

An Investigation into The KSA Environmental Safety using The Novel Microwave Pyrolysis for Recycling Waste Engines Oil

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ABSTRACT

Used automotive engine oil was treated using a microwave-induced pyrolysis process, with the intention of assessing the suitability of the process in recovering valuable products and investigating the characteristics of the pyrolysis oils i.e. elemental analysis, hydrocarbon composition, and potential fuel properties. The microwave-heated pyrolysis fuel properties (e.g. density, calorific value and kinematic viscosity) are compared to both waste and fresh oils. Examination of the composition of the oils showed the formation of light aliphatic and aromatic hydrocarbons that could also be used as a chemical feedstock. Our results indicate that microwave- heated pyrolysis shows exceptional promise as a means for recycling and treating problematic waste oil. The effect of the microwave power on the pyrolysis temperature is carried out and investigated at different test periods. The chemical composition of the pyrolysis products (liquid oil and gas) were analyzed using gas chromatography/mass spectrometry (GC/MS). The effects of both N₂ and waste oil flow rates on pyrolysis products of C, H₂, O₂, N₂ and S are obtained and compared with that of fresh and waste oils. The effect of pyrolysis temperatures on the pyrolysis calorific values of pyrolysis oil gases, liquids and solids masses are obtained and compared with the fresh oil. The calorific value of the pyrolysis gases and liquids constituents are estimated and compared.

1. INTRODUCTION

All nations have been confronted with the energy crisis due to depletion of finite fossil fuels reserves. Waste oils pose a very serious environment challenge because of their disposal problems all over the world. Waste oils are currently receiving renewed interest. The properties of the oil derived from waste plastics, cooking and engines oils were analyzed and compared with the petroleum products and found that it has properties similar to that of diesel[1-2]. Nasim et al. [3], focused on finding alternative new energy resources and utilizing them. Lam et al. [4], possessed a significant treatment and

disposal problem for modern society. Treatment of waste has become one of the central problems of our age, as traditional waste repositories, such as landfills and ocean dumpsites, become less and less available, [5-7]. Abo-Dief and El-Shamy [8] improved petroleum oil quality using nonionic surfactants and studies their inhibition effect on mild steel pipeline. Sharaf et al. [9], showed that the used engine oils can be used in engine as engine oil after purifying it. Conesa et al. [10], compared between different emission rates of various pollutants obtained from various wastes. Sarkar et al. [11] practiced to remove the pollutants from waste oil.

Omer [12], deduced that dependence upon oil and this will continue for a few more decades. Hamawand et al. [13], recycled waste engine oils using acetic acid. Ogbeide et al. [14] and Abo-Dief and Mohamed [15], identified a unique method by which the spent oil is adequately recycled for reuse. Emam and Shoaib [16], re-refined base oil characteristics using solvent extraction have a slight difference, compared to the virgin oil and the Egyptian standard. Wongkhorsub and Chindaprasert [17] discussed the current status of pyrolysis technology and its potential for commercial applications for bio-fuel production. Manasomboonphan and Junyapoon [18], described a comparison of the use of pyrolysis oils which are the tire pyrolysis oil, plastic pyrolysis oil and diesel oil in the assessment of engine performance, and feasibility analysis. Rasul and Jahirul [19] paralyzed Waste lube oil in a batch stirred bed reactor using heat at different temperatures under vacuum. Lam et al. [20] discussed status of pyrolysis technology and its potential for commercial applications for bio-fuel production. Lam et al. [21], investigated the characteristics of the pyrolysis oils produced from microwave-heated-pyrolysis of wasted oil. Jamjumras and Amornraksa [22], indicated that microwave pyrolysis shows extreme promise as a means for disposing of problematic waste oil. Abo-Dief et al. [23] and Ashraf and Abo-Dief [24], discussed the effect of three sulphur compounds on white technical oil as a corrosion medium. The aim of the present work is the analyzing of the chemical composition of the pyrolysis products (liquid oil and gas) using gas chromatography/mass spectrometry (GC/MS). The effects of both N_2 and waste oil flow rates on pyrolysis products of C, H_2 , O_2 , N_2 and S are obtained and compared with that of fresh and waste oils. The effect of pyrolysis temperatures on the pyrolysis calorific values of pyrolysis oil gases, liquids and solids masses are obtained and compared with the fresh oil. The calorific value of the pyrolysis gases and liquids constituents are estimated and compared.

2. EXPERIMENTAL WORK

The oil was collected from a Daihatsu Grand Terious car oil change after 4000 km in use. The type of base oil used in this study is GULF MAX API SL (SAE 10W-30), run on unleaded fuel in Albaha, KSA. The present work based on comparison of that used oil and pyrolysis oil shown in Fig. 1. The experiment was carried out with heating the oils collected to a temperature of over 250 °C for one hour, for the purpose of evaporating the water and the volatile substances in the used oil. The oil was then cooled to room temperature (16°C, winter) and then equal amounts of this oil (10 mL) were added to a

number of beakers. Before pyrolysis, the waste oil samples were filtered such that the size of any remaining particulates (i.e. metal particles, carbon soot's, and other impurities) were less than 100 µm. Microwave-heated pyrolysis of waste oil device and principles are described in our work, [2]. All the pyrolysis experiments were repeated several times and the data recorded is the average of the results obtained from three valid repeated runs performed under identical conditions. The fresh oil (FO), the waste oil, and the pyrolysis oils were examined for hydrocarbon composition by gas chromatography coupled with a mass selective spectrometry detector and a flame ionization detector. The oil samples were also analyzed by Fourier Transform Infrared Spectroscopy and elemental analyzer to identify their chemical functional group and elemental content (C, H, N, S, and O). In addition, the fuel properties of the oil samples (i.e. calorific value) was determined. The temperature of the carbon bed in the system was carried out using two thermocouples; one ducted into the middle layer of the carbon bed through the center of the shaft that protrudes from the bottom of the stainless steel stirrer shaft, the other enters the reaction chamber through a side port on the top of the reactor and is positioned at the top of the carbon bed. Later, the pyrolysis products were analyzed by gas chromatography mass spectroscopy (GC-MS) to identify their chemical composition. The GC-MS was not calibrated for the individual compounds in the samples; the compounds are quantified as total ion content percentage (TIC%) - an integration of the chromatogram's peaks. The estimated calorific value was calculated based on the TIC%, GCV and gas or liquid hydrocarbon product yield, i.e.;

$$\text{The estimated calorific value} = (\text{TIC\%} \times \text{GCV} \times \text{gas or liquid yield}) / 100.$$

Where; GCV is the gross calorific value of compound obtained from NIST Chemistry Web Book.



(a) Waste oil.



(b) Pyrolysis oil.

Fig. 1. Microwave pyrolysis and waste oils.

3. RESULTS and DISCUSSIONS

3. 1. Effect of Microwave Power

The effect of temperature on the activated carbon under microwave power of 200, 400, 600, 800, 1000, and 1200 Watts at different test periods are shown in Fig. 2. It can be seen that, in the most cases, the temperature increased rapidly during the first 5 minutes and the temperatures were relatively stable after 10 minute. Also, the target operating temperatures of about 600, 800 and 1000 ° C were easily achieved in 10 minute under 600, 800, and 1000 W, respectively. The stability and reproducibility of temperature profile were also obtained under those microwave power. After 10 minutes of reaction, there was almost no significant change in the temperature. Therefore, the experiment results obtained under microwave power of 400, 600, and 800 W for operating temperature 600,700 and 800°C were primarily selected.

3. 2. Effect of Waste oil and N₂ Flow Rate on the Oil Properties

The oil products derived from microwave-heated pyrolysis were examined and compared for both waste and fresh oils properties as shown in Fig. 3. The pyrolysis oil shows a low

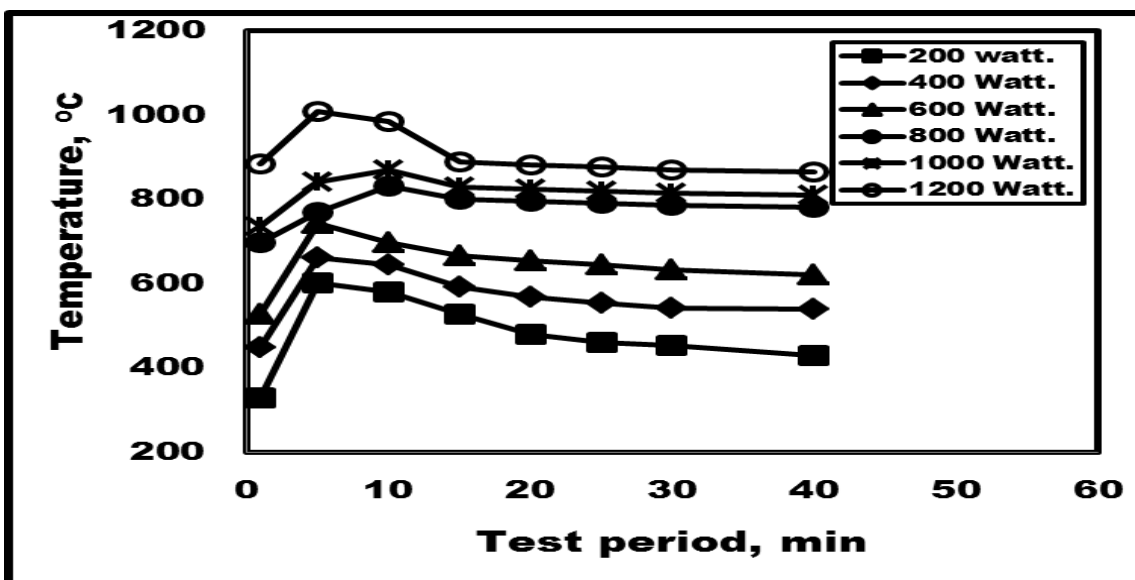


Fig. 2. Effect of microwave power on temperature at different test periods.

density but higher calorific value than the virgin oil due to the decomposition of the heavier hydrocarbons in virgin oil into lighter hydrocarbons in pyrolysis oil. The densities and viscosities of the pyrolysis oils were found to be lower than those of the waste oil due to the cracking of heavy hydrocarbons to lighter compounds. The densities of the pyrolysis oils (760–780 kg/m³), except for that from the experiments conducted at a N₂ purge rate, it reaches 900 Kg/m³ at 1000 ml/min, which is quite close to that for

gasoline, and it is also within the prescribed range. Also it is clear that the effect of N₂ flow rate on the density increment is higher compared to the waste oil flow rate.

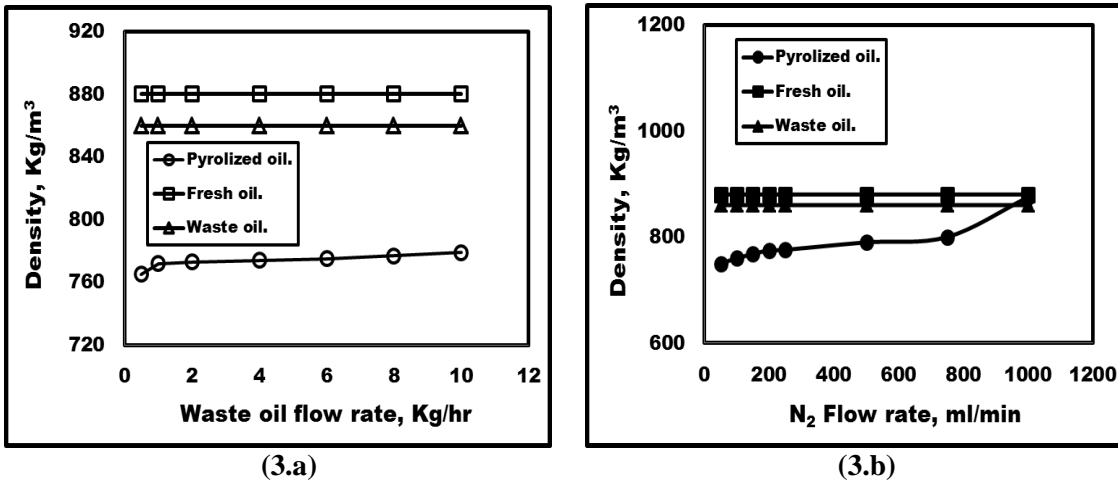


Figure 3. Effect of various types of oil on oil density.

Figure 4 illustrates that the pyrolysis oils possess slightly higher kinematic viscosities (6–8mm²/s), but are considerably higher than that of gasoline (0.7 mm²/s). Further treatment may be needed to reduce the viscosity of the pyrolysis oil since a lower viscosity is desirable and represents a favorable feature when it comes to handling and transportation. Also it is clear that the effect of N₂ flow rate on the density increment is lower compared to the waste oil flow rate. The use of a bed of carbon as the heating medium in our set-up, which also provides a reducing chemical environment at the operational temperatures, appears to decrease the formation of undesired oxidized species during the pyrolysis, and thus leading to the decreased oxygen content in the pyrolysis oil. This is desirable since oxidized species (e.g. acids and reactive peroxides) may catalyze undesired polymerization reactions of unsaturated compounds in the pyrolysis oil during storage, generating larger molecules (e.g. tar or sludge from polymerization of olefins) that have poor mutual solubility with other compounds in the oil, resulting in increased viscosity.

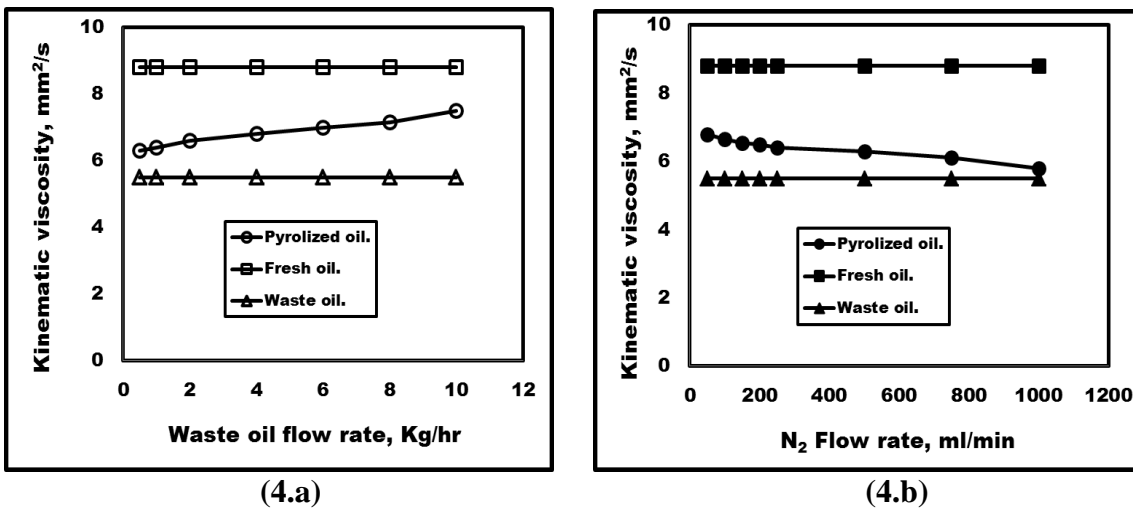


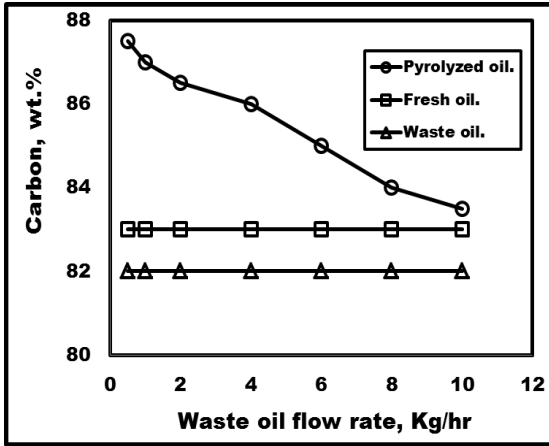
Figure 4. Effect of various types of oil on oil kinematic viscosity.

3. 3. Pyrolysis Oil Elemental Composition

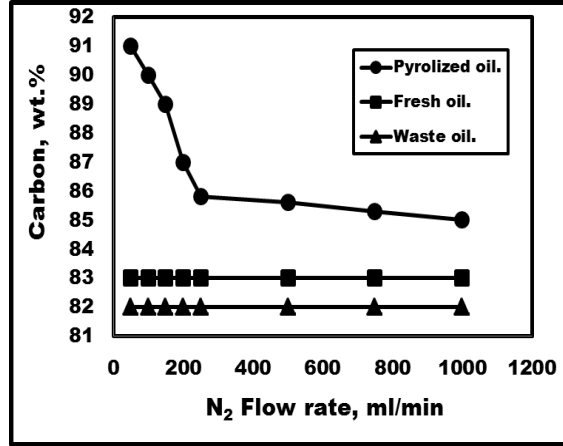
Figures 5 to 8 show the elemental composition of the fresh oil, waste oil before pyrolysis treatment and the pyrolysis oils obtained at different N_2 purge and waste oil feed rates. Carbon and hydrogen represented the main elements present in waste oil, whereas nitrogen, sulphur, and oxygen were detected in very low concentrations. Figure 5 shows a higher carbon wt.% at the beginning of feed rate of both N_2 and waste oil followed by a rapid decrement but the value of the carbon wt.% in the pyrolysis oil is still higher than that in both fresh oil and waste oil in both feed rate of N_2 and waste oil cases due to the used carbon in the pyrolysis process and that The carbon is mainly formed the base oils from which the lubricating oil is formulated. Figure 6 shows the variation of hydrogen wt.% at various purge and waste oil feed rates. Hydrogen is mainly formed the base oils from which the lubricating oil is formulated, whereas nitrogen, sulphur and oxygen are likely to originate from the additives (e.g. antioxidants) present in the engine oil. A decrease in hydrogen was observed for pyrolysis oils compared to the waste oil, suggesting that dehydrogenation and aromatization had occurred to some extent to form compounds containing carbon double-bonds (e.g. alkenes, aromatics. The purge and feed rates seem to have had only a minor influence on the elemental composition of the pyrolysis oils; however, at lower purge rates, increased secondary reactions as a result of the longer residence times of the pyrolysis volatiles in the reactor are likely to increase the degree of random scission thermal cracking and aromatization as indicated by the lower hydrogen in the oils obtained under these conditions in agreement with [4].

Figure 7 indicated that the pyrolysis oils showed a much lower content of oxygen due to the use of a bed of carbon as the heating medium in our set-up, which also provides a reducing chemical environment at the operational temperatures, appears to decrease the formation of undesired oxidized species during the pyrolysis, and thus leading to the decreased oxygen content in the pyrolysis oil. On the other hand, it is likely that some metals in the waste oil may have reacted with the oxygen present in the additives in waste oil to form metal oxides that are retained within the carbon bed during pyrolysis. The reduction in oxygen content is also likely to be due to decarboxylation commonly occurring during thermal treatment processes; this agrees with the findings of [7] in their waste oil pyrolysis study. The low oxygen content in the pyrolysis oils represents a favorable feature in producing a potential fuel source with high calorific value. Also, Figure 7 showed a higher value of N_2 in the pyrolysis oil followed by waste and fresh oil respectively due to the higher rates of N_2 purge gas resulted in a more rapid flow of pyrolysis volatiles out of the reactor and to the higher pressure created in the reactor. The results show that extended heating of the generated pyrolysis volatiles in the reactor could promote different product compositions due to secondary reactions of the primary pyrolysis product; hence it was observed that some waste oil is consumed in the production of pyrolysis gases and char in addition to pyrolysis oil. Whereas nitrogen, sulphur and oxygen are likely to originate from the additives (e.g. antioxidants) present in the engine oil [23].

Figure 8 showed that the pyrolysis oils contain a lower sulphur content compared to the waste oil; this suggests that sulphur, although present in very low concentrations in waste

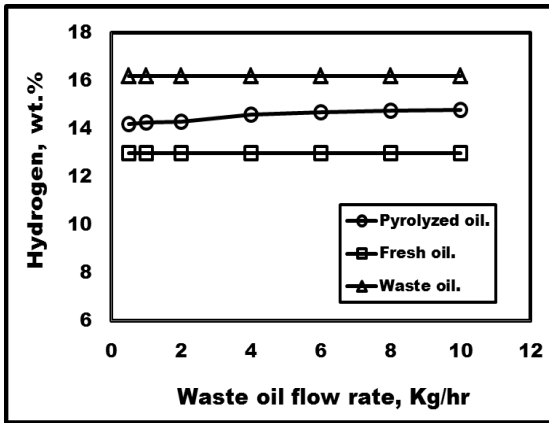


(5.a)

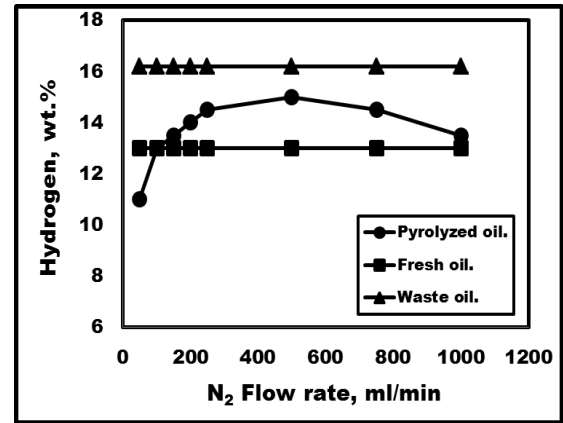


(5.b)

Figure 5. Variation of carbon wt.% at different waste oil and N₂ flow rates.

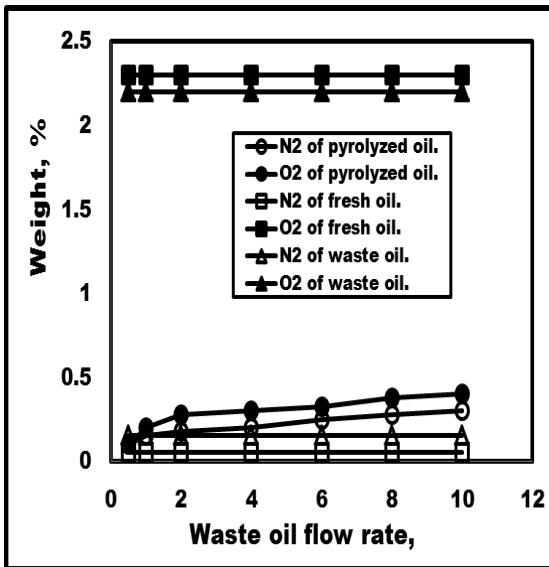


(6.a)

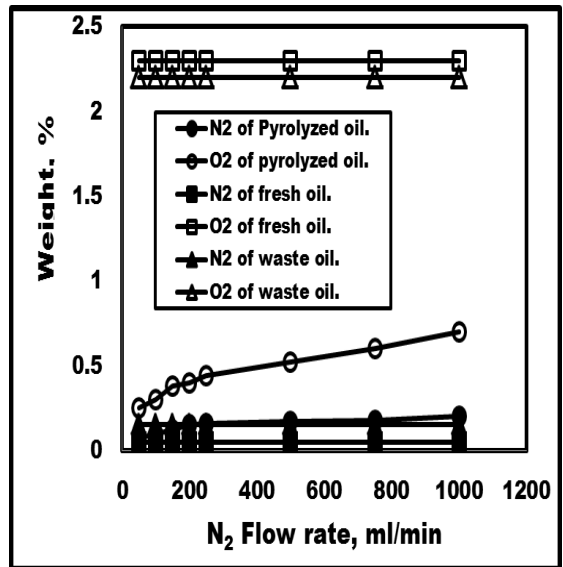


(6.b)

Figure 6. Variation of hydrogen wt.% at different waste oil and N₂ flow rates.



(7.a)



(7.b)

Figure 7. Variation of N₂ and O₂ wt.% at different waste oil and N₂ flow rates.

oil is likely to have reacted with oxygen during pyrolysis to form sulphur oxides which subsequently escape to the atmosphere during engine operation. In addition, new sulphur compounds may be formed during pyrolysis, e.g. metal or non-volatile inorganic sulphides [6], which remain in the carbon bed; these reactions lead to decreased sulphur content in the pyrolysis-oils. The results from elemental analysis show that the microwave-heated pyrolysis generated a pyrolysis oil with a low sulphur and oxygen content. The low sulphur and oxygen content is beneficial to upgrading the pyrolysis oil to transport-grade fuels.

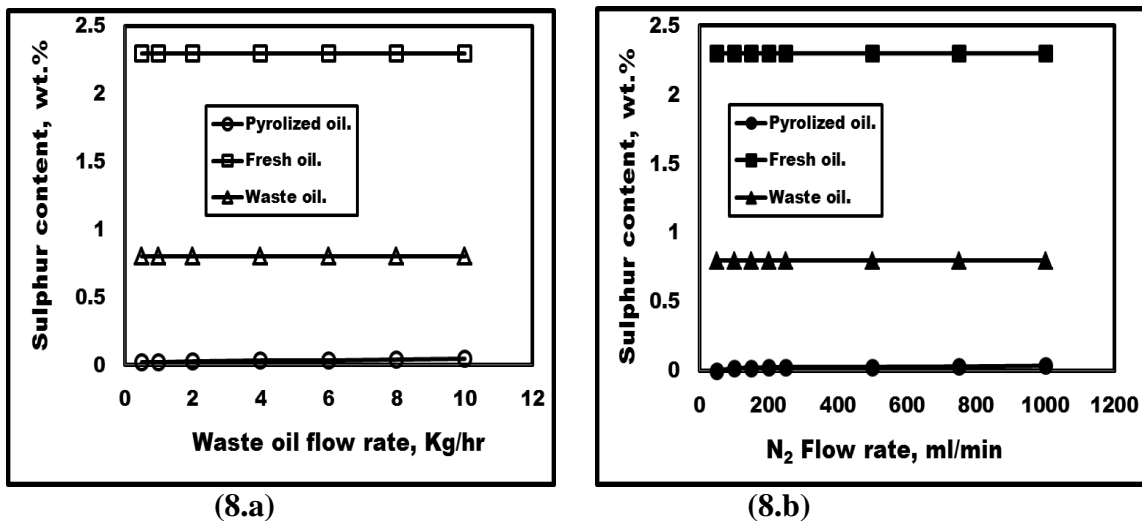


Figure 8. Variation of sulphur wt.% at different waste oil and N₂ flow rates.

3. 4. Calorific Value

Figure 9 compares the compounds amounts of fresh and pyrolysis oils. It is clear that pyrolysis oil contains higher gases, higher solids and lower liquids amounts compared to fresh oil, this may be due to the shorter time that causes more rapid flow of those gases out of the reaction zone. The decreased residence time decreases the potential for the compounds to be cracked and helps to explain the greater liquid yield and smaller gaseous yield observed in fresh oil over pyrolysis oil in agreement with [6], who noticed in their waste oil pyrolysis study that higher yields of gaseous products were achieved when the primary volatiles remained in the high temperature reaction zone for a longer period of time, and has also been observed during the pyrolysis of other materials such as plastic wastes. The calorific value of a fuel is another important fuel property that indicates the gross energy output of combustion in the engine chamber. The calorific value of the pyrolysis oils was higher than those of waste oil and close to those of traditional liquid fuels derived from fossil fuel, indicating that pyrolysis oils with high combustion energy can be obtained by microwave-heated pyrolysis. In particular, the pyrolysis oil obtained shows the closest calorific value to that of gasoline, representing an ideal process condition to obtain gasoline-like fuel. The decrease in oxygen content compared to the original waste oil is likely to contribute to the increase in the calorific value of the pyrolysis oils. Figures 10 to 12 show that microwave-induced pyrolysis of waste automotive engine oil is able to produce significant quantities of commercially

valuable products such as light olefins, gaseous hydrocarbon and liquid hydrocarbon oils containing BTX and benzene derivatives; these products can be treated and used as an energy source or industrial feedstock, [2]. Also higher amounts of light olefins (i.e. ethylene and propylene) compounds were obtained with our microwave pyrolysis process compared with other conventional pyrolysis, suggesting that cracking reactions are enhanced in microwave pyrolysis. Six hundred degree Celsius seems to be the ideal temperature for waste oil pyrolysis based on the highest yield of valuable compounds in the liquid product and lower heating energy requirements at this temperature.

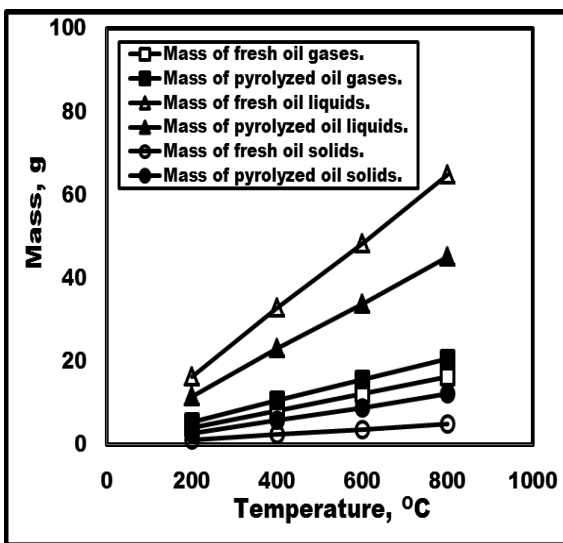


Fig. 9. Mass of oil compounds.

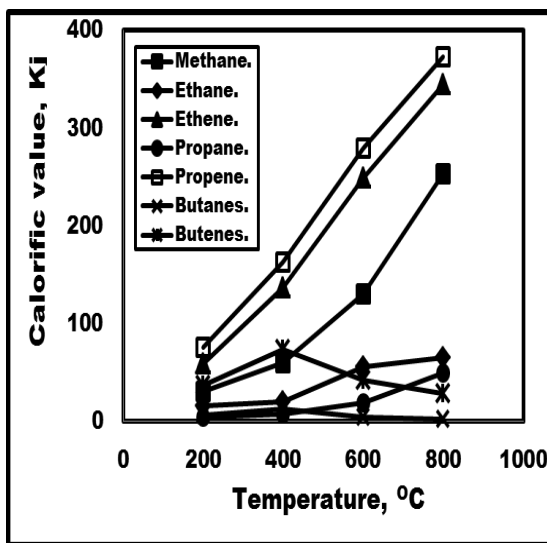


Fig. 10. Calorific value of pyrolysed gases.

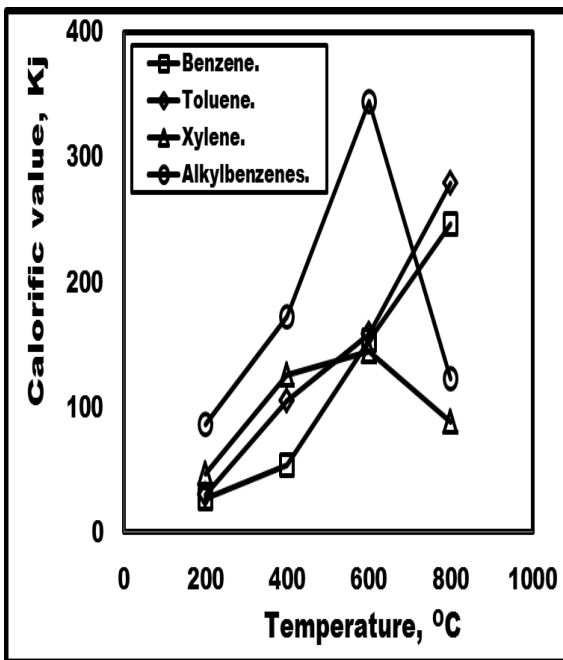


Fig. 11. Pyrolysed liquids calorific value.

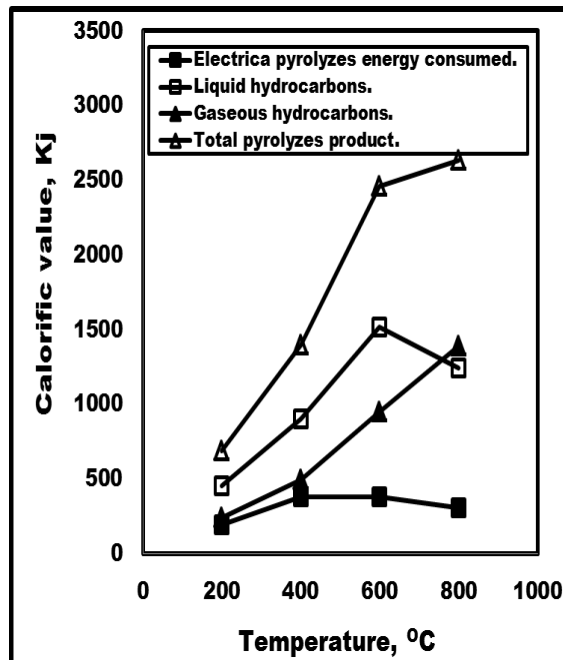


Fig. 12. Comparison of pyrolysis products.

4. CONCLUSIONS

From the present work, the following conclusions are obtained;

1. Microwave-induced pyrolysis has huge potential as a means of recovering commercially valuable products from waste oil.
2. Valuable products were obtained from pyrolysis of the waste oil, and the microwave pyrolysis process showed improved cracking reactions.
3. Microwave-induced pyrolysis of automotive oils produces significant amounts of valuable products: gaseous hydrocarbons with light olefins, and liquid hydrocarbon oils containing BTX and benzene derivatives.
4. Increasing the temperature was found to enhance the production of light gaseous and aromatic compounds, although the amount of liquid products was lower at higher temperatures.
5. Both N₂ and waste oil flow rates were found to have effects on the fraction of original waste oil converted to pyrolysis gases, pyrolysis oils, and residues.

REFERENCES

- [1] K. Naima and A. Liazid, "Waste oils as alternative fuel for diesel engine: A review", *J. of Petroleum Technology and Alternative Fuels* Vol. 4(3), pp. 30-43, March 2013.
- [2] Hala M. Abo-Dief, Amal A. Altalhi and Ashraf T. Mohamed, "Waste Oil Recycling Using Microwave Pyrolysis Reactors", *Journal of Industrial and Intelligent Information* Vol. 2, No. 4, pp. 314 – 319, December 2014.
- [3] M. Nasim, M. Pervez, R. Yarasu, and N. Lotia "Recycling waste automotive engine oil as alternative fuel for diesel engine: A Review", *IOSR Journal of Mechanical and Civil Engineering (IOSR-JMCE)* PP 46-50, 2014.
- [4] S. Lam, A. Russell, C. Lee, and H. Chase, "Microwave-heated pyrolysis of waste automotive engine oil: Influence of operation parameters on the yield, composition, and fuel properties of pyrolysis oil", *Fuel* 92, pp. 327–339, 2012.
- [5] A. Singh, D. Pant, S. Olsen, and P. Nigam, "Key issues to consider in microalgae based biodiesel production", *Energy Education Science and Technology Part A: Energy Science and Research*, Volume (issues) 29(1), pp. 687-700, 2012.
- [6] A. Naz, M. Ullah, S. Ali, T. Mahmood, M. Siddiq, A. Bano, Z. Tariq, "Nano Catalytic Conversion of used Lubricating Oil into Diesel Fuel", *International Journal of Enhanced Research in Science Technology & Engineering*, Vol. 3 Issue 4, pp. 438-446, April-2014.
- [7] M. Sharma, and N. Soni, "Production of Alternative Diesel Fuel from Waste Oils and Comparison with Fresh Diesel:-A Review", *The International Journal Of Engineering And Science (IJES)*, Volume3, Issue 4, Pages 54-58, 2013.
- [8] Hala Abo-Dief, and Omnia El-Shamy, "Improving petroleum oil quality using nonionic surfactants and studies their inhibition effect on mild steel pipeline (Part 1)", *Materials Science An Indian Journal, MSAIJ*, 10(5), pp. 182-191, 2014.

- [9] J. Sharaf, B. Mishra, and R.Sharma, "Production of gasoline-like fuel obtained from waste lubrication oil and its physicochemical properties", *Int. J. of Eng. Res. and Applications (IJERA)*, Vol. 3, Issue 3, pp.113-118, May-Jun 2013.
- [10] J. Conesa, R. Font, A. Fullana, I. Martí'n-Gullo´n, I. Aracil, A. Ga´lvez, J. Molto´, M. Rico, "Comparison between emissions from the pyrolysis and combustion of different wastes", *J. Anal. Appl. Pyrolysis*, pp.1-8, 2008.
- [11] A. Sarkar, M. Langanki, and R. Chowdhury, "Studies on pyrolysis of spent engine oil in a quartz load cell", *Int. J. of Res. in Eng. & Tech.*, V. 03, 6, pp. 222-226, Jun. 2014.
- [12] A. Omer, "Sustainable renewable energy resources, their development and applications", *J. of African Studies and Development*, V. 2(2), pp. 035-057, March 2010.
- [13] I. Hamawand, T. Yusaf and S. Rafat, "Recycling of Waste Engine Oils Using a New Washing Agent", *Energies*, 6, pp. 1023-1049, 2013.
- [14] S. Ogbeide, "An Investigation to The Recycling of Spent Engine Oil", *Journal of Engineering Science and Technology Review*, 3 (1), pp. 32-35, 2010.
- [15] Hala M. Abo-Dief, and Ashraf T. Mohamed, "Recycling Waste Engine Oil using The Microwave Pyrolysis Technique", *The 29th annual meeting of the Saudi Biological Society which will be held in Dammam, Saudi Arabia on February 25- 27*, p. 426, 2014.
- [16] E. Emam and A. Shoaib, "Re-Refining of Used Lube Oil, I- by Solvent Extraction and Vacuum Distillation Followed By Hydrotreating", *Petroleum & Coal* 55 (3), pp.179-187, 2013.
- [17] C. Wongkhorsub and N. Chindaprasert, "A Comparison of the Use of Pyrolysis Oils in Diesel Engine", *Energy and Power Engineering*, 5, pp. 350-355 2013.
- [18] W. Manasomboonphan, and S. Junyapoon, "Production of Liquid Fuels from Waste Lube Oils Used by Pyrolysis process", *2012 2nd International Conference on Biomedical Engineering and Technology IPCBEE*, Vol. 34, pp.130-133, 2012.
- [19] M. Rasul and M. Jahirul, "Recent Developments in Biomass Pyrolysis for Bio-Fuel Production: Its Potential for Commercial Applications", *Recent Researches in Environmental and Geological Sciences*, pp. 256-265, 2013.
- [20] S. Lam, A. Russell, and H. Chase, "From Waste To Valuable Fuel: How Microwave-Heated Pyrolysis Can Recycle Waste Automotive Engine Oil", *Prep. Pap.-Am. Chem. Soc., Div. Fuel Chem.* 56 (1), pp. 19-21, 2011.
- [21] S. Lam, A. Russell, and H. Chase, "Microwave pyrolysis, a novel process for recycling waste automotive engine oil", *Energy*, 35, pp. 2985-2991, 2010.
- [22] A. Jamjumras and S. Amornraksa, "Microwave Pyrolysis of C6 Non-aromatic Hydrocarbons", *4th Int. Conf. on Chemical, Biological and Environmental Engineering IPCBEE*, Vol.43, pp. 26-30, 2012.
- [23] Hala Abo. Daif, Elham Eissa , Nagy Moustafa and , Ebaa El.Shamy, "Minimize Corrosion and Scratching of Carbon Steel Specimens in Spindle Oil by Improving Its Oxidation Stability", *Int. J. of Academic Res.*, BaKu, Azerbaijan, Sept., 2010.
- [24] Ashraf T. Mohamed, and H.M. Abo-Dief, "Analysis of H₂S Environmental Pollutant in The Oil Industry using The Electrostatic Polarization Technique", *The 27th Meeting of The Saudi Biological Society, Jazan University - Jazan.*, 6-8 March2012.