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Nano Catalytic Conversion of used Lubricating Oil into Diesel Fuel

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Abstract: Alternative fuels have become increasingly important due to diminishing petroleum reserves, increasing economical situations and awareness of the increased environmental consequences of emissions from petroleum-fuelled engines. In this study, a diesel fuel was synthesized by the catalytic pyrolysis of used lubricating oil at 500^{o}C temperature in a muffle furnace using zeolite as catalyst. The prepared diesel was characterized by FT-IR, GC-MS and fuel properties. The functional groups analysis of the diesel was carried out by using FT-IR, which showed the presence of alkanes and alkenes. The chemical composition of the prepared diesel was determined by GC-MS analysis. Saturated and unsaturated hydrocarbons with carbon chain in the range C_9-C_{27} were found. Fuel properties such as flash point, kinematic viscosity, sulfur contents, cloud point, pour point, cetane number, and density were investigated using ASTM methods. The prepared diesel showed significantly high recovery (85-90%) of the energy present in the used lubricating oil, and is also relatively contaminant free with low levels of sulphur, oxygen, and toxic PAH compounds.

Keywords: catalytic pyrolysis, diesel, nanoparticles used lubricating oil, zeolite.

Introduction

In recent years, diminishing of fossil fuel sources, growing of demand and cost of petroleum-based fuels, and environmental hazards as a result of burning of them have encouraged researchers to investigate possibility of using alternative fuels instead of the fossil fuels. Therefore, the researchers have focused on finding alternative new energy resources and utilizing them. They have stated that it is necessary to reduce consumption of the petro fuels due to the negative effects on human life by producing alternative renewable fuels. As known fossil energy sources have been exhausted rapidly nowadays, it is predicted that fossil fuel sources will be depleted in the near future.[1] According to some studies, it is estimated that crude oil will last only for roughly 80 more years, gaseous fuels for about 150 years, and coal for 230 years.[2] Therefore, scientists and researchers all over the world are now working hard to discover new sources of energy for the future, and also try to develop new technologies that allow recycling or reusing waste material as a source of energy. [3] Many research works addressed the utilization of waste oils that are of lubricating oils originated from crude oil [3] and biomass origin waste oils for the case of diesel engine applications .[4-6] as sources of energy. The gaseous yield from steam gasification and pyrolysis of biomass have been investigated experimentally, the results of steam gasification have been compared to that of pyrolysis.[7-13] The temperature range investigated at elevated temperature in the range of 550–1000 °C. Hydrogen is produced from steam gasification and pyrolysis at the elevated temperatures .[7-9]

Mineral waste lubricating oil sources, particularly engine oils have attracted much attention as an alternative energy source. The lubricating oils can be recycled as lubricating oil, and re-used as fuel or made into diesel-like fuel.

Production of diesel-like fuel from waste oils such as industrial and engine waste oils, wood pyrolysis oils, fresh and waste fats and vegetable oils is an excellent way for producing alternative fuel sources. Industrial and engine waste oils [14], wood pyrolysis oils [15], fresh and waste fats and vegetable oils [16] have been proposed as pyrolysis raw material to produce gasoline and diesel-like fuels. There is plenty of the waste engine oil in the world. Abundant amounts of used engine lubricating oils are produced worldwide every year. [17] Annually, about 40 million metric tones are produced,

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and around 60% of the production becomes waste .[18] Less than 45% of available waste oil was collected worldwide in 1995, and the remaining 55% was either misused or discarded by the end user in the environment .[19] It should be collected and re-used in order to decrease detrimental effects on environment, and underground and surface waters, since it pollutes the atmospheric air as a result of burning, and has negative effects on living organisms, underground and surface waters when it is discharged into soil or water. Conversion of the waste engine oils into diesel like fuel by using pyrolitic distillation, and by utilization of the product as a diesel fuel has positive effects on environment and atmospheric air, and also has economical value.

Recently, recycling and utilizing of waste oils have received significant attention all over the world, since waste lubricant oils are considered toxic and hazardous because of the presence of metal particles remaining from the additives such as phenols, compounds of zinc, chlorine and phosphorus, chlorinated compounds, polycyclic aromatic hydrocarbons and other residues .[17] Waste oils can be reconstructed chemically by being heated in an oxygen-free environment .[18] The most important advantage of this method is that it does not pollute the environment when carried out in an appropriate way.

In this study, used lubricating engine oil samples were purified from contaminants, and the clean oil samples were blended with zeolite. The oil samples with the additive were heated in the muffle furnace. They were exposed to thermal treatment in order to convert them into a diesel-like fuel during the heating process. After that process, typical characteristics of the fuel, such as density, viscosity, flash and fire point, sulfur content, heating value and distillation temperatures were tested. The effects of the zeolite additive on these characteristics were discussed. Also it was discussed whether the obtained fuel can be used in a diesel engine or not.

Experimental

1. Materials and Reagents: Muffle furnace, L-shaped tube, condenser and beaker, measuring cylinder, round bottom flask, zeolite catalyst, filter paper. Waste lubricating oil (WLO) used for diesel synthesis was taken from local market.

2. Pre-treatment: The waste lubricating oil was highly viscous having carbon soot and gum type material. The waste lubricating oil sample was filtered using Whatman filter paper to remove the suspended particles including dust and metals.

3. Experimental Procedure: The catalytic pyrolysis experiment of waste lubricating oil (WLO) was carried out in a round bottom flask, equipped with L- shaped tube, connected with a condenser as shown in Figure 1. About 100 ml of pre-treated WLO was taken in round bottom flask and 2% (w/w with respect to weight of WLO) zeolite catalyst was added and mixed with WLO. The flask was placed in the furnace and started the reaction. The temperature of the furnace was increased from room temperature to 500^{o}C with a rate of 10^{o}C/min. The temperature was maintained at 500^{o}C for one hour. The WLO starts to crack and vaporized in L-shaped tubes which were condensed by condenser and collected in a beaker. This liquid product was named as diesel fuel.

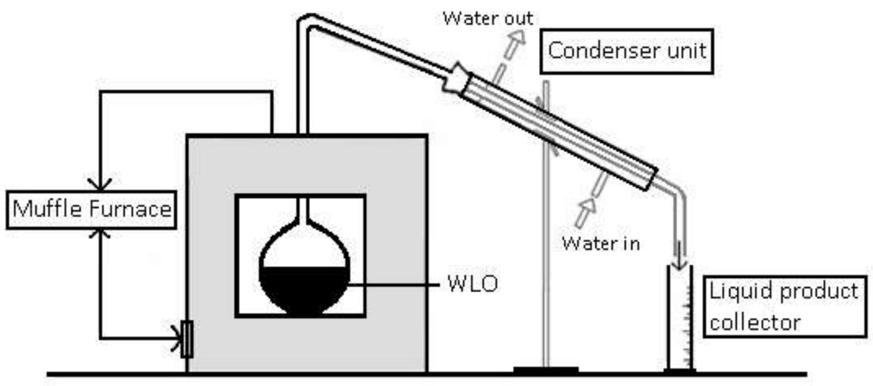

Figure 1. Experimental setup for the conversion of used lubricating oil into diesel fuel

2. Characterization

The prepared WLO diesel was characterized by Fourier Transform Infrared Spectroscopy (FT-IR), Gas Chromatography coupled with Mass Spectrometry (GC-MS) and fuel properties such as kinematic viscosity, flash point, pour point, cloud point, specific gravity, density, acid value, sulfur contents etc.

2.1. Fourier Transform Infrared Spectroscopy (FT-IR)

The analysis of diesel was carried out by FTIR using Bruker vector 22 spectrophotometer. The spectra were collected in the range of 4000-500 cm^{-1}. The resolution was 1 cm^{-1} and number of 15 scans.

2.2. Gas Chromatography-Mass Spectrometry (GC-MS)

Gas chromatography was used to determine the chemical composition of the prepared WLO diesel using GC-6890N model coupled with mass spectrometer; model MS-5973 MSD (mass selective detector). For the separation of different compounds present in diesel, a DB-5MS capillary column of internal diameter of 0.2 mm having length of 30 m and film thickness of 0.2 m was used. With a flow rate of 1.5 ml/min, helium was used as a carrier gas in GC-MS. The temperature of capillary column was raised from 120-300^oC at a fixed rate of 10^oC/min. A volume of 0.1 µL of diesel in chloroform was injected as a sample using split mode with split ratio of 1:10. The scan rate of mass spectrometer was set from 50-550 m/z. Electron impact (EI) mode of ionization was used.

3. Fuel Properties of Diesel

The fuel properties of the WLO diesel were evaluated as per ASTM standards. To evaluate the quality of prepared diesel, properties like kinematic viscosity (D445), cetane number (D613), pour point (D97), cloud point (D2500), specific gravity (D4052), flash point (D93), ash content (D482), sulphur content (D4294) and density (D5002) were analyzed. The data of fuel properties of diesel fuel are summarized in **Table 3**.

Results and Discussions

The diesel prepared from waste lubricating oil was analyzed using Fourier Transform Infrared Spectroscopy (FTIR), Gas Chromatography coupled with Mass Spectrometry (GC/MS) and fuel properties.

1. Fourier Transform Infrared Spectroscopy

The functional group analysis of pyrolysis oil was carried out by using Fourier Transform Infrared Spectroscopy (FTIR). The FTIR spectra obtained for pyrolysis oil is given in Figure 2. FTIR analysis was performed on a BRUKER VECTOR 22 spectrophotometer device. Table .1 shows the functional group obtained from FTIR spectra.

Table 1. FTIR results of waste lubricating oil diesel

S. No	Frequency Range (cm^{-1})	Functional Group	Classification of Compounds
1	2851.3-2920.2	C-H Stretching	Alkanes & Alkenes
2	1459	CH_2 Bending/Deformation	Alkanes
3	720.3	C-H Out of plane bending	Single ring aromatics
4	1376	CH_3 Bending	Alkanes

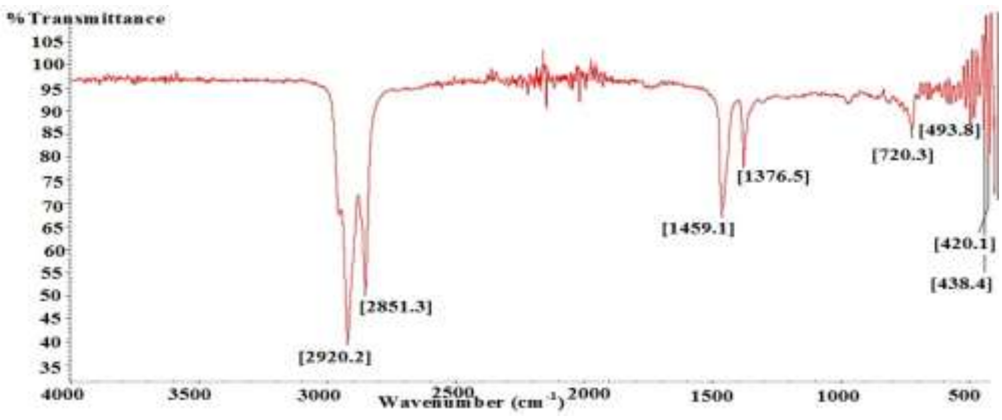

Figure 2. FTIR of waste lubricating oil diesel

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FTIR analysis showed the presence of different hydrocarbons which includes alkanes, alkenes and single ring aromatics. The presence of alkanes was confirmed by C-H stretching vibration between 2851.3-2920.2 cm^{-1}. The peaks at 1376.5 and 1459.1 cm^{-1} indicated C-H bending vibrations which is also another evidence of presence of alkanes. The peak at 720.3 showed C-H out of plane bending indicating the presence of single ring aromatics.

2. GC-MS Analysis

The GC/MS study was performed to determine the chemical composition of diesel fuel. The gas chromatogram of diesel fuel is given in **Figure 3**. The gas chromatogram revealed about 26 peaks which correspond to various alkanes and alkenes. The identification of these hydrocarbons was done by library match software (NO.NIST 02). The identified hydrocarbons were confirmed by mass spectrometric analysis and are given in **Table 2.**

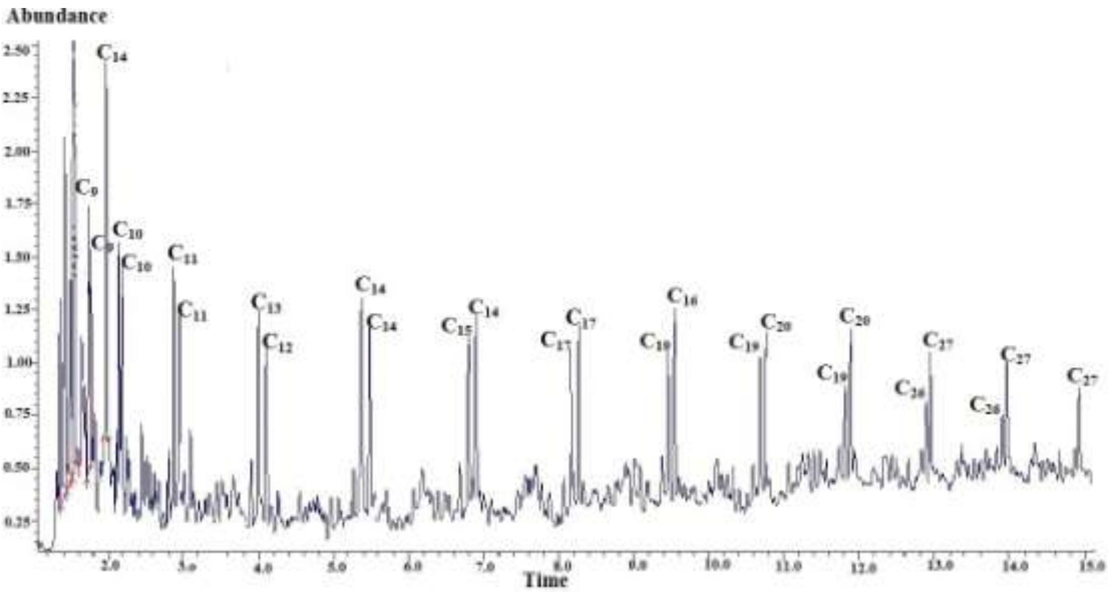

Figure 3. Gas chromatogram of waste lubricating oil diesel

Table 2. Compounds identified in diesel & their corresponding percentage composition

S.No	Compound	Retention time	%age composition
1	Nonene	1.75	4.26
2	Nonane	1.78	4.34
3	Cyclotetrasiloxane	1.97	4.80
4	Decene	2.15	5.24
5	Decane	2.19	5.34
6	Undecene	2.86	6.97
7	Undecane	2.94	7.17
8	Tridecene	4.00	9.75
9	Dodecane	4.10	10
10	Tetradecene	5.37	13.10
11	Tetradecane	5.48	13.36
12	Pentadecene	6.79	16.56
13	Tetradecane	6.900	16.83
14	Heptadecene	8.16	19.90
15	Heptadecane	8.26	20.15
16	Nonadecene	9.45	23.05

17	Hexadecane	9.55	23.29
18	Nonadecene	10.67	26.03
19	Eicosane	10.75	26.22
20	Nonadecene	11.81	28.98
21	Eicosane	11.88	28.98
22	Hexacosane	12.88	31.59
23	2-methylhexacosane	12.95	31.59
24	9-hexacosane	13.90	33.91
25	2-methylhexacosane	13.96	34.05
26	2-methylhexacosane	14.93	36.42

2.1. Identification of Saturated Compounds

Nonane

The peak at m/z value of 128 is the molecular ion peak of Nonane (C_9H_{20}) which is very short lived and undergoes fragmentation simultaneously due to which its intensity is very low. The molecular ion peak with very low intensity is only present in the mass spectra of linear alkanes and is totally absent in alkanes with heavy branching because cleavage in branched is more favored. This molecular ion peak is due to loss of one electron which result very short lived two centered one electron bond is formed which simultaneously cleaved into its fragments. By loss n-pently group from the molecular ion, a carbocation is left behind which gave a base peak at m/z value of 57. A peak appeared at 85 is due to loss of n-propyl group from molecular ion peak. Similarly by losing n-butyl group, a peak appeared at m/z value of 71.

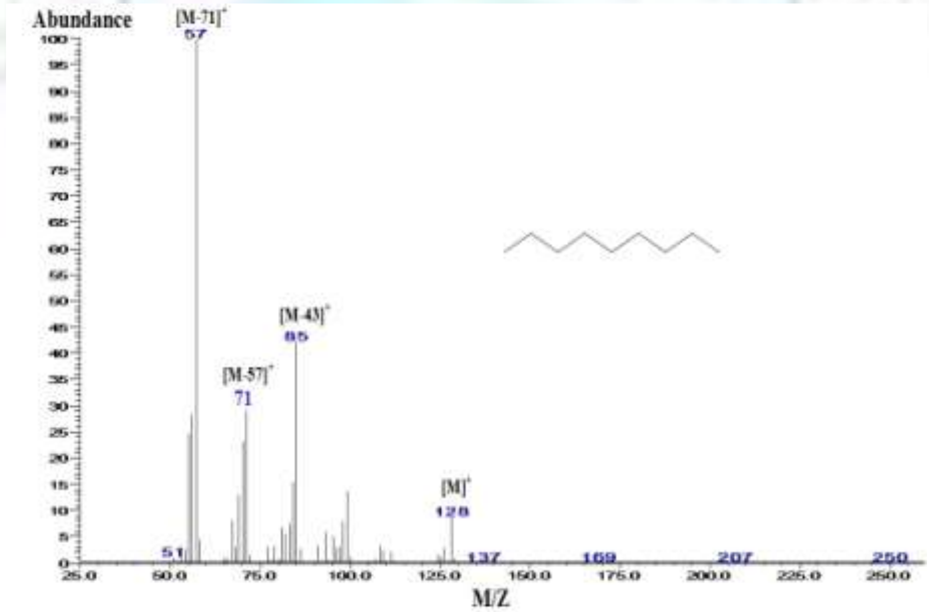

Figure 4. Mass spectrum of Nonane

Tetradecane

As the chain length increases the fragmentation of molecular ion become more favor. This is the reason that although this hydrocarbon is linear but yet the molecular ion peak is not present. There is a loss of propyl group from the molecular ion which result a peak at m/z value of 155 with a low intensity. This fragment losses (C_2H_4), (CH_2), 2 (C_2H_4) stepwise which leads the formation of peaks at m/z values of 127, 113, 85 and 57 respectively. The peak at m/z value of 57 represents the base peaks having maximum intensity.

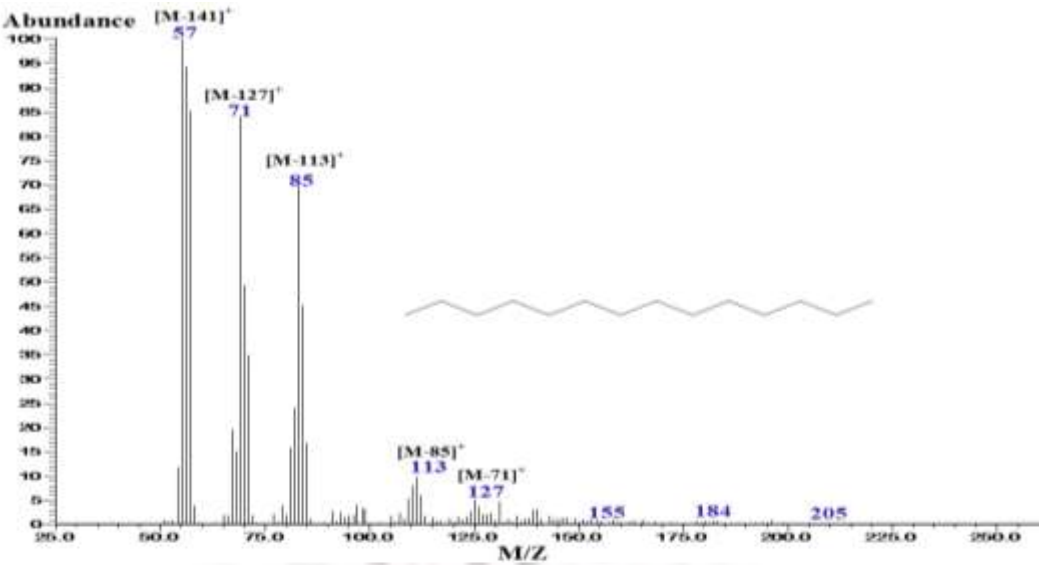

Figure 5. Mass spectrum of Tetradecane

2.2. Investigation of unsaturated hydrocarbons (Alkenes)

Nonene

The linear alkenes also give a molecular ion peak with very low intensity. The peak having m/z value of 126 represents the molecular ion peak. Just like in alkanes, fragmentation in branched alkenes is favored over in linear alkenes that's why molecular ion peak is absent in heavy branched alkenes. Here the presence of molecular ion peaks shows that this monounsaturated alkene is linear type. The molecular ion losses a propyl group which result the formation of carbocation having m/z value of 83 with the general formula of $[C_6H_{11}]$. The base peak which is appeared at m/z value of 56 is due to $[C_4H_8]^+$group which are formed by the loss of two groups simultaneously from the molecular ion. In the first step it loss an ethyl group and then a propenyl group.

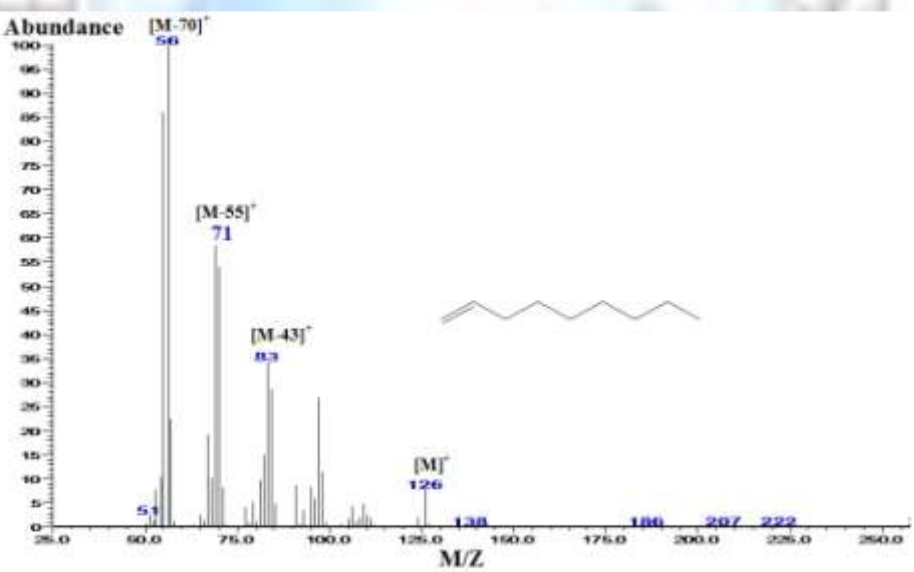

Figure 6. Mass spectrum of Nonene

Pentadecene

Here again the molecular ion peak is absent as the hydrocarbon chain length is long. The molecular ion immediately lose undecanyl group which result a base peak at m/z value of 55. The peak at m/z value of 83 is obtained by losing a nonyl group from the molecular ion. The peak which is appeared at m/z equal to 71 is obtained by the loss of decenyl group from the molecular ion. The other peak having m/z value of 111 appeared as a result of loss of heptyl group from molecular ion.

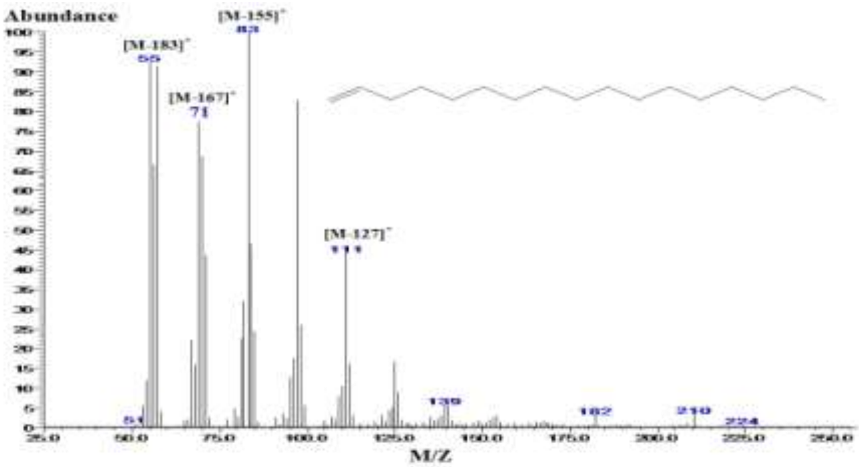

Figure 7. Mass spectrum of 1-pentadecene

Heptadecene

In the mass spectra of 1-heptadecene the peak at the m/z value of 55 is obtained as a result of loss of tridecanyl group from the molecular ion immediately as it is formed. By the loss of undecanyl group from the molecular ion, a peak having m/z value of 83 is appeared. The other peak at the m/z value of 111 is obtained by loss of nonyl group from the molecular ion.

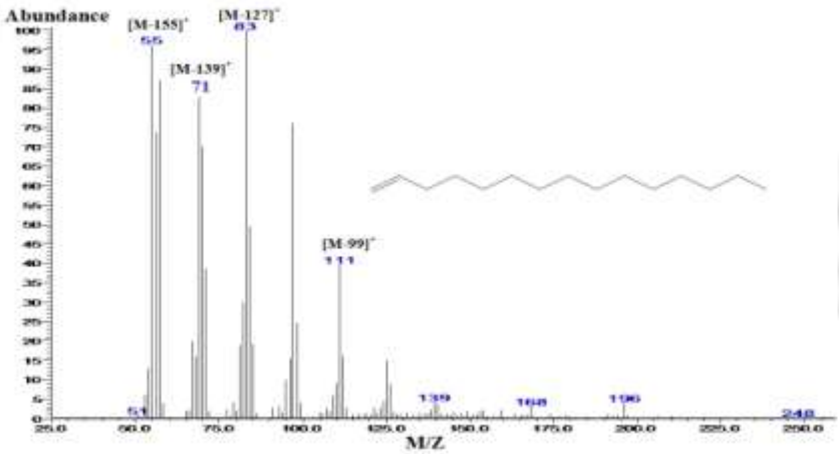

Figure 8. Mass spectrum of 1-heptadecene

3. Fuel properties of Diesel

Fuel properties diesel obtained from lubricating oil was carried out using of American Society for Testing & Materials (ASTM) methods and then results were compared with diesel standards (ASTM D975). **Table 3** shows results of diesel fuel along with the values that are recommended for for diesel standards (ASTM-D975). The characterization of fuels was carried out by their flash point, ash contents, kinematic viscosity, sulphur contents, cloud point, pour point, cetane number, density and acid value. Each of these parameters which define the quality of diesel is discussed individually in order to have a detailed discussion as given below:

Table 3: Fuel Properties of Waste Lubricating Oil Diesel

S. No	Fuel property	ASTM Method	Limit	Waste Lubricating Oil Diesel
1	Flash Point [^oC]	D-93	54 min	64
2	Kinematic Viscosity @40^oC,cSt	D-445	6.5 max	4.68
3	Density@15^oC,Kg/L	D-1298	0.94	0.8480
4	Sulphur Content	D-4294	1.0 max	0.452
5	Cloud Point [^oC]	D-2500	+6	-1
6	Pour Point [^oC]	D-97	+3	-9
7	Cetane Number	D-976	45 min	50

3.1. Flash Point

The flammability hazards of fuel in the presence of air are indicated by flash point. The measurement of flash point of fuel was carried out because this parameter is essential for handling, storage and safety purposes. Results showed that flash point of diesel was 64^{o}C which is higher than its limit. This higher value indicated that WLO diesel is safer than petroleum fuel because higher value of flash point shows its less volatility of diesel which makes it safer for transportation and storage. The results showed that flame hazards related with transportation, storage and utilization of diesel is much lesser than normally used fuels.

3.2. Kinematic Viscosity

Kinematic viscosity is another important property of fuel that shows the flow characteristics and controls the fuel atomization. The flow of fuel is affected by viscosity. Higher viscosity leads poorer atomization of fuel and unnecessary coking is which decreases the engine life. If the viscosity of fuel is lower then it will be easier to propel and atomize it and attainment of fine droplets. The fuel which has higher viscosity does not burn fully and deposits may be formed in fuel injector of diesel engine. So viscosity of fuels must be low. Results showed that viscosity of WLO diesel is within the limit.

3.3. Sulphur Content

The presence of sulphur content in the fuel has been associated with the negative effects. Diesel prepared from waste lubricating oil was almost free from sulphur and value of sulphur for WLO diesel was much less than the standard values. Therefore sulphur oxide would not be produced by the burning of these fuels and hence there would be no problems related with diesel so production of diesel is environmentally friendly.[17]

3.4. Cloud Point and Pour Point

Cloud point is the temperature at which cloud of wax crystals appeared in the oil when it is cooled while pour point is the minimum temperature at which fuel can flow. The values of pour point and cloud point of prepared diesel fall within the range of standards. It means that use of prepared fuels is suitable for high and moderate temperature climate.

3.5. Cetane Number

Another property of fuel is cetane number by which ignition quality of fuel can be measured. Ease of combustion and smoothness of combustion can also be measured by cetane number. Higher is the cetane number better will be the ignition property and there will be less occurrence of knocking. Various other parameters like noise, emission of CO and hydrocarbons and white smoke can also be affected by cetane number. The prepared diesel has a cetane number greater than its limiting values which shows a good indication of ignition quality and ultimately higher combustion efficiency.

3.6. Density

Another property of fuel is density which is important in the designing of fuel injection system. Greater mass delivery of fuel takes place due to higher density and hence larger consumption of fuel which is not favorable. Results showed that density of WLO diesel was less than its given limit which is favorable.

Conclusion

The used lubricating oil was converted into diesel fuel by the pyrolysis techniques in the presence of 2 wt.% zeolite catalyst. A round bottom flask was used as batch reactor and yield of about 85% was obtained. Highly viscous and bulky used lubricating oil was converted into saturated and unsaturated hydrocarbon with carbon chain ranging from C_9 to C_{27}. The FT-IR and GC-MS analyses confirmed the presence of saturated and unsaturated hydrocarbons. The fuel properties of the prepared diesel were investigated using ASTM methods and found within the standard limits. Hence, the prepared diesel is an excellent substitute of petro diesel and plays an important role to minimize the energy crisis in the world.

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