

Iron-Zirconium Catalyzed Liquid Fuel from Used Engine Oil Doped With Activated Petroleum Coke

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Abstract:

Effective combustion-liquid fuel was prepared from used engine oil doped with activated petroleum coke and enhanced with a homogeneous combustion catalyst based on FeO₂/ZrO₂. The bi-metal catalyst was compared to nitrate salts of different metals of period 4 groups 4 through group 12. Steam activation of the coke at ≈ 950 °C improves the homogeneity of the components in terms of sediments. The calcium sulphonate 0.05-1 % by weight confirmed a good stability role. The obtained liquid fuel is smokeless with low ignition temperature and high calorific value. Results indicated that the fatty acid salts of iron/zirconium oxide (FeO₂/ZrO₂) are thermally stable and the fuel has a low viscosity. The Fe/Zr catalyst displays an effective combustion catalysis overweighing the metals nitrate. The prepared liquid fuel, catalyzed and stabilized with calcium sulphonate has a high calorific value of 56.8 MJ/kg and low ignition temperature (≈ 186 °C) with low cost.

Keywords:

Waste Engine Oil, Combustion, Bimetal Fe/Zr Catalyst, Liquid Fuel, Metal Nitrate

1. Introduction

The Institute of Petroleum [1] in the United Kingdom and the American Society for Testing and Materials [2] had put forward laboratory tests for fuels standard. In respect of the design of apparatus, experimental procedure, reporting of results, etc., by such bodies, as in the United States, the working details of the tests are published annually. The petroleum-based fuels are fairly closely related to each other in molecular structure. An interrelationship is found between the measured fuel properties, particularly those concerned with volatility. The six basic property tests have been selected and arranged in the following manner.

- a. Relative density (formerly specific gravity)
- b. Viscosity ‘
- a. The calorific value expressed as recovered heat pour point

- c. Pour point
- d. flash point (Spontaneous-ignition temperature)
- e. Vapour pressure

1.1. The Relative Density

The density of a liquid sample is defined as the mass of the sample occupying a unit volume at the stated temperature of 15 °C. The density of a liquid sample relative to that of pure water is thus derived as follows

$$\text{Relative density at } t_1/t_2 = \frac{\text{mass of a given volume of sample at } t_1}{\text{mass of an equal volume of distilled water at } t_2}$$

The relative density at t_2 is the mass of an equal volume of distilled water at t_2

$$\frac{\text{the density of the sample at } t_1}{\text{the density of distilled water at } t_2}$$

One value of the standard reference temperature t_2 is 60 °F. (4 °C). The density of water is unity; hence density and relative density of a sample then become numerically equal. Knowledge of relative density immediately gives a broad indication of the fuel type (for example, gasoline or gas oil) together with the mass appropriate to a given storage volume. For fuels of a known type, it serves as a general inspection check for the presence of contaminants. For the present study, however, relative density serves as a valuable basis for comparison of fuel properties generally and, for this reason, has been selected as the first property. Full conversion to SI units has not been affected in the drawing up of specifications, although a complete set of SI-type units has been recommended by the Institute of Petroleum [3]; hence two types of unit are used where appropriate. A comment is also made on the two current general trends in fuel testing towards miniaturization and automation.

1.2. The Calorific Value

The EP Patent 0946681, 1999 and Bureau of Mines estimation, US and Caines, [4] had reported that the calorific value of liquid fuel is the quantity of heat released upon combustion of a unit mass of fuel burned in oxygen under pressure at constant volume when the combustion products are cooled to the initial temperature of 25 °C. The initial temperature of the calorimeter is arranged to be about 2 °C below ambient. In practice, exhaust gases invariably leave the combustion chamber at high temperature, carrying the latent heat of water with them. The net calorific value = gross calorific value - 0.212 (H) MJ/kg where H is the mass per cent of hydrogen in the sample. appears as follows gross calorific value = 22 320- 3780 d 2 B. t. u / lb. (= 51.916- 8.792 d 2 MJ/kg). Where d = relative density at 60/60 °F. The A.P.I. gravity system permits the use of a linear scale on the hydrometer stem Values of this product range from about 4500 to 9000 over the range 42.5 to 44.0 MJ/kg.

1.3. Distillation

The initial boiling point of liquid fuel was reported to be the temperature determined at the fall of the first drop of condensate. The final boiling point is the maximum temperature reached during the test (Van den Neste et al [5]). The extent of the distillation range for any given fuel is representative of the availability of that

fuel from the parent crude oil. A maximum distillation temperature limit of 370 °C has to be conducted.

1.4. The Absolute Vapour Pressure

According to Burgoyne [6], the absolute vapour pressure of liquid fuel may be defined as the pressure exerted by the vapour above the free surface of the liquid at the given temperature. The standard Reid apparatus for this test is given by the bomb is heated in a water bath controlled thermostatically to 100 °F (37.8 °C). When equilibrium conditions have been established, the vapour pressure is read off the gauge, and corrections made for ambient pressure.

1.5. Flash Point

The adjunct of energy to molecules of liquid fuel permits them to escape from the free surface into the vapour-air mixture above. Consequently, a fuel concentration can be envisaged that eventually becomes sufficient to support combustion on the application of some source of ignition. The flashpoint of the fuel represents the weak mixture limit of flammability, and the fuel temperature at which it occurs is the weak temperature limit of flammability was reported by Bell [7]. Tests with variable mixtures of air and fuel vapour (in the absence of liquid) show that these mixture limits are roughly common (at about 1 per cent and 6 per cent by volume) to all the commercial fuels of interest in the petroleum liquid range. Several methods exist for the determination of flashpoint. All involve the controlled heating of the fuel sample in a standardized container, with the repeated addition of a standard-sized test flame to the vapour space until the appearance of a flame that flashes the available air-vapour mixture and then extinguishes. Flash point provides an indication of fire risk in storage under ambient conditions, and the Abel test was incorporated in the Petroleum Act of 1879 in view of the dangers of using low flash-point kerosene in lamps. The kerosene's are flammable at ambient temperature, whereas the gasoline is over ich [7].

1.6. Spontaneous-ignition Temperature (SIT)

The SIT of liquid fuel is the temperature to which the fuel must be heated in the presence of air to promote spontaneous ignition in the absence of spark. It was reported [8] that the test method involves an open heated flask into which a measured volume of sample is injected. A stop-watch is started at the instant of injection and is stopped on the appearance of ignition. The temperature of the flask is plotted against the reaction-delay period, and the test repeated at progressively reduced temperatures to determine the minimum level for ignition. Spontaneous ignition is a property in which liquid fuel and an oxidant mixture can be raised to a temperature above ambient in the absence of any concentrated source of ignition [9,10].

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1.7. The Viscosity

The resistance of molecules of liquid fuel to internal displacement and flow is termed the viscosity. Upon heating the liquid fuel, the molecules expand with temperature rise, intermolecular distances increase, and the viscosity falls. The kinematic viscosity (symbol ν) may be defined as the quotient of the dynamic viscosity and the density of the sample. Hence $\nu = \tau/\rho$, where ρ = the density of the sample. It may be measured as an 'absolute' property of the fuel. The direct measure of the kinematic viscosity in centistokes is $\nu = Ct - B/t$ eSt where C = the instrument calibration constant, B = the instrument type constant, depending on the capillary diameter, and t = efflux time in seconds and St is the stokes [11].

1.8. Mazut

Mazut fuel is the low-quality heavy fuel oil. It is categorized into 4 grades based on its sulfur content. The very low-sulfur type contains < 0.5% sulfur whereas the high-sulfur grade contains up to 3.5% [12], Oxford, 2019 [13], Mazut 1984, [14]. Beskoski et al. [15] showed that the biodegradation of mazut would occur during bioremediation when stimulated with zymogenous microorganisms. Aliev et al. [16] showed that the addition of $\leq 0.1\%$ pour depressant to the crude mazut lowered its solid point by 20-30 °C. The use of the pour depressant in the export and marine mazut released up to 10-15% of the diesel fuel cuts. The specifications of heavy fuel oil mazut M100 are given by RUSSIAN GOST 30582 [12] (density at 20 °C amounts to 870 Kg/m³, flash point 57 -62 °C, ash 0.01 % and total Sulphur amounts to 0.02- 0.05 % by weight).

1.9. The Used Engine Oil

Some countries are using spent motor oil to conceive plant boilers, industrial blast furnaces and/or cement kilns. It had been shown that spent diesel oil could be recovered from a dirty motor oil by heating it at a temperature suiting the best diesel quality (Belo Egyptian oil petroleum Environmental Co. 2019 [17]). The used engine oil may contain some toxic components referred to as technologically enhanced radioactive material (Chen et al. 2013 [18] and Apa. O, et al. 2010 [19] reported two techniques to recycle used engine oil using composite solvents made up of butanol-propane and butanone-propane. The authors reported that nearly 80-85% of used diesel oil would be reused for heavy machinery and boiler operation. Maceiras, et al. 2016 [20] studied the recovery of diesel oil from waste engine oil by frequent distillations. They concluded that the best results were undertaken after two successive distillations of the spent oil with 2% sodium carbonate. Taajuddeen and Umer 2019 [21] studied the recycling of used engine oil using the acid-clay method as a newly developed green technology approach. The authors showed that the best results were obtained with 2% of sodium carbonate in two successive distillations. They also disclosed that pyrolytic distillation of waste engine oil demonstrated an excellent way to recover diesel fuel for safe use in engines.

1.10. The Petroleum Coke

Petroleum coke is the raw material for the production of artificial electro-graphite, smelting and chemical industries. Low sulfur high-quality coke such as needle coke is used in the manufacture of ultrahigh power graphite electrodes and some special carbon products. Needle coke is an essential material for the development of new technology of electric arc furnace in the steelmaking industry. Medium sulphur ordinary coke is used in the aluminium refining process. High sulphur ordinary raw coke is used in the manufacture of calcium carbide, silicon carbide, etc. The petroleum coke produces active carbon by steam activation at about 950°C but the activated coke showed low surface area. The low-sulphur coke is mainly used for aluminium refining and graphite manufacturing industries. It is also used in the production of carbon products, such as graphite electrodes for non-ferrous metals, anode arcs for steelmaking and carbonized silicon products. The production of commodity calcium carbide for synthetic fibres, acetylene and other products. The graphite petroleum coke has carbon content 98-99.5% with sulphur content is 0.05-0.03%

1.11. Additives to the Used Engine Oil

The addition of organic compounds to the used engine oil aims to improve its properties. Some of the important additives are those used for controlling viscosity and lubricity such as N-methyl aniline and other traditional compounds [22]. The typical detergents additives are magnesium sulfonate. Antioxidant additives are usually added to retard the degradation of the oil stock by oxidation like organic amines and phenols. Metal deactivators or metal de-activating agents (MDA) are also mixed as oil additives to stabilize fluids. Fuels are desulfurized by copper sweetening.

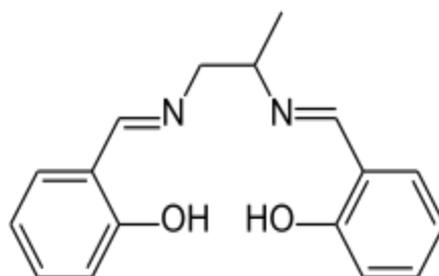


Figure 1. The chemical structure of N-methyl aniline.

Alkaline additives are also used to neutralize the acids and to prevent the formation of sulphates during working of the oil. Additives also may include magnesium and calcium sulphonate, salicylate, and phenate. The Total Base Number (TBN) in mg of KOH per gram of oil is a measure to estimate the alkalinity of the engine oil as declared in the following [23].

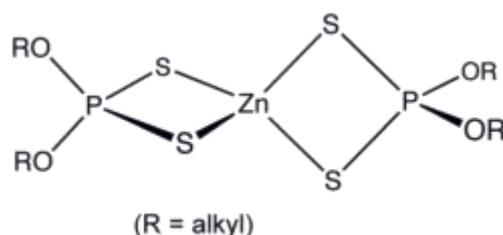


Figure 2. Total chemical structure of alkyl phenate of engine oil.

The aim of this work is to make use of the used engine oil to prepare liquid fuel having the properties complying with the standard specification. Along with such aim, the target includes increasing the calorific value of the liquid fuel in terms of heat recovery. This target has been investigated by doping the used engine oil with low-ranking petroleum coke either calcined or steam-activated. The reason for such a step is to enrich the components of the liquid fuel with a combustible and smokeless element like carbon. Other additives decreasing the liquid fuel viscosity, the flashpoint, the pour point, and the sediments upon storage for 6 months and the smokes purging during combustion were studied. Preliminary cost analysis was also considered.

2. Materials and Methods

2.1. The Used Engine Oil

About 50 kg sample of used engine oil of different types was collected randomly plus one fresh sample of each type. The used oil samples were kept for one week to allow any solid impurities to settle down by gravity. The solid contaminants-free samples were heated up to 120 °C in a Pyrex 6 L glass beaker while stirring to boil off any emulsified water. The collected sample was then contained in a clean plastic container and left for one month stagnant without any treatment before further process. Table 1 shows the chemical composition of the used engine oil.

Table 1 shows the chemical composition of the petroleum coke used in this work.

Table 1. Chemical composition of the petroleum coke used in this work.

| property | Green coke | Calcined coke | remarks |
|-------------------------|------------|---------------|---|
| Colour | Dark black | Light black | |
| Grain size, mm | <5 | >0.5 <1.8 | |
| Moisture content, wt. % | 0.8 max | 0.0 | Calcination at 950 °C under N ₂ gas atmosphere for 2 hours |
| Fixed carbon, wt. % | 89.88 | 92.57 | |
| Volatile matters, wt. % | 1.2 max | 0.0 | |
| Sulphur, wt. % | 6.17 | 5.98 | |
| Ash content, wt. % | 0.85 | 1.45 | |



Figure 3. Image of used and fresh oil sample.

2.2. The Petroleum Coke

A sample weighing 25 Kg of green petroleum coke was purchased from local supplier. It was examined visually to pick up foreign contaminants. The sample was steam-activated using a tube furnace type Nabertherm, R 120/500/13 Germany, max temperature up to 1300, fitted with an electronic control unit.

The coke sample was activated by steaming with super-heated steam at 950° in the tube furnace after connection to a superheat-steam generator for 2 hours. The activated coke was wet-milled in a ball mill for 6 hours to pass a mesh size of 10um. The undersize fraction was dried and used to dope the waste engine oil. The chemical properties of the activated coke are; fixed carbon 90.5 %, volatile matters 0.2%, max ash 6.5 %, sulphur 1.45 % and the residual is the moisture. Table 1 shows the chemical composition of the steam activated coke.

2.3. The Pour Depressant

Sulphonated compounds of calcium, potassium and ammonium are used as the pour dispersant. They were prepared by chemical reaction of pure sulphonic acid and the respective hydroxides at 75 °C for 3 h while stirring. The obtained sulphonate was used as a pour depressant. The prepared sulphonate compounds are transparent and colorless liquids readily homogeneous with the oil.



Figure 4. A photograph of the tube furnace used for steam activation of coke.

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| property | Green coke | activated coke | remarks |
|-------------------------|------------|----------------|--|
| Colour | black | Light black | Steam-activation at 950 °C under super-heated steam 18g H ₂ O/ 100 g coke 2 hours |
| Grain size, mm | <5 mm | >0.5 <1.8 mm | |
| Moisture content, wt. % | 0.8 max | 2.0 | |
| Fixed carbon, wt. % | 89.88 | 89.57 | |
| Volatile matters, wt. % | 1.2 max | 0.0 | |
| Sulphur , wt. % | 6.17 | 4.98 | |
| Ash content, wt. % | 0.85 | 5.45 | |

Preparation of iron-based Fe/Zr catalyst for fuel combustion:

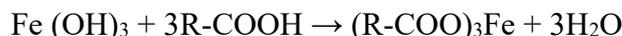
A new group of metallic catalysts dissolved in an organic solvent will allow their introduction to the liquid fuel, thus enabling significant reduction of the emission of pollutants from local sources [24]. In this study, two compounds were comparatively tested as a catalyst for combustion. The first was copper nitrate. The second was iron-based zirconium metals (FeO₂/ZrO₂). The combustion catalytic activity of the two catalysts was investigated. The preparation procedure of the iron-zirconium catalyst was as follows.

a. Ferrous sulphate (pickling liqueur) was obtained from Iron and Steel Co. Helwan. Egypt. ZrO₂ was obtained from broken zirconia brick (used for lining the inner walls of sodium glass fusing furnace, Lo'oloaa Co. at 6th October City, Cairo Egypt).

- a. The block was crushed and ground in a ball mill to pass 10 um mesh size.
- b. The powdered Zr oxide was reacted with 100% nitric acid for one week.

c. The obtained acidic nitrate salts was filtered and neutralized with urea to a pH of 6.7.

d. The synthesis of an iron-based catalyst proceeds according to the two successive reactions:



Iron (III) hydroxide obtained in reaction I was filtered and reacted with thall oil (Palmitic 36%, oleic 32% and linoleic 23%) acids dissolved in fuel oil. The Fe–Zr precursors with $\text{Fe}_2\text{O}_3/\text{ZrO}_2$ molar ratio of 5 : 1, 3 : 1 and 1 : 1 were prepared by the microwave-hydrothermal method described by Tic [24] using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ as raw materials.

The metallic catalysts were obtained from water-soluble salts of Fe^{3+} and Zr^{3+} . In reaction (I), ammonia water was added to a solution obtained by dissolving in water either iron(II) sulphate monohydrate or a mixture of iron(III) sulphate monohydrate and zirconium (III) nitrate hexahydrate. A solution obtained by dissolving thall oil in fuel oil was added to the resulting solution. The mixture was heated at about 80°C for 5 hrs. while stirring vigorously. When the reaction was complete, the organic phase was separated from the aqueous one by centrifuge. The organic phase is the catalyst

2.4. Description of the Method for the Preparation of the Targeted Liquid Fuel

Figure 5 shows the sequential experimental flow sheet applied for the preparation of the liquid fuel.

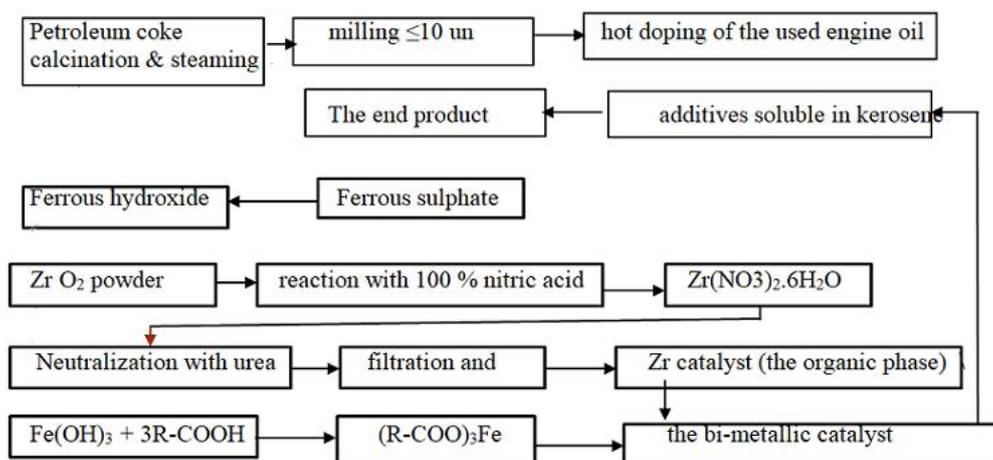


Figure 5. Sequential experimental flow sheet applied for the preparation of the Fe-base catalyst.

2.5 Methods of Measurement of the Physicochemical PROPERTIES

The standard analytical methods are used to determine the physicochemical properties are as follows.

Density @15 °C, test method: ASTM D1298

Atmospheric distillation, test method: ASTM D86. Apparatus: D86 – atmospheric distillation unit (batch unit) with thermometer (400°C) and receiving flask.

Viscosity at 40°C and 100°C , test method: ASTM D 445-06.

Flash point, test method: ASTM D 93 – 02.

Pour point: test Method: ASTM D97.

Total base number, test method: ASTM D4739.

3. Results and Discussion

The TGA study of the green coke as a function of temperature under a nitrogen atmosphere and the weight change upon steaming for 30 minutes were carried out. The TGA curve displays three horizontal segments. The segments are seen at $>100 < 300$ °C, $>400 < 600$ °C and $>800 < 950$ °C. The apparent density of the coke calcined at 1200 °C is 1.34 g/cm³. The calcined coke was then activated at 950 °C using a superheated steam flowing at a rate of 18 g steam/h/100 g coke. The activation process was executed for 2 h. Figure 6 shows a linear relationship curve with a slope of 0.544 % carbon loss / 10 °C. The maximum surface area amounts to 460 m²/g.

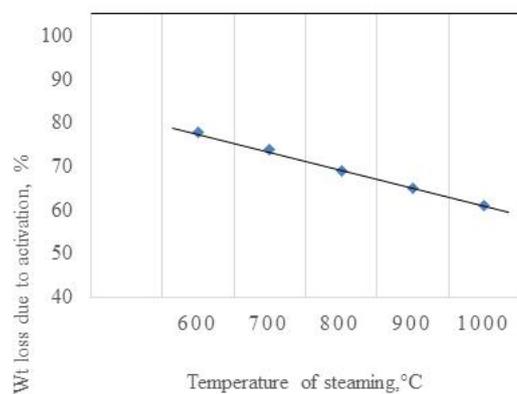


Figure 6. Effect of steaming temperature on the weight loss of coke.

Figure 7 shows the viscosity of the used engine oil measured at room temperature, as affected by doping of 10 μ m of the calcined and activated petroleum coke particles. The initial viscosity value amounts to 119 cP. The viscosity increases with the increase of the weight percentage of the doped petroleum coke up to 32 % to 154 cP. Doping with the activated coke, the viscosity only slightly increases to 126 cP.

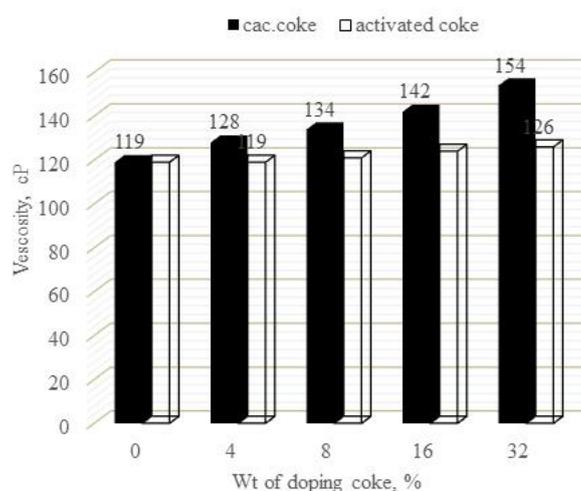


Figure 7. Viscosity of the spent engine oil as affected by doping petroleum coke.

Figure 8a shows the effect of adding nitrate salts of different metals as a catalyst on the viscosity of the ised engine oil free of petroleum coke and the oil doped with

calcined and activated coke. It can be seen that addition of the Fe/Zr catalyst up to ≥ 0.5 percent decreases the viscosity of the liquid fuel.

Figure 8a, b shows the effect of using nitrate salts (Figure 8a) and Fe/Zr as catalysts on the viscosity of the liquid fuel free of petroleum coke and doped with calcined and activated coke. It can be seen that the copper nitrate is an active material decreasing the viscosity of the liquid fuel. The decreasing effect of the tested nitrate salts is in the order Cu, Fe, Co, Cr, Ti, Ni, Zn, V and Mn. Comparative results of using the Fe/Zr catalyst to the activated coke-doped liquid fuel have a marked effect decreasing the viscosity of the liquid fuel.

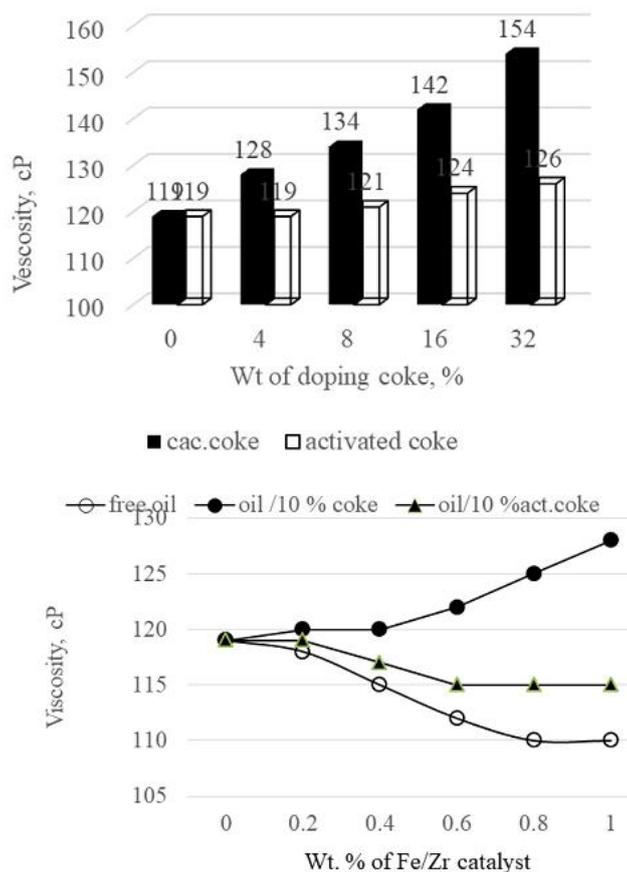
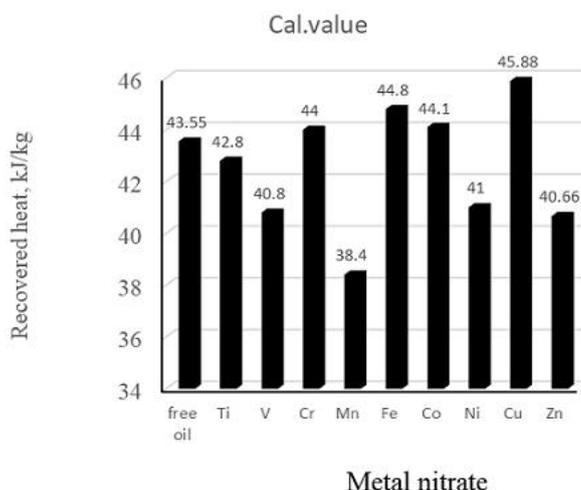


Figure 8. The catalytic effect of metals nitrate (8a) and bi-metallic Fe/Zr on the viscosity of the liquid fuel.



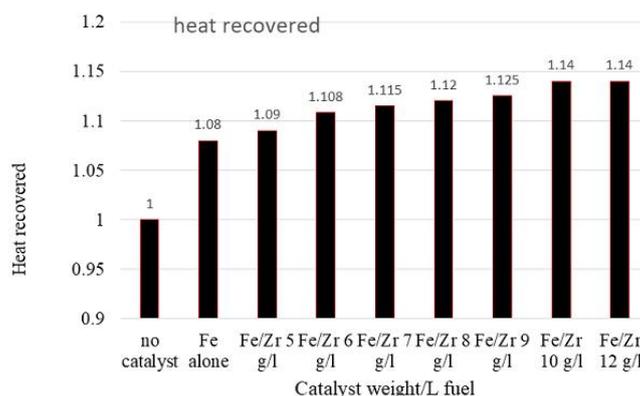


Figure 9. a, b. The effect of nitrate and bimetal catalysts on combustion in terms of heat recover.

Figure 9a, b shows the effect of catalysts on combustion in terms of heat recovery. It is shown that the heat recovery value of the liquid fuel as affected by using of 0.5 % nitrate salt of some metals in period 4 of groups 4 through group 12 (Figure 9a). The analogous results using bimetal Fe/Zr catalyst are given in Fig. 5b. It is seen that the heat recovery decreases in the order Cu, Fe, Co, Cr, Ti, Ni, Zn, V and Mn. The application of Fe/Zr catalyst on the heat recovery of the liquid fuel (Figure 4b) shows that the catalyst improves the extent of heat recovery by 14 % with 1 g/l fuel.

Figure 10 shows the effect of doping calcined and activated petroleum coke up to 20 Wt. % on the pour point of the liquid fuel. It is seen that the calcined coke increases the pour point from -32 °C to +10 °C and +14 °C with 5% and 10% od doped calcined coke. The corresponding values obtained with activated coke are +4 °C and + 7 °C respectively.

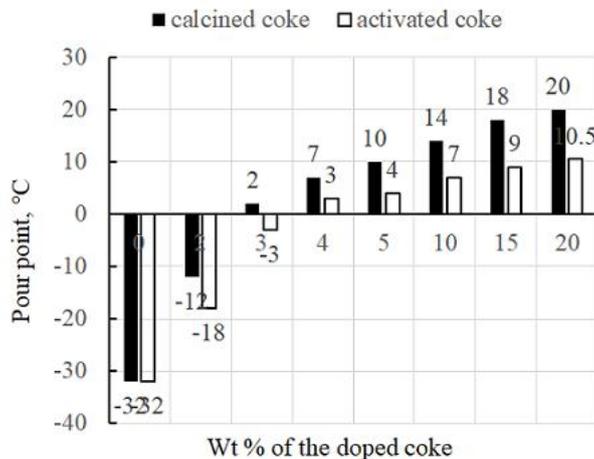


Figure 10. Effect of doping calcined and activated petroleum coke up to 20 Wt. %.

Figure 11 shows the effect od addition of some nitrate catalyst of different metals as well as the bimetal Fe/Zr catalyst on the pour point of the liquid fuel. It can be seen that the addition of catalyst – in general- increases the pour point of the liquid fuel to an extent that decreases in the order doped-coke, nitrate salts and bimetal Fe/Zr. For one and the same catalyst, the decreasing effect is highly related to the weight percent added.

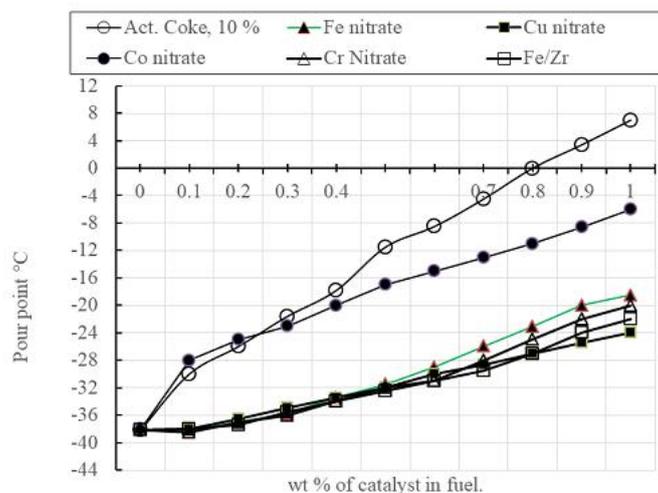


Figure 11. Effect of using nitrate salts of some metals and bimetal Fe/Zr catalysts on the pour point of the liquid fuel.

Figure 12a, b shows the flash point of the liquid fuel as affected by doping petroleum coke. It is seen that the initial flash point (238 °C) increases with increasing the percentage of the doped calcined coke (248 °C). Such effect becomes less pronounced with the use of activated coke (242 °C (with 8 Wt. % coke)). Bimetal Fe/Zr catalyst decreases the flash point to a lower value (205 °C)

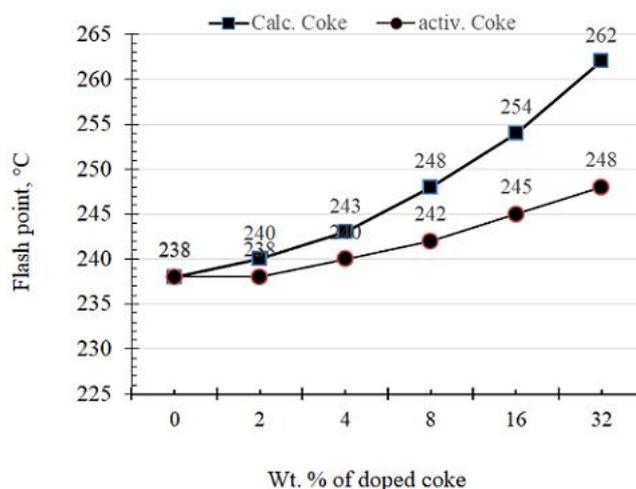


Figure 12a. The effect of doping coke on the flash point of the liquid fuel.

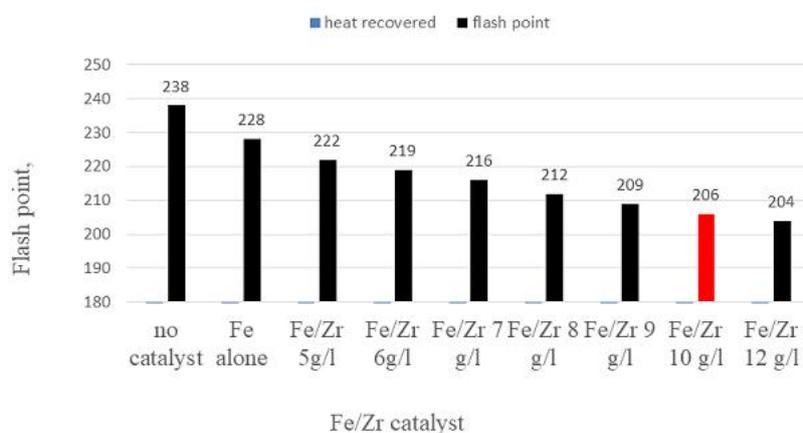


Figure 12b. The flash point of the liquid fuel as affected by addition of bimetal Fe/ Zr catalyst.

Figure 13 shows that the flash point of the liquid fuel decreases upon diluting with kerosene oil down to 222 °C and 204 °C with 10 wt. % and 20 Wt. % kerosene respectively. The flashpoint of the liquid fuel gradually decreases approaching that of pure kerosene. (59 °C) with further addition of kerosene.

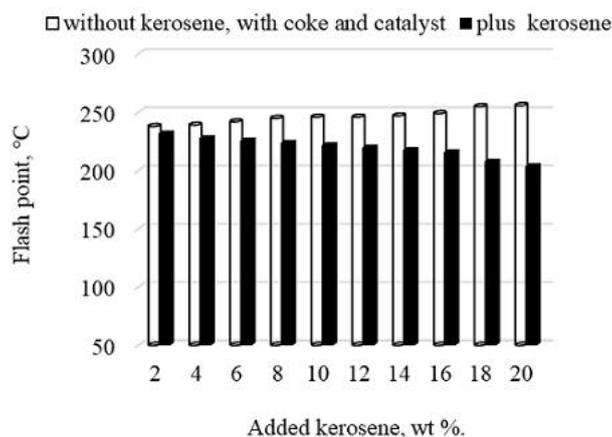


Figure 13. The flash point of the liquid fuel as a function of diluting with kerosene oil.

Figure 14 shows the the effect of using calcium sulphonate as a stabilizing agent on the stability of the coke-doprf liquid fuel in terms of the extent of solid sedement taking place upon storage of the liquid fuel stagnant for 6 months. It is seen that blending of the liquid fuel regularly decreases the weight of sediments with the increase of the blended calcium sulphonate. Addition of 5-6 wt per cent of calcium sulphonate improves the fuel stability so that only 2 % of the sedement was traced back.

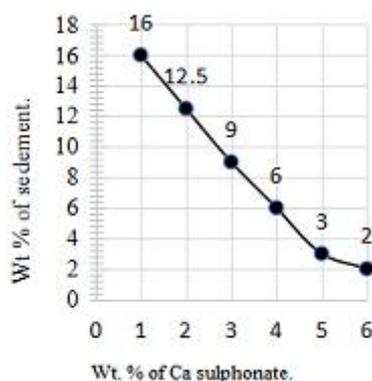


Figure 14. Effect of calcium sulphonate on the stability of the liquid fuel.

4. Discussion

Motor oil is the distilled product obtained from petroleum-based and not-petroleum-synthesized chemical compounds. Most motor oils are made from a heavier, thicker petroleum hydrocarbon base stock derived from crude oil, with some additives to improve certain properties [24,25]. The used engine oil, or engine lubricant is any of various substances comprising base oils enhanced with various additives. Anti-wear additive(s) in addition to detergents, dispersants and viscosity index improvers are also used. Typical engine oil properties are given in Table 2 [26,27].

Table 2. Typical engine oil properties.

| Test` | value |
|-------------------------------|-------|
| Kinematic viscosity at 40 °C | 12.9 |
| Kinematic viscosity at 100 °C | 2.91 |
| Flashpoint, °C | 82 |
| Pour point, °C | -7 |
| Density, g/cm ³ | 0.900 |

The waste engine oil may contain some inclusions as shown in Table 3 [17,18].

Table 3. Specific gravity of things found in waste oil.

| Material | Sp. Gr/cm3 |
|--------------------------------|------------|
| Oil | 0.88 |
| Water | 1.00 |
| Propylene Glycol | 1.036 |
| Brake Fluid | 1.05 |
| Ethylene Glycol | 1.10 |
| Glycerol | 1.129 |
| Calcium* | 1.55 |
| Magnesium* | 1.738 |
| Zinc dialkyl di-thio-phosphate | 1.60 |
| Teflon* | 2.20 |
| Iron | 7.85 |
| Copper | 8.96 |
| Lead | 11.35 |

*oil additives, anti-friction, detergents or anti corrosives

These inclusions that discourage the use of spent engine oil for heating a broad scope area of application and therefore decrease its price as well [29,30]. It becomes legitimate to investigate possible challenges to make use of the used engine oil and maximize its benefits of preparing useful product(s). Such aim may help to remove the hazards of depleting mineral resources of petroleum distillates. The disadvantages of using spent engine oil for heating objectives are because of the undesirable combustion products when the spent oil is used as it is. Combustion of this oil would proceed in a multi-step sequence as follows.

- a. Heating the oil up to its boiling point
- b. Latent heat to convert the boiling oil to a vapour
- c. Heating the vapour reaching the flash point
- d. Catching fire of the hot vapour in the presence of sufficient atmospheric oxygen
- e. Heat transfers from the flame vicinity to the unburnt oil vapour by radiation and partly by convection.
- f. Efficient removal of the combustion products especially the solid carbon particles away to allow new air diffusing to the oil vapour to keep the flame propagation.

Step (c) may be the rate-determining step to keep the flame glowing whereas the insufficiency of step (e) may smother the heat energy from igniting the hot vapour of the oil and the so-called self-distinguish phenomenon of the flame would take place.

The use of activated petroleum coke to enrich the engine oil with carbon content has its background on that the combustion of the coke is a smoke-free material with a good calorific value to avoid the self-distinguish phenomenon. The added coke should be freed from incombustible ingredients. For this reason, calcination of the coke would be done before doping to inhibit inflammable volatiles and densify the coke fines. In this context, activation of coke allows the coke particles having larger surface area to help adsorption of the oxidizing agent (atmospheric oxygen) enhancing combustion reactions to propagate.

The purpose of the use of combustion catalysts like metals nitrate or base-iron bimetal Fe/Zr or organic compounds such as hydrocarbonyl succinimide and hydrocarbonyl amine or a combination of the hydrocarbonyl amine and N, N'-disalicylidene-1,2-di-amino-propane is to enhance steps (d) and (e) of the suggested combustion model given above.

The visibility of any combustion catalyst is based on its power to enhance the fuel ignition process. In this work, the selected catalyst materials are distinguished to decreasing the flash point of the liquid fuel. The tested materials perform rapid ignition at low temperatures by catalyzing step (c) of the suggested combustion model. In this context, metal nitrate and bimetal Fe/Zr compounds are highly recommended. The choice of the nitrate salt of different metals of period 4 groups 4 through group 12 has its background of their atomic configuration. All these metals have two electrons in the outmost S-shell as follows:

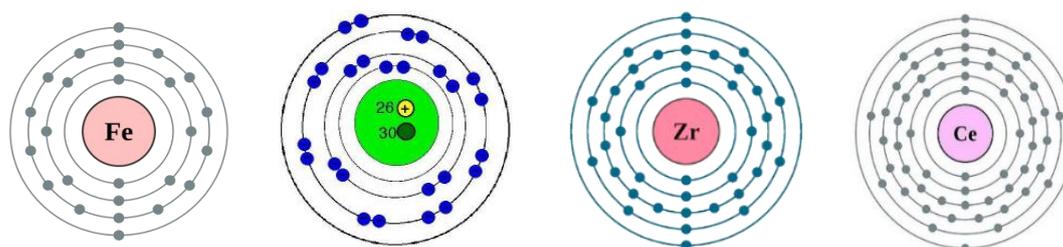
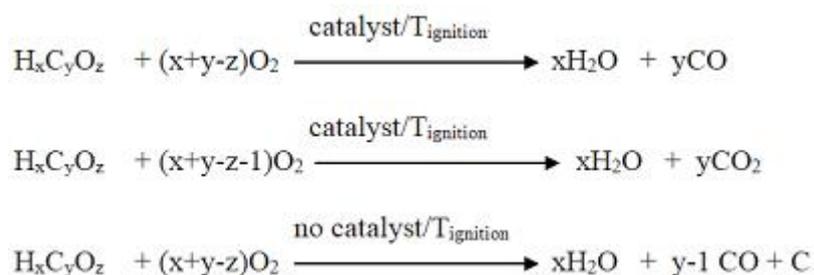


Figure 15. The atomic configuration of Fe, Sr, Zr and Ce elements.

The two electrons in the outer S shell help coordination with the atmospheric oxygen atom and easily donate to the reacting hydrocarbon compounds in the liquid fuel to release water and CO or CO₂ according to equations 3-5.



Iron-base bimetal catalyst enhances combustion according to equation 3. Inferior catalysts undergo combustion according to equation 4 and partly according to equation 5.

The combustion products would indicate the efficiency of the catalyst to carry out the combustion process according to any of these equations. The catalytic efficiency decreases in the order Fe/Zr, Cu, Fe, Co, Cr, Ti, Ni, Zn, V and Mn. The weight per cent of copper nitrate added to the liquid fuel oil showed that <10 % by weight is the

proper percentage to achieve convenient ignition extent. However, organic compounds of hydrocarbyl succinimide and hydrocarbyl amine or a combination of the hydrocarbyl amine and N, N'-disalicylidene-1,2-di-amino-propane are found less-active combustion catalyst.



Figure 16. Image of smokes purging from incomplete combustion of fuel.

Doping with activated carbon coke and the addition of combustion catalyst such as bimetal Fe/Zr or copper nitrate to the used engine oil decreases the viscosity of the liquid fuel. This effect was ascribed to the marked capacity of the coke to adsorb high-molecular weight hydrocarbons in the liquid fuel. In contrary, doping of calcined coke increases the viscosity of the liquid fuel because coke is immiscible in the oil without any adsorption activity. Such disadvantage was partially modified by diluting of the viscous fuel with kerosene oil. The role displayed by kerosene addition is to modify the overall vapour pressure of the fuel [19]. The vapour pressure of kerosene amounts to 0.7 kPa as compared to heptane, 6 kPa, and hexane, 17.6 kPa. Kerosene is the light flammable oil. Above 37°C explosive vapour/air mixtures may be formed. [28,31,32]. Results revealed that the characteristics of the prepared liquid fuel highly recommend it be acceptable fuel with a good pour point, flash point and stability for storage for long times. A preliminary cost study was carried out. The price of the prepared liquid fuel is competitive to the price of mineral fuel. Preliminary cost study revealed that the production cost of one barrel of the prepared liquid fuel amounts to \$ 15.5 as compared to \$42.8 for the fuel oil obtained from the petroleum refinery enterprise.

5. Conclusion

The conclusion of this research is that liquid fuel has been prepared from used engine oil, fine particles of activated petroleum coke, bimetal Fe/Zr catalyst, calcium sulphonate and diluted with kerosene oil has proved a convenient liquid fuel for heating purposes. The used engine oil is a recurring mineral and has a little reuse possibility as it is. This limited reuse is because of its inclusions of degraded organic lubricating compounds besides the metals fines that resulted from the mechanical wear of the contacting articles. This work has proved that liquid fuel prepared from the used engine oil by doping with activated petroleum coke fines and some other additives is a convenient fuel for heating purposes. The characteristics of the prepared liquid fuel showed that it has high calorific value, good pouring point, convenient flashpoint, smoke less with low price as compared to similar fuel obtained from mineral petroleum refinery enterprises.

Conflicts of Interest

The author declares that there is no conflict of interest regarding the publication of this article.

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