

Quality Improvement of Waste Tyre Pyrolysis Oil by Using Cu/HMOR as a Catalyst

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Metal-loaded zeolites are interesting catalysts for the improvement of the quality and quantity of waste tyre pyrolysis products. Since the catalysts exhibit multi-functions in catalysis, including hydrogenation, dehydrogenation, ring-opening, cracking, etc. that can be acquired from metal and zeolite properties. This work studied the effect of 5 wt%Cu/HMOR catalyst on waste tyre pyrolysis products. Since copper is widely used in several applications such as selective hydrogenation of undesired unsaturated hydrocarbons in a mixed-C₄ stream, and sulphur removal from liquid fuels, etc. Catalytic pyrolysis of waste tyre was operated in a bench reactor. GCxGC-TOF/MS and SIMDIST-GC instruments were used to analyze the liquid products. Sulphur distribution in the pyrolysis products was determined by using an S-analyzer. As compared with the HMOR catalyst, the Cu/HMOR decreased the amount of olefins, naphthenes, poly-aromatics, and polar aromatic compounds in oils while the amounts of paraffins, di- and mono-aromatics in oils were increased because the presence of copper can promote hydrogenation, ring-opening, and cracking activities of HMOR zeolite. Furthermore, Cu/HMOR catalyst not only reduced heavy compounds in the oil but also sulphur content in the oil (reduced from 1.08 wt% to 0.907 wt% in the HMOR case), indicating that the quality of the oil as a combustion fuel was improved by using copper as a promoter of HMOR zeolite. An interesting result was that the valuable products produced in the Cu/HMOR case were benzene (1.14 wt% in oil), toluene (2.65 wt% in oil), and ethylbenzene (5.39 wt% in oil), which have never been found in the non-catalytic case or in the case when the parent HMOR was used.

1. Introduction

From the past to present, waste tyre elimination has been an important problem because tyres are highly stable in chemicals and environments. Pyrolysis is a thermal degradation method of waste tyres, which is more effective process than other waste tyre elimination methods because it can not only eliminate waste tyres but also recover usable products (Williams, 2013); so, waste tyre pyrolysis is widely adopted nowadays in many countries where land and resource are limited. The waste tyre pyrolysis can produce three parts of products consisting of gases, oils and char. The interested product is pyrolysis oil that can be fractionated according to boiling points into gasoline, kerosene, gas oil, heavy gas oil, light vacuum gas oil, and heavy vacuum gas oil (Dũng et al., 2009a). Furthermore, some components in oil can be used as chemicals (Boxiong et al., 2007) such as benzene, toluene, xylenes, etc.

Zeolites are widely used as a commercial catalyst in the production of petrochemicals because they have several interesting properties such as catalytic cracking and hydrocracking (USY), catalytic dewaxing (ZSM-5, ZSM-22, and SAPO-11), cracking and alkane isomerization (BETA) (Martinaz and Corma, 2011), and transalkylation and paraffin skeletal isomerization using HMOR (Busca, 2007), etc. For catalytic pyrolysis of waste tyre, zeolites can be effective catalysts for increasing desired products as proven by many researchers. For examples, Williams and Brindle (2003) found that ZSM-5 and Y zeolites can increase the amount of value added products in pyrolysis oils; for examples, benzene, toluene, xylene, styrene, etc. HBETA zeolite can produce the high amount of saturated hydrocarbons and the naphtha fraction of tyre-derived oil (Saeae and Jitkarnka, 2012). Dũng et al. (2009a) studied the effect of HMOR

zeolite on catalytic pyrolysis oils. HMOR zeolite can increase the amount of mono-aromatics in the oil, and gasoline and kerosene yields, while heavier fractions and total-aromatics were also decreased, indicating that the oil quality can be upgraded. Furthermore, an introduction of metal onto a zeolite might improve some quality of pyrolysis products as well. Copper is widely used as a selective hydrogenation catalyst and adsorbent in sulphur removal from liquid fuels. Copper-loaded catalysts can be used in selective hydrogenation that can remove undesired compounds in the process. For examples, Cu/SiO₂ catalyst was used to remove alkynes and butadiene in C₄-stream by partial hydrogenation by converting them into butenes (Setiawan and Cavell, 1995). Copper loading on hydrotalcite, malachite, SiO₂ and Al₂O₃ supports was used to convert propyne into propylene at high selectivity and undesired products at low selectivity (Bridier et al., 2010). In the other applications, Cu(I)-exchanged zeolites can be used as an adsorbent for thiophene removal from liquid fuels as well (Tang and Shi, 2011). For catalytic pyrolysis of waste tyre, copper was expected to promote hydrogenation that might cause cracking and ring-opening reactions to occur easily. Furthermore, copper was expected to enhance sulphur reduction of the pyrolysis oil as well. In this work, the effect of copper on waste tyre pyrolysis products was therefore studied, using HMOR zeolite as the support.

2. Experiment

2.1 Catalyst and sample preparation

HMOR zeolite (Si/Al = 9.5) supplied by TOSOH Company (Singapore) was calcined in static air with the heating rate of 5 °C/min from room temperature to 500 °C with holding for 3 h after the final temperature was reached. The calcined zeolite was subsequently impregnated with the copper solution (Cu(NO₃)₂·3H₂O) at the copper loading of 5 wt%, dried overnight in an oven at 120 °C, and calcined again at the same calcination condition. Next, the calcined catalyst was reduced at 600 °C for 2 h in hydrogen atmosphere. Finally, the catalyst powder was pelletized, crushed, and sieved to the size range of 40-60 mesh. A waste tyre sample, Bridgestone TURANZA GR-80, was shredded and then sieved into a particle size of 20-40 mesh.

2.2 Waste tyre pyrolysis process

The pyrolysis system employed in the experiment was the same as in Dũng et al. (2009b). The catalytic pyrolysis of waste tyre was operated at atmospheric pressure from room temperature to a temperature of 500 °C (the pyrolysis zone) and 350 °C (the catalytic zone) with a ramping rate of 10 °C/min and a holding time of 2 hours after the final temperatures were reached. 30 g of shredded tyre (20 - 40 mesh) and 7.5 g of HMOR or 5 wt%Cu/HMOR catalyst (40 - 60 mesh) were packed in the pyrolysis zone and the catalytic zone, respectively, (at catalyst/tyre ratio = 0.25). Nitrogen gas was used as carrier gas. Liquid products were condensed in the condensers immersed in an ice-salt (NaCl) bath, while the gas products were collected by using a gas sampling bag.

2.3 Catalyst characterization

XRD machine (Rikagu) was used to acquire the XRD patterns of the catalysts using CuK α radiation operated at 40 kV and 30 mA. The angles in the range of 5-65° were scanned at a scanning speed of 5 °/min. Surface area and pore volume of catalysts were determined by N₂ physisorption using Thermo Finnigan Sorptomatic 1990 equipment. The amount of coke on spent catalysts was determined by using Perkin Elmer/Pyris Diamond (Thermogravimetric/Differential Thermal Analysis, TG/DTA). The temperature was ramped up from room temperature to 900 °C with the heating rate of 10 °C/min. Sulphur content on catalyst surface was determined by using LECO®Elemental Analyzer (TruSpec®S).

2.4 Product analysis

Liquid and solid products were weighed for calculating the product yield. Before analysis, asphaltene was firstly precipitated from the liquid products via mixing with *n*-pentane in the oil/*n*-pentane mass ratio of 40:1. After that the precipitated asphaltene was filtered from the solutions using a Teflon membrane (0.45 μ m) in a vacuum system, and then the maltene solutions were analyzed for the composition by using Gas Chromatography-Mass Spectrometry (GCxGC-TOF/MS). The Agilent gas chromatograph 6890 system consists of a cryogenic modulator and a Pegasus 4D TOF/MS. The 1st column was a non-polar Rtx®-5 Sil MS with 30 m x 0.25 mm ID x 0.25 μ m film thickness. The 2nd column was an Rxi®-17 MS with 1.10 m x 0.10 mm ID x 0.10 μ m film thickness. Furthermore, the true boiling point curves of maltene solutions were also analyzed by using a Varian GC-3800 simulated distillation gas chromatograph (SIMDIST-GC) conformed to the ASTM-D2887 method. The instrument equipped with FID and WCOT fused silica capillary column (15 m x 0.25 mm x 0.25 μ m) The true boiling point curves were cut into petroleum fractions according to their boiling points; full range naphtha (< 200 °C), kerosene (200-250 °C), light gas oil (250-300 °C), heavy gas oil (300-370 °C) and long residue (> 370 °C). The gas products were analyzed

for hydrocarbon species and concentrations by using a GC-FID, Agilent Technologies 6890 Network GC system (HP-PLOT Q column: 20 μm film thickness and 30 m x 0.32 mm ID). Furthermore, the liquid and solid products was also analyzed for their sulphur content by using a LECO®Elemental Analyzer (TruSpec®S); whereas the sulphur content in gas products was calculated via mass balance.

3. Results and discussion

3.1 Catalyst characterization

XRD patterns of HMOR and Cu/HMOR catalysts are displayed in Figure 1. The results show that the introduction of copper onto the zeolite does not affect the zeolite structure. The peaks of copper appear at the 2θ of 43.47° and 50.67° . The BET specific surface area and pore volume of catalysts are shown in Table 1. These results indicate that the introduction of copper onto HMOR zeolite reduces the specific surface area and pore volume because copper might partially block the pore of zeolites (Garrido Pedrosa et al., 2006).

3.2 Effect of Cu/HMOR on waste tyre pyrolysis products

Figure 2 shows that HMOR does not increase the gas yield even though the liquid yield decreased because the catalyst generates a considerable amount of coke on the surface. The presence of copper on HMOR zeolite promotes gas production, and reduces the liquid yield while the solid yield is constant. Furthermore, the amount of coke is increased with using the copper-loaded catalyst as well. It can be concluded that copper promotes the cracking activity of the zeolite.

Table 1: BET specific surface area and pore volume of catalysts

Catalyst	Specific surface area (m^2/g)	Specific pore volume (cm^3/g)
HMOR	395	0.199
Cu/HMOR	345	0.180

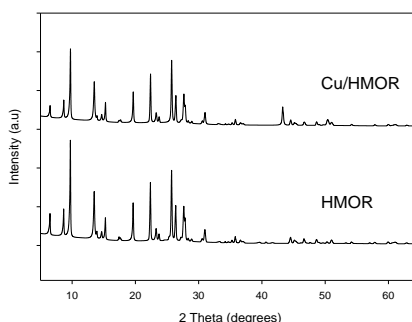


Figure 1: XRD patterns of HMOR and Cu/HMOR catalysts

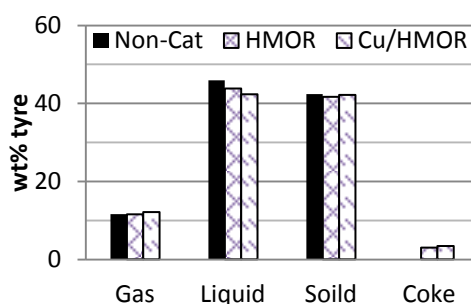


Figure 2: Product distribution in HMOR and Cu/HMOR cases

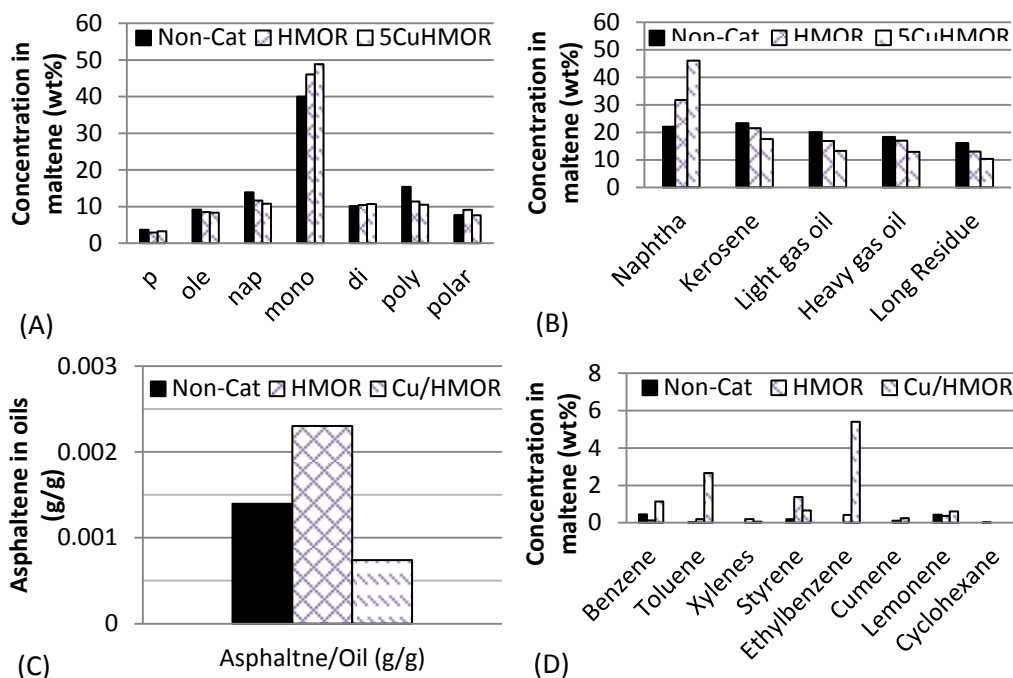


Figure 3: Oil analysis in HMOR and Cu/HMOR cases; (A) Concentrations of each group in maltene, (B) Petroleum cuts, (C) Asphaltene content in oils, and (D) Petrochemical valuable products

Table 2: Average carbon number of each group in maltenes in HMOR and Cu/HMOR cases

Catalyst	P	O	Nap	Mono	Di	Poly	Polar	Total
No catalyst	15.7	12.2	12.3	11.8	12.1	14.7	11.4	12.5
HMOR	16.1	11.9	12.1	11.6	11.9	14.7	11.6	12.2
Cu/HMOR	14.1	11.3	11.0	10.9	11.8	14.4	11.7	11.6

For oil analysis (Figure 3A), the oil components were categorized into seven groups: paraffins (P), olefins (O), naphthenes (Nap), mono-aromatics (Mono), di-aromatics (Di), poly-aromatics (Poly), and polar-aromatics (Polar). HMOR reduces the concentrations of olefins and naphthenes while the concentration of mono-aromatics is highly increased as compared with the non-catalyst case, indicating that HMOR catalyst exhibits aromatization ability. Furthermore, the concentration of poly-aromatics is decreased because the catalyst might also exhibit hydrogenation and ring-opening abilities (Du et al., 2005) that it can convert poly-aromatics into mono-aromatics. The oil obtained from HMOR has the lower overall average carbon number (Table 2) than that from the non-catalyst case, resulting in a significant increase in full-range naphtha and subsequent decrease in heavier petroleum cuts as shown in Figure 3B. As compared with HMOR zeolite, copper promotes the production of mono-aromatics in the oil (Figure 3A) possibly via hydrogenation and ring-opening of poly-aromatics, and via aromatization of olefins and naphthenes. Full-range naphtha (Figure 3B) is also increased because copper promotes cracking activity, resulting in the decrement of the overall average carbon numbers of the maltene (Table 2). Furthermore, Cu/HMOR also reduces polar-aromatic concentration and asphaltene content. As observed from the species in mono-aromatics shown in Figure 3D, the valuable petrochemicals highly produced are styrene (1.37 wt% in oil) in the HMOR case, and benzene (1.14 wt% in oil), toluene (2.65 wt% in oil) and ethylbenzene (5.39 wt% in oil) in the Cu/HMOR case. It can indicate that the catalytic pyrolysis of waste tyre has high potential for chemical production as well.

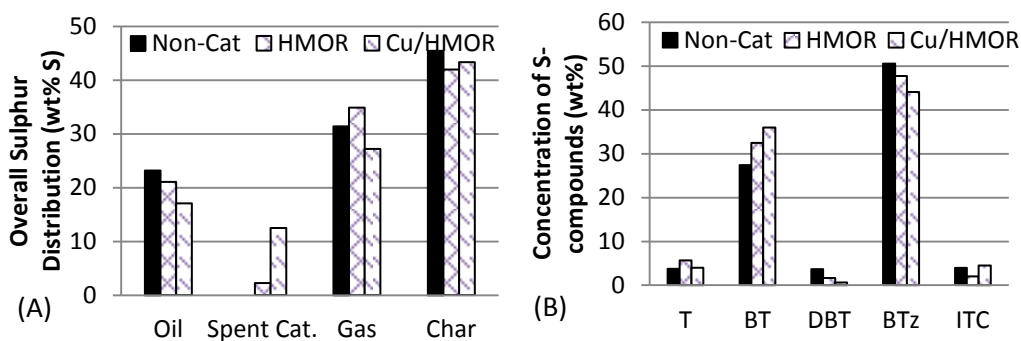


Figure 4: Sulphur analysis in HMOR and Cu/HMOR cases; (A) Overall sulphur distribution, and (B) Distribution of major groups of sulphur-containing compounds in maltenes

3.3 Quality improvement of pyrolysis oil

The quality of pyrolysis oil can be improved using Cu/HMOR not only due to light oil production and the reduction of concentration of poly- and polar-aromatics, and asphaltene content in the oil, but also due to the reduction of sulphur content in the oil. HMOR can reduce sulphur content in the oil (Figure 4A) by converting sulphur-containing compounds in the oil, and releasing sulphur into gas and coke. The increment of sulphur in gas indicates that the catalyst also exhibits cracking and desulphurization abilities. Furthermore, HMOR catalyst can reduce the average carbon number of all groups of sulphur-containing compounds in maltene (Table 2), indicating that the sulphur-containing compounds in the oils can be removed easily via desulphurization. Sulphur-containing compounds found in the oils were classified into five groups: thiophenes (T), benzothiophenes (BT), dibenzothiophenes (DBT), benzothiazoles (BTz), and isothiocyanates (ICT). For sulphur species in the maltenes, the proportions of benzothiazoles and isothiocyanates are decreased with using HMOR, indicating that HMOR can promote breaking C-S and C-N bonds, and/or can adsorb these species more on the catalyst surface. Cu/HMOR gives lower sulphur content (0.907 wt%) in the oil than HMOR zeolite (1.08 wt%) because copper can adsorb sulphur-containing compounds in both oil and gas onto the catalyst surface, subsequently forming coke, which is similar to the work of Twigg and Spencer (2001) reporting that copper is rapidly deactivated by sulphur-containing compounds. For the species of sulphur-containing compound (Figure 4B), Cu/HMOR reduces benzothiazoles, and thiophenes more than HMOR zeolite. Moreover, the reduction of average carbon numbers in all groups of sulphur-containing compounds also indicates that copper can help remove sulphur atoms more easily.

4. Conclusions

Cu/HMOR catalyst was studied in this work to determine its effect on the quality of waste tyre pyrolysis oil. It was found that the introduction of copper on HMOR zeolite can promote gas and full-range naphtha productions, indicating that copper promoted cracking activity. Cu/HMOR also enhanced the selectivity of mono-aromatics due to the increasing activities in hydrogenation and ring-opening of poly-aromatics, as well as the aromatization of olefins and naphthenes. Interestingly, the introduction of copper highly promoted the production of valuable products in oils. HMOR was found to be more selective for styrene production (1.37 wt% in oil) than thermal pyrolysis. Cu loading to HMOR resulted in better production of benzene (1.14 wt% in oil), toluene (2.65 wt% in oil) and ethylbenzene (5.39 wt% in oil). So, the catalytic pyrolysis of waste tyre using HMOR or Cu/HMOR as catalysts had high potential for chemical production as well. However, the presence of copper on HMOR zeolite increased coke formation possibly occurred from the deposition of polar-aromatics and asphaltene on the catalyst surface. Nevertheless, the quality of pyrolysis oil using Cu/HMOR can be improved since the poly-, polar-aromatics, and asphaltene contents in the oil was reduced in conjunction with the production of lighter and sweeter oil. Cu/HMOR catalyst can reduce sulphur content in the oil from 1.08 wt% to 0.907 wt%.

Acknowledgements

The authors would like to acknowledge the financial supports from The Petroleum and Petrochemical College, Chulalongkorn University, Center of Excellence on Petrochemical and Materials Technology, and Thailand Research Fund (TRF).

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