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Changes in Components of Tyre-derived Oil after Sulphur and Heteroatom Removal Using Three Acids

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Tyre-derived oil consists of many types of hydrocarbons such as aromatic hydrocarbons and sulphur compounds. Aromatic hydrocarbons can generate gum in the engine, which results in a lower efficiency of the engine and causes black smoke. Moreover, sulphur compounds can also cause air pollution. Conventionally, acid treatment has been adopted by small companies that aimed at reducing aromatics, but it also gives undesired compounds in the tyre-derived oil. It has been reported that sulphuric acid can remove impurity and sulphur compounds in waste lube oil. However, it is suspicious that sulphuric acid used in the acid treatment can also form heteroatom-containing hydrocarbon molecules, such as S compounds, in the oil. So can other acids. In this work, sulphuric acid, nitric acid, and hydrochloric acid were used as chemicals in acid treatment in order to investigate the changes in components in tyre-derived pyrolysis oil. The products were analyzed by using SIMDIST-GC, GC×GC-TOF/MS, and S analyzer. The results showed that the volume of tyre-derived oils decreased about 50 wt.% together with 50 % sludge formation when sulphuric and nitric acids were used. For hydrochloric acid, the volume of tyre-derived oil decreased about 10 wt.%. The tyre-derived oil contained 5 % gasoline, 25 % kerosene, 35 % gas oil, LVGO 8 % and HVGO 27 %. The results from GC×GC-TOF/MS were used to explain the changes in oil components before and after treatments.

1. Introduction

The growth of transportation in the world, a number of cars have been increased, there have directly with proportional to the quantity of tyres. Globally, an estimated one billion tyres reach the end of their useful lives every year. In Thailand, an estimated three hundred thousand tyres reach the end of their term of four hundred kilometres around Bangkok every year. The tyres are made of non-biodegradable material. The waste tyres were used mainly in cement plants because they have high energy content and a better source of energy than other solid fuels. The combustion of tyres may involve the emission of hazardous pollutants extremely harmful to human health and the natural environment. Tyres contain synthetic and natural rubber, metal wire, carbon, nitrogen; sulphur compounds and other additives used in production process. A pyrolysis process can be an alternative way to dispose waste tyres without oxygen, produces pyrolysis gas, pyrolysis oil (tyre derived oil) and pyrolysis char. Tyre derived oil (TDO) is mainly constituted by aliphatic hydrocarbons such as saturated hydrocarbons (Alkanes) and unsaturated hydrocarbons (Olefins), alicyclic hydrocarbons such as saturated naphthenes and unsaturated naphthenes, aromatic hydrocarbons such as mono-aromatic hydrocarbons, di-aromatic hydrocarbons, poly-aromatic hydrocarbons and aromatic heterocyclic compounds, with some properties such as calorific value and density, similar to light fuel oil, but that more contain metal, sulphur, nitrogen compounds and aromatic hydrocarbons than light fuel oil. A colour of tyre-derived oil is dark brown or black (Sakollapath et al., 2014) with medium viscosity (Stefano et al., 2014). The problems of tyre-derived oils come from sulphur compounds and aromatic hydrocarbons. Sulphur compounds in the forms of

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polar-aromatic hydrocarbons can cause corrosion and knocking of engine. Aromatic hydrocarbons moreover generate gum, blocking efficiency in engine and releasing black smoke into atmosphere. Conventional acid treatment can improve quantity of waste lube oil. In small tyre pyrolysis plants in Thailand, some conventional strong acids were used to treat tyre-derived oil without awareness of side reactions that can cause more serious problems to the oil product and the environment. The objectives of current research study were therefore to study the changes in compositions and properties of tyre-derived oils that may impact to environment after treatments using conventional strong acids.

2. Experimental

2.1 Acid treatment

The experiments were carried out using conventional strong acids; that are sulphuric acid, nitric acid, and hydrochloric acid, aiming to extract contaminants from tyre-derived oils. The concentrations of acids and bases were 10 M. Tyre-derived oil and a strong acid were first mixed in the beaker at the ratio of 10 (25 g of TDO/2.5 g of acid). After an hour, acid sludge was drained off from the beaker, and the oil was neutralized with sodium hydroxide with the oil to base ratios of 10. The reaction was carried out at 45 °C with stirring at 800 rpm for 2 h in acid-base treatment. The temperature was maintained constant to enhance proper mixing in the beaker and allow for layers of sludge to be formed at the end of the reaction. Centrifugation was carried out to extract the impurities dispersed in the oil at 4,000 rpm and 10 min.

2.2 Product analysis

The liquid product was first dissolved in n-pentane (mass ratio of n-pentane/oil = 40:1) to precipitate asphaltene. Asphaltene was filtered by using a polyamide membrane (0.45 μm). The maltene solution was analyzed using Comprehensive Two- Dimension Gas Chromatography (Agilent Technologies 7890) with Time-of-Flight Mass Spectrometer (LECO, Pegasus® 4D TOF/MS) (GCxGC-TOF/MS) equipped with the 1st GC column was an Rxi®-PAH MS (60 m × 0.25 mm ID × 0.1 μm), and the 2nd GC column was a non-polar Rxi®-1HT (1 m × 0.25 mm ID × 0.1 μm). The simulated true boiling point curves were determined by using a Perkin Elmer Clarus 580 simulated distillation gas chromatography (SIMDIST-GC) equipped with FID detector and an Elite®SimDist 10 m × 0.53 mm × 2.65 μm WCOT fused silica capillary column. The petroleum fractions were separated based on their boiling point ranges according to the ASTM D2887; gasoline (<149 °C), kerosene (149 - 232 °C), gas oil (232 - 343 °C), light vacuum gas oil (343 - 371 °C) and heavy vacuum gas oil (>371 °C). Moreover, sulphur content in tyre-derived oils and sludge were determined by LECO®Elemetal Analyzer (TruSpec®S), following the ASTM D1552

3. Results and Discussion

3.1 Acid treatment

Acid treatments in tyre-derived oils were conducted using different types of acids; namely, sulphuric acid, nitric acid and hydrochloric acid in order to investigate the changes in components in the oils. The result in Figure 1 shows that the quantities of tyre-derived oils after the acid treatments are reduced because some sludge is generated. In addition, the sulphuric, nitric, and hydrochloric acids produce the amount of sludge about 50.0 wt.%, 38.9 wt.% and 5.69 wt.%, respectively. Treatment using hydrochloric acid was found to lose the oil yield less than the other acid. Treatment of tyre-derived oil using the acid generates some sludge that needs further treatment, which is a disadvantage of this method.

Figure 1: Percentage of products obtained from acid treatments

3.2 Grouping of chemical components in tyre-derived oils

The chemical components in tyre-derived oils using Comprehensive Two- Dimension Gas Chromatography with Time-of-Flight Mass Spectrometer were divided to 3 groups: (1) Hetero compounds, (2) Aromatic compounds, and (3) Non-aromatic compounds. Saturated hydrocarbons, olefin hydrocarbons, terpene hydrocarbons, sulphur compounds, nitrogen compounds and oxygen compounds were combined in one non-aromatic compound group. The result in Figure 2 shows that the treated tyre-derived oils using sulphuric acid is better than the others conventional strong acids because the hetero compounds was decreased about 3.29 %, and the non-aromatic compounds group was decreased about 2.07 %, but the aromatic compounds group was increased about 5.36 %. Figure 3 shows the total ion chromatogram of tyre-derived oil.

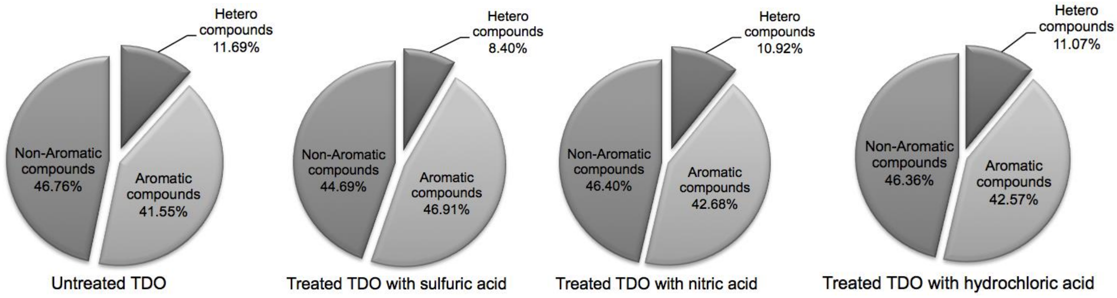

Figure 2: Contents of aromatics, non-aromatics and hetero compounds in tyre-derived oils.

3.3 True boiling point curve of tyre-derived oils

Petroleum fractions in maltenes are classified according to boiling point distillation conformed with ASTM D-2887 into 5 fractions: gasoline (<149 °C), kerosene (149-232 °C), gas oil (232-343 °C), and light vacuum gas oil (343 - 371 ° C), and high vacuum gas oil (>371 °C). The results in Figure 4 show that the maltenes before and after acid treatments are mainly distributed in the range of gas oil, heavy vacuum gas oil and kerosene. Figure 5 shows the true boiling point curve of tyre-derived oils. The acid treatments slightly affect to the petroleum fractions. The treatments result in slightly-heavier oil than no treatment.

3.4 Sulphur compounds in liquid and solid products

The analysis of total sulphur compounds in tyre-derived oils and sludge was conformed with ASTM D1552. The results in Figure 6(a) show that the after acid treatments, the sulphur compound in tyre-derived oils was increased about 9 - 12 % when compared with that in the untreated tyre-derived oil. The results in Figure 6(b) show that the attempts on removal of sulphur compounds from tyre-derived oil using the three acids are not successful. In addition, they resulted in higher contents of sulphur.

4. Conclusions

The study has proven that treatments using conventional strong acids such as sulphuric acid, nitric acid and hydrochloric acid as done by small waste tyre pyrolysis companies were not appropriate for improving the quality of tyre-derived oil because of the sludge that needs further treatment and the increasing aromatics and sulphur contents after the treatments. The acid treatments also resulted in slightly-heavier oils. The results of this study will be used as the evidences for educating owners of tyre pyrolysis plants not to adopt the treatments using the three acids.

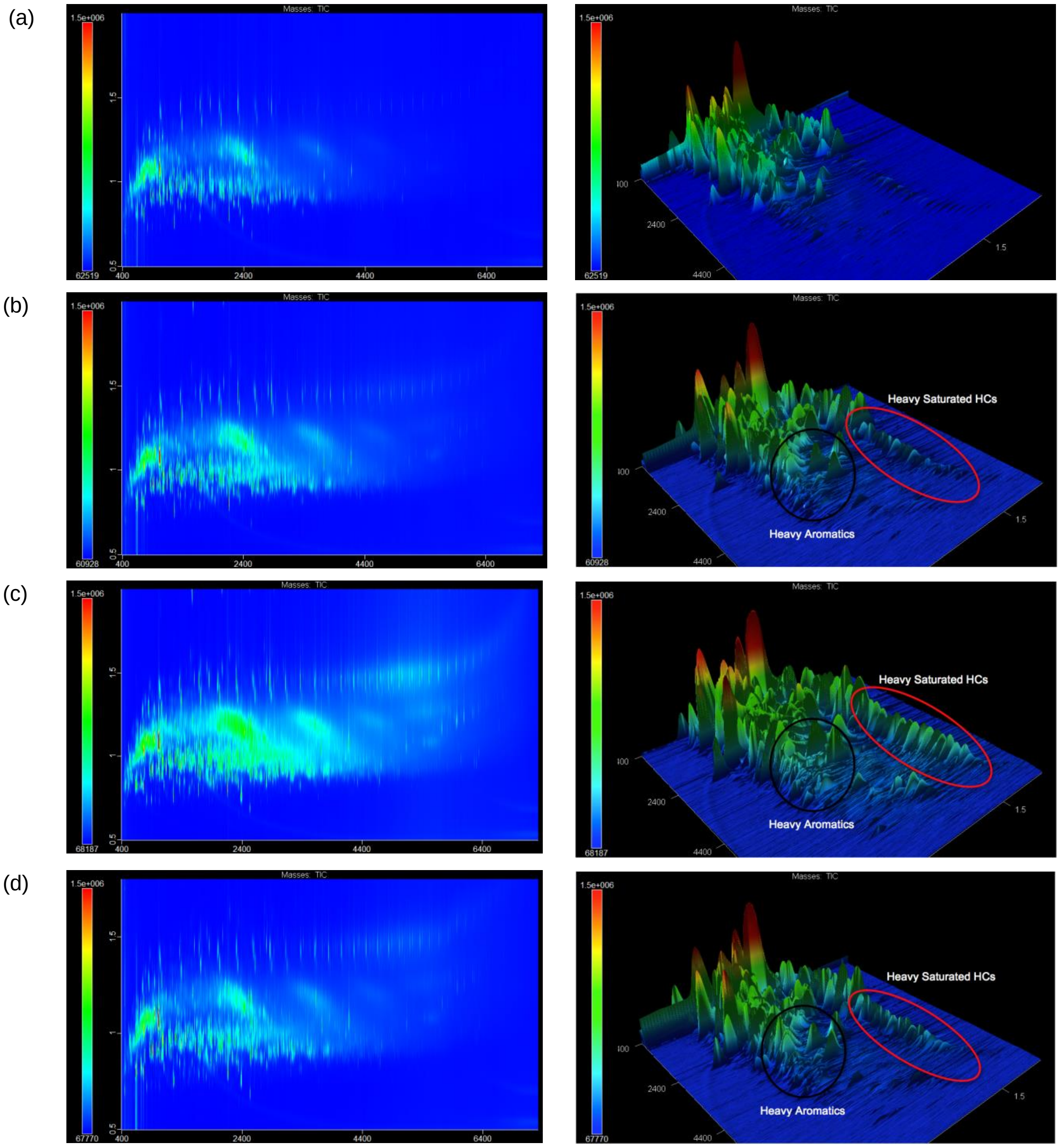

Figure 3: Contour plot and surface plot of total ion chromatograms: (a) untreated TDO (b) treated TDO with H_2SO_4 (c) treated TDO with HNO_3 and (d) treated TDO with HCl

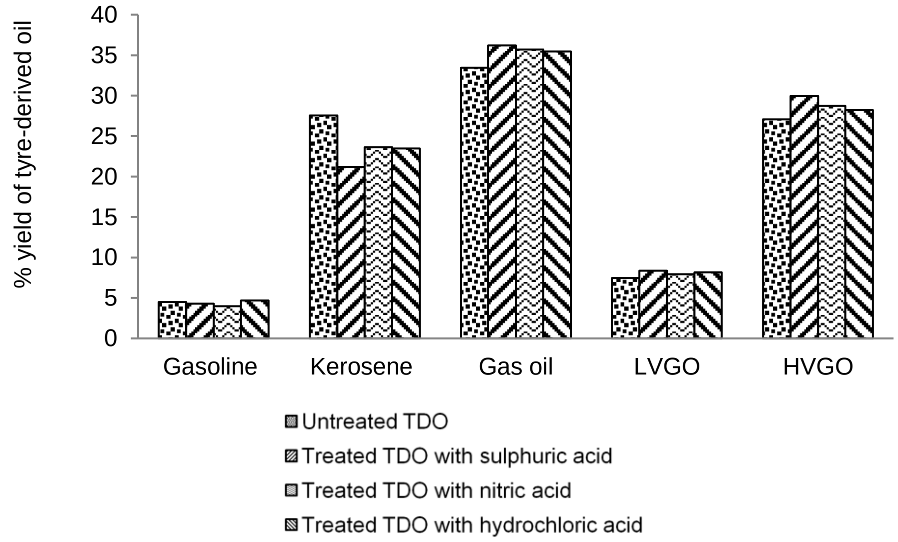

Figure 4: Petroleum fractions in maltenes of untreated and treated tyre-derived oils

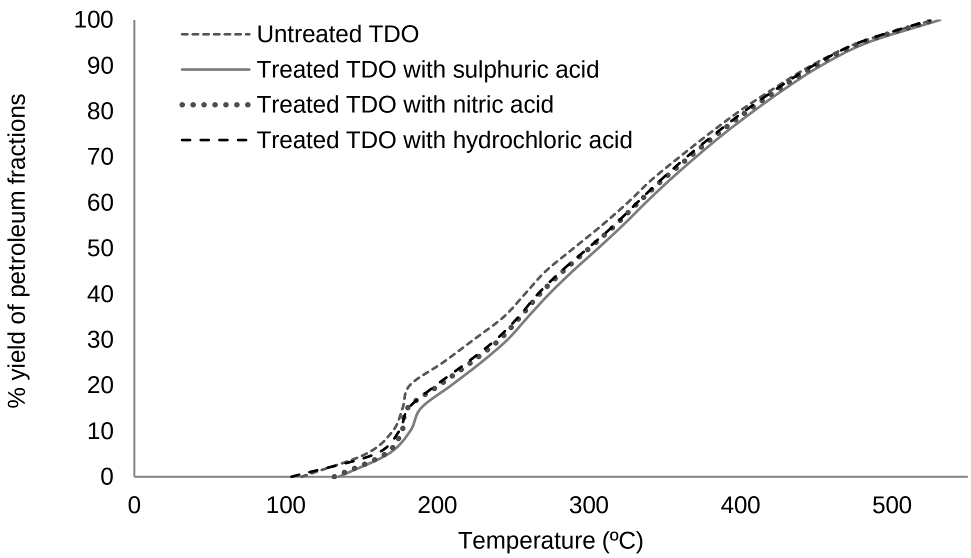

Figure 5: True boiling point curve of untreated and treated tyre-derived oils

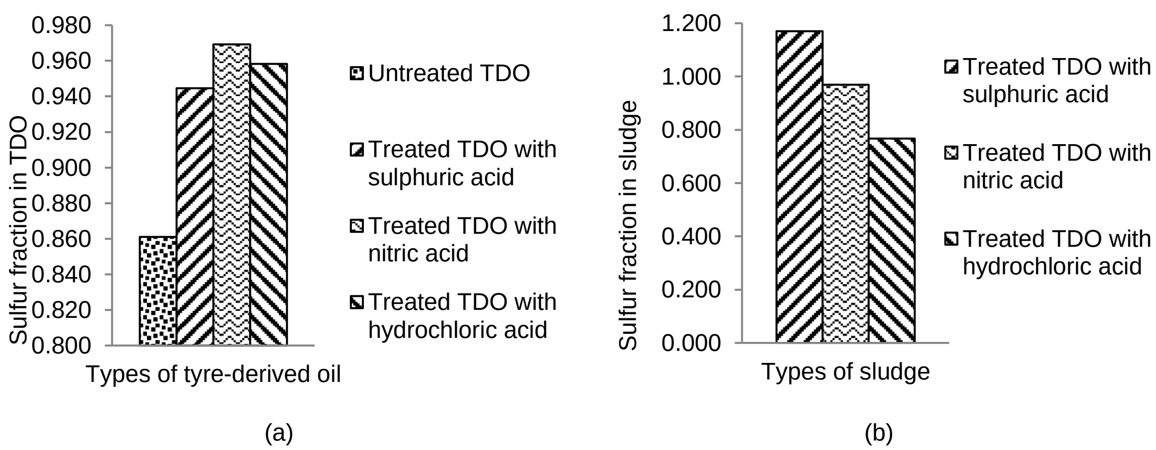

Figure 6: Sulphur content in products: (a) tyre-derived oils (b) sludge

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