# CHAPTER IV
## UPGRADING OF WASTE TYRE-DERIVED OIL FROM WASTE TYRE PYROLYSIS OVER Ni CATALYST SUPPORTED ON HZSM-5 ZEOLITE

## 4.1 Abstract

The catalytic pyrolysis of waste tyre was investigated using Ni-doped HZSM-5 zeolite as a catalyst in a bench-scale reactor ramped from room temperature to 500 °C (pyrolysis zone) and 350 °C (catalyst bed), aiming to improve the quality of tyre-derived oil in terms of sulphur reduction and enhancement of valuable petrochemical production. 5 wt% of nickel was introduced on HZSM-5 zeolite using incipient wetness impregnation, and characterised using XRD, BET, and XPS. Gaseous products were analysed by GC-FID. The GCxGC-TOF/MS and SIMDIST-GC were used for analysis of pyrolysis oil. The sulphur content in tyre-derived oil was determined by S-analyzer. The introduction of metallic nickel on HZSM-5 zeolite significantly changed textural properties, also modified the catalytic behavior. When compared to parent HZSM-5 zeolite, Ni/HZSM-5 catalyst significantly improved gasoline and kerosene production in waste tyre-derived oil, whereas the heavy fractions, such as gas oil and light vacuum gas oil, drastically decreased. In addition, Ni doping drastically reduced sulphur contents in tyre-derived oil by 29.2 %. Benzothoiphenes, dibenzothiophenes, and naphthothiophene were the sulphur species that significantly decreased. Furthermore, with Ni loading, the production of cumene, ethylbenzene, toluene, and mixed xylenes in oil was also enhanced. These results indicated Ni/HZSM-5 was a promising catalyst for enhancement of tyre-derived oil quality.

## 4.2 Introduction

Due to the petroleum resources that continuously decrease with a rapid rate in association with the growth of waste tyre that constantly increases, the pyrolysis of waste tyre is one of alternative ways for producing of chemicals and fuels. Recent study has reported that waste tyre-derived oil contains a relatively-high concentration

of aromatics such as mono-, di-, poly- and polar aromatics, which cannot be directly used as vehicle fuels (Yuwapompanit *et al.*, 2015). However, the aromatic compounds in oil are valuable chemicals such as benzene, toluene, xylenes, styrene and ethylbenzene, which can be utilized as a petrochemical feedstocks in refinery. As a result, several catalysts have been used in catalytic pyrolysis of waste tyre in order to improve of valuable chemical production in waste tyre-derived oil, and reduce of polycyclic aromatics and sulphur-containing compounds. Many acidic zeolites, such as Mordenite, Y, and Beta have been tested in catalytic pyrolysis of waste tyre, and provided interesting results. Dung *et al.* (2009) stated that HMOR increased the concentration of mono-aromatics in oil, whereas the polycyclic aromatics, especially polar-aromatics significantly decreased. In addition, HMOR also increased the naphtha fraction in oil, whereas the heavy fraction drastically decreased. HBETA and HY zeolites increase naphtha and kerosene fractions, whereas the heavier fraction slightly decreased (Manchantrarat and Jitkarnka, 2012). Thus, these studies indicate that different zeolites provide different product distribution because each zeolite has unique properties. In particular, HZSM-5 zeolite is commonly used as a catalyst in the petrochemical industry due to its pore size, strong acidity and strong resistance to deactivation. Boxiong *et al.* (2007) found that the HZSM-5 enhanced the production of benzene, toluene and xylenes. In general, the addition of a transition metal on a catalyst can modify the catalyst activity. Nickel is favourable to hydrogenation/dehydrogenation reactions, or promotes aromatization and cracking reactions (Botas *et al.*, 2014). For example, Ni over hierarchical ZSM-5 and Beta zeolites enhanced the production of gas and gasoline from hydroreforming of polyethylene-derived thermal cracking oil. In addition Ni/HZSM-5 catalyst can promote the transformation of olefins into aromatics and iso-paraffins (Yin *et al.*,2005). Another common application of nickel-based catalyst is desulfurization. The sulphur removal efficiency increased with the increase of nickel loading on SBA-15 in adsorptive desulfurization of diesel (Ko *et al.*, 2007). The aim of this work was therefore to investigate the effect of nickel on waste tyre pyrolysis products in terms of oil quality improvement and enhancement of valuable petrochemical production. HZSM-5 zeolite was selected as the support since the pore size and channel structure are suitable for producing valuable aromatic hydrocarbons.

Furthermore, the introduction of nickel on HZSM-5 was expected to promote the formation of valuable chemicals and reduction of polycyclic compounds in oil, especially sulphur containing-compounds. Moreover, the sulphur content in pyrolytic oil might be reduced with nickel doping.

## 4.3 Experimental

### 4.3.1 Catalyst Preparation

ZSM-5 zeolite (840NHA, Si/Al=20, $NH_4$-form) was purchased from TOSOH Corporation (Singapore). Prior to activity testing and metal impregnation, HZSM-5 was calcined in standing air at 500 °C for 3 h (Ramping rate of 10 °C/min). Ni-promoted HZSM-5 was prepared by incipient wetness impregnation of nickel compound $(NiNO_3)_2 \cdot 6H_2O$) with 5 wt% metal loading based on the mass of catalyst. The catalysts were then dried overnight at 105 °C and calcined at same condition as mentioned above. The catalyst powders were pelletized, crushed and sieved to 40-60 mesh of particle size. The Ni/HZSM-5 catalyst was activated by reduction under hydrogen flow (30 ml/min) at 600 °C for 2 h (heating rate 10 °C/min)

### 4.3.2 Catalyst Characterization

The catalyst samples were characterized by different physicochemical characterization methods. X-Ray diffraction (CuK$\alpha$ radiation), carried out in a Rikagu SmartLab X-Ray Diffractometer, was used to identify the crystallinity of catalysts. XRD patterns were recorded in the 5-65 ° (2$\theta$) range using a scan speed of 10° (2$\theta$)/min. The species of nickel was determined by using XPS with an AXIS ULTRADLD (Kraros) equipped with a monochromatic Al X-ray source and a hemispherical analyser. The spectrometer was carrier out at the pass energy of 160 eV and 80 eV to acquire wide scan and core level spectra, respectively. All peaks were calibrated from C1s spectra (Binding energy = 285.0 eV). The surface area and pore volume of catalyst were measured using $N_2$ adsorption-desorption isotherms with Thermo Finnigan Sorptomatic 1990 instrument.The amount of coke deposition on the spent catalysts was measured by thermogravimetric analysis (TGA), carrier out under flowing of nitrogen (10 ml/min) and oxygen (20 ml/min) on a Perkin Elmer/Pyris Diamond (Thermogravimetric/Differential Thermal Analysis, TG/DTA)

The samples were heated up from room temperature to 900 °C with 10 °C/min ramping rate. CHNS analyser was used to determine the sulphur and nitrogen content on spent catalysts using LECO®Elemetal Analyzer.

### 4.3.3 Waste Tire Pyrolysis

The schematic pyrolysis system is displayed in Figure 4.1. Firstly, 30 g of shredded tire (20-40 mesh) is pyrolyzed in the lower zone of the reactor at 500 °C under atmospheric pressure. The pyrolysis products are carried by 30 ml/min of nitrogen flow to the catalytic bed filled with 7.5 g of catalyst and be heated to 350 °C. After the temperatures of lower and upper zones reaches to the desired one, the temperature of two zones is kept at desired temperature for 2 h. The resulting products were separated into gas and liquid fraction by condensers (ice-salt condensing system). Gas product was collected in Tedlar PVF bag.
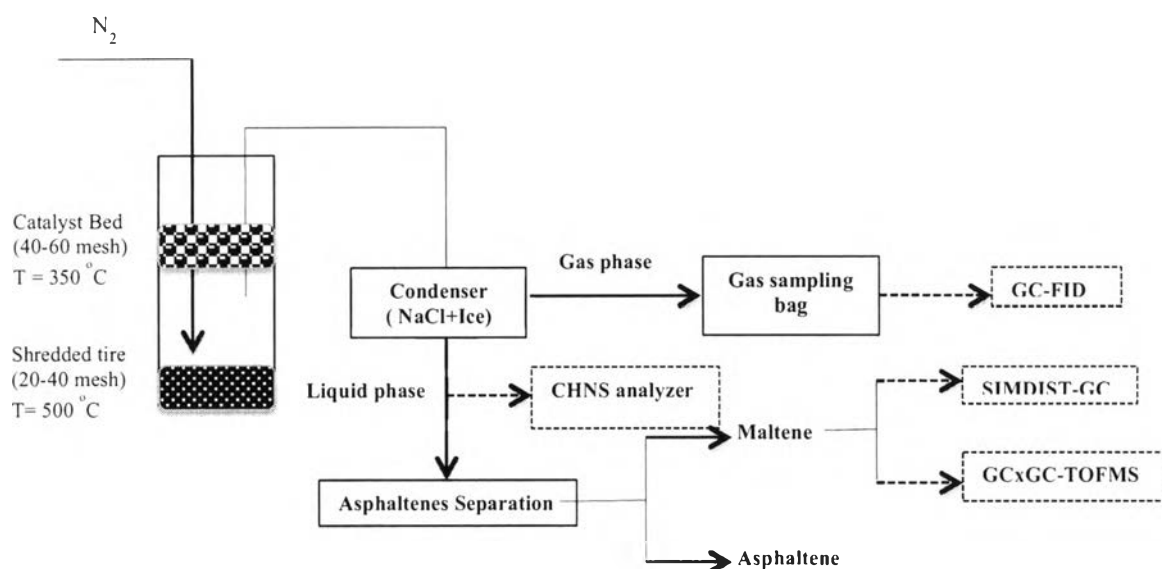


**Figure 4.1** Schematic of waste tire pyrolysis system for collection and analysis of products.

### 4.3.4 Product Analysis

Liquid and solid products were weighed to determine the product yield. The liquid product was dissolved in n-pentane (mass ratio of n-pentane/oil = 40:1) to precipitate asphaltene. Asphaltene was filtered by using a polyamide membrane (0.45 μm). The maltene solution was then analysed by Comphehensive Two-Dimension Gas Chromatography (Agilent Technologies 7890) with Time-of-

Flight Mass Spectrometer (LECO, Pegasus® 4D TOF/MS) equipped with the 1st GC column was a non-polar Rtx®-5Sil MS (30 m x 0.25 mm ID x 0.25 μm) and the 2nd GC column was an Rxi®-17 MS (1.790 m x 0.1 mm ID x 0.1 μm). The simulated true boiling point curves were determined by using a Varian GC-3800 simulated distillation gas chromatography equipped with FID detector and a 15m x 0.25 mm x 0.25 μm WCOT fused silica capillary column. The petroleum fractions were separated based on their boiling point ranges according to the ASTM D2887; 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). Moreover, sulphur content in tire-derived oils and char were determined by LECO®Elemetal Analyser (TruSpec®CHNS). Moreover, sulphur content in a gaseous product was determined by mass balance.

## 4.4 Results and Discussion

### 4.4.1 Catalyst Characterization

The XRD patterns of the parent HZSM-5 zeolite and the supported Ni catalyst in Figure 4.2 clearly display the characteristic XRD patterns of MFI structure. Therefore, the introduction of nickel on zeolites seems not to destroy the structure, but slightly affects the zeolite crystallinity. From Table 4.1, the decreases in BET surface area and micropore volume clearly indicate that Ni cluster might be located inside the zeolite channels, and partially block the zeolite channels (Maia et al., 2010).
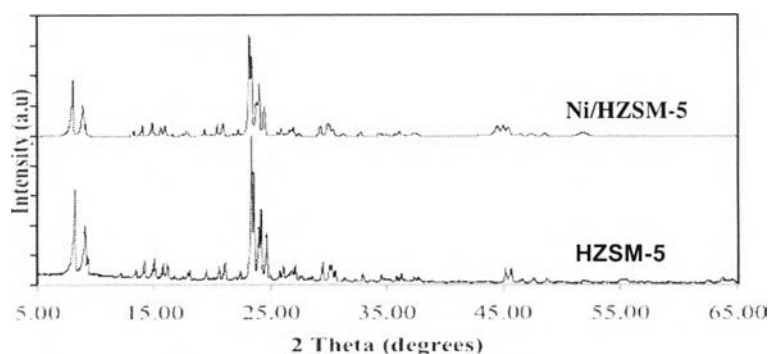


**Figure 4.2** XRD patterns of HZSM-5 zeolite and impregnated catalysts.

**Table 4.1** BET specific surface area and pore volume of catalysts

| Catalyst | Surface Area (m²/g) | Micropore Volume (cm³/g) |
|---|---|---|
| HZSM-5 | 365 | 0.178 |
| Ni/HZSM-5 | 290 | 0.142 |



**Figure 4.3** XPS spectrum of Ni-promoted catalyst.

**Table 4.2** XPS result of Ni-promoted catalyst

| Ni species | Ni 2p$_{3/2}$(eV) | Ni 2p$_{3/2}$(sat) (eV) | Ni 2p$_{1/2}$ (eV) | Relative Amount of Nickel Species (%) |
|---|---|---|---|---|
| Ni$^0$ | 852.7 | - | 870.1 | 57.45 |
| Ni$^{2+}$ | 856.1 | 861.5 | 872.4 | 14.82 |
| NiAl$_2$O$_4$ | 857.4 | - | 874.3 | 27.73 |

The XPS spectrum of supported Ni catalyst in Figure 4.3 has three peaks assigned to Ni 2p$_{3/2}$ with binding energies of 852.7, 856.1 and 857.4 eV, indicating the presence of metallic nickel, Ni$^{2+}$ and NiAl$_2$O$_4$, respectively (Karthikeyan *et al.*, 2008) as shown in Table 5.2. The reduction of nickel on HZSM-5 zeolite is rather difficult since the multiple species of nickel are formed on the surface of HZSM-5 zeolite. Moreover, it is very difficult to reduce Ni$^{2+}$ specie due to the strong interaction between Ni$^{2+}$ and support (Xiao and Meng., 1994).

### 4.4.2 Pyrolysis Yields

When metallic nickel was introduced on HZSM-5 zeolite, the liquid yield is suppressed from 42.5 to 39.4 %, whereas the gas yield slightly increases from 10.8 to 12.0 %. These results indicate that the incorporation of nickel over HZSM-5 zeolite promotes the cracking activity of HZSM-5 zeolite. Furthermore, coke formation on Ni/HZSM-5 catalyst drastically increases roughly twice as much as that on the parent HZSM-5 zeolite. These results show that the introduction of metallic nickel on HZSM-5 zeolite greatly increases surface activity and hydrogen transfer, which favors for coke formation.
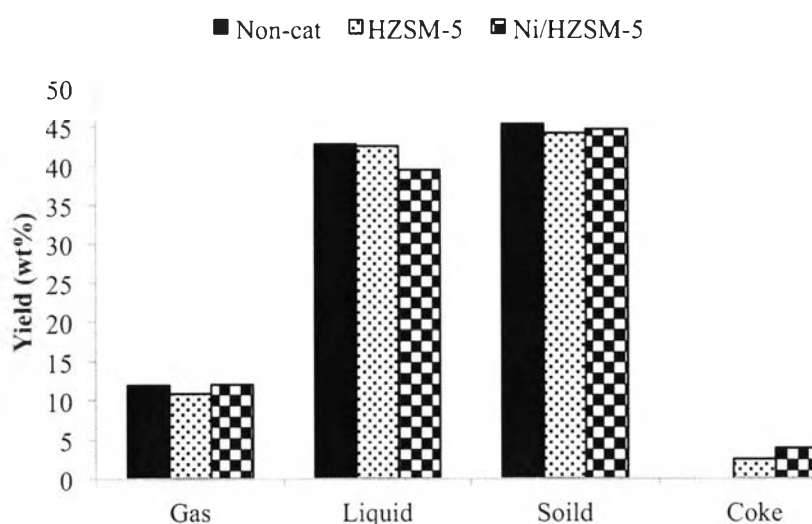


**Figure 4.4.** Effect of nickel loaded on HZSM-5 on pyrolysis yields

### 4.4.3 Waste Tyre-derived Oil

Figure 4.5(a) provides the information about the petroleum fractions in maltenes. The HZSM-5 zeolite gives a higher concentration of gasoline, whereas the kerosene, gas oil and HVGO are lower than the non-catalytic case. These results indicate that the medium pore size and acidity of HZSM-5 can promote the cracking of heavy fractions. Significant differences are observed in the proportion of petroleum fractions with using HZSM-5 zeolite loaded with nickel. The impregnation of ZSM-5 with nickel drastically increases the production of gasoline and kerosene whereas gas oil, LVGO and HVGO fractions significantly decrease. This clearly indicates that metallic nickel on the HZSM-5 zeolite strongly promotes

cracking of heavy fractions, leading to formation of lighter fractions. Figure 4.5(b) displays the maltene composition. The maltene compositions are classified into 7 groups; that are, paraffins (para), olefins (ole), naphthenes (nap), mono-aromatics (mono), di-aromatics (di), poly-aromatics (poly) and polar-aromatics (polar). For the parent HZSM-5, the concentrations of mono-aromatic and naphthenes significantly decrease, whereas the concentration of poly-aromatics drastically increases. The HZSM-5 catalyst enhances the production of bi-phenyl species such as 4,4'-dimethylbiphenyl and 2-methyl-biphenyl. This result indicates that HZSM-5 catalyst might promote the combination of naphthenes and/or mono-aromatics via oligomerization/aromatization reactions, resulting in high formation of poly-aromatics. However, kinetic diameters molecules of 4,4'-dimethylbiphenyl and 2-methylbiphenyl calculated from Joback method are 6.81 and 6.52 Å, respectively, which are larger than the pore size of HZSM-5 zeolite. There are two possible reasons that can explain the formation of poly-aromatics over HZSM-catalyst. First, it is well known that the pore-size of HZSM-5 zeolite is 5-6 Å. However, it can be expanded at a high temperature. The effective pore size of ZSM-5 zeolite can expand between 6.62 Å and 7.27 Å at 300 °C, and can increase to 7.64 Å at 370 °C (Borm *et al.*, 2010). This fact can explain the high formation of poly-aromatics in ZSM-5 pore. In addition, the formation of poly-aromatics possibly occurs at acid sites located at the external surface of HZSM-5 zeolite. On the other hand, the impregnation of HZSM-5 catalyst with nickel strongly increases the production of mono-aromatics, whereas the yields of olefins, naphthenes and poly-aromatics decrease. These results indicate that the Ni/HZSM-5 exhibits hydrogenation and ring opening of poly-aromatics, which transforms poly-aromatics to mono-aromatics. Furthermore, the introduction of nickel on HZSM-5 zeolite might promote cyclization and dehydrogenation of olefins and aromatization of naphthenes, leading to the high formation of mono-aromatics.
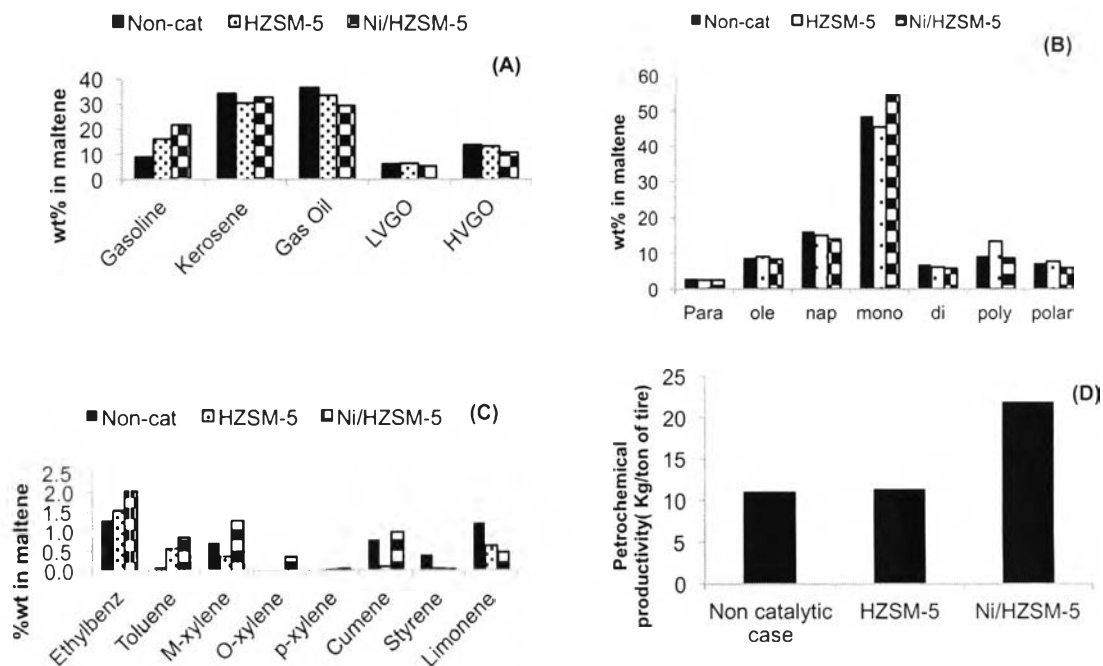
**Figure 4.5** Oil analysis: (A) Concentrations of each group in maltenes, (B) Petroleum fractions, (C) Petrochemicals in maltenes, and (D) Petrochemical productivity.

Although waste tyre-derived oil is not suitable for using as vehicle fuel due to the high content of aromatics as displayed in the Figure 4.5(b), but there are some valuable chemicals in waste tire-derived oil, which can be easily separated in refinery. As a result in Figure 4.5(c), HZSM-5 catalyst clearly enhances the yields of ethylbenzene and toluene, whereas yields of styrene, cumene and limonene significantly decrease. On the other hand, Ni doping significantly enhances the yields of ethylbenzene, toluene, mixed-xylenes, and cumene, whereas the yields of styrene and limonene decrease. Furthermore, Ni/HZSM-5 enhances the overall petrochemical productivity roughly twice as much as HZSM-5 catalyst. The introduction of nickel on HZSM-5 might transform limonene to petrochemical species such as ethylbenzene and m-xylene (Pines and Ryer, 1995). In addition, it can be clearly seen that the formation of ethylbenzene is favored over HZSM-5 and Ni-impregnated HZSM-5 since these two catalysts might promote the dehydrogenation of styrene. Moreover, naphthalene, 1,3-dimethyl naphthalene, and

1-methyl naphthalene also decrease with doping of nickel on HZSM-5. This indicates that some of these di-aromatics might be transformed to valuable mono-aromatics via these two steps. First, one ring of naphthalene might be hydrogenated into tetralin at a nickel site, and then the naphthenic ring of tetralin was cracked to form valuable products such as benzene, toluene, ethylbenezene, xylenes and etc.

**Table 4.3** Sulphur content in oils

| Catalyst | Sulphur content in oil (wt%) | Sulphur reduction (%) |
| --- | --- | --- |
| Non-catalytic | 0.96 | Base |
| HZSM-5 | 0.78 | 18.8 |
| Ni/HZSM-5 | 0.68 | 29.2 |

Table 4.3 shows the sulphur content in oil and sulphur reduction of the HZSM-5 and Ni/HZSM-5. it can be seen that when catalysts are used, the sulphur content in oil is lower than in non-catalytic case. HZSM-5 mainly removes the sulphur compounds from oil with the formation of coke on the spent catalyst, similar to the results reported by Al-Bogami and De Lasa (2013). Furthermore, the modification of HZSM-5 zeolite by nickel species significantly decreases the sulfur content in oil by 29.2 %. It can be clearly seen that the increase of sulphur deposition on the spent Ni/HZSM-5 catalyst causes the reduction of sulphur content in oil (see in Figure 4.6(a)). Therefore, it is reasonable to conclude that Ni species selectively remove sulphur compounds via adsorption of sulphur species on the metallic site. It can be suggest that sulphur-containing compounds are more preferably adsorbed on Ni/HZSM-5 catalyst than HZSM-5 zeolite since the incorporation of nickel with HZSM-5 zeolite might increases the Lewis acidity of zeolites, which promote the adsorption of sulphur containing compounds (Pang *et al.*, 2007). The main sulphur-containing compound found in waste tyre-derived oil is benzothiazoles species (BTz), which is commonly used as an accelerator in vulcanization process. Thiophenes (Th), benzothiazoles (BTz) and isothiocyanate strongly decrease, whereas benzothiophenes (BT), dibenzothiphene (DBT) and naphthothiophene (NTH) slightly increase with using HZSM-5 catalyst. This result indicates that HZSM-5 catalyst is active for breaking C-S and C-N bonds of benzothiazole and

isothiocyanate and breaking C-S bonds of thiophenes. On the hand, the formations of BT and DBT slightly increase since the acidity of HZSM-5 catalyst might promote formation of poly-thiophenic compounds via thiophenic speices (Dung *et al.*, 2009). The different result is observed in the case of Ni/HZSM-5 catalyst. In this case, the sulphur-containing compounds, except BT, DBT and NTH, significantly increase since the Ni might reduce the active sites of HZSM-5 zeolite that favors for C-S and C-N breaking of thiophenic compounds. In addition, the reduction of benzothiophenes might cause the formation of ethylbenzene and styrene (Yao *et al.*, 2005). The ethylbenzene can be formed via the hydrogenation of BT, followed by hydrogenolysis of dihydrobenzothiophene. Styrene can be directly formed via hydrogenolysis of BT.
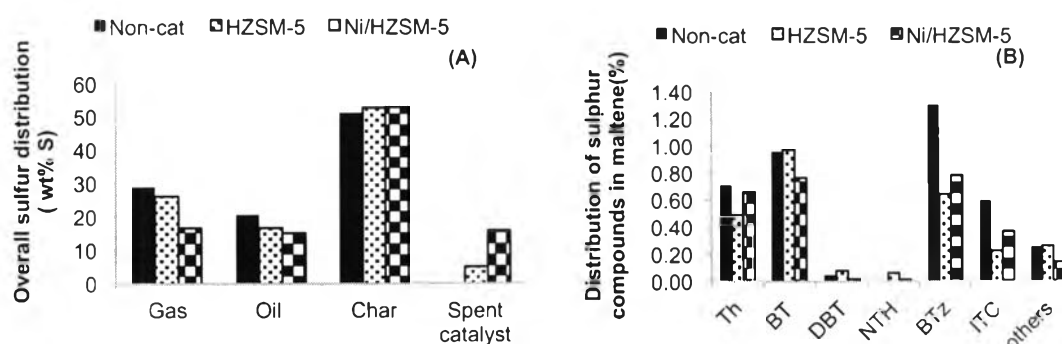
**Figure 4.6** Sulphur analysis: (A) Overall sulphur distribution, and (B) Distribution of sulphur-containing compounds in maltenes.

## 4.5 Conclusions

Ni-loaded HZSM-5 zeolite can be considered an interesting catalyst for the improvement of quality of waste tyre-derived oil via conversion of polycyclic aromatics to lighter hydrocarbons and reduction of sulfur from waste tyre-derived oil. The results indicated that the incorporation of nickel over HZSM-5 zeolite strongly promoted the production of gasoline, indicating that with nickel loading the cracking activity of catalyst highly increases. Moreover, Ni/HZSM-5 favored the conversion of polycyclic aromatics, naphthenes and olefins to mono-aromatics, whereas parent HZSM-5 catalyst favored the formation of poly-aromatics. In

addition, the production of petrochemicals in oil was enhanced with using Ni/HZSM-5. HZSM-5 provided a slightly better production of ethylbenzene and toluene than the non-catalytic case. On the other hand, Ni doping strongly enhanced the production of ethylbenzene, toluene, cumene and mixed-xylenes. It is reasonable to conclude that nickel on HZSM-5 has the ability on improving the petrochemical production from waste tyre-derived oil. Furthermore, the introduction of nickel on HZSM-5 also reduced sulphur content in waste tyre-derived oil from 0.78 to 0.68 wt%.

## 4.6 Acknowledgements

## 4.7 References

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