

CHAPTER IX

CONCLUSIONS AND RECOMMENDATIONS

There are three main drawbacks of pyrolytic products. First, heavy compounds especially aromatic hydrocarbons are highly present in tire-derived oil (TDO); thus, it is not suitable for uses in vehicle engine. Second, char remaining from pyrolysis is highly obtained, but it has only a few applications. Third, heteroatoms such as nitrogen in TDO can cause the catalyst poisoning and environment problems. Therefore, the objectives were to (1) estimate molecular size for designing oil-upgrading catalysts, (2) study the effect of pore size and pore structure of the selected catalysts for removal of heavy compounds, (3) upgrade pyrolysis char for using as a catalyst in catalytic pyrolysis of waste tire, and (4) identify N-containing compounds for better understanding in further treatment.

Estimation of molecular sizes of hydrocarbons in 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. As a result, using the $\text{Ø}_{k,\text{avg}}$ for catalyst design in pyrolysis of waste tire was found not suitable. Thus, the $\text{Ø}_{m,\text{avg}}$ estimation of compounds in TDOs must be acquired in this work. Aromatics (size 6.6-14.6 Å) were mainly in gas oil and vacuum gas oil fractions. Therefore, some selective catalysts such as aluminophosphate catalysts (6-15 Å) or mesoporous materials such as MCM (20-30 Å) families were suggested. Bulky aromatic compounds were expected to be removed when the selected catalysts were introduced.

The effect of pore size was investigated between commercial Al-MCM-41 (pore size = 33.1 Å) and Al-SBA-15 (pore size = 60.5 Å) on conversion of heavy compounds, especially large-size aromatic hydrocarbons into lighter oil products. The results indicated that the pore size of 33.1-60.5 Å can provide the almost complete cracking of large-size poly- and polar-aromatics in tire-derived oil. However, the pore size of 33.1 Å showed more impressive reduction of heavy

fractions (gas oil, LVGO, and HVGO) and large-size aromatics (DAHs, PAHs, and PPAHs) than the pore size of 60.5 Å. Moreover, the pore size of 33.1 Å was not only better in removing those heavy compounds but also in producing a higher quality of petrochemicals. This is because the pore size of 33.1 Å better fits with the size of aromatic compounds in oil than the pore size of 60.5 Å, driving higher sticking possibility on the active sites, and then higher reactivity. Furthermore, Al-MCM-41 and Al-SBA-15 can drastically remove sulfur in oil.

The effect of pore structure was studied using synthetic Si-MCM-41 (hexagonal structure) and Si-MCM-48 (cubic structure) on the removal of heavy fractions. The results indicated that both catalysts can highly decrease gas oil and vacuum gas oil fractions, leading to a substantial enhancement of gasoline and kerosene. Interestingly, Si-MCM-41 and Si-MCM-48 can open rings of aromatics because the large porosity of Si-MCM-41 and Si-MCM-48 can contribute in the high diffusion of large-size aromatics to access the active site in pore. Then, protons in the silanol groups in the pore of these materials can be highly promoted to the molecules, forming carbenium ions for further cracking. However, the cubic structure better performed on heavy compound removal because its three-dimensional interconnected cubic pore structure performed the reaction with a higher retention time inside the pore.

Possibility of using untreated and 5 M HNO₃-treated pyrolysis chars as catalysts for waste tire pyrolysis was investigated. It was found that the 5MHNO₃ treatment can enhance the acidity, surface area, pore size, and sulfur removal of char. Interestingly, the untreated and 5 M HNO₃-treated chars can convert heavy portions (gas oil and gas oil) into lighter fractions (gasoline and kerosene), caused by the reduction of aromatics (DAHs, PAHs, and PPAHs) in oil. However, the 5 M HNO₃-treated char gave the higher performance on catalytic cracking than untreated char due to higher acidity, higher surface area, and larger pore size.

Identification of nitrogenous compounds in TDO using powerful GCxGC/TOF-MS was successfully accomplished. Approximately, 87 nitrogenous species in PPAHs group were detected, and classified into 10 groups, according to their structures and carbon numbers; that are, amines (An), amides (Ad), azo compounds (Az), indoles (ID), isothiocyanates (ITC), nitro compounds (N), nitriles

(NT), pyridines (PD), quinolines (QL), and especially diazabicycloheptenes (DBCH) that was firstly detected in tire-derived oil. Most of N-containing species are distributed in the carbon numbers of 6-18 (99.0 %), and are mostly in the Azo groups of compounds (42.9 %). Diazabicycloheptenes was the new group, firstly found in TDOs. Most of nitrogenous compounds were found distributed in kerosene and gas oil fractions.

There are 5 recommendations for future studied. First, a catalyst with cubic structure should be further study on the effect of pore size between 30-60 Å for removal of heavy fraction, petrochemical productivity, and hetero-atom removal. Second, pyrolysis char should be further studied on the conditions of treatment/modification methods, structure stability, and metal doping. Then, the optimized catalyst should be prepared in the industrial form. Third, it is recommended that hetero-atoms such as sulfur and nitrogen be removed from TDO by using hydrated iron (III) chloride-clay adsorbent, hydrodenitrogenation (Wei *et al.*, 2015), ultrasound-assisted oxidative desulfurization process (Nunes *et al.*, 2014) or ionic liquid methods (Laredo *et al.*, 2015). Fourth, hydrotreating process should be introduced for oil upgrading. Finally, it is recommended that the obtained oil be refined and tested in a vehicle engine.