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SPECTRAL ANALYSIS OF BIODIESEL FROM COTTON OIL USING SULFATED ZIRCONIA PROMOTED WITH ALUMINUM

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ABSTRACT

The biodiesel synthesis using cottonseed oil with aluminum-promoted sulfated zirconia catalyst was studied to analyze the quality of fuel produced. The various catalyst weight percent studied produced more than 75% biodiesel yield. Fourier transform infrared spectroscopy of biodiesel provides a C-O strong stretch of esters at 1745.520cm^{-1}. The ester peak was observed at 1745cm^{-1}, CH peaks from 2800cm-1 to 3000cm$^{-1,}$ and the OH^{-} peak was absent, indicating the long fatty acid esters chain. The gas chromatography-mass spectrometer analysis shows the presence of methyl ester of tetradecanoic acids, hexadecanoic acids, and octadecadienoic acids, which make up the majority of the composition and 8, 11-octadecadienoic acids methyl ester makes up 58% of the product biodiesel. The physical properties were determined for biodiesel which provides a flashpoint at 172ºC and fire point at 197ºC. The ^{1}H nuclear magnetic resonance observation of the singlet signal of proton at 3.640ppm signals the availability of methyl ester group in biodiesel synthesized.

Keywords: Aluminum Promoted Sulfated Zirconia; Biodiesel; Cottonseed Oil; Transesterification; Nuclear Magnetic Resonance

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INTRODUCTION

Biodiesel is fatty acids containing methyl esters or ethyl esters obtained from vegetable oil by transesterification process. Biodiesel is an alternative source of energy to crude-based fuels in driving the engines of automobiles. It is a non-toxic fuel and biodegradable, which is advantageous for environmental causes.[1] The main byproduct of the transesterification process is glycerol, which is helpful as animal feed, lubricants, polymers, and surfactants.[2] The homogeneous catalysts used in biodiesel synthesis include sodium methoxide, sodium hydroxide, and potassium hydroxide alkali catalysts.[3,4,5,6] The various heterogeneous catalysts studied extensively include enzymes[7,8], titanium silicates, anionic resins, barium titanate, and barium-modified zeolite.[9,10], clam shells[11], CaO, $ZnCl_2$, and ZnO[1213,14], shells of eggs[15] and ZrO2.[16] The acid-catalyzed reactions have a lower reaction rate than base-catalyzed transesterification and operate at high-temperature conditions.[17] The use of heterogeneous catalysts reduces the process cost and water usage in the process.[18] The heterogeneous catalysts are non-corrosive and address the environmental concerns in the transesterification process.[19] The biodiesel is obtained from vegetable oils such as cottonseed oil[20,21], waste oil fryed[22], sunflower oil[23], and waste soybean oil.[24] In this study, transesterification with oil from seeds of cotton using sulfated zirconia catalyst promoted with aluminum. The biodiesel synthesized is characterized using FTIR and Gas chromatographic spectroscopy to analyze various groups of functions existing in biodiesel. The catalytic surface is analyzed with scanning electron microscopic studies. The flashpoint, fire point, kinematic viscosity of biodiesel, iodine, and saponification values were determined as per standards.

EXPERIMENTAL

Catalysts Preparation

Aluminum-promoted sulfated zirconia catalyst (Al_2O_3/S-ZrO_2) was prepared using a solvent-free method. Zirconium Oxychloride ($ZrOCl_2.8H_20$), Aluminum Sulfate ($Al_2(SO_4)_3.18H_2O$), and Ammonium Sulfate

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$(NH_4)_2SO_4$ were taken in the ratio 1:1:6, the mixture was ground in a porcelain mortar for 15 min. The catalyst is maintained at 25^{O}C for 16-20 hours. The calcination was done in a muffle furnace at 700°C for a calcination time of 6 hours. The physical properties of biodiesel were characterized using ASTM standards.

General Procedure

The transesterification process converts alcohols and oils to esters. Biodiesel is produced from oil obtained from seeds of cotton with methanol using sulfated zirconia. Biodiesel contains esters produced from the reaction of methanol with cottonseed oil. Cottonseed oil and methanol are mixed in the molar ratio of 1:9 and 3% weight of oil is added as catalyst. This mixture is stirred at 55°C and 600rpm in a magnetic stirrer for 3hrs stirring time. The catalyst added was an acid-based catalyst containing aluminum-promoted sulfated zirconia. The glycerol phase is separated from the ester phase, and further analysis was carried out.

Analytical Discussion

FTIR spectra were obtained using Nicole iS-10 (FTIR Spectrometer) in the region 4000-400 cm^{-1}. The biodiesel formed by transesterification of oil obtained from seeds of cotton using sulfated zirconia catalyst is analyzed with Shimadzu Gas Chromatography Mass Spectrometer-QP 2010 Ultra equipment. The length of the gas chromatograph column is 30 meters, the diameter of the gas chromatograph column is 0.25milli meters and the thickness of film is 0.25 micrometers. The flow rate of helium a carrier gas in the column is 15mL/min. The temperature rises from 60°C to 280°C at 12°C/min. The volume of sample injection is 1µl. Surface analysis of zirconia catalyst was obtained using scanning electron microscopy (SEM) VEGA3 TESCAN device, which functions at 5 and 30kV voltage to analyze the particle's size, shape, and distributions.

RESULTS AND DISCUSSION

Surface Morphology of Aluminum-Promoted Sulfated Zirconia Catalyst

The SEM images obtained for the zirconia catalyst after the thermal treatment are shown in Fig.-1. The SEM images revealed that the zirconia particles were aggregated together to form rod-like structures along with irregular solids. The rod-like structures found were as big as 4.6 microns in length and 1 micron in thickness. The particle agglomerations were polydisperse in the irregular solids and did not show any specific structure. Also, the particle agglomerations were seen as lumps in the solids in a few places. However, more rod-like structures found between the irregular solids could have been formed from the zirconia particles by the slow annealing after the thermal treatment.

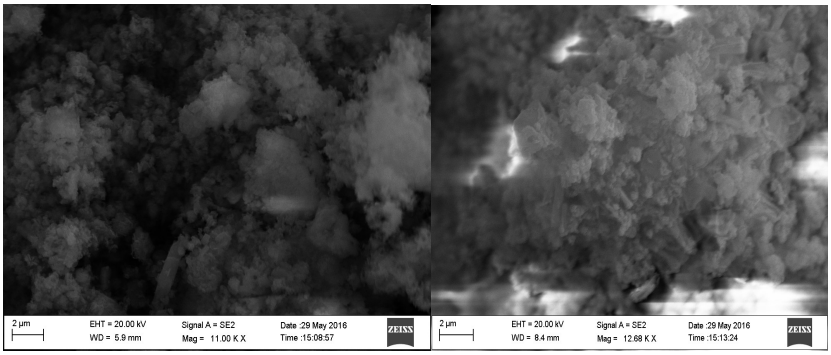

Fig.-1: Surface Morphology of Aluminum Promoted Sulfated Zirconia Catalyst

Effect of Concentration of Zirconia Catalyst on Biodiesel Synthesis

The biodiesel percentage yield for different aluminum-promoted sulfated zirconia catalyst weights and the ratio of alcohol to oil parts is provided in Table-1. It is seen that the concentration increases of heterogeneous catalysts in the mixture result in an increased fatty acid methyl ester yield due to the increased number of sites that are active. The various catalyst weight % studied produced biodiesel yields larger than 75%. The increase in catalyst weight from 1% to 2% resulted in an increase in yield from 77% to 79% for the six parts of alcohol to one part of the oil in the mole ratio. The methyl ester synthesized increased with a change in a mole ratio of alcohol to oil, as observed in the experiments studied. For ratios

of 6:1 and 9:1 alcohol to oil with a catalyst weight of 1%, the yield varies by 1.630%. The yield difference is 1.44% when the catalyst is increased to 2% by weight. The cottonseed oil is converted to biodiesel at different alcohol-to-oil molar ratios (X_1) and catalyst amounts (X_2) were studied. The regression coefficients for the % yield of biodiesel (Y) are shown in Table-2 given below

% Molar Yield of Biodiesel $Y = 79.790 + 0.738X_1 + 1.832X_2 – 0.512\ X_2^2 – 0.067\ X_1X_2$

Where Y is the predicted response, the effect of catalyst weight is more predominant (+1.832) than alcohol to oil molar ratio (+0.738), as observed in the correlation. The response surface methodology is used to analyze the results obtained in MINITAB statistical software. The catalyst weight % with P- value 0.006 as shown in Table-2, affects biodiesel synthesis as P values are close to zero. The analysis of variance shown in Table-3 justifies the above observation. The linear effect is more predominant on the yield of biodiesel than quadratic and interaction effects. The P value of regression is 0.012 is low and shows the statistical significance of the results obtained. Figure-2 shows the contour plot for the weight percentage of catalyst versus the ratio of alcohol to oil on a mole basis. The biodiesel yield was 80% for the ratio of alcohol and oil at 7.5:1 and the catalyst weight percentage of 2.5%.

Table-1: Biodiesel Synthesis for Change in Alcohol and Oil Amount and Catalyst Percentage

Methanol: Oil (X_1)	Catalyst percentage by weight (X_2)	Yield percentage of biodiesel (Y)
6:1	1	77
6:1	2	79
6:1	3	81
9:1	1	78
9:1	2	81
9:1	3	82

Table-2: Coefficients, t and P Values for the Synthesis of Biodiesel

Term	Coefficient	Standard Error coefficient	t	P
Constant	79.790	0.022	3553.542	0.000
Alcohol: Oil (X_1)	0.738	0.012	56.954	0.011
Catalyst % (X_2)	1.832	0.015	115.418	0.006
X_2^2	-0.512	0.027	-18.636	0.034
X_1X_2	-0.067	0.015	-4.251	0.147

Table-3: ANOVA for Synthesis of Biodiesel using Aluminum Promoted Sulfated Zirconia

Analysis	Variables degrees of freedom	Sum of the squares (Sequential)	Sum of the squares (Adjusted)	Mean of the squares (Adjusted)	F	P
Regression	4	17.071	17.071	4.267	4232.600	0.012
Linear	2	16.703	16.703	8.351	8282.500	0.008
Square	1	0.350	0.350	0.350	347.310	0.034
Interaction	1	0.018	0.018	0.018	18.070	0.147
Residual Error	1	0.001	0.001	0.001		
Total	5	17.072				

Fourier Transforms Infrared Spectroscopy of Biodiesel Synthesized.

Fourier transforms infrared spectroscopy (FTIR) spectra of biodiesel samples are provided in Fig.-3. The various peaks seen in the spectra can be interpreted as follows, at 3471.6cm^{-1} is an O-H bond which is H-bonded, stretch vibration with strong and broad intensity. At peaks with wavenumber 3007.440cm^{-1}, 2925.480$cm^{-1,}$ and 2856.540cm^{-1} C-H weak stretches of alkanes were observed. The C-H weak fingerprint region is shown at wavenumber 2359.100cm^{-1}. C-O strong stretch of the ester is seen at 1745.520cm^{-1}. At 1458.120cm^{-1} C-H medium bend of alkanes and the C-H rocking bond of alkanes at 1369.960 cm^{-1} were observed. The peaks having wavenumber 1235.700cm^{-1}, 1163.630$cm^{-1,}$ and 1105.420cm^{-1} are weak stretches of C-C/C-O bonds. C-C strong bend of aromatics at 913.327cm^{-1}, C-H medium rocking bond of alkanes at 722.350$cm^{-1,}$ and O-H broad bends at 591.070cm^{-1} were observed. Figure-3 shows the presence

of an ester peak at 1745cm^{-1}, CH peaks from 2800cm^{-1}to 3000cm^{-1}and the non-existence of OH^{-} peak indicates methyl esters are present in the biodiesel synthesized.

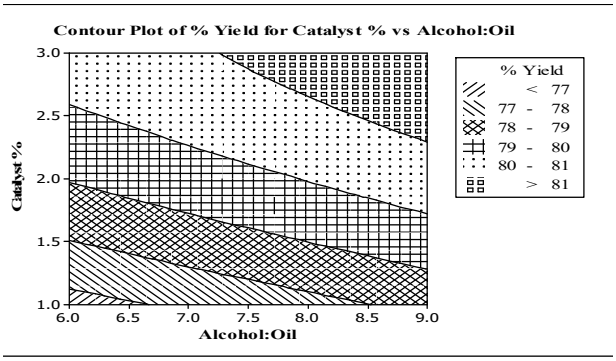

Fig.-2: Contour Regions for Biodiesel Yield using Sulfated Zirconia

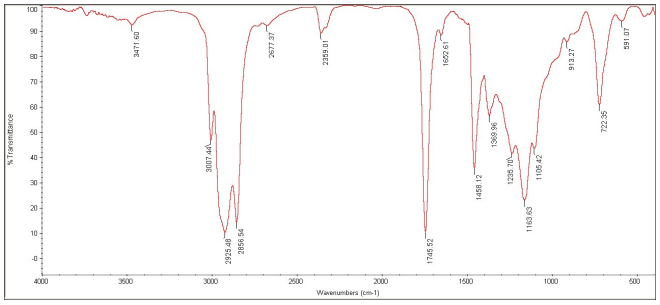

Fig.-3: FTIR Spectra for Biodiesel Synthesized using Aluminum Promoted Sulfated Zirconia Catalyst

Gas Chromatography-Mass Spectrometer of Biodiesel Synthesized

Figure-4 shows gas chromatography and mass spectrometer (GC-MS) analysis of biodiesel showing various methyl esters of fatty acids. Table-4 provides the composition, and retention time of multiple components in the synthesized biodiesel obtained from GC-MS analysis. The methyl esters of decanoic acid (tetra and hexa) and octa decadienoic acid remain a major proportion of the composition where 8, 11-octadecanoic acid methyl ester makes up 58.01% of the biodiesel sample and small quantities of stearic acid methyl ester (methyl stearate) 2.39% is present. The 2,4 Decadienal, an aromatic substance at 6.04%, is a product of degradation resulting from oil heating and not observed in pure oil which may cause biodiesel toxicity. The presence of esters of methyl alcohol such as decadienoic acid (tetra and octa) and hexadecanoic acid shows that the trans-esterified product is biodiesel.

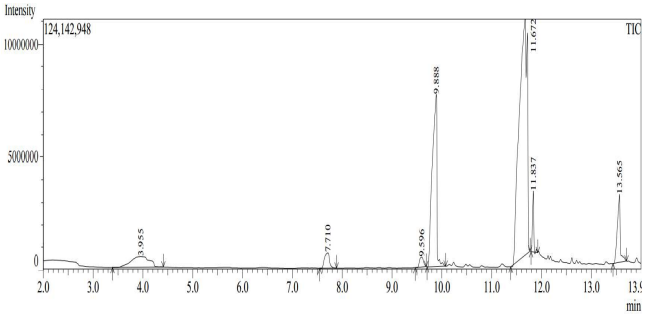

Fig.-4: GC-MS Analysis of Biodiesel Synthesized using Aluminum Promoted Sulfated Zirconia Catalyst

Table-4: Composition And Retention time of Various Components in the Synthesized Biodiesel

Peak No.	Name	Composition (%)	Retention Time (min)
1	2,4-Decadienal	6.040	3.955
2	Tetradecanoic acid of esters of methyl alcohol	2.320	7.710
3	9-Hexadecanoic acid of esters of methyl alcohol	1.180	9.596

4	Hexa decanoic acid of esters of methyl alcohol	24.170	9.888
5	8,11-Octadecadienoic acid of esters of methyl alcohol	58.010	11.672
6	Methyl Stearate	2.390	11.837
7	9-Octadecenoic acid 12-hydroxy-methyl esters	5.890	13.565

Nuclear Magnetic Resonance of Biodiesel Produced

The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy of the biodiesel obtained using aluminum-promoted sulfated zirconia catalyst was obtained in a Bruker 400MHz NMR machine. Figure-5 and Fig.-6 show the ^{1}H and ^{13}C NMR spectra of biodiesel, respectively. From Fig.-5 of ^{1}H NMR, the peaks observed within 1-2.500ppm are assigned to the aliphatic protons. The characteristic peak signals observed between 4 and 5.5 ppm are due to the presence of olefinic protons. The singlet proton obtained at 3.640ppm signals the existence of methyl ester and clearly matches the peaks for the esters of decadienoic acid (octa). It is observed from Fig.-6 showing the carbon NMR spectra of the biodiesel with peaks at 172.900ppm prove the existence of acid ester group. The peaks at 128ppm and 130ppm reveal the existence of olefinic groups. The esters of the methyl alcohol group recorded a peak at 61.900ppm, which matches the existence of esters of octadecadienoic acid. The signals group occurring within 15-35ppm is due to the presence of aliphatic carbon within 50 and 70ppm due to carbons having oxygen attached to them. The various peak assignments of ^{1}H and ^{13}C NMR of biodiesel synthesized are provided in Table-5.

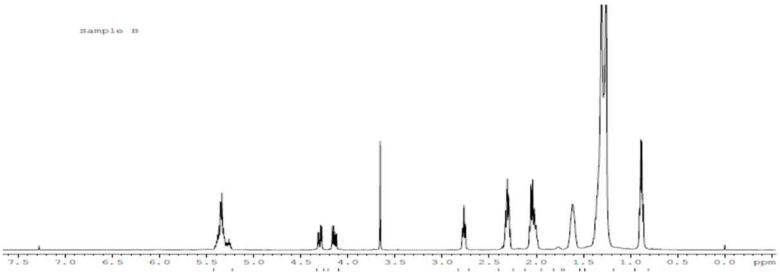

Fig.-5: ^{1}H-NMR of Biodiesel Observed in Chloroform

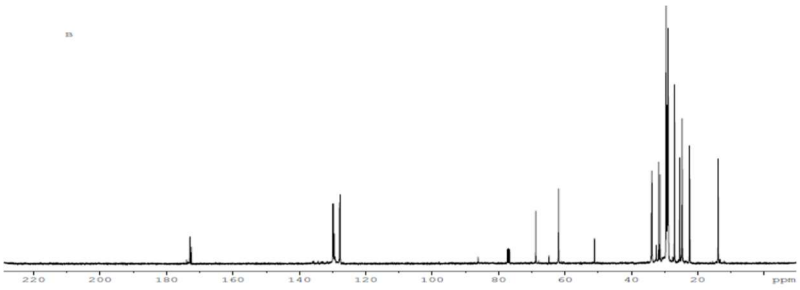

Fig.-6:^{13}C-NMR of Biodiesel Observed in Chloroform

Table-5: NMR Wavelengths for Biodiesel Produced

^{1}H- NMR Spectral for Biodiesel	
Groups of olefins	δ range 5.300ppm
Groups of methyl ester	δ range 3.640 ppm
^{13}C-NMR spectral for biodiesel	
Groups of acid ester	δ range 172.900ppm
Groups of olefins	δ range 128ppm to 130ppm
Groups of methyl ester	δ range 61.900ppm
aliphatic carbon atoms	δ range 15 to 35ppm

Physical properties estimation of biodiesel synthesized: The properties determined for biodiesel synthesized using aluminum-promote- sulfated zirconia catalyst are shown in Table-6, and these values were as per the European standards EN14214 and American Society for Testing and Materials standards ASTM D6751.

Table-6: Physical Properties Determined for Biodiesel Synthesized

Property	Values for cottonseed oil	ASTM D6751 (B100) Biodiesel standard values	EN 14214 Biodiesel standard values	Values (Biodiesel from Al-promoted sulfated zirconia)
Density of biodiesel (kg/m^3)	---	860-900	860-900	888
Flash point of biodiesel (°C)	260	93-170	>101	172
Fire point of biodiesel (°C)	--	--	--	197
Moisture percentage (%wt)	0.020	0.050 max	0.050 max	0.041
Iodine value of biodiesel (mgI_2/100g)	101.550	--	120	129.220
Saponification values of biodiesel (mg potassium hydroxide/g)	184.970	164-220	--	172.840
Acid values of biodiesel (mg potassium hydroxide /g)	0.420	0.500	0.500	0.300
Kinematic viscosity of biodiesel produced (cSt)	--	1.900-6	3.500-5	4.200

CONCLUSION

The transesterification of oil from seeds of cotton reacted with methanol using sulfated zirconia, resulting in the yield of biodiesel higher than 75%. FTIR spectra analysis of biodiesel provides the existence of an ester peak at 1745 cm^{-1}. GC-MS analysis of biodiesel shows the presence of methyl esters of decanoic acid (tetra and hexa) and acids of octadecadienoic, which remains a major composition where 8, 11-octadecanoic acid methyl ester makes up 58.010% of the biodiesel sample. The flashpoint of 172°C was obtained for the biodiesel synthesized using aluminum promoted sulfated zirconia, which is within the prescribed ranges of ASTM D6751. SEM images revealed that the zirconia particles were aggregated together to form rod-like structures and irregular solids as big as 4.600 microns in length with 1 micron in thickness. The ^{1}H nuclear magnetic resonance observation of singlet proton recorded at 3.640ppm signals the existence of methyl ester in biodiesel synthesized.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID IDs, given below:

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