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PRODUCTION OF BIO-DIESEL FROM WASTE COOKING OIL BY USING HOMOGENEOUS CATALYST

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ABSTRACT

Waste cooking oil (WCO) was used as bio-diesel feedstock. WCO with methanol was heated at different temperature with the help of conventional mechanical stirrer. Potassium hydroxide (KOH) and sodium hydroxide (NaOH) was used as catalyst. The effect of different operational parameters such as, catalyst loading, reaction temperature, and reaction time were evaluated. From the results, it was clear that the bio-diesel fuel produced from waste cooking oil (WCO) was within the recommended standards of biodiesel fuel. The trans-esterification reaction using potassium hydroxide (KOH) catalyst was more effective than sodium hydroxide (NaOH) catalyst for the higher yields conversion. With potassium hydroxide 0.4 wt. %, yield was 94.4% and conversion was 97.76% at 60^{o}C, in three hours reaction time.

Key words: Bio-diesel, Waste cooking oil, Trans-esterification reaction, Homogeneous catalyst.

INTRODUCTION

With the increase in population, there has been consistent demand in every arena for fuel. Human life is largely dependent on material things. These material things are produced and transported with the help of fuel driven mediums, but fuel is largely amassed in very few countries of the world especially middle-East countries. With the growth of the economy and consumption, the governments of many countries of the world are striving hard to find an alternative to the fossil fuel, which is slow & gradually depleting. Moreover, the fossil fuel leads to pollution and bad effects on human health. Keeping this into mind, bio-diesel would be natural choice for countries largely dependent on import so as to utilize the natural resources in the optimum manner for other basic needs.[1] An alternative fuel for diesel engines and for heating oil burners could be vegetable oil. For engines designed to burn petrol, diesel fuel, vegetable oils has high viscosity must be lowered to run these engines and

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heating oil burners; otherwise will face many problems (A) Starter problem (B) Incomplete combustion (C) Carbon build up on the piston (D) Engines knocking (E) Damage the engines[2]. When the mono-alkyl esters of fatty acids derived from vegetable oils or animal oils, it is called Biodiesel. Bio-diesel was synthesized from edible (Veg or animal) oils and non edible (Veg or animal) oils[3]. For bio-diesel production edible vegetable oils such as canola, soybean, sun flower and corn were used and could be used as diesel substitutes[4,5]. Biodiesel was produced from the non-edible oil of Karanja by trans-esterification of the waste karanja oil with methanol in the presence of NaOH as catalyst. In this reaction, conversion of biodiesel was 92%. Waste cooking oil (WCO) is cheaper than edible vegetable oil so can be used for biodiesel production[6]. Waste cooking oil from restaurants was used to reduce the cost of feedstock to produce biodiesel. By use of base catalyst conversion was 95%. Effect of different variables such as methanol-to-oil ratio, acid-to-oil ratio, reaction temperature was studied for acid catalyzed pretreatment of crude Jatropha oil[7,8]. When the feedstock has high free fatty acid to produce biodiesel with less acid value two steps had been followed in which first was acid catalyst for ester-faction and second step was base catalyst for trans-esterification[9]. The production of biodiesel was studied from waste cooking oil feed stock in ultrasound cavitation, conventional mechanical stirrer, alcohol and different catalysts weight (0.5%, 0.75% and 1%). High yield (94.2%) was obtained from waste cooking oil through ultrasound cavitation[10]. Different aspects such as optimization of methanol for trans-esterification, design parameters were studied using waste cooking oil as feed stock[11-13]. In this work, experiments were carried out for the bio-diesel production from waste cooking oil (WCO) using conventional trans-esterification processes. Waste cooking oil (WCO) contains high FFA content, so that alkali trans-esterification was employed using methanol and (KOH & NaOH) catalysts. This work aims to evaluate the effect of different operating parameters on the methyl ester yield.

EXPERIMENTAL

Materials and methods

15 Liters waste cooking oil (WCO) from Ruby Hall Clinic, Pune, was collected. Potassium hydroxide (KOH), sodium hydroxide (NaOH) flakes and methanol (AR Grade) were used. The mixture was stirred at the constant speed for all experiments. All experiments of trans-esterification reaction were carried out in a 2 Liters round-bottom flask endowed with a water-cooled reflux condenser. Heating mantle with conventional mechanical stirrer method was used for heating the mixture in the flask.

Equipment

Trans-esterification experiments were carried out in a 2 Liters three-necked (first one for thermo well and second for stopper third for stirrer) batch reactor. With a conventional mechanical stirrer, a thermocouple connected to a heater plate, and two necks, one is stopper to remove samples and to feed the raw materials such as (waste cooking oil, catalyst and methanol) and another for the thermometer (thermo well), respectively. The experimental set-up is shown in Fig. 1.

Fig. 1: Experimental set-up for bio-diesel production

Experimental procedure

The trans-esterification reaction was carried out in 2 Liters reaction flask with mechanical stirrer, thermometer, stopper and heating mantle. The trans-esterification process was studied for catalyst (0.4 wt. %, 0.7 wt. % and 1.0 wt. % KOH), at a reaction time (1-3 h) at 50, 60, 70 and 80 ± 2°C and at atmospheric pressure. Feed was made free from water, as any water or moisture in the system will consume some of the catalyst and slow the trans-esterification reaction. Hence, Feed (WCO) was preheated after collection at 110 ± 2°C in order to ensure no water in the waste cooking oil (WCO). Waste cooking oil (WCO) sample was weighed carefully on weighing machine. The sample was found to be 400 mL waste cooking oil (WCO), 100 mL methanol and 0.4 wt. % of KOH. The same was followed for NaOH. The mixture was heated up to 60 ± 2°C with continuous agitation for 3 hr. The reaction mixture was feculent. The product was kept in the separating funnel for 12 hrs. Two phases having a different density were formed as a result of trans-esterification. Upper layer consisted of bio-diesel, alcohol and soap and down layer consisted of glycerin, excess alcohol, catalyst, impurities and traces of unreacted oil. Two layers were separated and measured. Purification of upper layer was done i.e. alcohol was removed by heating mixture at 80°C and washed with warm distillated water three times.

RESULTS AND DISCUSSION

A base catalyst was studied for 0.4 wt. %, 0.7 wt. % and 1 wt. % KOH and same for NaOH. Figure 2 and 4 showed the effect of base catalyst on the yield. The maximum yield was obtained for waste cooking oil (WCO) at 0.4 wt. % of catalyst. Trans-esterification reaction could not occur properly with an insufficient amount of a base catalyst was proved during experimentation. Yield was slightly decreased above 0.4% of catalyst. Mass transfer became more important at higher concentrations. The temperature effect on the yield was studied for 50^{o}C, 60^{o}C, 70^{o}C and 80^{o}C at atmospheric pressure. The maximum yield was achieved at a temperature of 60^{o}C for waste cooking oil (WCO). From the result shown in the Table 1, the maximum yield was 94.4% and conversion was 97.76% at 60^{o}C and 0.4 wt. % KOH concentration.

Table 1: Yield and conversion of bio-diesel produced from waste cooking oil by using KOH catalyst

Sample No.	Temperature (^{o}C)	Catalyst (wt. %)	Yield (%)	Conversion (%)
1	50	0.4	94.38	97.02
2	50	0.7	88.8	91.06
3	50	1.0	86.4	88.08
4	60	0.4	94.4	97.76
5	60	0.7	93.1	96.27
6	60	1.0	87.3	90.3
7	70	0.4	90	91.8
8	70	0.7	87.39	91
9	70	1.0	86.5	88
10	80	0.4	90.9	91.05
11	80	0.7	87.8	89.5
12	80	1.0	86.5	88.8

Similarly from Table 2, the maximum yield 93.45% and conversion 96.47% was obtained at 60^{o}C and 0.4 wt. % NaOH concentrations. From Figures 2-5, it can be concluded that by using KOH catalyst, the bio-diesel yield and conversion was greater than the NaOH catalyst. The suitable operating conditions were obtained at 60^{o}C reaction temperature, 3 hr reaction time and 0.4 wt. % KOH catalyst concentrations. Methyl ester conversion was good as the temperature was increased. The operating temperature for reaction was higher than that of boiling point of methanol so the alcohol was evaporated and thus resulted in fewer yields.

Table 2: Yield and conversion of bio-diesel produced from waste cooking oil by using NaOH catalyst

Sample No.	Temperature (^oC)	Catalyst (wt. %)	Yield (%)	Conversion (%)
1	50	0.4	90.17	94.04
2	50	0.7	80.68	82.12
3	50	1.0	82.09	85.09
4	60	0.4	93.45	96.47
5	60	0.7	86.6	89.57
6	60	1.0	86.4	88.08
7	70	0.4	91.4	96.27
8	70	0.7	89.9	92.55
9	70	1.0	84.02	85.09
10	80	0.4	89.8	92.5
11	80	0.7	88.3	91.05
12	80	1.0	84.5	87.4

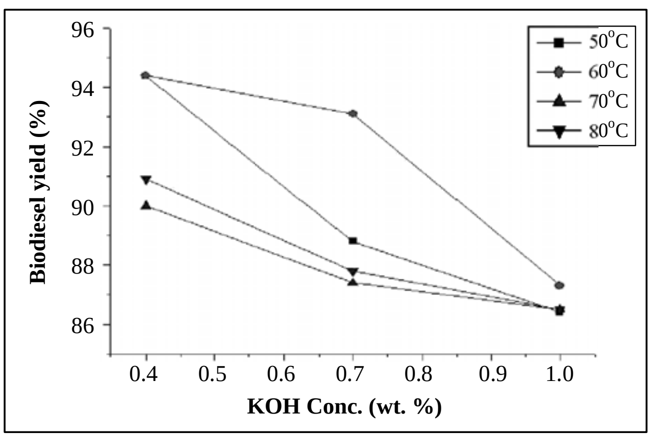

Fig. 2: Effect of KOH catalyst on bio-diesel yield

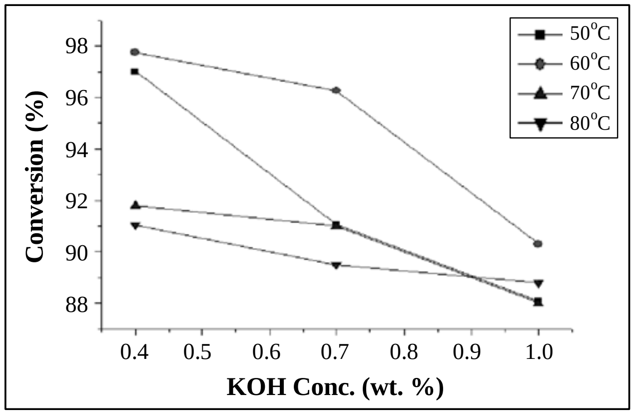

Fig. 3: Effect of KOH catalyst on conversion

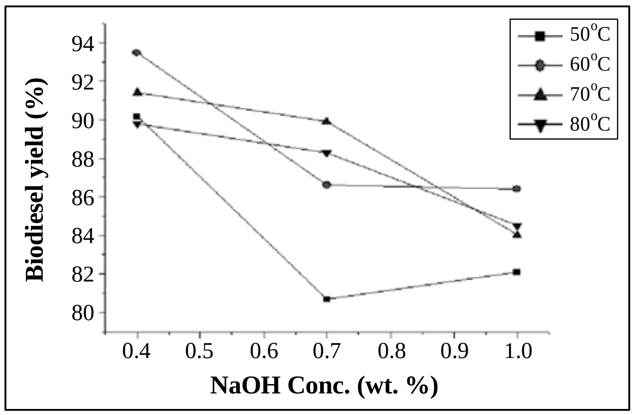

Fig. 4: Effect of NaOH catalyst on bio-diesel yield

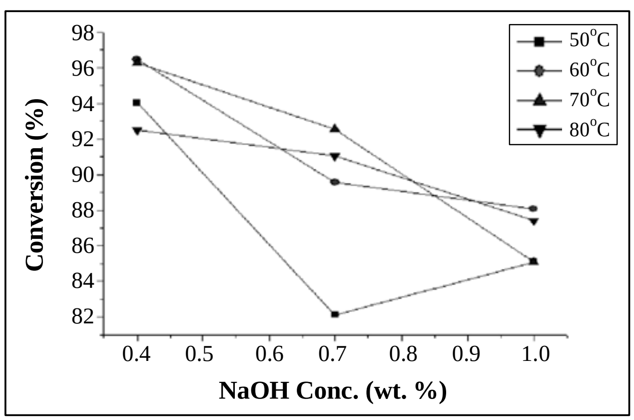

Fig. 5: Effect of NaOH catalyst on conversion

In Table 6, it is shown that elemental content of methyl ester (bio-diesel) fuel produced from waste cooking oil was different than this elemental content for petrol, diesel fuel. These differences in elemental contents between bio-diesel and the petrol diesel cause difference in the characteristics. The Gross Calorific Value (GCV) of petrol diesel fuel according to Indian standard is 10000 cal/g and in experimental study it was found 9870 cal/g for bio-diesel. Presence of the elements Ca, Mg, K and Na in less amount for bio-diesel than conventional diesel fuel, therefore the effect of bio-diesel on engine will be less than the effect of conventional diesel.

Table 3: Yield and conversion of bio-diesel produced from waste cooking oil by using 0.4 wt. % KOH catalyst at 60^{o}C

Sample No.	Time (Hr)	Yield (%)	Conversion (%)
1	3	94.4	97.76
2	2	92.3	93.2
3	1	93.48	95.53

Table 4: Yield and conversion of bio-diesel produced from waste cooking oil by using 0.4 wt. % NaOH catalyst at 60^{0}C

Sample No.	Time (Hr)	Yield (%)	Conversion (%)
1	3	93.45	96.47
2	2	90.2	94
3	1	91.5	95.2

Table 5: Properties of methyl ester from waste cooking oil

Sample	Cloud point (^{o}C) ASTM D2500 Test jar method	Pour point (^{o}C) ASTM D7683 Test jar method	Flash point (^{o}C) Pensky Marten flash point apparatus	Viscosity (cP) Brookfield DVII + Pro viscometer
1	11	-3	126	6.3
2	10	-2	130	7.49
3	10	-4	140	6.36
4	4	-3	145	4.77

Cont…

Sample	Cloud point (^oC) ASTM D2500 Test jar method	Pour point (^oC) ASTM D7683 Test jar method	Flash point (^oC) Pensky Marten flash point apparatus	Viscosity (cP) Brookfield DVII + Pro viscometer
5	5	-1	128	4.92
6	6	-1	120	5.01
7	0	-4	108	4.58
8	4	-2	98	4.43
9	12	-2	123	4.74

Table 6: Elemental analysis of methyl ester from waste cooking oil

S. No.	Test description	Test result for sample 1	Test method
1	Aluminium content ppm	0.5	ASTM D 4737-10
2	Antimony content ppm	< 0.1	ASTM D 6595-11
3	Barium content ppm	< 0.1	ASTM D 6595-11
4	Boron content ppm	< 0.1	ASTM D 6595-11
5	Cadmium content ppm	< 0.1	ASTM D 6595-11
6	Calcium content ppm	4.5	ASTM D 6595-11
7	Chromium content ppm	0.2	ASTM D 6595-11
8	copper content ppm	8.6	ASTM D 6595-11
9	Iron content ppm	0.4	ASTM D 6595-11
10	Lead content ppm	11.5	ASTM D 6595-11
11	Magnesium content ppm	0.3	ASTM D 6595-11
12	Manganese content ppm	< 0.1	ASTM D 6595-11
13	Molybdenum content ppm	2.1	ASTM D 6595-11
14	Nickel content ppm	0.1	ASTM D 6595-11
15	Phosphorous content ppm	< 0.1	ASTM D 6595-11
16	Potassium content ppm	146	ASTM D 6595-11
17	Silicon content ppm	4.1	ASTM D 6595-11

Cont…

S. No.	Test description	Test result for sample 1	Test method
18	Silver content ppm	< 0.1	ASTM D 6595-11
19	Sodium content ppm	5.3	ASTM D 6595-11
20	Tin content ppm	< 0.1	ASTM D 6595-11
21	Titanium content ppm	< 0.1	ASTM D 6595-11
22	Vanadium content ppm	< 0.1	ASTM D 6595-11
23	Zinc content ppm	13	ASTM D 6595-11
24	Gross calorific value cal/g	9870	IS 1448(P6)2013

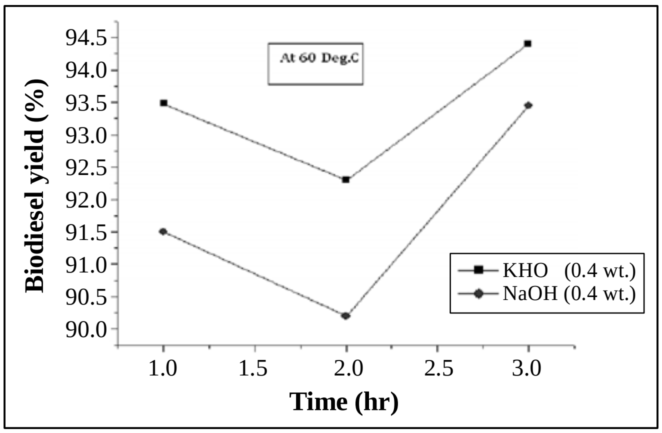

Fig. 6: Effect of time on yield at 60°C

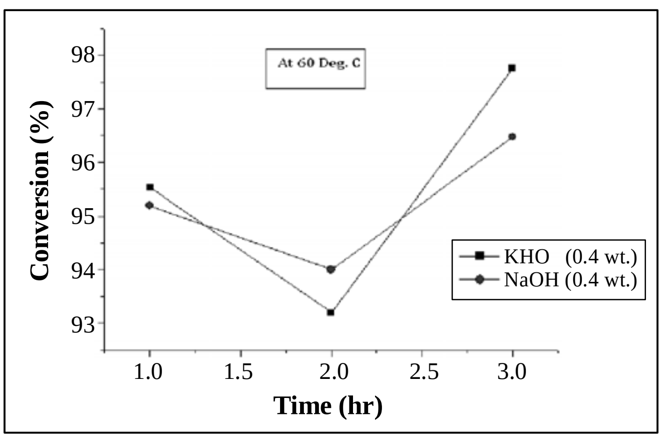

Fig. 7: Effect of time on conversion at 60°C

CONCLUSION

Results showed that using KOH catalyst the bio-diesel yield and conversion obtained was greater than the NaOH catalyst. With potassium hydroxide reaction, less soap formation was obtained than sodium hydroxide. The suitable operating conditions were obtained at 60^{o}C reaction temperature, 3 hr reaction time and 0.4 wt. % KOH concentrations. Reduction in the reaction time was effected on the bio-diesel characteristic such as viscosity and specific gravity as present slight unreacted raw materials (WCO). Also, it was concluded that increasing the catalyst concentration bio-diesel yield was reduced due to the formation of soap. Bio-diesel characteristics like viscosity, flash point, cloud point, specific gravity, gross calorific value, elemental analysis and pour point were comparable to diesel.

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