

## CHAPTER V

### CONCLUSIONS AND RECOMMENDATIONS

The pyrolysis of waste tire was operated in a bench-scaled autoclave reactor. The effects of Rh supported on different zeolites, with especially differences on acidity of acidic (HY, HBETA) and non-acidic (KL) zeolites were investigated. 0.25 wt% Rh on each supports and 1 wt% Rh on HBETA were prepared by incipient wetness impregnation technique. Furthermore, the role of commercial regenerated NiMoS/Al<sub>2</sub>O<sub>3</sub> and fresh CoMoS/Al<sub>2</sub>O<sub>3</sub> catalysts obtained from a refinery on the catalytic pyrolysis of waste tire were also investigated. With their desulfurization ability, the quality and quantity of pyrolysis oil were expected to improve in terms of a lower sulfur level. There were 10 experiments (including batch of non-catalyst and pure zeolite supports), performed for this work by using the controlled parameters as the following; the used tires were sieved into particle size range of 8-18 mesh and process conditions, holding time, N<sub>2</sub> flow rate, heating rate, pyrolysis zone temperature, catalytic zone temperature, weight of scrap tire and catalyst were fixed to 30 min, 30 ml/min, 10 °C/min, 500 °C, 350 °C, 30 g and 7.5 g (ratio of tire per catalyst = 4:1), respectively

In order to compare the acidity effect, KL and HBETA were selected as the support for Rh loading. It was found that 0.25 wt% Rh/KL did not much affect to the pyrolysis products while the liquid product extremely decreased to the short-chain hydrocarbons by using 0.25 wt% Rh/HBETA. It can be explained that the acidity of acidic catalyst promoted the cracking activity, resulting in high amount of gas yield (remarkable in cooking gas) and coke formation, but 1 wt% Rh/HBETA did not further increase the cracking reaction. Likewise, 0.25 wt% Rh/HBETA gave the best result for desulfurization of oil because of the hydrogenation and hydrodesulfurization of Rh and high cracking activity of HBETA by removing the sulfur from oil and releasing it in the form of H<sub>2</sub>S. However, the oil obtained from using 0.25 wt% Rh/KL remained high quality as same as using 0.25 wt% Rh/HBETA since the low-molecular weight sulfur was considerably observed. The sulfur species found the most in 0.25 wt% Rh/KL and HBETA cases were benzo[b]thiophene, 2,7-dimethyl- and 3-Methylbenzothiophene.

The effects of pore structure of HY and HBETA were also investigated. Both 0.25 wt% Rh/HY and Rh/HBETA affected to the pyrolysis products, but 0.25 wt% Rh/HBETA produced more gas yield than 0.25 wt% Rh/HY because of greater acid strength. The highest cracking activity of 0.25 wt% Rh/HBETA caused the large hydrocarbon molecules blocking the one-dimensional (strength pore) of HBETA support; so, poly-aromatics were found the most in 0.25 wt% Rh/HBETA case due to coke blocking. However, the introduction of Rh led to decrease in specific surface area, pore specific volume, and acidity of the catalysts, but it induced mono-aromatics formation. The sulfur content obtained from using 0.25 wt% Rh/HY was higher than that obtained from using 0.25 wt% Rh/HBETA, and also low quality of oil was found because of less of sulfur-containing light molecules. 2,7-dimethylbenzo[b]thiophene was the most found sulfur species obtained from using 0.25 wt% Rh/HY.

The roles of regenerated NiMoS/Al<sub>2</sub>O<sub>3</sub> and fresh CoMoS/Al<sub>2</sub>O<sub>3</sub> hydrodesulfurization catalysts on catalytic pyrolysis of waste tire were investigated since the catalysts contained both acid and metal sulfide functions that could potentially benefit cracking and sulfur removal simultaneously, and the use of regenerated catalyst was exclusive of the economic benefit. It was amazing that the regenerated NiMoS/Al<sub>2</sub>O<sub>3</sub> had a bit cracking activity less than fresh CoMoS/Al<sub>2</sub>O<sub>3</sub>, possibly due to the excellent activity for hydrogenation of Ni catalyst (Kim *et al.*, 2003). The oil obtained from CoMoS/Al<sub>2</sub>O<sub>3</sub> had less poly- and polar-aromatics than NiMoS/Al<sub>2</sub>O<sub>3</sub> due to its higher Brønsted acid density that could be explained from IPA-TPD analysis. However, NiMoS/Al<sub>2</sub>O<sub>3</sub> showed high selectivity in full range naphtha while CoMoS/Al<sub>2</sub>O<sub>3</sub> gave remarkable mono-aromatics amount, and both of the two catalysts caused the prominent light alkane gas product (ethane, propane). For the desulfurization ability, CoMoS/Al<sub>2</sub>O<sub>3</sub> gave the lowest sulfur in the oil.

It can be concluded that all catalysts had both cracking and desulfurization, but the best results for catalytic pyrolysis of waste tire and sulfur removal ability were obtained 0.25 wt% Rh/HBETA and commercial CoMoS/Al<sub>2</sub>O<sub>3</sub> catalysts, respectively. However, the sulfur species found the most in this study were benzothiophene derivatives, which is different from Williams and Bottrill (1995) who found dibenzothiophene derivatives in majority.

It is recommended that the further study about the improvement of catalysts be investigated for the modified catalysts that have both the best in cracking and desulfurization by combining the Rh/HBETA with commercial CoMoS/Al<sub>2</sub>O<sub>3</sub> hydrodesulfurization catalyst as the additive, aiming to further enhance desulfurization ability of the best cracking catalyst. Moreover, the economic valuation should also be concerned.