Estimation of Average Kinetic and Maximum Diameters of Hydrocarbon Groups in Tyre-Derived Oil for Catalyst Design Purpose

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Estimation of molecular sizes of hydrocarbons in tyre-derived oil (TDO) is necessary for selecting an oil upgrading catalyst. Generally, the size of a hydrocarbon mixture can be described using average kinetic and maximum diameters. Due to molecular movement, average kinetic diameter ($Ø_k$) is absolutely needed. However, maximum diameter ($Ø_m$), defined as the longest part of a molecule, can ensure that all molecules in the mixture can pass through the catalyst pore. Therefore, the objectives were to estimate average kinetic ($Ø_{k,avg}$) and and average maximum ($Ø_{m,avg}$) of hydrocarbons in TDOs, and then suggest selective catalysts to handle them, aiming to decrease heavy fraction especially aromatic compounds and increase lighter products. $Ø_k$ was calculated using critical parameters from Joback method, whereas $Ø_m$ was estimated using published data from Chemspider. More than 800 species detected by GCxGC-TOF/MS were classified into saturated hydrocarbons (SATs), olefins (OLEs), naphthenes (NAPs), terpenes (TERs), mono-aromatics (MAHs), di-aromatics (DAHs), poly-aromatics (PAHs), and polar-aromatics (PPAHs). As a result, the $Ø_{k,avg}$ of all hydrocarbon groups is in the range of 6.5 - 8.1 Å. The $Ø_{m,avg}$ of SATs and OLEs is 8.1 - 34.7 Å, whereas that of the other groups is in the range of 6.6 - 14.6 Å. Hence, in order to handle aromatic groups (6.6 - 14.6 Å), aluminophosphate catalysts (6 - 15 Å) or mesoporous materials such as MCM (20-30 Å) families are recommended.

1. Introduction

Nowadays, the growth rate of transportations has rapidly increased. The following problem is that the large space of landfill for waste tyre is required. Therefore, the recycle of end-of-life tyre should be considered. Pyrolysis is one of the effective processes for end-life tyre elimination. Gas, oil, and char are the obtained solutions from this process. Indeed, tyre-derived oil (TDOs) is the attractive product since it can be directly used as fuel oil. However, the recent research work of Yuwapornpanit and Jitkarnka (2015) stated that the improvement of oil qualities was the important issue because heavy fractions (gas oil and LVGO, and HVGO) (60 - 65 %), and especially large-size aromatics (DAHs, PAHs, and PPAHs) (20-25 %) still remained in tyre-derived oil from thermal pyrolysis. In order to convert heavy fractions into light products, the estimation of molecular sizes of hydrocarbons in tyre-derived oil (TDO) is necessary for selecting an oil-upgrading catalyst with an appropriate pore size that can handle all molecules in the feed. Generally, kinetic diameter is commonly referred in catalysis literatures as the size of a molecule, which is used a criterion in selecting pore size of a selective catalyst. Since the TDO is a complex mixture of a large number of bulky molecules, the estimation of average molecular size is not simple, and has not been accomplished. Jae et al. (2011) suggested that if the value from literatures has not yet been available, the properties of a compound at the critical point including temperature, pressure, and volume, can be used to calculate its kinetic diameter. The estimation of the molecular size can be also determined from molecular weight; however, the method can be only applicable for a spherical molecule such as aromatic and symmetric compounds (Bird et al., 2007). Furthermore, the molecular sizes can be estimated by using Lennard-Jones calculation (Marcus, 2003). However, Lennard-Jones parameters for evaluation are limited for bulky molecules, like in TDOs. Additionally, kinetic diameter can be observed from commonly available

computational programs; for examples, Spartan'02 and GAUSSIAN 98 using quantum mechanic calculation for a complex mixture in gasoline (Jiménez-Cruz and Laredo, 2004), and Turbomole V6.5 electronic structure package using for simulation of kinetic diameter of small gaseous molecules (Mehio et al. 2014). For a multi-component mixture, the average kinetic diameter ($Ø_k$) of the compounds in the mixture is absolutely needed to describe the average molecular size. However, the maximum diameter ($Ø_m$) of a molecule, defined as the longest part of a molecule, can indicate the maximum size of catalyst pore that would allow the longest part of a molecule to pass through. Then, the $Ø_{m,avg}$ of compounds in a mixture is calculated to ensure that all molecules in the mixture can pass through a selective catalyst pore. This present research work was aimed at estimating the average molecular sizes of compounds in TDO for selecting a selective catalyst with a suitable pore for the conversion of TDOs to lighter products. From the molecular composition of TDO obtained from GCxGC/TOF-MS, the kinetic diameter of all molecules was calculated by using critical volume, obtained from Joback method, whereas the maximum diameter was estimated using the published data from ChemSpider (Royal society of chemistry, 2015). Then, the average molecular sizes of every group of compounds in TDO were reported, and some catalysts selective to convert TDO were finally suggested.

2. Experimental

2.1 Pyrolysis process of waste tyre
The tyre pyrolysis experiment was conducted using the same pyrolysis system as in the research of Yuwapornpanit and Jitkarnka (2015). First, the waste tyre sample, Bridgestone TURANZA GR-80, was scraped and then sieved (20-40 mesh). Then, thirty grams of scraped tyre were loaded into the pyrolysis zone. After that scraped tyre was heated from room temperature to 500 ^{o}C with heating rate of 10 ^{o}C/min. The operating time was held of 120 min at final temperature. Nitrogen was used as carrier gas in order to carry the product effluent to condensers to condense the oil products, and the incondensable gas was kept in a Tedlar gas bag.

2.2 Analysis of waste tyre products
First, TDO was dissolved in n-pentane (RCI Labscan, Thailand, 99 %) in the oil to n-pentane mass ratio of 1:40 for asphaltene separation. A GCxGC/TOF-MS, the Agilent gas chromatograph 6890 system equipped with a cryogenic modulator and a Pegasus 4D TOF/MS, was employed to analyze the maltene composition. The 1st column was a non-polar Rtx®-5 Sil MS with 30 m x 0.25 mm ID x 0.25 µm film thickness. The 2nd column was an Rxi®-17 MS with 1.79 m x 0.10 mm ID x 0.10 µm film thickness. The mass rage 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, and required the similarity more than 700. The dt method was used to calculate the percentage of area. Data were recorded and analyzed using the LECO ChromaTOF® software. The NIST library provided with the instrument was used for spectral searching. The components in maltene obtained from GCxGC/TOF-MS were categorized into 8 groups; that are saturated hydrocarbons (SATs), olefins (OLEs), naphthenes (NAPs), terpenes (TERs), mono-aromatics (MAHs), di-aromatics (DAHs), poly-aromatics (PAHs), and polar-aromatics (PPAHs) (Pithakratanayothin and Jitkarnka, 2014). A SIMDIST GC, a Varian GC-3800 simulated distillation gas chromatograph conformed to the ASTM-D2887 method, was used to determine the simulate true boiling point of TDO. The instrument was equipped with FID and WCOT fused silica capillary column (15 m x 0.25 mm x 0.25 µm). The true boiling point curve was cut into petroleum fractions according to their boiling points; gasoline (< 149 ^{o}C), kerosene (149 - 232 ^{o}C), gas oil (232 - 343 ^{o}C), light vacuum gas oil (343 - 371 ^{o}C) and heavy vacuum gas oil (> 371 ^{o}C).

2.3 Determination of sampling size
Yamane method was used to determine the sampling size (n) of hydrocarbons in each molecular group as seen in Eq(1) (Israel, 2013). A ninety percent confidence level was assumed for this equation (e = 0.1), where N is the population of hydrocarbons in each group.

$$n = \frac{N}{1+N(e)^2}$$
(1)

2.4 Determination of molecular diameters
The components in the condensed oily phase from pyrolysis of waste tyre were the outcome from GCxGC/TOF-MS. These molecules were assumed as a rigid feed. First, all the components were classified into the 8 molecular groups, and then the representative components from each group were selected using the sampling technique based on Yamane's method. The kinetic diameter ($Ø_k$) of each all

representative molecules was next calculated using its critical volume at critical point based on Joback method. The critical volume was manually calculated according to the functional group within molecular structure (Pirika, 1999). Then, it was used to calculate the kinetic diameter as shown in Eq(2) (Bird et al. 2007), where V_c is defined as the critical volume (cm^3/mol).

$$\phi_k = 0.841 V_c^{\frac{1}{3}} \tag{2}$$

The maximum diameter, defined as the longest part of molecular structure, was next evaluated using the published data from ChemSpider (Royal society of chemistry, 2015) conformed to NIST, SMILES, InChI, API, etc databases. Then, the area percentages of sampling species were normalized, and the distribution of kinetic and maximum diameters of each molecular group were plotted with the increment 0.5 Å, in order to calculate the average molecular sizes from the distributions. The average kinetic and average maximum diameters in each distribution range were subsequently determined using Eq(3), where ω and m are defined as the weight fraction of each species and the number of species in each range.

$$\phi_k = \frac{\sum_{i=1}^{m} \omega_i \phi_i}{\sum_{i=1}^{m} \omega_i} \tag{3}$$

3. Results and Discussion
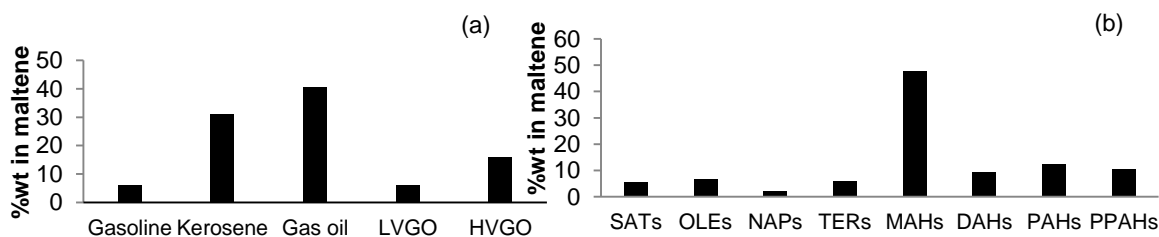
3.1 Analysis of tyre-derived oil

Figure 1: (a) Petroleum fractions analyzed by using SIMDIST GC, and (b) Maltene compositions of each component group detected by using GCxGC-TOF/MS

From the analysis, tyre-derived oil contains 6.2 wt% gasoline, 31.0 wt% kerosene, 40.6 wt% gas oil, 6.4 wt% LVGO, and 15.9 wt% HVGO. The aromatics (MAHs, DAHs, PAHs, and PPAHs) account for 78.5 wt%, followed by 12.7 wt% aliphatics (SATs and OLEs), and 8.7 wt% alicyclics (NAPs and TERs).

3.2 Determination of sampling size

Table 1: Sampling size and representatives from each group of compounds

Molecular group	Number of detected compounds	Number of sampling size[a]	Range of carbon number	Range of sampling carbon number	%Area of detected compounds	%Area of sampling
SATs	42	30	5 - 27	8-27	5.31	5.15
OLEs	110	52	5 - 19	8-18	7.42	6.21
NAPs	42	30	6 - 16	7-15	2.04	1.92
TERs	100	50	6 -15	6-15	6.68	5.79
MAHs	231	70	8 - 26	8-16	46.90	40.63
DAHs	27	21	10 - 16	10-16	9.22	9.12
PAHs	96	49	10 - 30	12-25	12.06	11.19
PPAHs	174	64	5 - 23	6-21	10.36	9.03
Total	822	365			100.00	89.04

[a]Yamane (Israel, 2013)

A total of 822 hydrocarbon compounds were detected in tyre-derived oil using GCxGC-TOF/MS. The Yamane method was used to calculate the sampling size (Israel, 2013). Moreover, molecules with a high percent area (high concentration) were considered. As a result, the sampling size of 365 species was selected as representatives to estimate the diameters. The representatives of molecules were carefully

selected to cover all groups of compounds based on their concentration in all range of carbon number. The information about the representative molecules is shown in Table 1. The total percent area of representative compounds accounts for 89.0 % of total area.

3.3 Determination of molecular diameters

The diameters of all representative compounds were calculated. The distributions of molecular sizes were then plotted, as displayed in Figure 2. Subsequently, the average molecular diameters were estimated from the molecular size distributions as reported in Table 2.
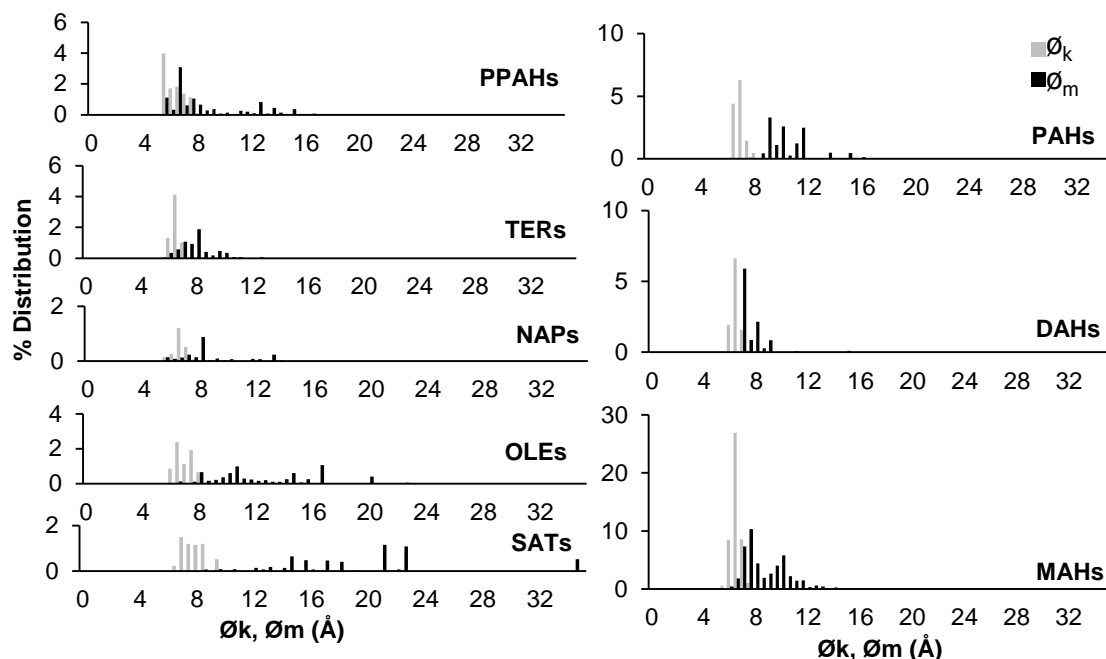

Figure 2: Molecular size distributions of components

Table 2: Average kinetic and maximum diameters of compositions in each group

Group of components	Average kinetic diameter ($\varnothing_{k,avg}$; Å)[a,b]	Average maximum diameter ($\varnothing_{m,avg}$; Å)[b,c]		
		Small (< 8 Å)	Medium (8-16 Å)	Large (>16 Å)
SATs	8.1	-	9.8, 15.7	23.4, 34.7
OLEs	7.2	-	8.1, 10.9	21.0
NAPs	6.8	7.8	13.0	-
TERs	6.7	-	8.2	-
MAHs	6.6, 7.2	6.6	9.0	-
DAHs	6.7	7.6	13.5	-
PAHs	7.2	-	8.6, 10.4, 14.6	
PPAHs	6.5	7.2	13.3	-

[a]Eq(2), [b]Eq(3), and [c]Royal society of chemistry, 2015

As a result, the molecular sizes of each hydrocarbon group are distributed in more than one range of distributions, except those of TERs. The uni-modal distribution of $\varnothing_k$ is observed in all groups of hydrocarbons, except MAHs whose $\varnothing_k$ are distributed in bi-modal distribution. The $\varnothing_{k,avg}$ of all hydrocarbon groups is in the range of 6.5-8.1 Å. The maximum diameters, $\varnothing_m$, are distributed in tri-modal distribution. Therefore, the average maximum diameters, $\varnothing_{m,avg}$, were classified into 3 sizes; that are, small (< 8 Å), medium (8-16 Å), and large sizes (> 16 Å) as reported in Table 2. Furthermore, the $\varnothing_{m,avg}$ of aliphatic (SATs and OLEs), alicyclic (NAPs and TERs), and aromatic (MAHs, DAHs, PAHs, and PPAHs) groups are in the range of 8.1-34.7 Å, 7.8-13.0 Å, and 6.6-14.6 Å, respectively. Based on the $\varnothing_{m,avg}$, the components with the medium sizes (8-16 Å) are the majority in the TDO.

3.4 Design of catalyst

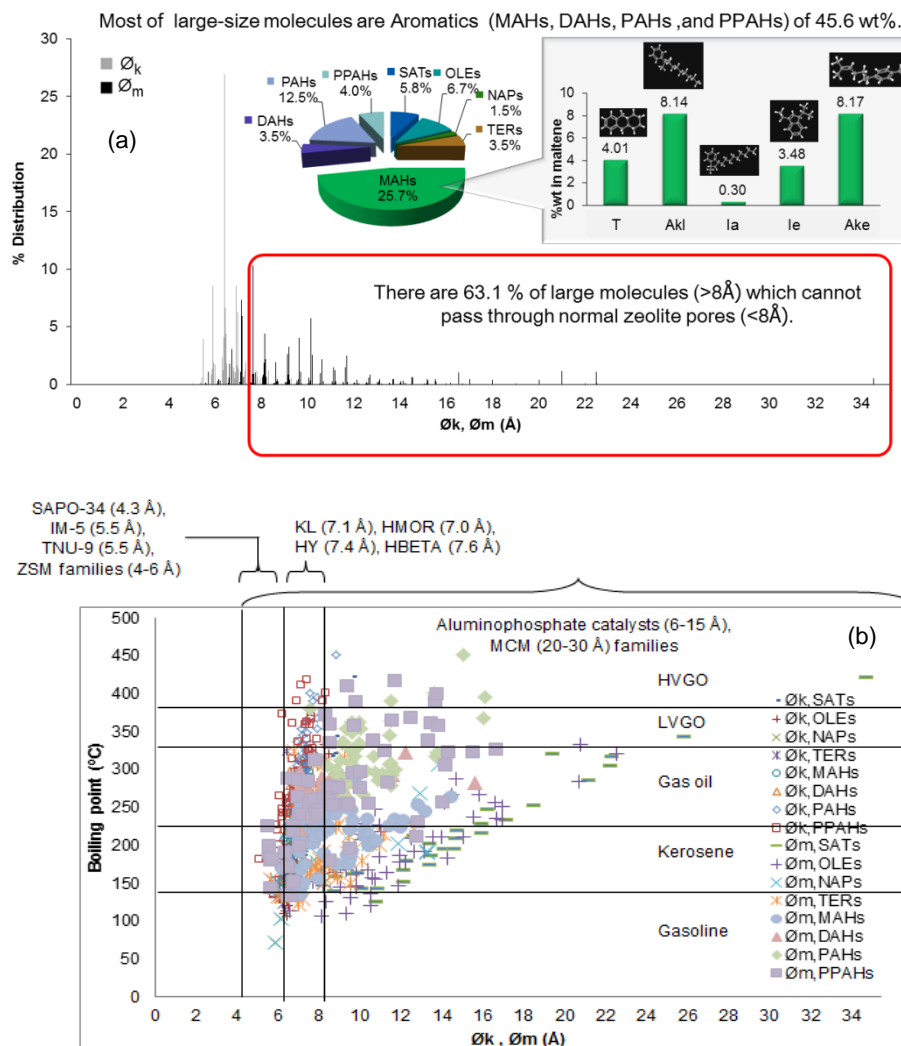Figure 3: (a) Distribution of molecules with large sizes (T = Tetralines, Akl = Akylbenzenes, Ia = Indanes, Ie = Indenes, Ake = Akenylbenzene), and (b) Distribution of molecular sizes of compounds in TDO in all petroleum fractions

In the previous work Yuwapornpanit and Jitkarnka (2015) used the zeolites with the pore size of 6-8 Å, which were HBETA, HY, and HMOR, in the pyrolysis of waste tyres. The results showed that LVGO and HVGO were still remained. Therefore, it can be stated that the catalyst with pore size less than 8 Å cannot highly convert heavy fractions into lighter products. It can be observed that the $\varnothing_{k,avg}$ obtained from calculation is in the range of 6.6-8.1 Å; therefore, some catalysts with this range of pore size, like HBETA, HY, and HMOR, should have been able to handle the heavy fractions, but they could not have. Thus, the $\varnothing_{k,avg}$ may not be suitable for using in catalyst design for catalytic pyrolysis of waste tyre. That is why the estimation of the $\varnothing_{m,avg}$ of compounds in tyre-derived oil must be acquired in this work.

The molecular size distributions of all groups are illustrated in Figure 3(a). There is approximately 63.1 % of large-size molecule distributing in the tyre-derived oil. Most of them are aromatics (45.6 %) distributing in MAHs, DAHs, PAHs, and PPAHs. The major large-size aromatic group is MAHs (25.7 %), which is mainly composed of include akenyl- and alkyl-benzenes, followed by tetralines, indenes, and indanes.

Figure 3b shows that hydrocarbons within the $\varnothing_{m,avg}$ of 8-16 Å account for more than half amount of total representative hydrocarbons. Most of them are in gas oil, HVGO, and LVGO fractions, mainly comprised of aromatic compounds as reported in Table 3. PAHs contributes the highest amount, followed by PPAHs, MAHs, and DAHs. Thus, the catalysts such as aluminophosphate (6-15 Å) and MCM (20-30 Å) may be

used to selectively convert these fractions, especially aromatic compounds, into lighter products. Using these catalysts, not only can aromatic groups be cracked in the inner pore, but also other bulky compounds can be handled. Since the sizes of the feed fit with the pore sizes of the catalysts; thus, aromatic compounds can be transformed into the lighter products with lower boiling points. Furthermore, the hydrocarbons with the molecular size in the range of 6-8 Å in NAPs, MAHs, DAHs, and PPAHs can be handled by KL, HMOR, HY, and HBETA pores, according to the $Ø_{m,avg}$ as seen in Table 2. The small-microporous catalysts such as SAPO-34, IM-5, TNU-9, and ZSM-5 families with the pore sizes of 4-6 Å have a very low potential to convert the hydrocarbons in TDO since most of molecules have sizes larger than 6 Å.

Table 3: Molecular composition of each petroleum cuts (%) of thermal pyrolysis case

Group of components	Gasoline	Kerosene	Gas oil	LVGO	HVGO
SATs	3.0	3.6	5.7	35.0	28.4
OLEs	27.6	6.1	6.4	-	-
NAPs	3.1	3.5	0.5	-	-
TERs	13.1	8.8	3.5	-	-
MAHs	49.8	64.0	26.9	-	-
DAHs	-	3.8	21.3	-	-
PAHs	-	-	26.5	41.4	50.5
PPAHs	3.5	10.3	9.2	23.6	21.1

4. Conclusions

The molecular sizes of complex hydrocarbons in TDOs were estimated, and then used for selecting some reactant-selective catalysts suitable for converting bulky hydrocarbon into lighter products. As a result, using the $Ø_{k,avg}$ for catalyst design in pyrolysis of waste tyre may not suitable. Thus, the $Ø_{m,avg}$ estimation of compounds in TDOs must be acquired in this work. Aromatics (MAHs, DAHs, PAHs, and PPAHs) with the $Ø_{max,\ avg}$ of 6.6-14.6 Å were mainly in gas oil, LVGO, and HVGO fractions. Therefore, some selective catalysts such as aluminophosphate catalysts (8-15 Å) or mesoporous materials such as MCM (20-30 Å) families can be employed. Using these catalysts, bulky aromatic compounds are expected to be reformed or cracked into products with lower boiling point.

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