Development of Mg-SO$_4^{2-}$/ZrO$_2$ Heterogeneous Catalyst forming Biodiesel from Karanja Oil

Sunder Lal[1], Richa Tomer[2], Deeptiraj Pant[3], Ramswaroop Singh Thakur[4]

[1] Assistant Professor, Chemical Engineering, Maulana Azad National Institute of Technology Bhopal, INDIA
[2] B.Tech, Chemical Engineering, Maulana Azad National Institute of Technology Bhopal, INDIA
[3] M.Tech, Chemical Engineering, Maulana Azad National Institute of Technology Bhopal, INDIA
[4] M.Tech, Chemical Engineering, Maulana Azad National Institute of Technology Bhopal, INDIA

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Abstract – *We have studied transesterification of karanja oil with heterogeneous catalyst and found that the heterogeneous catalyst Mg-SO$_4^{2-}$/ZrO$_2$ worked very well for transesterification of oils. The maximum conversion was above 90% at Temperature 80^{0}C and the GCMS analysis of biodiesel showed that the biodiesel consisted of ten major products viz. Methyl Palmitate, Methyl Stearate, Methyl Oleate, Methyl Linolenate, Methyl Linoelate, Methyl Eicosanonate, Methyl Archidate, Methyl Tetra deconate, Methyl Pentyl hexonate and Methyl Behenate. The first order plots were found to be fit the conversion versus time data. Along with this yield of different components of the biodiesel versus time data showed the reaction is first order. It is also found that the the value of rate constant approximately 1 min^{-1}. We have also purposed the reaction mechanism of biodiesel formation and explain with the results. The catalyst was characterized by FTIR, TGA, BET and SEM and we used this catalyst continuously for 1000 hours of reaction time without effecting conversion and yield which shows the catalyst activity remained unchanged at least for 1000 h.* Therefore this catalyst can be used to produce biodiesel at industrial scale.

Keywords: Transesterification[1], Karanja Oil[2], Biodiesel[3]

1. Introduction

Due to the increase of petroleum price, the use of biodiesel for fuel has now become economical, in some countries, it has become mandatory to mix it with regular diesel in about 5-10%. In addition to becoming economical in some cases it has positive environmental impacts. This is because they have higher cetane number which gives shorter ignition delay. For it is use for period of time, the emission has lower particulate matters giving longer minimum carbon deposits on injector.

Homogenous base- catalyzed transesterification of oils (or triglycerides) are mostly used method for the biodiesel production. In spite of all advantages, this technology requires rigorous control of raw materials; the raw material must have very limited presence of water and no free fatty acids (FFAs). This is because presence of water and FFA leads to saponification and the soap formation which reduces the formation of biodiesel. In the production of biodiesel, glycerol is the main byproduct and it increases difficulties of separation of glycerol is emulsified. We have reviewed the current literature on the selection of heterogeneous catalyst so that these difficulties can be overcome. It was observed that in the reaction mass, there exists a water layer having glycerol and organic layer consisting of biodiesel and the solid layer has the catalyst. Due to formation of slight amount of soap, the powdered catalyst tends to be entrained and is carried away with the product layer hence giving the loss of the catalyst. In view of this difficulty, the literatures show the absence of true heterogeneous catalyst which could be repeatedly recycled.

An alternate route of biodiesel production could be esterifcation of free fatty acid by acid catalyst. This reaction may occur in the presence of triglycerides or conjugated with transesterification reaction. Since the free fatty acids are the reactants of esterification hence no limit of FFA is bonded. In addition of this, there is exists raw material such as used oil and beef tallow oil without need of neutralization. In such reaction, soap is not formed since the catalyst is not base and separation of glycerol is avoided. In view of this, we study a review of heterogeneous catalysts for esterification reaction [1-26]. Various catalysts suggested are Montmorrilonite clay [1], hydrotalcite clay [2], cation exchange resin [3,6,8,9,11,12], nano-magnetic solid catalyst [15], metal oxides [4,10 and 17], Heteropoly acids (HPAs) [5,10,16 and 20] and zeolites [7,8,10 and 13] and The picolinic acid modified 12-tungstophosphoric acid (PA-HPW) can be easily recovered and reused [21] etc. Form the literature; it is found that catalysts have low the reusability. It is also found that the catalytic activities of all

catalysts are relatively slow and temperature needed to operate between 100-200⁰C. There are few reactions that occur at temperatures less than 100⁰C as in reference 5, 6, 9, 10, 13 and 18-26. In this paper we report heterogeneous catalyst which can be recycled for long number of cycles. We used three supports viz. modified alumina, hydrotalcite clays and Raney nickel support and out of these the modified alumina served the best with HPA catalyst. The oil tested was Karanja (10.56 % FFA).

2. Experimental Section

2.1 Material used

The crude Karanja oil is purchased from New Market, Bhopal. Zirconium Oxychloride and Magnesium nitrate extra pure were purchased from Loba Chemie, Mumbai and used as received. Methanol and liquor Ammonia (10%w/v) were obtained from Central Drug House, New Delhi and used as received.

2.2 Preparation of catalyst:

2.2.1 Preparation of support

To prepare the support, 20g of hydrated zirconyl oxychloride $ZrOCl_2$ were dissolved in about 100 ml of deionized water and a drop wise addition of aqueous solution of ammonia resulted in the precipitation. A necessary amount of ammonia solution was added so that the pH value could be adjusted to be approximately in range of 9–12. The precipitate was aging for 3h in water bath at 100⁰C, filtered by vacuum and washed several times until a negative test of chloride ion was achieved and then dried for about 12 h at 120⁰C. Then it is calcined at 500⁰C for 3 h. the final product is named as zirconium dioxide.

2.2.2 Preparation of supported catalyst

Sulfated zirconia was prepared by wet impregnation method of 4g of ZrO_2 with 60 ml aqueous solution of 1N sulfuric acid for 8 h with occasional stirring. The solution was then filtered and the obtained materials were dried at 110⁰C for 12 h. The catalyst was calcined at 500⁰C for 3 h. The resulting materials were designated as sulfated zirconia.

Magnesium doped sulfated zirconia was prepared by sequential impregnation method. Sulfated Zirconia was impregnated by grinding with magnesium nitrate with addition of 1-2ml of H_2O.then the final solid was dried at 110⁰C for 12h and calcined at 500⁰c for 3h. The final catalyst is designed as magnesium doped sulfated zirconia ($Mg-SO_4^{2-}$ / ZrO_2).

3. Catalyst Test

3.1 Reaction Procedure

A round bottom flask (500ml) with water- cooled reflux condenser arrangement was used as laboratory-scale reactor for the experimental studies in this work, and a hot plate with magnetic stirrer was used for heating the mixture in the flask. For the simultaneous transesterification and esterification reaction of oil, the mixture was stirred at the same agitation speed of 1000 rpm for all the test runs.

The reactor was initially charged with 100 ml oil, 2g of catalyst and heated to 50⁰C then methanol (30 ml) is added drop wise and further it is heated to the required temperature (60-80⁰C) before running the reaction for desired reaction time (1-10h). An on/off controller was used for controlling the temperature with a chrome alloy thermocouple for temperature sensing. The reaction mixture was withdrawn after the desired reaction time by stopping the reaction and reaction mixture was collected through a separating funnel. It has the two layers, the first being methyl ester, oil and methanol and second is glycerol. The third phase is solid catalyst at the bottom of the reactor. The upper layer is collected and heated upto 60⁰C to removes methanol from the methyl ester and oil mixture.

Now conversion is determined by the following procedure 1 ml of mixture is added to 40ml of alkali (NaOH, 0.1N) and reacted for 12h. After completion of the reaction, the sample was titrated with H_2SO_4 (0.1N) to get the percentage of esters in the upper layer [21].

$$\text{Percentage of esters (w/v)} = \frac{(V_O\text{-}V_B)*N*MW_{ME}*100}{1000}$$

Where Above, V_B is volume o H_2SO_4 required for titration of Biodiesel sample (ml), V_O is volume of H_2SO_4 required for titration of blank oil (ml), N is Normality of acid and MW_{ME} Molecular weight of the ester, which is approximately taken as 292.20 assuming it is methyl ester of lauric acid. The products obtained after reaction were also analyzed by gas chromatography (GC) using a HPINNO-Wax capillary column 0.25mm × 60m film thickness 0.20 micron with flame ionization detector. The components of the biodiesel were analyzed by using a Shimadzu QP-2000 GCMS.

4. Result and Discussion:

4.1 Characterization of the final Catalyst

4.1.1 FTIR Analysis of Catalyst

The loading of the Mg-SO$_4{}^{2-}$/ZrO$_2$ on the support has been confirmed by the FTIR of the catalyst.
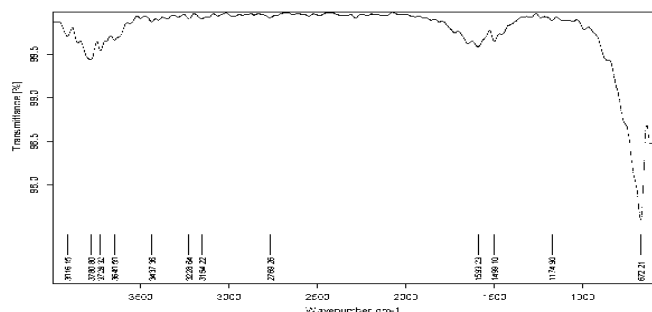

Fig-1 FT-IR image of Mg-SO$_4{}^{2-}$/ZrO$_2$ catalyst

4.1.2 Scanning Electron Microscopy of the catalyst

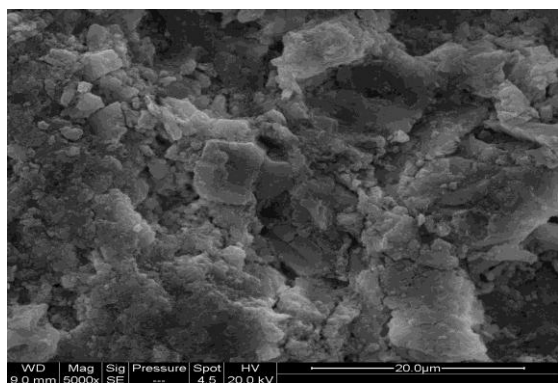SEM of final catalyst and used magnesium doped sulfated zirconia has been shown in fig. 2.

Fig-2 SEM image of Mg-SO$_4{}^{2-}$/ZrO$_2$ catalyst

4.1.3 Thermogravimetric analysis (TGA) of Mg-SO$_4{}^{2-}$/ZrO$_2$)

The TGA analysis of the complex catalyst was carried out using a Perkin –Elemer instrument in N$_2$ atmosphere. The TGA graphs of Mg-SO$_4{}^{2-}$/ZrO$_2$) catalysts are given in figure 4.1. About 10-15 mg of the sample (Mg-SO$_4{}^{2-}$/ZrO$_2$) was taken and heated from 40° C to 950°C at the rate of 10°C/min and the weight loss was measured in this temperature range. Table 3.4 gives the temperature until which the catalyst (Mg-SO$_4{}^{2-}$/ZrO$_2$) is thermally stable. The catalyst showed considerable weight loss (more than 35%) on heating till 250°C while the corresponding catalysts is found to be stable till 500 °C.
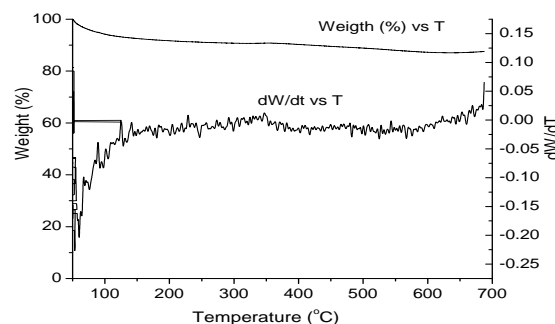

Fig-3 TGA image of Mg-SO$_4{}^{2-}$/ZrO$_2$ catalyst

4.1.4. Surface area Analysis

The surface area (SA) of the catalyst at various stages of the catalyst preparation has been measured on a Coulter SA 2100 instrument and is analyzed by the BET method. The surface area of the Mg-SO$_4{}^{2-}$/ZrO$_2$ was found to be 226m^{2}g^{-1}.

We ran our experiments at reactor size of 200ml as well as 20 liter batch reactor and the oil conversion data were not found to be affected by the reactor size which signifies that the overall reaction remains in reaction kinetics controlled regimes and is independent of diffusion. The reaction product could be easily separated in a settling tank by leaving it over night and the biodiesel layer separated from the glycerin phase The product formed was separated and subjected to GCMS analysis using GC column HPINNOWAX and the product was shown to consists of ten major constituents which are given below.

Methyl Palmitate, Methyl Stearate, Methyl Oleate, Methyl Linolenate, Methyl Linoelate, Methyl Eicosanonate, Methyl Archidate,Methyl Tetra deconate, Methyl Pentyl hexonate,and Methyl Behenate.
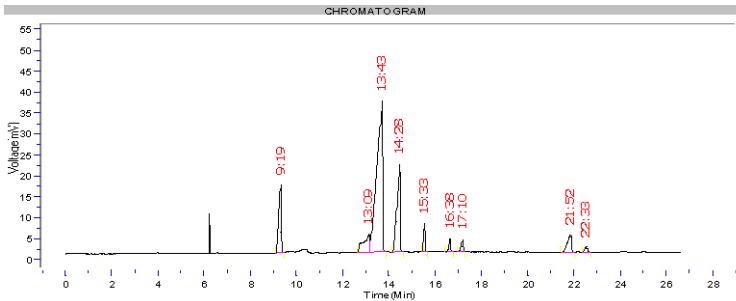
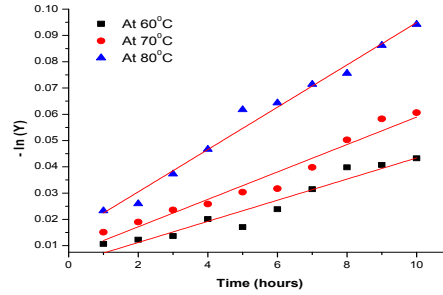Fig-5: Chromatogram of Biodiesel produced by using Mg-SO$_4^{2-}$/ZrO$_2$

5. Conversion and Yield Graphs for Karanja Oil:

The reaction results of transesterification of oil are given in fig. 4 and for their components of Karanja oil given in fig.5-9.
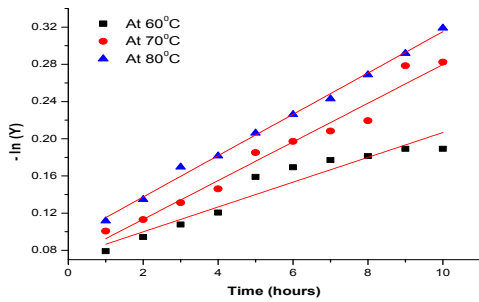

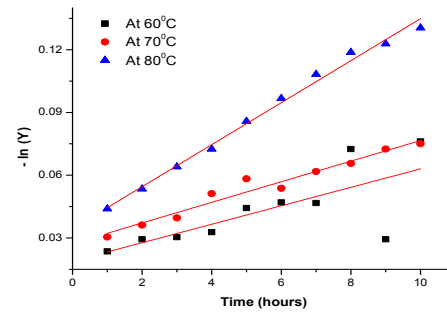Fig-4: Conversion of karanja oil at different temp

Fig-5: Yield for the Methyl Stearate in Biodiesel Obtained from Karanja Oil
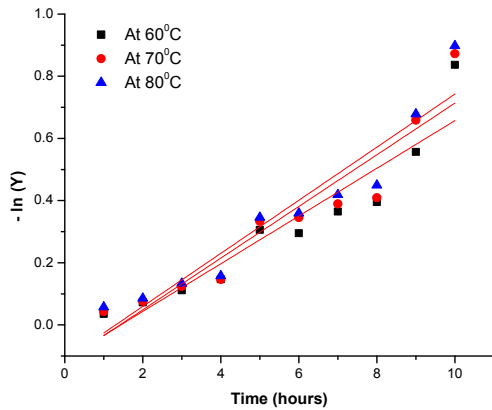

Fig–6: Yield for the Methyl Oleate in Biodiesel Obtained from Karanja Oil

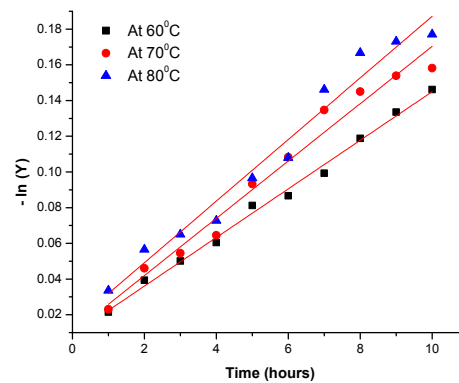Fig–7: Yield for the Methyl Linoleate in Biodiesel Obtained from Karanja Oil

Fig–8: Yield for the Methyl Linoelate in Biodiesel Obtained from Karanja Oil
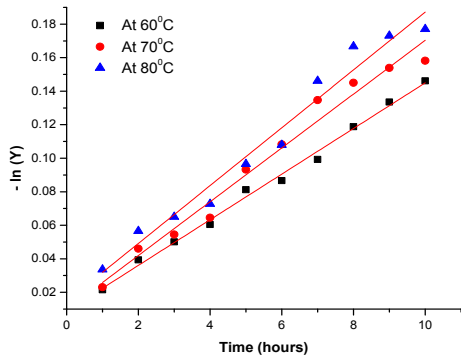
Fig- 9: Yield for the Methyl Eicosanonate in Biodiesel Obtained from Karanja Oil

We have attempted to determine the rate constants from the experimental data using zero order, first order and second order kinetics. The first order kinetics has been seen to give the best results. In figure 4-8 for Karanja oil (except data for methyl linoleate for which R^2 is 0.2) a first order is good representation because the value of R^2 is more than 0.8. Tables 1 also show the first order rate constants for various components and the overall rate constants cannot be obtained as some weighed average of rate constants of various components. In fact, the overall first order rate constant is higher as compared to the rate constants of individual components. This suggests that the overall mechanism as first order is correct and there must be some additional mechanism of reaction leading to biodiesel formation.

Table 1: Reaction Kinetics of Karanja Oil for First order

emp	Product name	$10^{-2}h^{-1}$	Values
0°C	verall	36	95
	ethyl Palmitate	33	91
	ethyl stearate	6	88
	ethyl oleate	36	99
	ethyl linolenate	9	97
	ethyl linoelate	4	47
	ethyl eicosanonate	4	93
	ethyl archidate	2	80
	ethyl tetra deconate	1	91
	ethylpentyl hexonate	7	73
	ethyl behenate	.46	88
0°C	verall	03	815

	ethyl Palmitate	3	96
	ethyl stearate	33	88
	ethyl oleate	6	97
	ethyl linolenate	0	99
	ethyl linoelate	49	95
	ethyl eicosanonate	5	95
	ethyl archidate	4	63
	ethyl tetra deconate	18	77
	ethylpentyl hexonate	65	66
	ethyl behenate	.35	76
0°C	verall	5	81
	ethyl Palmitate	2	99
	ethyl stearate	53	89
	ethyl oleate	7	96
	ethyl linolenate	6	95
	ethyl linoelate	0	99
	ethyl eicosanonate	3	98
	ethyl archidate	6	98
	ethyl tetra deconate	49	93
	ethylpentyl hexonate	3	98
	ethyl behenate	.40	965

6. CONCLUSIONS

In this paper we have tested heterogeneous Mg-SO$_4^{2-}$/ZrO$_2$ catalyst. Main focus of the work was made on zirconia supported catalyst which was tested for more than 1000h without loss of activity of purposed catalyst does not affect by the presence of free fatty acid (FFA) content in the Karanja oil. Therefore this catalyst has novelty over other same class of catalyst for transesterification reaction. The GCMS analysis shows that there are ten major components in biodiesel even though they are present in different concentrations and their conversion with yields of individual components as a function of time. For temperatures less than 60 °C, reaction was negligible or very small while above 80 °C, the overall pressure in the reactor is very high (due to methanol. In view of this, the temperature variations studied were 60 °C, 70 °C and 80 °C. Using gas chromatography, concentration of individual components was determined and the data fitting using first order plot was carried out. The goodness of fit was measured by R^2 values which are also reported in Table 1 most of the R^2 values are more than 0.8, this way confirming the goodness of the fit. The overall rate constant was considerably higher than individual rate constant of components for all oil indicating some side reactions also occurred which followed first order kinetics. The concentration of methyl behenate in some cases is seen to fall after undergoing a maximum. It is likely that it may have diffused to the glycerol phase.

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BIOGRAPHIES

Dr. Sunder Lal is Assistant Professor in Chemical Engineering Department, MANIT Bhopal, INDIA. He obtained his PhD from IIT Kanpur, India. He has more than ten years experienced of teaching and research. He has published more than ten international and national journal research papers.

Ms. Richa Tomer is pursuing M.Tech in Chemical Engineering department from MANIT, Bhopal, India. She has published two research papers.

Mr. Deeptiraj Pant is pursuing PhD in Chemical Engineering Department from MANIT, Bhopal, India. He has published three research papers.

Mr. Ram Swaroopsingh Thakur is pursuing PhD in Chemical Engineering Department from MANIT, Bhopal, India. He has published two research papers.