CHAPTER VII

COMPARISON BETWEEN Cu/KL AND Zn/KL ON SULFUR REMOVAL FROM TIRE-DERIVED OIL, AND PRODUCTION OF PETROCHEMICALS

7.1 Abstract

Nowadays, waste tire is increasingly produced in every year. Furthermore, the amount of petroleum in the world is deteriorating. Tire-derived oils obtained from pyrolysis of waste tire are an alternative way for producing petrochemicals and reducing waste in the same time. Recently, bifunctional catalysts have been used in several research works, which can improve the properties and quantity of pyrolysis products, especially oil products composed of value added chemicals such as benzene, toluene, xylenes, etc. Furthermore, sulfur reduction is a necessary process, since sulfur compounds have corrosive property and undesired odor. Since several properties of copper and zinc, especially sulfur removal ability in adsorption and hydrodesulfurization processes are need for tire-derived oils; therefore, Cu- and Zn-loaded KL zeolite were expected to increase hydrodesulfurization activity because potassium in KL can help promoting hydrogen spill-over content on the catalyst surface that can be used to remove sulfides of the metals, and then possibly enhance sulfur removal from tire-derived oils as well. The results showed that the presence of copper and zinc on KL zeolite can highly promote the production of petrochemicals, especially benzene and cumene, and ethylbenzene and cumene, respectively. For sulfur removal, Cu addition on KL can reduce sulfur content in oils from 1.11 wt% to 0.844 wt% while Zn loading can also reduce sulfur content in oils to 0.854 wt%, indicating that Cu or Zn on KL can exhibit hydrodesulfurization ability.

7.2 Introduction

Pyrolysis is a potential method for waste tire elimination because the method can convert waste tires into gas fuels, oils, and char. Tire-derived oils are an alternative energy source for the uses as fuels, and have a high possibility for producing petrochemical feedstocks as well. Bifuctional catalysts are attractive because metals and supports can exhibit several interesting ability such as cracking, hydrogenation, ring-opening, hydrodesulfurization, etc. For example, some researchers such as Williams and Bottrill (1995), Qu *et al.* (2006), and Boxiong *et al.* (2007) studied the effect of zeolites on petrochemicals in waste tire pyrolysis products. The petrochemicals from waste tire pyrolysis can be benzene, toluene, xylenes, limonene, styrene, ethylbenzene, and cumene, for examples. However, the quality of tire-derived oils still need to be improved in terms of sulfur content; so, the oils have to be treated for reducing the corrosion and pollution problems of the oil usage. Sulfur-polycyclic aromatic hydrocarbons (PASH) in tire pyrolysis oil were reported by Williams and Bottrill (1995). Main PASH found were benzothiophene, and the groups of dibenzothiophenes and their derivatives. Dũng *et al.* (2009) revealed that Pt/HBETA and Pt/HMOR can reduce sulfur content in forms of polar-aromatics via hydrogenation of platinum converting polar-aromatics and their precursor into saturated hydrocarbons before further cracking via zeolites.

Copper is a metal that is widely used as a catalyst for selective hydrogenation of undesired unsaturated light hydrocarbons (Setiawan and Cavell, 1995; Bridier *et al.*, 2010). Furthermore, a copper-exchanged zeolite has high ability to deep desulfurize thiophene from liquid fuels (Gong *et al.*, 2009) such as gasoline, etc. Another interesting metal that is in the same period in the periodic table of element is zinc. Zinc is used in many applications because it has several outstanding properties. For examples, zinc can promote dehydrogenation reaction rate of a light alkane, and increase C_{6+} aromatic selectivity of HZSM-5 catalysts (Berndt *et al.*, 1996; Viswanadham *et al.*, 1996). Moreover, zinc-exchanged zeolites have ability to remove sulfur-containing compounds in liquid fuels (Hernández-Maldonado *et al.*, 2005; Villarroel *et al.*, 2008; Oliveira *et al.*, 2009; Shangguan *et al.*, 2013).

KL is an interesting zeolite because KL can exhibit dehydrogenation and aromatization for catalysis, and potassium can increase hydrogen capacity in hydrogen storage application. So, the uses of KL zeolite as a support for copper and zinc might increase hydrogen spill-over content on the catalyst surface, while the metals might exhibit desulfurization; so, the metal-loaded KL catalysts might reduce sulfur-containing compounds in tire-derived oils. Furthermore, the formation of valuable petrochemicals might be promoted as well.

This work studied on the effect of Cu/KL and Zn/KL catalysts on tire-derived oil, petrochemical production, and sulfur removal. Tire-derived oils were analyzed to determine their compositions and quantity, and petroleum cuts by using GC×GC-TOF/MS and SIMDIST-GC, respectively. Gas products were analyzed their compositions by using GC-FID. All three pyrolysis products (gas, oil and char) and spent catalysts were analyzed and/or calculated sulfur distribution by using S-analyzer.

7.3 Experimental

7.3.1 Catalyst Preparation

KL zeolite supplied by TOSOH Company (Singapore) was calcined in air from room temperature to 500 °C with a heating rate of 10 °C/min. The final temperature was held for 3 hr. The calcined zeolite was then impregnated with solutions of copper precursor ($(Cu(NO_3)_2).3H_2O$ or zinc precursor ($Zn(NO_3)_2.6H_2O$) at the metal loading of 5 wt%, dried overnight in an oven at 120 °C, and calcined again at the same calcination condition. The calcined Cu- and Zn-loaded catalysts were subsequently reduced at 600 °C and 500 °C, respectively, for 2 hr in hydrogen environment. Finally, the catalysts were pelletized, crushed, and sieved into a particle size of 40-60 mesh.

7.3.2 Catalyst Characterization

The XRD patterns of the catalysts scanned from 5° to 65° with a scanning speed of 5 °C/min were acquired from XRD machine (Rikagu) using CuKα radiation operated at 40 kV and 30 mA. Specific BET surface area and specific pore volume of catalysts were determined by using Thermo Finnigan Sorptomatic 1990 equipment that N_2 gas was used as an adsorbate. Thermo Finnigan TPDRO 1100 was used to determine metal-support interaction and basicity of the catalysts via comparison among temperature programmed reduction (TPR) profile under 4.99 % H_2/N_2 flow at 20 ml/min with a heating rate of 20 °C/min from room temperature to 900 °C, and 99.999 % CO_2-temperature programmed desorption (TPD) profile under 99.999 % He flow at 10 ml/min with a heating rate of 10 °C/min from room temperature to 600 °C, respectively. Thermogravimetric/Differential Thermal

Analysis, TG/DTA (Perkin Elmer/Pyris Diamond), was used to determine the amount of coke deposited on spent catalysts with the ramp rate of 10 °C/min from room temperature to 900 °C. Sulfur content on catalyst surface was acquired from LECO®Elemetal Analyzer (TruSpec®S).

7.3.3 Waste Tire Pyrolysis

Pyrolysis apparatus was the same as the work of Dũng *et al.* (2009). The reactor was divided into lower zone (pyrolysis zone) and upper zone (catalytic zone) which wer loaded with 30 grams of shredded tire (20-40 mesh), and loaded with 7.5 grams of a catalyst, respectively. Two zones were heated from room-temperature to 500 °C and 350 °C with a heating rate of 10 °C/min at atmospheric pressure, respectively, and the final temperatures were held at the target temperatures for 2 hr. Nitrogen gas was used as a carrier gas. Pyrolysis oils were collected in the condensers immerged in an ice-salt bath. A gas sampling bag was used to collect gas products, while solid products or chars remained in the bottom of the reactor.

Gas yields were calculated from mass balance, which equals to initial weight of tire abstracted by liquid and solid yields, and the amount of coke on the catalyst surface determined from the TG/DTA instrument. Asphaltene in oil products was precipitated via mixing the oils with *n*-pentane in the oil/*n*-pentane mass ratio of 40:1 for 18 hr, and filtered through a teflon membrane (0.45 μm). The remained oils called maltenes were analyzed their qualities and determined oil compositions in the next steps. GC×GC-TOF/MS equipped an Agilent gas chromatograph 7890 (Agilent Technologies, Palo Alto, CA, USA), a Pegasus® 4D TOF/MS (LECO, St. Joseph, MI, USA) and a thermal modulator was used to analyzed oil compositions. The instrument was operated by the cooperation of two GC columns (Thames Restek, Sounderton, UK). The 1st GC column was a non-polar Rtx®-5Sil MS, 30 m × 0.25 mm ID × 0.25 μm film thickness. The 2nd GC column was an Rtx®-17 MS, 1.10 m × 0.10 mm ID × 0.10 μm film thickness. 1 μL of maltene in 2 ml of CS_2 solution was analyzed by injection into the instrument via a splitless injector operated at 250 °C using 1.0 mL/min of helium as a carrier gas. Moreover, the true boiling point curves of maltene solutions were obtained from a Varian GC-3800 simulated distillation gas chromatograph (SIMDIST-GC) conformed to the ASTM-D2887 method. The instrument was equipped with FID and WCOT fused silica capillary column, 15 m ×

0.25 mm × 0.25 μm. The true boiling point curves were next cut into petroleum fractions according to their boiling points; gasoline (<149 °C), kerosene (149-232 °C), gas oil (232-343 °C), light vacuum gas oil (343-371 °C) and heavy vacuum gas oil (>371 °C). A GC-FID, Agilent Technologies 6890 Network GC system (HP-PLOT Q column: 20 μm film thickness and 30 m × 0.32 mm ID) was used to determine the compositions and concentrations of the gas products. Furthermore, sulfur contents in the liquid and solid products were also determined by using a LECO®Elemetal Analyzer (TruSpec®S); whereas the sulfur content in gas products was calculated via mass balance.

7.4 Results and Discussion

7.4.1 Basicity and Metal-Support Interaction on Sulfur Removal

Potassium ions in KL zeolite are active species for S-compound adsorption because they have more electrophilic properties than the metal species on the catalyst surface. CO_2-TPD in Figure 7.1 shows that the introduction of copper or zinc can increase the basicity of KL, which can adsorb CO_2 as acid probe molecules. The surface activity of metal-loaded catalysts might also increase, resulting in the increase of the sulfur removal ability of catalysts as shown in Table 7.1. For Cu/KL and Zn/KL catalyst cases, the introduction of Cu or Zn on KL can reduce sulfur content in the oil to 0.844 wt% and 0.854 wt%, respectively, which might be caused from the individual sulfur adsorption ability of Cu or Zn sites. The adsorption of S-compounds on Cu or Zn sites can eventually form sulfides with Cu or Zn after a S-free hydrocarbon leaves the surface due to C-S bond cleavage as well. The surface cleaning of sulfur on metal sites can be indicated metal-support interaction by using TPR profiles (Figure 7.2). The peak at a higher temperature demonstrates the higher metal-support interaction of a catalyst. The results show that the reduction temperature of zinc oxide on KL zeolite is higher than that of copper oxide on KL zeolite; so, the interaction between Cu-KL is weaker than that between Zn-KL. Furthermore, the metal sulfide bond strength can be determined by the heat of formation of the sulfides (Chianelli *et al.*, 2009). Copper sulfides have a low heat of formation (kcal/mole of metal) as shown in Table 7.2. Sulfur depositing on the spent

Cu/KL can be removed easily, resulting in high hydrodesulfurization activity, as supported by the increasing sulfur content in the gas phase for the Cu-loaded catalyst as shown in Figure 7.3. The hydrodesulfurization activity on Cu/KL can cause regenerating active sites for sulfur removal from the oils as well.

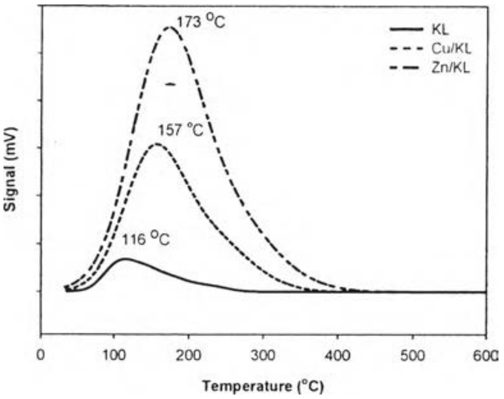

Figure 7.1 CO_2-TPD profiles of Cu/KL and Zn/KL catalysts.

Table 7.1 Sulfur content in oil (wt%)

Catalyst	wt% Sulfur in oil
No Catalyst	1.22 ± 0.0404
KL	1.11 ± 0.0520
Cu/KL	0.844 ± 0.0121
Zn/KL	0.854 ± 0.0262

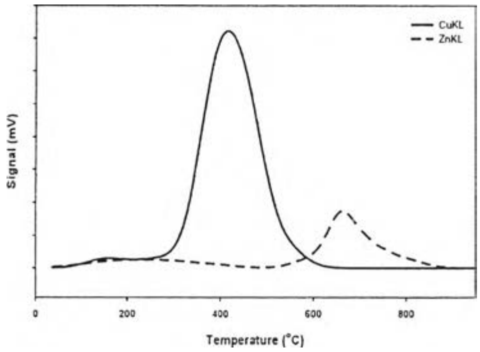

Figure 7.2 TPR profiles of Cu/KL and Zn/KL catalysts.

Table 7.2 Standard molar heat of formation (Green and Perry, 2008)

Metal Sulfide	**ΔH_f° at 25 °C (kcal/mol)**
CuS	-11.6
Cu_2S	-18.97
α-ZnS (Wurtzite)	-45.3

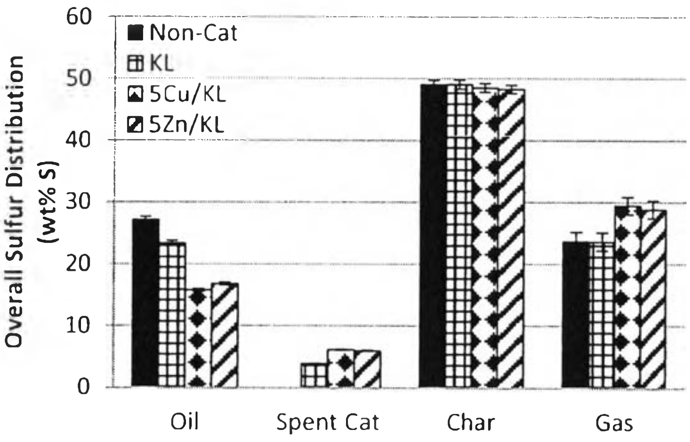

Figure 7.3 Overall sulfur distribution (wt% S in tire).

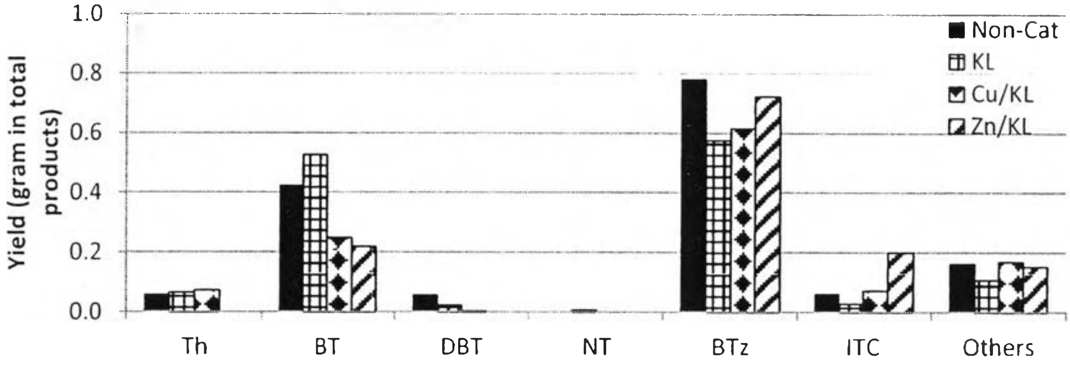

Figure 7.4 Yields of sulfur-containing compound species.

7.4.2 Sulfur Compound Species

Sulfur-containing compounds in waste tire pyrolysis oils can be classified into six major groups: thiophenes (Th), bezothiophenes (BT), dibenzothiophenes (DBT), naphthothiophenes (NT), benzothiocyanates (BTz), and isothiocyanates (ITC).

Figure 7.4 shows that the presence of copper or zinc on KL zeolite can reduce the amounts of BT and DBT, and increase the amounts of BTz and ITC, indicating that the increment of basicity in the Cu/KL and Zn/KL can promote the adsorption of BT and DBT molecules on the potassium ions. Furthermore, copper can also promote the adsorption of the molecules of S-compounds, and form the thermodynamically stable forms (Hassan *et al.*, 2008) as shown in Table 7.2.

7.4.3 Tire-derived Oils and Petrochemicals in Oils

The SIMDIST-GC results can provide the petroleum cuts: gasoline (b.p. = 15.5-149 °C), kerosene (b.p. =149-232 °C), gas oil (b.p. = 232-343 °C), light vacuum gas oil (b.p. = 343-371 °C), and heavy gas oil (b.p. = 371-566 °C). Figure 7.5 shows that copper and zinc additions can highly promote gasoline fraction, indicating that copper and zinc can clearly increase cracking activity of KL zeolite. However, the oil compositions in each petroleum cuts are mainly aromatics as shown in Table 7.3. So, tire-derived oils are suitable for petrochemical production rather than the fuel production because the quality of tire-derived oils has to be upgraded for reaching the international standard fuel specifications. Moreover, the increment of gasoline in the metal-loaded catalyst cases also increases the amount and selectivity of petrochemicals as compared with the KL and the non-catalyst cases (Figure 7.6 and Table 7.4).

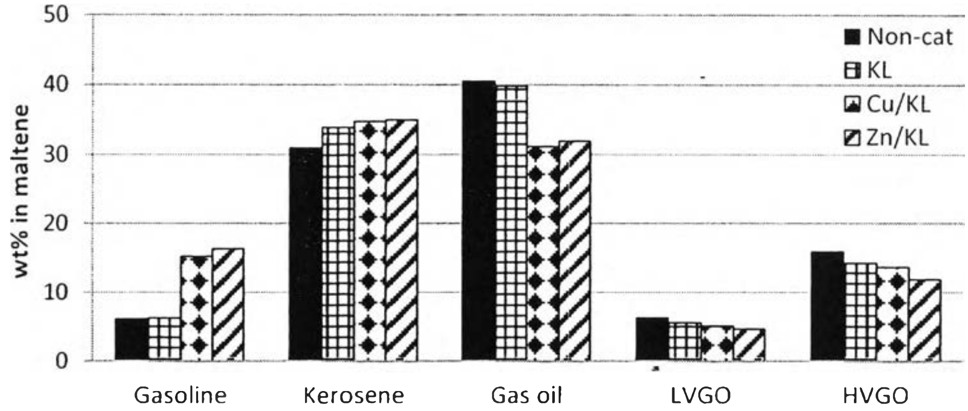

Figure 7.5 Petroleum fractions in maltenes.

Table 7.3 Compositions (wt%) of paraffins, olefins, naphthenes, and aromatics in each petroleum cut for all cases (obtained from GC×GC-TOF/MS results)

	Gasoline	Kerosene	Gas oil	LVGO	HVGO
Paraffins	0.00-0.944	0.511-2.11	8.27-26.1	0.00-13.5	0.00-22.1
Olefins	1.41-14.2	2.81-9.04	2.31-14.1	0.00-9.17	0.00-7.49
Naphthenes	6.72-15.0	6.30-13.0	3.67-23.3	0.00-25.1	0.00-7.49
Aromatics	69.8-91.9*	76.3-89.7	58.9-68.0	74.9-100	77.9-100

* Mono-aromatics in Gasoline = 29.0–60.5 wt%

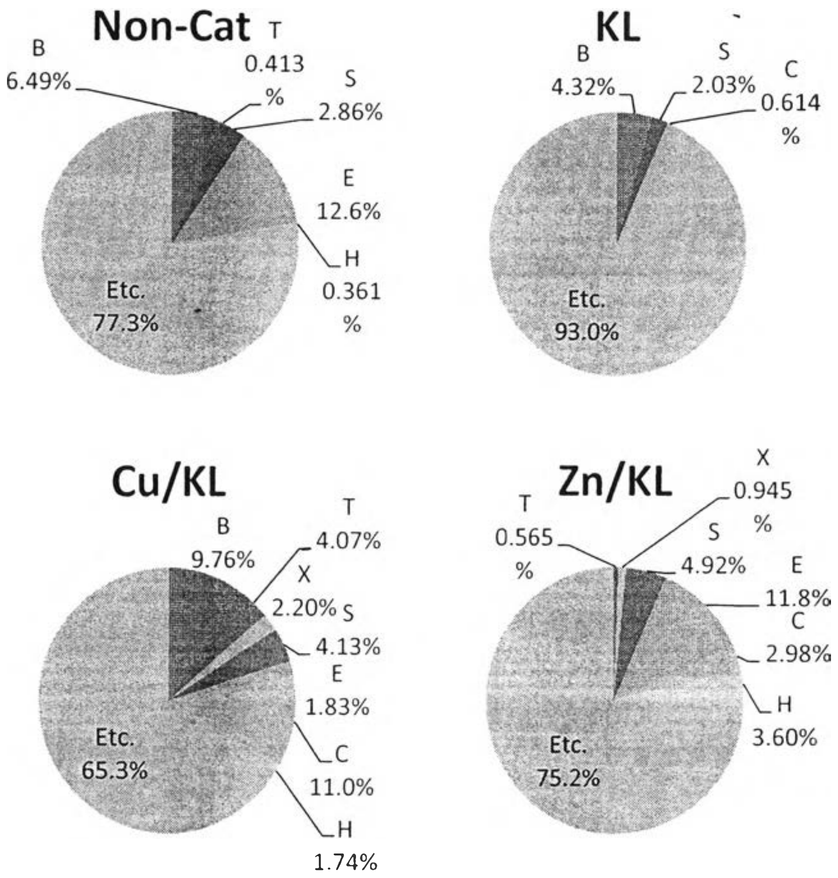

Figure 7.6 Petrochemicals in gasoline (wt%).

Table 7.4 Petrochemical productivity from waste tire pyrolysis

Catalyst	kg of total petrochemicals per ton of tire
No Catalyst	7.15
KL	1.91
Cu/KL	20.5
Zn/KL	16.5

Petrochemicals that can be produced in the catalytic pyrolysis of waste tire are benzene (B), toluene (T), xylenes (X), ethylbenzene (E), styrene (S), cumene (C) and cyclohexane (H). BT and BTz are considered only because these groups are present in a high amount as compared with other groups. The petrochemicals are produced from sulfur-containing compounds via desulfurization, and from other reactions of hydrocarbons in pyrolysis. Unfortunately, the number of chemical species in maltenes is very large, the exact pathways of petrochemical production are very difficult to be investigated.

7.5 Conclusions

This work studied the effects of Cu/KL and Zn/KL catalysts on tire-derived oils. Cu and Zn additions onto KL zeolite increased lighter oil production, especially gasoline fraction. However, tire-derived oils were aromatic-based: so, the oils were suitable for petrochemical production. Furthermore, copper and zinc can promote sulfur reduction from the oil. Cu/KL was the better catalyst for sulfur removal from the tire-derived oil than the KL zeolite (from 1.11 wt% in oil to 0.844 wt% in oil). The presence of copper and zinc can increase basicity of potassium ions in KL zeolite that might cause highly remove benzothiophens (BT) from the oils. Interestingly, the valuable petrochemicals highly produced were benzene and cumene in the Cu/KL catalyst case, and ethylbenzene and cumene in the Zn/KL case.

7.6 Acknowledgements

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

7.7 References

Berndt, H., Lietz, G., Lücke, B., and Völter, J. (1996) Zinc promoted H-ZSM-5 catalysts for conversion of propane to aromatics I. Acidity and activity. Applied Catalysis A: General, 146, 351-363.

Boxiong, S., Chunfei, W., Binbin, G., Rui, W., and Liangcai (2007) Pyrolysis of waste tyres with zeolite USY and ZSM-5 catalysts. Applied Catalysis B: Environmental, 73(1–2), 150-157.

Bridier, B., López, N., and Pérez-Ramírez, J. (2010) Partial hydrogenation of propyne over copper-based catalysts and comparison with nickel-based analogues. Journal of Catalysis, 269, 80-92.

Chianelli, R.R., Berhault, G., and Torres, B. (2009) Unsupported transition metal sulfide catalysts: 100 years of science and application. Catalysis Today, 147(3–4), 275-286.

Du, H., Fairbridge, C., Yang, H., and Ring, Z. (2005) The chemistry of selective ring-opening catalysts. Applied Catalysis A: General, 294(1), 1-21.

Dũng, N.A., Wongkasemjit, S., and Jitkarnka, S. (2009) Effects of pyrolysis temperature and Pt-loaded catalysts on polar-aromatic content in tire-derived oil. Applied Catalysis B: Environmental, 91, 300-307.

Gong, Y., Dou, T., Kang, S., Li, Q., and Hu, Y. (2009) Deep desulfurization of gasoline using ion-exchange zeolites: Cu(I)- and Ag(I)-beta. Fuel Processing Technology, 90, 122-129.

Green, D.W. and Perry, R.H. (2008) Perry's Chemical Engineers' Handbook. USA: McGraw-Hill.

Hassan, K.H., Khammas, Z.A.-A., and Rahman, A.M. (2008) Zinc oxide hydrogen sulfide removal catalyst/preparation, activity test and kinetic study. Al-Khwarizmi Engineering, 4, 74-84.

Hernández-Maldonado, A.J., Yang, F.H., Qi, G., and Yang, R.T. (2005) Desulfurization of transportation fuels by π-complexation sorbents: Cu(I)-, Ni(II)-, and Zn(II)-zeolites. Applied Catalysis B: Environmental, 56, 111-126.

Oliveira, M.L.M., Miranda, A.A.L., Barbosa, C.M.B.M., Cavalcante Jr, C.L., Azevedo, D.C.S., and Rodriguez-Castellon, E. (2009) Adsorption of thiophene and toluene on NaY zeolites exchanged with Ag(I), Ni(II) and Zn(II). Fuel, 88, 1885-1892.

Qu, W., Zhou, Q., Wang, Y.-Z., Zhang, J., Lan, W.-W., Wu, Y.-H., Yang, J.-W., and Wang, D.-Z. (2006) Pyrolysis of waste tire on ZSM-5 zeolite with enhanced catalytic activities. Polymer Degradation and Stability, 91(10), 2389-2395.

Setiawan, I. and Cavell, K.J. (1995) Removal of unstaturated contaminants from an industrial C4-stream using Cu/SiO2 catalysts: Subsequent testing of the purified stream with an alkyne sensitive catalyst system. Applied Catalysis A: General, 131, 225-241.

Shangguan, J., Zhao, Y., Fan, H., Liang, L., Shen, F., and Miao, M. (2013) Desulfurization behavior of zinc oxide based sorbent modified by the combination of Al_2O_3 and K_2CO_3. Fuel, 108, 80-84.

Villarroel, M., Baeza, P., Escalona, N., Ojeda, J., Delmon, B., and Gil-Llambías, F.J. (2008) M_D//Mo and M_D//W [M_D = Mn, Fe, Co, Ni, Cu and Zn] promotion via spillover hydrogen in hydrodesulfurization. Applied Catalysis A: General, 345, 152-157.

Viswanadham, N., Pradhan, A.R., Ray, N., Vishnoi, S.C., Shanker, U., and Prasada Rao, T.S.R. (1996) Reaction pathways for the aromatization of paraffins in the presence of H-ZSM-5 and Zn/H-ZSM-5. Applied Catalysis A: General, 137, 225-233.

Williams, P.T. and Bottrill, R.P. (1995) Sulfur-polycyclic aromatic hydrocarbons in tyre pyrolysis oil. Fuel, 74, 736-742.