



## Comparison of Components in Oil Derived from Tyre Pyrolysis with and without KL Catalyst Using GC × GC / TOF-MS

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Typically, the products from waste tyre pyrolysis consist of (i) gas fraction (18 – 23 %wt), (ii) liquid fraction (41 – 49 %wt), and (iii) char fraction (38 – 40 %wt). The liquid amount is considered the highest among those obtained from waste tyre pyrolysis. The improvements of tyre-derived oils (liquid fraction) could be accomplished by increasing mono-aromatics as a result of the reductions in di-aromatics and poly-aromatics through hydrogenation and the conversion of terpenes through aromatization. A basic catalyst that has potassium as a cation such as potassium tert-butoxide ( $K^+(CH_3)_3CO^-$ ) can provide hydrogenation and aromatization. KL zeolite is a representative of a solid basic catalyst. It has a pore diameter 0.71 Å and 1-dimensional pore structure. Moreover, the 1-dimensional pore structure can align the incoming molecules parallel on the surface of KL, resulting in high yields of hydrogenated products. Two-Dimensional Gas Chromatography coupled with Time-of-Flight Mass Spectrometry (GC × GC / TOF-MS) that can separate and identify the chemicals that have same retention time and boiling points due to overlapped mass spectra was employed for better identification of components in tyre-derived oils. The objective of this research was thus to observe the changes the hydrocarbon species upon the use of a KL catalyst. The GC × GC / TOF-MS was used to investigate hydrocarbon species in the maltenes (liquid fraction without asphaltene) from the non-catalyst and KL batches. The liquid products were categorized into saturated hydrocarbons (SATs), olefins (OLEs), terpenes (TERs), mono-aromatics (MAHs), di-aromatics (DAHs), poly-aromatics (PAHs), and polar-aromatics (PPAHs), including sulphur compounds. The pyrolysis experiments were performed in a bench-scaled autoclave reactor from room temperature to 500 °C (for the pyrolysis zone) and 350 °C (for the catalytic zone) with the heating rate of 10 °C/min. As a result, KL was found to increase the MAHs from 20.1 to 26.8 %wt (mostly, 2-ethyltetralin) and decrease DAHs from 13.31 to 6.37 %wt (mostly, 2-ethylnaphthalene), and TERs from 4.06 to 2.56 %wt (mostly, d-limonene and 3-carene). The sulphur compounds in tyre-derived oils were found to be thiophenes, phenylthiophenes, benzothiophenes, methylbenzothiophenes, dibenzothiophenes, and naphthols.

### 1. Introduction

Questions concerning about the quality of tyre-derived oil have been arisen since tyre-derived oil was composed of a considerable amount of aromatics that can be pollutants and carcinogenic agents. Dai et al. (2001) studied the pyrolysis of waste tyres in a circulating fluidized-bed reactor, and reported that 12.10 %wt in aromatic fraction was di-aromatics, for examples, naphthalene and methylnaphthalenes. Laresgoiti et al. (2004) characterized the liquid products from tyre pyrolysis, and reported that poly-aromatics generally consisted of three main groups: fluorenes, phenanthrenes, and pyrenes.

To be converted, di-aromatics and poly-aromatics need to be first hydrogenated. Bianchini et al. (2004) studied the role of a single-site catalyst on the hydrogenation of thiophenes, and reported that it produced non-aromatic hydrocarbons and H<sub>2</sub>S. Piyawongpinyo and Jitkarnka (2013) reported that doping 10 and 20 %wt Mo on Ni/HBETA increased a high amount of saturated hydrocarbons and light petroleum fractions.

Moreover, Saeng-araku and Jitkarnka (2013) revealed the spent commercial NiMoS/Al<sub>2</sub>O<sub>3</sub> catalyst was effective enough to reduce the sulphur in oil from 1.36 to 0.60 %wt and produced lighter products.

A basic catalyst that has a K<sup>+</sup> as a cation such as potassium tert-butoxide (K<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>CO<sup>-</sup>) and K/Al<sub>2</sub>O<sub>3</sub> can provide both hydrogenation and aromatization. Stapp and Kleinschmidt (1965) studied the isomerization of cyclooctadienes to cis-Biscyclo[3.3.0]oct-2-ene, and reported that potassium tert-butoxide can hydrogenate linear dienes, like 1,5-hexadiene, to hexane. Moreover, Slaugh (1967) studied metal hydrides as hydrogenation and isomerization catalysts, and found that potassium hydride (KH) appeared to be several hundred times more active than sodium hydride. In addition, Slaugh (1968) studied the hydrogenation of benzene to phenylcyclohexane using supported alkali metal catalysts, and found that the catalytic properties of alkali metals could be changed drastically by depositing them on certain supports. Furthermore, Friedman et al. (1971) found that alkali metals and alkali metal alloys can be used as catalysts for the hydrogenation of poly-aromatic hydrocarbons to products containing an isolate aromatic ring. In addition, a basic catalyst can also provide aromatization of hydrocarbon compounds. Moreover, Brown (1973) revealed potassium hydride with amine can provide aromatization of *d*-limonene to *p*-cymene at room temperature.

The KL zeolite is a solid basic catalyst that contains K<sup>+</sup> as a cation. It has basic property and one dimensional channel of 12-membered rings with a pore size of 0.71 nm (Sato et al., 1999). KL has been employed as a support of Ru for the hydrogenation of unsaturated aldehyde (Álvarez-Rodríguez et al., 2005). Azzam et al. (2010) studied the aromatization of hexane over Pt/KL catalyst, and they found that L-zeolite channels inhibited the coke formation and catalyst deactivation. Previously, KL has been tested in our group as tyre pyrolysis catalyst, and its effects on pyrolysis products were reported in terms of petroleum cuts in tyre-derived oil. No details on chemicals in oils were reported.

Comprehensive two-dimensional gas chromatography (GC × GC) consists of two columns connected in series. The first column (a primary non-polarity column) can separate the components based on carbon number, and it consequently provides the second column (a secondary polar column) with a series of sub-samples containing the same carbon number that can be further separated based on the polarity. Time-of-flight (TOF/MS) instrument is able to scan at the high scan rates of ≥ 50 spectra/s. The data can be collected at high rates, which are shown obviously at separated retention time with accurate quantification (Dalluge et al., 2002a). The analysis of an unresolved complex mixture such as oil spill (Nelson et al., 2006), rich biodegraded crude oil (Melbye et al., 2009), cigarette smoke (Dalluge et al., 2002b), and standard polycyclic aromatics have been well accomplished by using this technique (Manzano et al., 2012). Therefore, in this work, the effect of KL zeolite on the chemical components of tyre-derived oil was determined using GC × GC / TOF-MS as an analysis instrument. The components in the oils derived from tyre pyrolysis with and without KL catalyst are hereby compared and discussed.

## 2. Experimental setup

### 2.1 Catalyst preparation

The zeolite, Linde Type L (LTL, K-form, Si:Al = 3) supplied by the TOSOH Company (Singapore) was first calcined in air at 500 °C with the heating rate of 5 °C min<sup>-1</sup> for 3 h. After that, the zeolite was pelletized, ground, and then sieved to a specific particle size range of 400-425 μm before use.

### 2.2 Pyrolysis of waste tyre

A used passenger tyre tread, Bridgestone TURANZA GR-80, was shredded and sieved to a size range of 8-18 mesh. The tyre pyrolysis experiments were conducted using the same pyrolysis system as in (Dũng et al., 2009). The tyre sample was pyrolyzed in the reactor where the temperature was ramped from room temperature to the final temperature of 500 °C with the ramping rate of 10 °C min<sup>-1</sup>, and kept at the final temperature for one hour to ensure the total conversion of tyre. 7 g of the KL catalyst was packed and heat at 350 °C in the catalytic zone. A 25 mL min<sup>-1</sup> nitrogen was used to purge the reactor before the experiment and to carry the product out of the reactor. The obtained product was passed through the ice-salt condensing system containing two consecutive containers in order to separate the liquid product from incondensable compounds. After the experiment, the solid and liquid were weighed to determine the product distribution. The amount of gas was calculated from mass balance. Only the oil was brought to analysis in this study. It was first dissolved in n-pentane with the ratio of 40:1 (n-pentane:oil) to separate asphaltene. The clear solution after filtration is called maltene.

### 2.3 Analysis using GC × GC – TOF/MS

The GC × GC–TOF/MS system was composed of an Agilent gas chromatograph 7890 (Agilent Technologies, Palo Alto, CA, USA), a thermal modulator, and a Pegasus® 4D TOF-MS (LECO, St. Joseph, MI, USA). The GC was installed with two columns: the first column was a non-polar Rtx 5 silms®

(30 m x 0.25 mm i.d. x 0.25  $\mu\text{m}$  film thickness), and the second column a Rxi®-17 ms (1.10 m x 0.10 mm i.d. x 0.10  $\mu\text{m}$  film thickness). Both columns were made by Thames Restek (Sounderton, UK). The main GC oven was operated from at 50  $^{\circ}\text{C}$  with 2 min holding at the beginning and then ramped to 310  $^{\circ}\text{C}$  at 5  $^{\circ}\text{C min}^{-1}$  with 10 min holding at 310  $^{\circ}\text{C}$ , and the secondary oven was operated at 60  $^{\circ}\text{C}$  held for 2 min at the beginning and ramped to 320  $^{\circ}\text{C}$  at 5  $^{\circ}\text{C min}^{-1}$  with 10 min holding at the final temperature. One  $\mu\text{L}$  of the 10 mg/mL maltenes in carbondisulfide ( $\text{CS}_2$ ) was injected via a spiltless injector at 250  $^{\circ}\text{C}$  using He as the carrier and a constant column flow rate of 1.0 mL/min. The modulator was operated under modulation timing of 4-s cycle time and 0.5-s holding time in the release position. The nitrogen cryogen coolant maintained the temperature of the modulation trap to at least 30  $^{\circ}\text{C}$ . A Pegasus 4D® TOF/MS instrument was used to acquire mass spectral data, using -70 V electron impact ionization. The ion source temperature was set at 250  $^{\circ}\text{C}$ . The detector voltage was set at 1,600 V. The transfer line temperature was 250  $^{\circ}\text{C}$ . The mass range collected was from 35 to 500  $m/z$ , with 100 spectra/s transferred to the data station. The data processing was set S/N value of 10, match required to combine 500, and dt that was used to calculate the percentage area. Data were recorded and analyzed using the LECO ChromaTOF® software. The NIST library provided with the instrument was used for spectral searching. The analysis was repeated for 3 times.

### 3. Results and discussions

#### 3.1 Total ion chromatograms and grouping of components in tyre-derived oils

Figure 1 shows the contour plots of total ion chromatogram (2D TIC) of maltenes from (a) non-catalyst and (b) KL batches. They indicate that the conditions used to analyze the tyre-derived oil are satisfied to separate the complex components, which were found in a total of more than 1,500 compounds. As the structural complexity of the components increases, partial overlapped for component classes can occur even though they are shown by GC x GC/TOF in the total ion chromatogram. For examples, the compounds in the circle are identified by the NIST database as monoaromatic hydrocarbons (MAHs). After using the KL catalyst, the contour plot in the circle appears darker than that from the non-catalyst batch. It means that the concentration of MAHs is increased with using the KL catalyst. However, the GC x GC/TOF can reveal the separation of components in overlapped chromatograms as seen on the surface plots of total ion chromatogram (3D plots) in Figure 2 since the secondary column (the polar column) can separate the components with different polarities, which emerge at the same retention. These components are separated layer by layer as seen in the profile on the contour plot, continuing as the carbon number increases.

For the analysis of TICs, the components are thus categorized into groups, according to their chemical structures; namely, saturated hydrocarbons (SATs), mono-aromatics (MAHs), di-aromatics (DAHs), poly-aromatics (PAHs), polar-aromatics (PPAHs), terpenes (TERs), and olefins (OLEs). MAHs are the most valuable chemicals in the petrochemical industry. Some of them play an important role as upstream petrochemicals in either polymer or advanced material industries. It can be seen that the MAHs increases when the KL catalyst is used. Two main groups of MAHs are mono-aromatics with saturated substituents (MAHs-SS) and mono-aromatics with unsaturated substituents (MAHs-US). Mono-aromatics with saturated substituents are classified into four sub-groups; that are, benzene, alkylbenzenes, indanes, and 1,2,3,4-tetrahydronaphthalenes (tetralins), and those with unsaturated substituents are classified into two sub-groups; that are, indenes and alkenylbenzenes. SATs consist of aliphatic hydrocarbons starting at C14 to C17. OLEs consist of unsaturated hydrocarbons also starting at C14 to C17. TERs consist of 3-carene and d-limonene. DAHs consist of naphthalene and alkylnaphthalenes. PAHs consist of 1-1'biphenyl, anthracene, pyrene, and benzopyrene whereas PPAHs consist of thiophenes, benzothiophenes, and dibenzothiophenes.

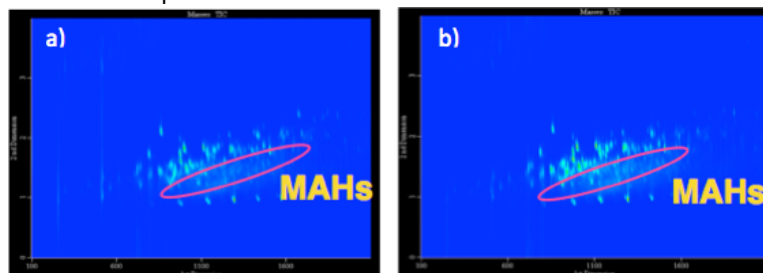


Figure 1: 2D-Total ion chromatogram (contour plot) of the maltenes from (a) non-catalyst and (b) KL batches

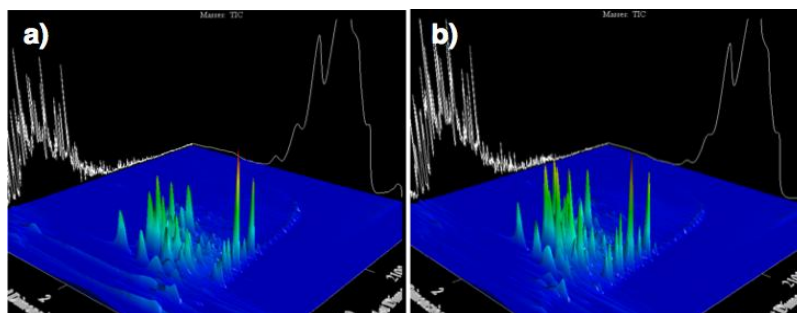


Figure 2: 3D-Total ion chromatogram (surface plot) of the maltenes from: a) non-catalyst b) KL

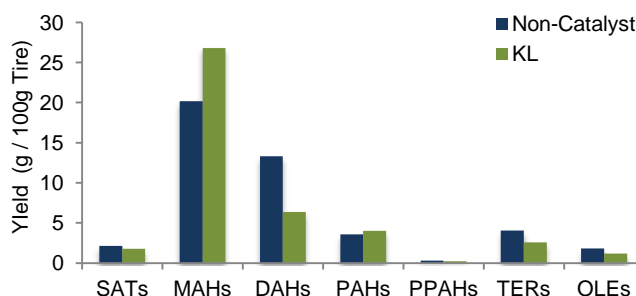


Figure 3: Yield of hydrocarbon species in tyre-derived oils from non-catalyst and KL batches

### 3.2 changes of oil components with using KL

Figure 3 indicates the changes of components upon the use of KL as follows. The yield of MAHs increases from 20.1 to 26.8 g/100 g tyre (mostly, 2-ethyl-1,2,3,4-tetrahydronaphthalene (2-ethyltetralin), ( $m/z = 160$ )). The yield of DAHs decreases from 11.3 to 6.3 g/100 g tyre (mostly, 2-ethylnaphthalene ( $m/z = 156$ )), whereas that of TERs from 4.0 to 2.9 g/100 g tyre (mostly, d-limonene ( $m/z = 136$ ) and 3-carene ( $m/z = 136$ )). SATs, PAHs, PPAHs, and OLEs are not found significantly changed upon using the KL catalyst.

#### 3.2.1 Changes of hydrocarbon species in MAHs

According to Figure 3, the significant decrements of DAHs and TERs are observed in conjunction with the increase in MAHs. Since a significant increase of MAHs is found with using the KL catalyst, the changes of compounds in MAHs are then examined in details. Figure 4 shows the changes of hydrocarbon species in the MAHs groups. It can be seen that benzene, alkylbenzenes, indanes, and 1,2,3,4-tetrahydronaphthalenes (tetralins) significantly increase; whereas indenenes and alkenylbenzenes dramatically decrease when the KL catalyst is used.

#### 3.2.2 Changes of hydrocarbon species in TERs

According to Figure 5(a), dominant components in the TERs (C<sub>10</sub>) group are d-limonene ( $m/z = 136.125$ ), 3-carene ( $m/z = 136.125$ ) and 3-methyl-4-methylenebicyclo[3.2.1]oct-2-ene (3-m-4-mb-2-e) ( $m/z = 136.125$ ). The others in the figure are described to the combination of all minorities in TERs. When the KL catalyst is used, the yields of d-limonene and 3-carene decrease.

#### 3.2.3 Change of hydrocarbon species in PAHs

From Figure 5(b), the yield of 1,2-dihydroacenaphthylene (ace) decreases with the increase in phenanthrene (phen). The yield of 4-methyl-1,1'-biphenyl (4-m-1,1'-bph) ( $m/z = 166.078$ ) decreases with the increase in 2-methyl-9H-fluorene (2-m-9-flu) ( $m/z = 180.094$ ). Finally, the yields of 9H-fluorene (9-flu), 2,2'-dimethyl-1,1'-biphenyl (2,2'-dbph), and 1,1'-biphenyl (1,1'-bph) decrease when the KL catalyst is used.

#### 3.2.4 Change of hydrocarbon species in SATs

It was found the SATs hydrocarbon species are tridecane (C<sub>13</sub>), tetradecane (C<sub>14</sub>), and hexadecane (C<sub>16</sub>). From Figure 6(a), the yield of tetradecane drastically decreases whereas the yield of tridecane increases when the KL catalyst is used.

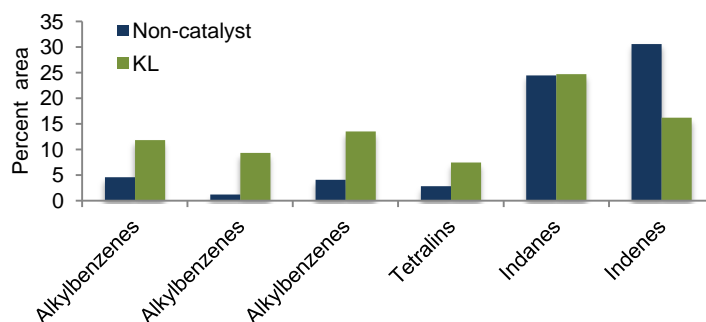


Figure 4: Changes of hydrocarbon species in the MAHs groups with using KL catalyst

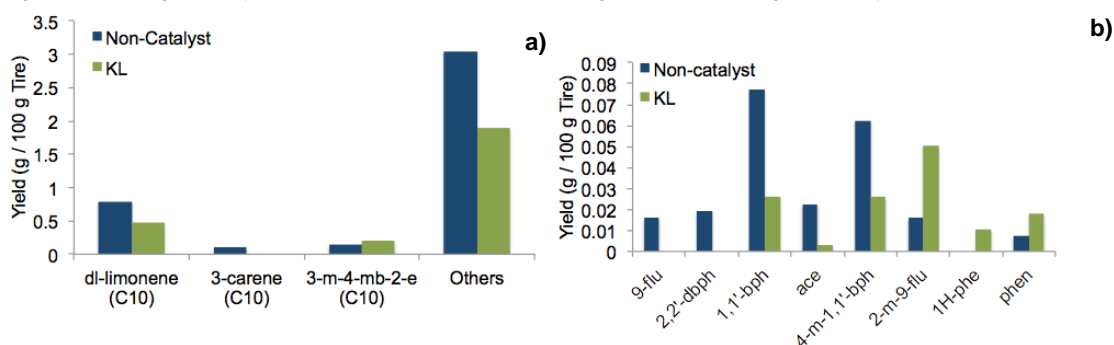


Figure 5: Changes of hydrocarbon species in (a) TERs (C10) and (b) PAHs with using KL catalyst

### 3.2.5 Change of hydrocarbon species in PPAHs

The sulphur compounds in PPAHs were found to be 2-(1-methylethyl)thiophene, ( $m/z = 126.050$ ), methylbenzothiophene ( $m/z = 148.035$ ), 3-phenylthiophene, ( $m/z = 160.035$ ), dimethylbenzothiophene ( $m/z = 162.050$ ), dibenzothiophene ( $m/z = 184.035$ ), dimethyldibenzothiophene ( $m/z = 212.066$ ), and naphtho[2,3-b]thiophene, 4,9-dimethyl- ( $m/z = 212.066$ ). Figure 6(b) shows that thiophenes (thos) and benzothiophenes (b-thos) are increased with the decreases in phenylthiophenes (p-thos), benzothiophenes (b-thos), and dibenzothiophenes (db-thos) when the KL catalyst is used.

## 4. Conclusions

The KL catalyst was found to increase the yield of MAHs (mostly, 2-ethyltetralin) from 20.1 to 26.8 %wt but decrease that of DAHs (mostly, 2-ethylnaphthalene) from 13.31 to 6.37 %wt. Moreover, the yield of TERs (mostly, d-limonene and 3-carene) decreased from 4.06 to 2.56 %wt. It was due to the fact that the KL catalyst can hydrogenate DAHs and aromatize TERs. Moreover, the bulky pyrolysis products decreased when the KL catalyst was used. The PPAHs, PAHs, SATs, and OLEs did not significantly change with using the KL catalyst. Finally, the sulphur compounds in tyre-derived oils were found to be thiophenes, phenylthiophenes, benzothiophenes, methylbenzothiophenes, dibenzothiophenes, and naphthols.

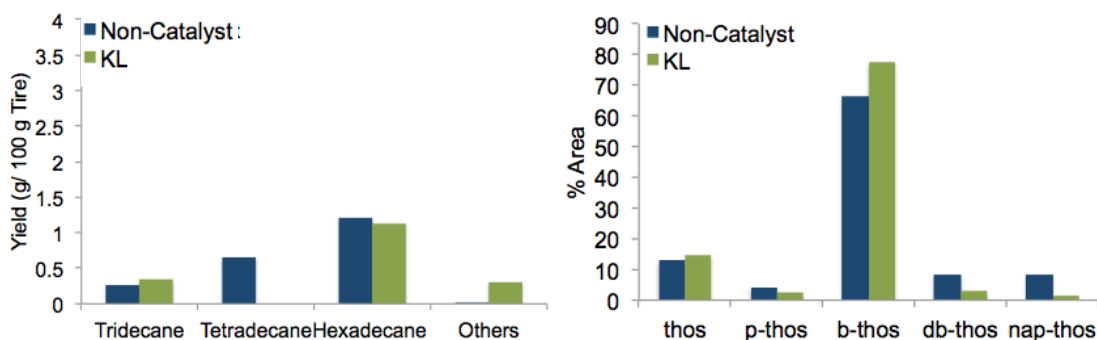


Figure 6: Changes of hydrocarbon species in (a) SATs and (b) PPAHs with using KL catalyst

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