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Influence of Red Mud Catalyst in the Catalytic Fuel Reformer

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Abstract

The hazardous waste material such as Waste engine oil (WEO) and red mud is recycled in this study. WEO is thermally cracked with red mud catalyst in the catalytic fuel reformer (CFR). The gas obtained from the CFR is condensed using water cooled condenser for analyzing purpose. The output of the condenser is named as WEORM. The different chemical properties such as density, kinematic viscosity, flash and fire point and calorific value of WEORM are analyzed and compared with those of diesel fuel. The compositional analysis for diesel and WEORM was made using Fourier transform infrared (FT-IR) and gas chromatograph-mass spectra (GC-MS). The results of FT-IR and GC-MS of WEOA revealed that it was similar to fossil diesel fuel. Thus this study concludes that environmentally hazardous waste material such as waste engine oil and red mud is recycled and converted into a useful resource and serves as an alternative source of fuel for CI engine.

Keywords: Waste Engine Oil, Pyrolysis, Red mud, Catalyst, Hazardous, Fuel reformer

1. Introduction

Nowadays the internal combustion engines are spread to the extent that they represent the main cause of pollutant production. Nevertheless, it is well known that the stocks of fuels traditionally used in this kind of engines will be able to satisfy the world's needs for few more decades. This explains the massive research activity, drawn all over the world, addressed to the utilization of innovative fuels and injection concepts in order to either replace the traditional ones or obtain a more efficient and clean combustion. Compared to diesel engines, characterized by a high efficiency but at the same time high levels of particulate, and to premixed charge gasoline engines, characterized by a low efficiency because of knock limitations and pumping losses, lean burn engines can reach a higher efficiency thanks to lower pumping losses and heat transfer [1–5].

On the contrary, lean mixtures generally imply higher levels of both total unburned hydrocarbons (THC) and carbon monoxide. Nevertheless, mixing the fuel with an increasing quantity of air, flame instability, sometimes leading to misfiring, is observed. Hence extraction of alternative fuel from the waste material is one of the best suitable methods not only because of the clean environment and also to recycle the waste material into useful source of energy. With this is aim in mind waste engine oil (WEO) is selected as useful energy source in this study.

Worldwide annually about 40 million metric tons of lubricating oil are used in different sectors out of which major consumption is from the automobile sector. About 60% of the oils used in lubricating are generated as waste [6]. Used engine oil contains metals and heavy polycyclic aromatic hydrocarbons that could contribute to chronic hazards including mutagenicity and carcinogenicity [7,8]. According to USEPA, one litre of used engine oil is enough to contaminate one million gallon of fresh water [9]. Used engine oil also increases the pollution threats to humans, animals and vegetation [10, 11]. Prolonged exposure to high oil concentration may cause the development of liver or kidney disease, possible damage to the bone marrow and an increased risk of cancer [12, 13].

In India, the Ministry of Petroleum and Natural Gas, Government of India, in 2012-2013, statistics stated that crude oil production is about 37.882 MMT, in that lubrication oil production is about 896 TMT. Around 60% of the production becomes waste. Less than 45% of available waste oil was collected for recycling and the remaining 55% was either misused or discarded by the end user in the environment [14].

The main objective of the work is to convert the WEO into useful form of energy source for the combustion in diesel engine. The hazardous waste material red mud is used as catalyst to crack the WEO thermally in the catalytic fuel reformer (CFR).

2. Materials and methods

The CFR was used to convert the WEO into gaseous state. To know the suitability of utilizing this gas in the diesel engine, the reformed gas was condensed using water-cooled condenser and the liquid sample was collected for analyzing purpose.

2.1 Preparation of red mud catalysts

The red mud samples were collected from aluminium plants located in different sites in India. The red mud was introduced into the shaker. The shaker had three different sizes of sieves. It removed the core particles present in the red mud and the powder form of red mud was collected. The NaOH was added as the bonding material into the sieved red mud. Then the red mud was prepared in the form of pellets. The size of the pellets was approximately 20 to 30 mm in diameter. The pellets are subjected to heating in an oven to about 80^{o}C for a period of one hour. Then the dried pellets were allowed to cool at room temperature.

2.2 Compositional analysis

2.2.1 GC-MS

Liquid samples were dissolved in methanol and analyzed using GC-MS instrument (Varian-Saturn-2200 MS/MS). GC-MS was operated in a non-isothermal mode, ramping at 250^{o}C using a 30 m fused silica capillary column (cross linked 5% PH ME siloxane, I.D. 0.25 mm, film thickness 0.25 μm).

The total ion chromatogram produced for each sample was analyzed using Varian analysis software and the NIST mass library. The chromatograph integrator was programmed in two different modes, allowing the quantification of compounds by both species and size. In this way, GC-MS analysis was permitted the identification of the products and the classification of the sample by chain length. GC-MS was not calibrated for the individual compounds in the samples; hence, the compounds were quantified as total ion content percentage (TIC%) - an integration of the chromatogram's peaks.

2.2.2 FT-IR

A Bruker-Alpha FT-IR spectrometer with a resolution of ±1 cm^{-1} was used. Spectra were recorded at room temperature (298 K) in the region of 4000 to 400 cm^{-1} and NaCl cell of path length 0.1mm was used. The spectrometer possesses auto-align energy optimization and dynamically aligned interferometer. It was fitted with a KBr beam splitter, a DTGS-Detector and Everlgo™ mid-IR source. A baseline correction was made for the spectra recorded.

2.3 Properties

Some of the important fuel properties such as density, kinematic viscosity, flash point, fire point, calorific value and specific gravity were analyzed as per their respective ASTM methods.

2.4 Catalytic fuel reformer

A CFR was designed and fabricated with suitable dimension which would convert the WEO into hydrocarbon fuel. The reformer of the system is connected with a water cooled condenser to condense the reformulated gas. The schematic representation of the system is shown in figure 1.

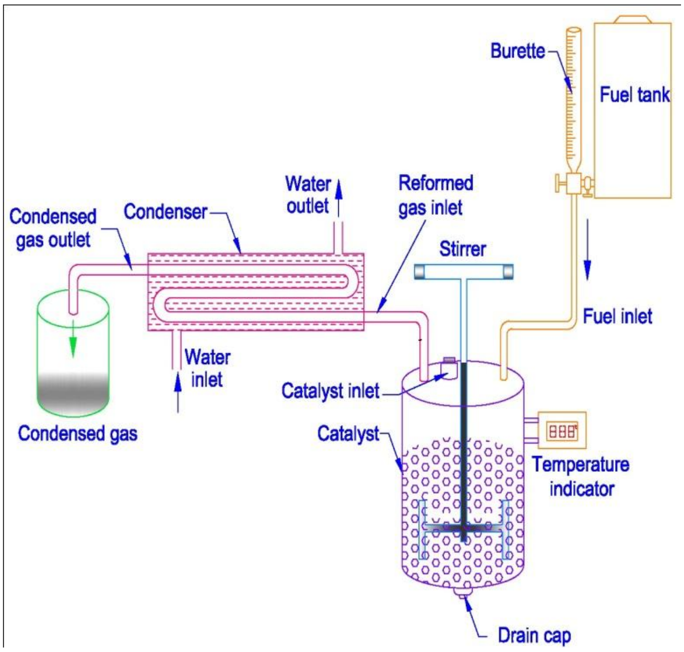

Figure 1. Catalytic fuel reformer

The system consists of several components such as fuel tank, control panel, reactor, thermocouple, stirrer, condenser and fuel storage tank. The fuel tank was used to supply WEO into the reactor. The reactor of the system had a cylindrical shape with an inner diameter of 15cm and a length of 45cm. The reactor was designed and fabricated to heat the WEO immersed with the catalyst. It includes an electrical heating unit which can be used to heat the WEO and catalyst to a temperature up to 1000^{o}C. The electrical heater panel consists of a resistance heater and a voltage control to adjust the heating rate. The heating control was performed by the control panel. The stirrer was used to mix the WEO with the catalyst uniformly and also to distribute the temperature uniformly. The temperature in the reactor was measured by a thermocouple. The condenser unit was used to condense the reformed gas which was collected at the end of the reactor. A water-cooled condenser was used to condense the reformed WEO gas.

3. Results and discussion

3.1 Fuel characterization

In this section, the different properties of the diesel fuel, fresh engine oil (FEO), WEO and WEORM are discussed. Fuel properties such as density, kinematic viscosity, flash point, fire point, calorific value and specific gravity were analyzed. The density was measured according to ASTM D1298 method, kinematic viscosity was measured according to ASTM D445 method, flash point and fire point were measured as per ASTM D93, calorific value was measured as per ASTM D5865 method, specific gravity was measured as per ASTM D1298 method and calorific value was measured as per ASTM D240. Some of the important properties of diesel fuel, FEO, WEO and WEORM are shown in table 1.

Table 1 Properties of Diesel, FEO, WEO, RM

Property	Diesel	FEO	WEO	WEORM
Specific gravity @ 27°C	0.8298	0.881	0.879	0.8312
Kinematic viscosity @40°C in CSt	2.57	85	52	1.65
Flash Point in°C	50	215	197	35
Fire Point in °C	56	-	-	37
Gross calorific value in MJ/kg	44.67	43.6	45.4	42.68
Density@15°C in gm/cc	0.8072	0.879	0.858	0.8121

The WEO showed a lower density but higher calorific value than that of the FEO. It is thought that some of the heavier hydrocarbons in FEO were decomposed into lighter hydrocarbons in WEO. The lower calorific value of the FEO was likely due to the presence of carbon and long-chain carbon compounds of lower calorific value in the oil matrix. The densities and viscosities of the WEORM were found to be lower than that of the WEO due to the cracking of heavy hydrocarbons to lighter compounds. The density of WEORM was quite close to that for diesel [15]. The flash point of the WEORM was found to be lower than that of diesel. The low flash points suggest that the unrefined WEORM contained components that have a lower boiling point range than diesel. WEORM possesses lower kinematic viscosity than that of diesel, since lower viscosity is desirable and represents a favorable feature when it comes in handling and transportation.

3.2 Chemical composition

WEO and WEORM are characterized by GC-MS. The results of GC-MS analysis are shown in figures 2 and 3. GC results show that the WEO containing C_8-C_{24} hydrocarbons was thermally cracked with red mud as the catalyst, comprising mainly C_{10}-C_{30} hydrocarbons with the presence of aliphatic hydrocarbons and aromatics. This shows that the cracking of compounds to produce some aromatic structures possibly derived from cyclization and aromatization reaction that occurred during thermal cracking.

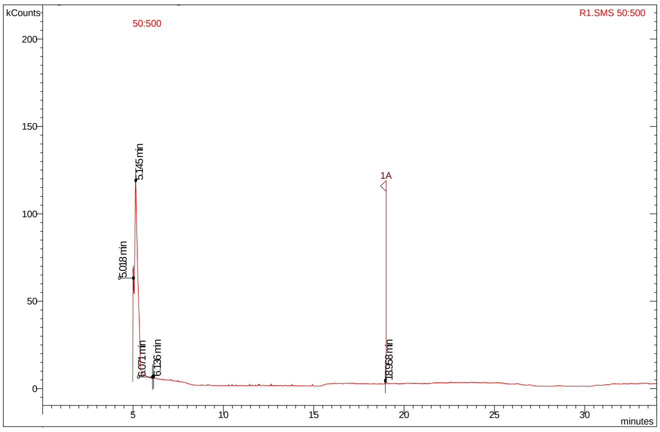

Figure 2. GC-MS of WEO

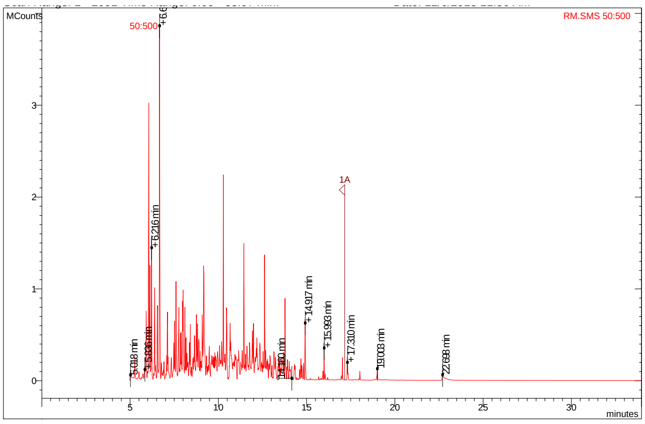

Figure 3. GC-MS of WEORM

Hence it is similar to diesel fuel, mainly containing paraffins, napthenes and aromatics. Aliphatic hydrocarbons are the most abundant component in WEORM. This indicates the cracking of WEO to small hydrocarbon components and heterogeneous reactions that occurred during thermal cracking process.

3.3 FT-IR analysis

FT-IR spectroscopy was used to identify the functional groups present in WEO and it can offer information regarding the chemical change of the functional groups which may play an important role in investigating the influence of catalyst with WEO. The representative FT-IR spectra of the diesel fuel and WEORM in the 4000–400 cm^{-1} wave number region are presented in figure 4.

The FT-IR spectrum reveals the presence of different functional groups. The two strong peaks observed at ~2921cm^{-1} and ~2853 cm^{-1} in the diesel fuel correspond to the asymmetric and symmetric stretching modes of C-H groups. These two strong bands indicate the presence of alkanes in the diesel fuel. The intense infrared bands observed at ~1460 cm^{-1} and ~728 cm^{-1} arise mainly from the C-H asymmetric bending and C-H out-of-plane bending, respectively, indicating the presence of alkanes. Further, the FT-IR spectra of WEORM showed the presence of bands similar to functional groups present in the diesel fuel. Hence, the FT-IR results confirmed that most of the hydrocarbons found in the WEORM are alkanes and thus has a potential to be used as an alternative fuel in the diesel engine.

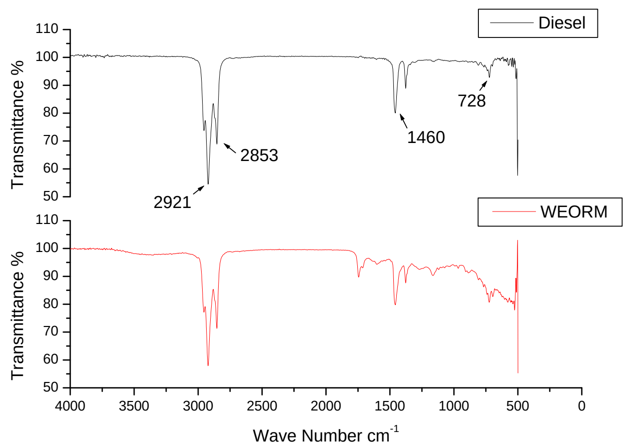

Figure 4. FTIR of Diesel and WEORM

4. Conclusion

In the present study, the suitability of using WEO as energy source for diesel engine was investigated. Dangerous hazardous materials such as WEO and red mud released into the environment and atmosphere were minimized by the way of utilizing these materials in this investigation. The collected WEO is allowed in to the CFR. Red mud ash is used as catalyst in the CFR. The reformulated gas from the CFR is condensed using condenser and the sample is analyzed. The properties of the oil obtained from CFR are tested and found to be close to that of the diesel fuel. The GC-MS results reveal that the heavier hydrocarbon present in the WEO is cracked into light hydrocarbon which is similar to that of diesel fuel. Similarly FT-IR results also confirmed that most of the hydrocarbons found in the WEORM are alkanes and thus have a potential to be used as alternate fuel in diesel engines.

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