An Analysis of The Biodiesel Production Process from Non-Edible Oils Using Heterogeneous Acid Catalysts

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Abstract-The esterification of Karanja oil with methanol was used to produce biodiesel from the oil. Biodiesel yields were determined by 1H NMR. Zeolite and Amberlite15, two heterogeneous acid catalysts, were observed to have different effects. Heat treatment of Karanja oil was observed. Dry Amberlyst15 was found to be most active catalyst. Co-solvents had no effect on the esterification reaction. A study was conducted on the leaching effect of dry Amb15. The esterification reaction is sensitive to temperature, with its rate increasing as the temperature rises. The effect of the methanol-to-oil ratio was also examined under a constant volume mixture condition. A non-monotonic behavior was observed, with two peaks appearing at ratios of 3:1 and 60:1. Additional studies are required to understand this phenomenon and improve on the operating conditions for efficient biodiesel production from Karanja oil

Index Terms— Amberlyst15; Biodiesel; Esterification; FFA; Karanja oil

I. INTRODUCTION

The production of biodiesel from edible and non-edible oil by esterification and transesterification reaction using methanol in the presence of various catalyst is being actively pursued. Various homogenous and heterogeneous catalysts have been used for this purpose. Due to many advantages of heterogeneous catalyst over homogenous catalyst, heterogeneous catalysts are more preferred [1]. Various types of heterogeneous catalyst used for production of biodiesel are listed in various journals [2, 3]. In this study Karanja oil, which is mainly found in rural parts of India where the average rainfall is low, was considered as the non-edible oil source. Production of biodiesel from Karanja oil, having high free fatty acids (FFA), mainly using homogeneous catalysts, has been reported [4, 5]. In this study several heterogeneous acid catalysts were considered for the production of biodiesel from Karanja oil.

II. PROCEDURE

Materials Used

Non–edible Karanja oil was purchased from the local market of Kanpur district, Uttar Pradesh, India. Several zeolite catalysts of varying silica to alumina ratio were used. Additionally, different grads of Amberlite catalyst, Amberlyst15 (wet, moisture up to 50%) referred to wet Amb15 and Amberlyst15 (dry, moisture up to 3 to 6%) referred to dry Amb15, were purchased from Sigma Aldrich Company. Methanol (99% purity) was purchased from Merck.

Determination of free fatty acid (FFA) content of the oil Initially, 50 ml of ethanol and few drops of phenolphthalein indicator were neutralized by few drops of 0.05N KOH. A known amount of non-edible oil, 7 gm, was then mixed with the neutralized ethanol and phenolphthalein indicator and warmed to about 60 oC. The acid value of the above oil was then determined by titrating with a solution of 0.1 N KOH. A 0.1 N solution of KOH was made by dissolving 0.56 gm of KOH in 100 ml of DW.

Experimental Setup

A 2.0 litre batch reactor (AmAr Equipments Ltd, Mumbai, India) was used in this study for esterification reaction. The reactor is equipped with a PID controller, RTD-PT100 temperature sensor, electrically heated jacket, a cooling water circulation system, magnetic stirrer and a reflux condenser with other valves and gauges. The valve at the bottom of the reactor was used for removing sampling for analysis.

Experimental Procedure

The experiment was performed with known amount of oil and a measured amount of methanol and catalyst placed in a closed agitated reactor described above. The mixture was heated to the reaction temperature. The reaction temperature was reached in the reactor in about an hour. The reaction was allowed to proceed for eight hours. After eight hours the heating was stopped and the reactor vessel was allowed to cool to room temperature. Samples were taken from the reaction mixture at room temperature and then washed with warm (about 70 ºC) distilled water (DW) The upper ester layers of the samples were analyzed with 1H NMR spectroscopy for the calculation of conversion/yield using published procedures [6]. The biodiesel yields were also determined for different methanol amounts (methanol:oil ratio) and reaction temperatures (80, 100 and 120 ºC).

III RESULT AND DISCUSSION

Free fatty acids in oil

FFA present in Karanja oil was measured and possessed an acid value of 11.78 of KOH/gm of oil and FFA of 5.8. The FFA of the biodiesel mixture after reaction was measured and was less than 1 for wet Amb15.The FFA of Karanja oil as a function of temperature was also studied. The FFA measured for Karanja oil heated at 80, 100, 120, 140 and 160 ℃ for 2 hrs revealed values similar to the raw oil suggesting no further degradation of the oil at these temperatures. The catalytic activity of several solid acid catalysts for the biodiesel production from Karanja oil was investigated and the results are shown in Figure 1. Comparing the biodiesel yield of different zeolites, it was observed that the maximum yield of about 11% was obtained for β-zeolite. The rest of the zeolites gave biodiesel yield values ranging from 3 to 6%. In contrast, Amberlite catalysts gave higher biodiesel yields, ranging from 30 to 40%. Specifically, the two Amberlite catalysts, wet Amb15 and dry Amb15 showed a biodiesel yield of about 30% and 38%, respectively. Thus, the most suitable solid acid catalysts was dry Amb15.

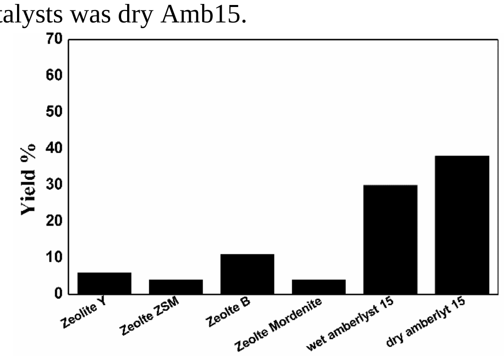


Figure 1: Biodiesel yield using different solid acid catalysts

Experimental condition: oil =50 g; methanol:oil = 30:1; catalyst amount = 6 wt% of oil, rpm =750; Time = 8hr

The difference in the biodiesel yield of wet Amb15 and dry Amb15 were studied by trying various pretreatment procedures with wet Amb15. Wet Amb15 of several forms was used: (i) without further washing and then crushed, (ii) washed with DW and then dried at 90 ºC, (iii) washed, crushed and dried at 90 ºC, and (iv) untreated and uncrushed (granular) particles. The surface areas of these samples were also determined. The biodiesel yields and surface area are shown in Table 1. The maximum biodiesel yield of 30% was achieved for the wet Amb15 sample that was untreated granular form of catalyst. Furthermore, the surface areas of the different pretreated wet Amb15 samples were similar, 33 to 36 m^2/g and did not correlate with the biodiesel yield values.

Table 1: Pretreatment effect of wet Amb15
Experimental condition: oil =50 g; methanol:oil = 30:1; catalyst amount = 6 wt% of oil, rpm =750; Time = 8hr

Catalyst nature	Surface area (m^2/g)	Yield (%)
Without washed & crushed	36	25
Washed & dried at 90 ºC	34	23
Washed, crushed and dried at 90 ºC	36	28
Un-treated, granular particle	33	30

Experiments were also preformed with Jatropha oil at the same reaction condition and a similar biodiesel yield of 30% was observed. Furthermore, there was no co-solvent Tetrahydrofuran (THF)) effect since similar biodiesel yields were observed with and without THF. Considering all the above observations further studies were conducted using dry Amb15 catalysts.

Effect of Temperature

The effect of temperature on the biodiesel yield from Karanja oil using dry Amb15 was studied. Reaction temperatures of 80, 100 and 120 ºC were considered and the results are shown in Figure 2. The results reveal that the as the reaction temperature increases the biodiesel yield also increases. Such an increase in biodiesel yield does indicate the kinetic influence of the reaction.

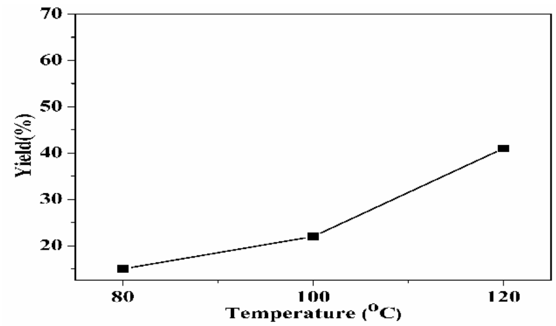


Figure 2: Effect of temperature with dry Amb15

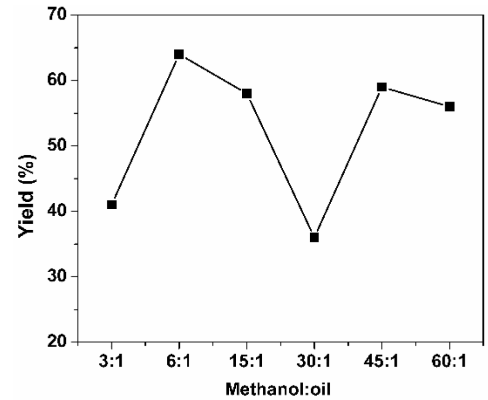
Experimental condition: oil =139 g; methanol:oil = 30:1; catalyst amount = 18 wt% of oil, rpm = 750; Time = 8 hr

Leaching Test

To test for leaching the catalyst was mixed with the required amount of methanol for 12 hr. The liquid part was collected and it was noticed that there was a significant amount of methanol retained in the catalyst. Furthermore, a hissing sound and heating was observed. Using a make-up amount of methanol corresponding to the 30:1 methanol:oil ratio, the reaction was conducted. The results reveal that the biodiesel yield was less than 4%. Thus, the effect of leaching was not significant.

Methanol: oil ratio effect

The methanol:oil ratio being an important factor in the production of biodiesel, its effect was studied using ratios ranging from 3:1 to 60:1. The total initial reaction volume was kept constant during these studies so that mixing effects were kept constant. The results of the different methanol:oil ratio are shown in Figure 4. The biodiesel yields at various methanol:oil ratios did not vary monotonically. Additional studies are required to ascertain the reason for this non-monotonic behavior.



Experimental condition: Reaction mixture volume 341 ml; catalyst amount = 18 wt% of Oil; rpm = 750; Time = 8 hr

CONCLUSION

In the present study several solid acid catalysts were studied for biodiesel production from Karanja oil containing FFA of about 6% (acid value 11.781 KOH/gm oil). It was observed that heating of Karanja oil up to 160 ºC for 2 hrs does not change the FFA content. Dry Amberlyst15 was found to be most active catalyst amongst those studied. Various catalyst pretreatments of wet Amberlyst15 was studied, however, the results were not as promising as those obtained using dry Amberlyst15. The effect of using a co-solvent (THF) revealed an insignificant effect suggesting the absence of mass transfer limitations in the reaction. The absence of mass transfer effect was also suggested in the studies dealing with the effects of temperature. The effect of leaching revealed that there was a small amount of biodiesel produced when using the liquid filtrate obtained from the mixture of methanol and dry Amberlyst15. Mixing of methanol with catalyst resulted in heating of the mixture suggesting some intrinsic changed in the catalyst. The effect of methanol:oil ratio revealed a non-monotonic behavior with two maxima in the range of 3:1 and 60:1. Additional studies are required to understand this phenomenon and improve on the operating conditions for efficient biodiesel production from Karanja oil.

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