high FFAs to esters. In the second stage, sodium hydroxide (NaOH) is taken as an alkaline catalyst because it is cheaper and reacts faster than acidic catalyst. Molecular weight of neem oil with substantial chemical constituents has etermined as 857.89 grams. As per transesterification process, 3 moles of methanol require to react with 1 mole of vegetable oil. Molecular weight of methanol is 32 and hence 96g of methanol required for transesterification of 1 mole (857.89 g) of neem oil, which amounts to 13.97 % methanol.

Experimental method

Clean neem oil (100 ml), which was collected from Science and Technology Entrepreneurship Park (STEP) of Basaveshwara Engineering College, Bagalkot (India). In this study, two stages transesterification process has successfully used for producing biodiesel. In the first stage, FFA of mixture reduced to 0.8 % by acid Transesterification process with methanol in the presence of acid (H_2SO_4) catalyst.

Stage 1 acid catalyzed Transesterification process

Table 1 shows the factors and their levels selected for stage 1 acid catalyzed transesterification process. In this stage, nine experiments have conducted by varying methanol quantity (5, 10, and 15 % v / v of oil or 1, 2 and 3 molar ratio) and reaction time (45 min, 60 min, and 75 min). Experiments have conducted by keeping acid catalyst concentration (H_2SO_4, 1 % v / v) and reaction temperature (55^0C to 60^0C) constant.

Table 1. Experimental factors and their levels for stage 1 acid catalyzed transesterification process

Factors	Unit	Levels		
		1	2	3
CH_3OH (% v /v of oil)	ml	5	10	15
Reaction time	minutes	45	60	75

Experimental procedure

Neem oil has taken into the biodiesel reactor. Water bath temperature is maintained at 55^0C to 60^0C. Required amount of CH_3OH added to the concentrated H_2SO_4 (1% v / v of oil). The mixture slowly added to the heated oil. Stirring and heating continued for 10 to 15 minutes. Stirring at low RPM and heating (55^0C to 60^0C) continued for different reaction times. Similar method used for all nine experiments which conducted according to the experimental matrix shown in Table 2 On completion of reaction, the mixtures have allowed to fall into two layers. The excess methanol, H_2SO_4, and impurities moved to the top surface and have taken out. The acid value of the product separated at the bottom has measured. Table 2 shows the FFA level for different combination of CH_3OH and reaction time for neem oil for stage -1 acid catalyzed transesterification process.

Table 2. Layout of experimental design and results for stage -1 acid catalyzed transesterification process

Experiment No	Samples	CH_3OH (% v / v of oil)	Reaction time in minutes	FFA (%)
1	S_1	5	45	6.2
2	S_2	5	60	5.3
3	S_3	5	75	4.5
4	S_4	10	45	3.3
5	S_5	10	60	2.1
6	S_6	10	75	2.2
7	S_7	15	45	2.4
8	S_8	*15*	*60*	*0.8*
9	S_9	15	75	1.6

Stage 2 Alkaline catalyzed transesterification process

In the second stage, sample No.8 of the first stage has chosen as its free fatty acid level (0.8%) is less than 1%. In this stage one – factor – at – time (OFAT) has been used to convert esterified neem oil into methyl ester. In order to optimize the amount of methanol required for the process, experiments have conducted with six samples of methanol (20, 25, 30, 35, 40, and 45 %). Process has been carried at constant reaction temperature, reaction time, and catalyst concentration. In several studies (Alacantara *et al*., 2000; Ma *et al*., 1998), NaOH (0.1 to 1.2 % by weight) has used for biodiesel production. Optimization of NaOH concentration carried out by taking five different catalyst concentrations (0.3, 0.5, 0.7, 1.0, and 1.5 %) by keeping methanol amount, reaction time, and reaction temperature constant. NaOH solution has prepared by dissolving NaOH pellets in methanol. Solution added to esterified neem oil. NaOH solution is prepared in alcohol because NaOH pellets would react with CO_2 and water present in the atmosphere and yield sodium carbonate, which would affect performance of the catalyst during transesterification process.

Reaction temperature should always be maintained below boiling point (65^0C) of methanol. Hence to optimize reaction temperature, three different temperatures (30^0C, 45^0C, and 55^0C) have been chosen, keeping alcohol, catalyst concentration, and time constant. Methyl ester conversion rate increases with reaction time (Ma *et al*., 1998). Hence to optimize reaction time, three different reaction times (60, 90, and 120 min) have been selected, keeping alcohol, catalyst concentration, and temperature constant. The sample has taken in each of six round bottom flasks and heated to 65^0C to dissolve solid fat if any. It is allowed to settle for 2 to 3 hour. Settled water is removed. In the mean time, sodium methoxide solution has prepared by dissolving required amount of NaOH pellets in selected quantity of methanol per liter of oil. Half of the prepared sodium methoxide solution has added to the mixture. The solution has heated to required temperature and then remaining half of sodium methoxide solution has added. Stirring continued up to selected hour by keeping reaction temperature constant. Mixture has allowed separating and settling overnight by gravity settling into a clear, golden color liquid biodiesel on the top and light brown glycerol at the bottom. Next day, glycerol has drained off, leaving biodiesel (yield, 85.50% v / v of oil) in the digester. Crude biodiesel has water washed to bring down pH (7). The remaining experiments were conducted as per the experimental matrix (Table 3).

RESULTS AND DISCUSSION

Figure 1 shows the effect of molar ratio of methanol to oil and reaction time on FFA level of neem oil. Figure 1.1 shows that the reaction progressed rapidly in the initial stage and became slower in the later phase. It also shows that the FFA level steadily decreased with an increase in the molar ratio at the same period of reaction time. Sample S_8 has minimum FFA (0.8%) at the optimized molar ratio of 3 (methanol quantity of 15 % v / v of oil) and reaction time (60 minutes). Sample (S_8) has used for Stage 2 acid catalyzed transesterification processes. Figure 2 shows the effect of molar ratio of methanol to neem oil on biodiesel yield. It indicates that with the increase in molar ratio of methanol to neem oil, the biodiesel yield has increased and reached maximum value at molar ratio of 7, and then yield has decreased.

Table 3. Optimized process parameters for the maximum yield of restaurant waste oil methyl esters

Samples	Oil (ml)	Methanol (ml)	Acidic Catalyst (H_2SO_4) (ml)	Basic Catalyst (NaOH) (g)	Reaction Temperature (^0C)	Reaction Time (min)	Biodiesel (ml)	Glycerol +Emulsion +Loss	Biodiesel (%)
S1	100	20	1.0	0.3	55	90	65.50	34.50	65.50
S2		25					70.50	29.50	70.50
S3		30					78.50	21.50	78.50
S4		35					85.50	14.50	85.50
S5		40					82.50	17.50	82.50
S6		45					80.50	19.50	80.50
S7		35	1.0	0.5	55	90	81.50	18.76	81.50
S8				0.7			83.50	16.66	83.50
S9				1.0			80.50	19.77	80.50
S10				1.5			78.50	21.75	78.50
S11		35	1.0	0.7	30	90	78.50	21.87	78.50
S12					45		80.50	19.77	80.50
S13		35	1.0	0.7	55	60	79.50	20.77	79.50
S14						120	80.50	19.88	80.50

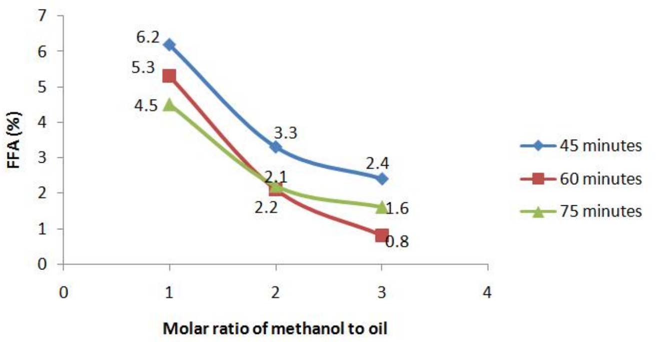

Figure 1. Influence of quantity of methanol and reaction time on FFA level of neem oil

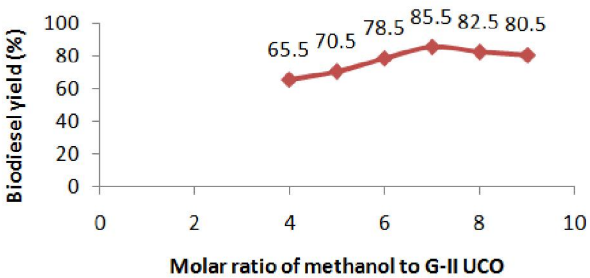

Figure 2. Effect of molar ratio of methanol to neem oil on biodiesel yield

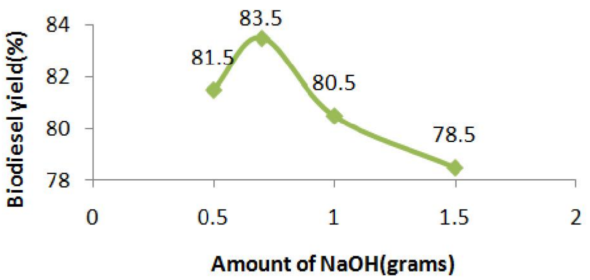

Figure 3. Effect of NaOH concentration on biodiesel yield

Figure 1.3 shows the effect of NaOH concentration on biodiesel yield. It indicates that the biodiesel yield increases with the increase in the concentration of NaOH and reaches maximum value at 0.7 gram NaOH. Figure 1.4 shows the effect of reaction temperature on biodiesel yield. It indicates that biodiesel yield increases with the increase in reaction temperature and reaches maximum value at 55^0 C. Figure 1.5 shows the effect of reaction time on biodiesel yield. It indicates that biodiesel yield increases with the increase in reaction time and reaches maximum value at 90minutes. Table1.3 shows the optimum values required for the transesterification of neem oil.

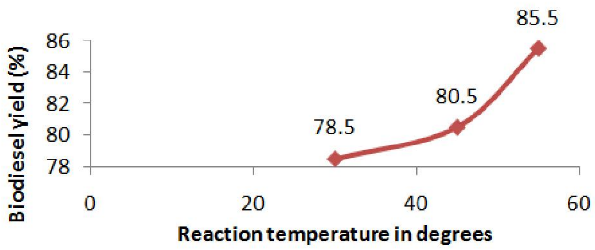

Figure 4. Effect of reaction temperature on biodiesel yield

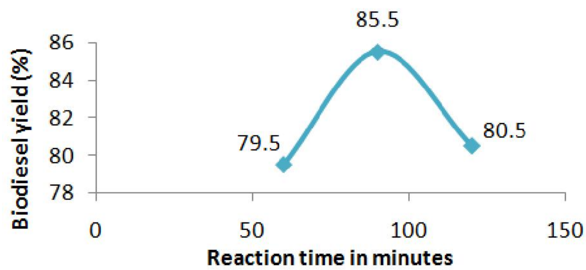

Figure 5. Effect of reaction time on biodiesel yield

Conclusion

FFA level of neem oil has reduced to 0.8% by acid Transesterification at the optimized molar ratio of 3 (methanol quantity of 15 % v / v of oil) and reaction time (60 minutes). Optimum value has obtained by varying the concentration of methanol (20% to 45%, by vol) or methanol to oil ratio from 4 to 9, NaOH concentration (0.3% to1.5%, by wt), reaction temperature (30^0C to 55^0C) and reaction time (60 min to 120 min). Maximum yield (85.50%) has obtained at optimum amount of methanol (35%) or at a molar ratio of 7, catalyst NaOH concentration (0.3%), temperature (55^0C) and reaction time (90 minutes).

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