

CHAPTER VII
POSSIBILITY OF USING UNTREATED AND HNO₃-TREATED
PYROLYTIC CHAR AS CATALYSTS FOR THERMOLYSIS OF SCRAP
RUBBER: IN-DEPTH ANALYSIS OF TIRE-DERIVED PRODUCTS AND
CHAR CHARACTERIZATION

7.1 Abstract

The pyrolysis char produced in the thermolysis of scrap rubber has few market outlets, reducing the economic viability. Thus, char properties was firstly studied in this research, and then untreated and 5 M HNO₃-treated chars were investigated their potentials as the catalysts in terms of product distribution as well as oil quality. The catalysts were characterized by using BET, XRD, XRF, FTIR, FE-SEM, and TG/DTA. The gas products were analyzed by using GC/FID whereas the oil products were analyzed by using SIMDIST-GC and GCxGC/TOF-MS. Sulfur and nitrogen contents were determined by using CHNS-analyzer. The results indicated that the surface area and pore size of treated char were enhanced. Furthermore, it can be noted that the increase in the total acidity of treated char was caused by the enhancement of carboxyl (-COOH) group on the surface. Additionally, the 5 M HNO₃-treatment can demineralize and significantly reduce sulfur content in the char. For product distribution, the 5 M HNO₃-treated char tended to decrease liquid fraction due to higher acidity, higher surface area, and larger pore size, promoting the greater cracking activity and then converting liquid into the gas phase. As compared with thermal decomposition, both untreated and 5 M HNO₃-treated chars dramatically decreased gas oil, light vacuum gas oil, and heavy vacuum gas oil, leading to drastically enhance of gasoline and kerosene. Moreover, even though these catalysts cannot reduce nitrogen content in oil, they can greatly remove sulfur in oil (approximately 26.6-27.3 %).

7.2 Introduction

With the strong global need in automobile usage, a huge amount of used tire rubbers has been increasingly generated. Due to the fact that the disposal of waste rubber is a serious environmental problem, reprocessing via pyrolysis process is an interesting alternative. However, waste solid or pyrolytic char from pyrolysis process, which is made up to 40-42 wt% (Yuwapornpanit and Jitkarnka, 2015) of all thermalytic products, has few market outlets, reducing the economic viability. With environmental concern, pyrolytic char can provide valid opportunities to be an alternative resource to produce adsorbents for water and air purification, fuel materials, or catalyst supports. The structure of pyrolytic char was similar to graphite, but covalent bonding between its graphene sheets showed imperfections in its production (On-x Life Technologies, Inc., 2013). The crystalline pyrolytic carbon has a distorted lattice structure with random unassociated carbon atoms (Wikipedia, 2014). López *et al.* (2013a) and Choi *et al.* (2014) reported that main elements of pyrolytic char were composed of carbon (81.5-82.8 wt%), hydrogen (0.32-1.0 wt%), sulfur (1.7-3.3 wt%), and nitrogen (0.2-0.5 wt%). Bunthid *et al.* (2010) and Bernardo *et al.* (2010) noted that pyrolytic char still contained the contaminants such as sulfur, heavy metal, volatile matter and trace oil, needed to be carefully removed. Normally, most of research work was focused on the production of commercial activated carbon from pyrolytic char, which was prepared by thermal treatment combined with carbonization and activation with activating agents such as steam, CO₂ or air (Antoniou *et al.*, 2014). The results showed that this method can provide high surface area, which was suitable for adsorption applications. Bernardo *et al.* (2012) suggested that acid leaching can be applicable to remove a trace of oil in activated carbon. Moreover, to decrease ash content of the chars, a demineralization procedure using hydrogen peroxide was successfully applied, which highly removed the majority of the metallic elements. Moreover, among the treatments using HCl, HCOOH, and H₂O₂, the result indicated that HNO₃-treatment of pyrolysis char provided the highest sulfur removal. The attractive point is that HNO₃ was able to maintain pore structure than other acids. Soltani *et al.* (2014) found that pyrolytic char from used cigarette filters, modified by using nitric leaching, had 57.8 % greater

surface acidity than the non-modified char, which was confirmed by Boehm titration method.

Since tire-derived char (TDC) is cheap and it is enormously produced from waste tire pyrolysis (40-60 % of all products), it is essential to find its potential usages and applications in order to avoid a gigantic inventory of TDC in a tire pyrolysis plant. One interesting application is to use TDC as a catalyst for catalyzing a reaction, and one perfect solution is to use TDC as the catalyst in waste tire pyrolysis plant. The objective of this work was therefore to investigate the potential of using untreated and 5 M HNO₃-treated chars as catalysts for waste tire pyrolysis with in-depth analysis of tire-derived products and char characterization. The pyrolytic chars were tested in the catalytic pyrolysis of scrap tire rubber. From this purpose, untreated and 5 M HNO₃-treated chars were expected to convert heavy oil fraction into lighter products, and then produce greater quality of oil.

7.3 Experimental

7.3.1 Catalyst Preparation

In order to treat tire-derived char (TDC), nitric acid was used as a surface cleaning chemical. The TDC was firstly immersed in a 5 M HNO₃ solution (commercial HNO₃: RCI Labscan, 65 % purity; density 1.39 g/mL) with TDC to acid ratio of 1 g : 7.5 mL at room temperature under stirring condition (300 rpm) for 1 h. The 5 M HNO₃-treated char was subsequently washed until pH 7, and then dried at 105 °C overnight. Finally, the catalyst was pelletized and then sieved to control particle sizes in the range of 40-60 mesh.

7.3.2 Catalyst Characterization

Thermogravimetric/Differential Thermal Analysis, TG/DTA, (Perkin Elmer/Pyris Diamond), was performed to determine the thermal characteristics as well as the amount of moisture (50-105 °C), volatility or coke deposited on spent catalysts (105-850 °C), and fixed carbon (> 850 °C). This analysis was conformed to ASTM D3172-07 and ASTM D3173-03. The contents of carbon, hydrogen, nitrogen, and sulfur in feed material and catalysts were acquired from using LECO®Elemental

Analyzer (TruSpec®S). X-ray fluorescence (XRF) spectrometry (AXIOS PW4400) was used to determine the concentrations of elements in waste tire feed and catalysts. The samples were mixed with boric acid with the sample to boric acid mass ratio of 1:3. X-ray diffraction (XRD) instrument (Rikagu) was used to determine the crystalline phase of catalysts. The scanned angle started from 5° to 60° with a scanning speed of 5°/min. Thermo Finnigan/Sorptomatic 1990 equipment was used to determine the physical properties of catalyst. The approximate 0.5 g catalysts were degassed under vacuum at 250 °C for 18 h prior to analysis. Scanning electron micrographs (FE-SEM, JEOL/JSM 5200) was used to examine the microstructure morphology of the catalysts. The samples were dried at 105 °C for 24 h, and then were coated by Pt for 150-200 sec. A Nicolet 6700 Fourier transform infrared spectrometer (FTIR) was used to collect the spectra and the wave range number of the functional group on pyrolytic chars. The samples were mixed with KBr with the sample to KBr mass ratio of 1:1200. In addition, total acidity was determined by using back titration (3 replicates) (Makrigianni *et al.*, 2015).

7.3.3 Pyrolysis Process

The wasted tire tread (Bridgestone TURANZA GR-80) was prepared as a raw material, which was free of fiber and steel. It was consequently scraped, and then sieved (20-40 mesh). Pyrolysis experiments were conducted using pyrolysis procedure as reported in Dũng *et al.* (2009). The reactor was divided into two zones; the lower zone (pyrolysis zone) was loaded with 30 g of tire, and the upper zone (catalytic zone) was loaded with 7.5 g of a catalyst. The two zones were heated from room temperature to 500 °C and 350 °C, respectively, with a heating rate of 10 °C/min at atmospheric pressure. After that the final temperatures were held for 120 min in order to ensure that the tire sample was completely decomposed. The evolved gas was purged using a 25 mL/min of nitrogen through two condensers, aiming to separate liquid product from incondensable gas. The liquid product was called tire-derived oil (TDO).

7.3.4 Product Analysis

TDO and TDC were weighed to calculate the amount of gas yield by using mass balance. As first, TDO was dissolved in n-pentane with the oil to n-pentane mass ratio of 1:40 for asphaltene separation. The obtained oil is called maltene. Then, a 30 μL maltene solution diluted in 2 mL carbon disulfide (CS_2) was analyzed for its composition by using Gas Chromatography with Time of Flight Mass Spectrometer (GCxGC/TOF-MS). GCxGC-TOF/MS apparatus 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. The 1st GC column was a non-polar Rtx®-5Sil MS and the 2nd GC column was a polar Rxi®-17 MS. After that the diluted maltene solution was analyzed for the true boiling point by using 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 \times 0.25 mm ID \times 0.25 μm film thickness). The true boiling point curves were 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). Finally, gas product was analyzed for its composition using a Gas Chromatography with FID detector, Agilent Technologies 6890 Network GC system (HP-PLOT Q column: 20 μm film thickness and 30 m \times 0.32 mm ID).

7.4 Results and Discussion

7.4.1 Characterization of Tire-derived Chars (TDCs)

The TDC used in this study was obtained from the thermolysis of scrap tire sample. Table 7.1 reports the proximate and ultimate analysis of waste tire sample, which was used as the feed material. The feed material consists of volatile matters nearly two third of total weight, while approximately one third remains as fixed carbon. Moreover, it is composed of carbon (77.10 wt%), hydrogen (6.75 wt%), sulfur (0.48 wt%), and nitrogen (2.05 wt%).

Table 7.1 Proximate and ultimate analysis of waste tire sample

Proximate Analysis ^a	wt%	Ultimate Analysis ^b	wt%
Moisture	0.50	C	77.10±0.00
Volatile	62.92	H	6.57±0.01
Fixed carbon	36.58	N	0.48±0.01
		S	2.05±0.00

(a) dry basis, (b) dry and ash free basis, s.d. = standard deviation

The FTIR spectrum of the 5 M HNO₃-treated char is illustrated in Figure 7.1. Its spectrum, revealing the broad peak of carboxyl groups, is similar to untreated char spectrum. The peak present at around 3500 cm⁻¹ can be attributed to the -OH stretching of carboxyl and phenolic groups. The stretching at 2915 cm⁻¹ can be attributed to the C-H stretching of aromatic ring whereas the present peak at 2847 cm⁻¹ is the -OH stretching in carboxylic functional group. The band at 1706 cm⁻¹ can be assigned to the C=O vibration of ketones, aldehydes, or carboxyl groups. Another band, detected at 1146 cm⁻¹, may be attributed to the C-O stretches in carboxyl groups (Soltani *et al.*, 2014). Chingombe *et al.* (2005) referred to this absorbed peaks as carboxyl group since char was oxidized its carbon structure by using nitric acid, causing ring opening phenomena in amorphous carbon by introducing new acidic group on activated carbon. Then, some part of char structure was further oxidized to form nitro group. Even though the pyrolysis char was treated by nitric acid, the treated char present a low absorbed peak of N-O vibration of nitro compound at 1558 cm⁻¹ and C-N stretching of aromatic amine at 1384 cm⁻¹ (Gokce and Aktas, 2014). This result may present the weak bond of nitro group. When 5 M HNO₃-treated char was tested for its total acidity by back titration, the result shows that the acidity of treated char is a bit higher than that of the untreated char by 0.26 mmol/g as seen in Table 7.2. These results indicate that nitric treatment significantly increases in carboxylic group on treated char surface.

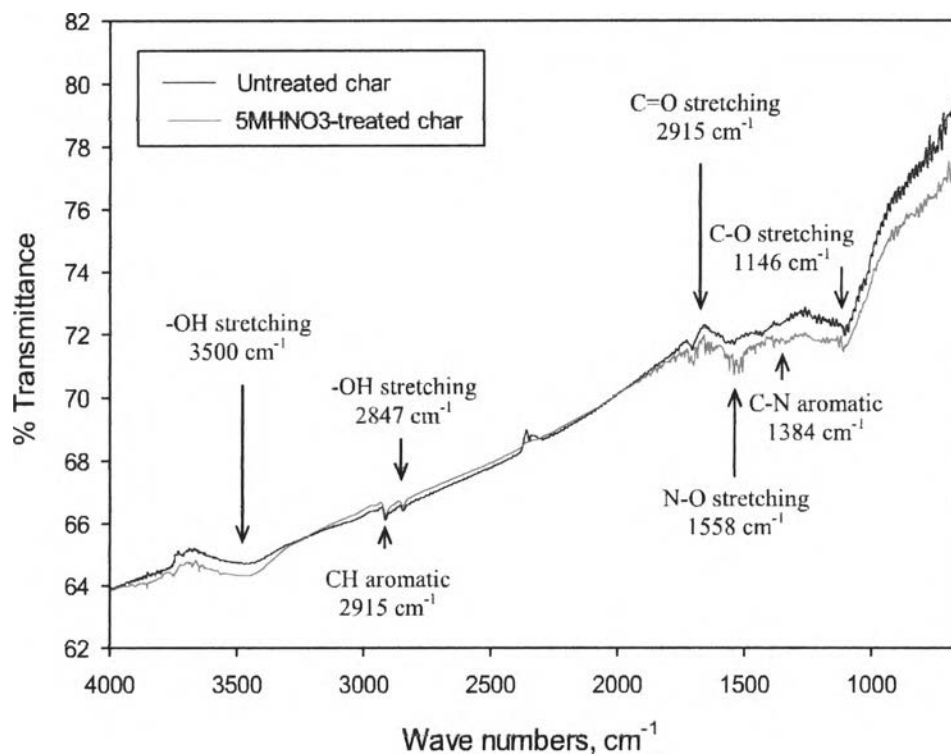


Figure 7.1 FTIR spectra of untreated and 5 M HNO₃-treated char.

Table 7.2 Physical properties of untreated char and 5 M HNO₃-treated char

Sample	S _{BET} (m ² /g)	Pore Volume (cm ³ /g)	Average Pore Diameter (nm)	Total Acidity (mmol/g)
Untreated char	70.06	0.39	22.97	49.98±0.60
5 M HNO ₃ -treated char	96.10	0.38	25.55	50.25±0.40

The isotherms, distributions of pore size, and porous textural properties are shown in Figures 7.2a, 7.2b and Table 7.2, respectively. It can be seen that nitric treatment causes the increase of surface area from 70.06 m²/g to 96.10 m²/g. In case of pore size distributions, it is agreed well with N₂ adsorption isotherms

because all the samples are the mesoporous structures, which are mainly distributed in the range of large mesopore (10-40 nm). However, nitric acid treatment does not give significant difference in pore volume as compared with untreated char.

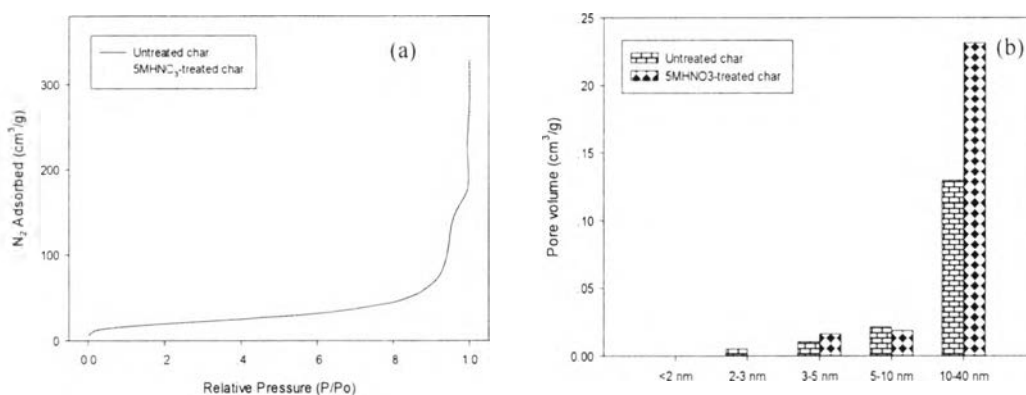


Figure 7.2 (a) Isotherms and (b) pore diameter distributions of untreated and 5 M HNO_3 -treated char.

Figure 7.3 exhibits that the XRD patterns of untreated and treated chars, which present two diffraction peaks corresponding to reflections of (0 0 2) ($2\theta = 10-30^\circ$) and (1 0 0) ($2\theta = 35-50^\circ$) graphite planes (López *et al.*, 2013b). Generally, the (0 0 2) plane is observed at $2\theta = 25^\circ$, which is attributed to the stacking of graphitic basal plane. In this work, the diffractions of untreated and 5 M HNO_3 -treated chars are observed at sharp $2\theta = 25.1^\circ$, and 24.6° , respectively, whereas the (1 0 0) plane of untreated and 5 M HNO_3 -treated chars are represented at 43.3° and 43.5° , respectively. Moreover, the α -ZnS and β -ZnS are also detected by using XRD instrument. López *et al.* (2013b) found that the formation of ZnS, causing from ZnO and H_2S , occurred during pyrolysis as a consequence of the sulfur decomposition. As a result, nitric acid treatment can reduce α -ZnS and β -ZnS contents, causing the reduction of Zn and S contents in the pyrolytic chars as seen in Table 7.3.

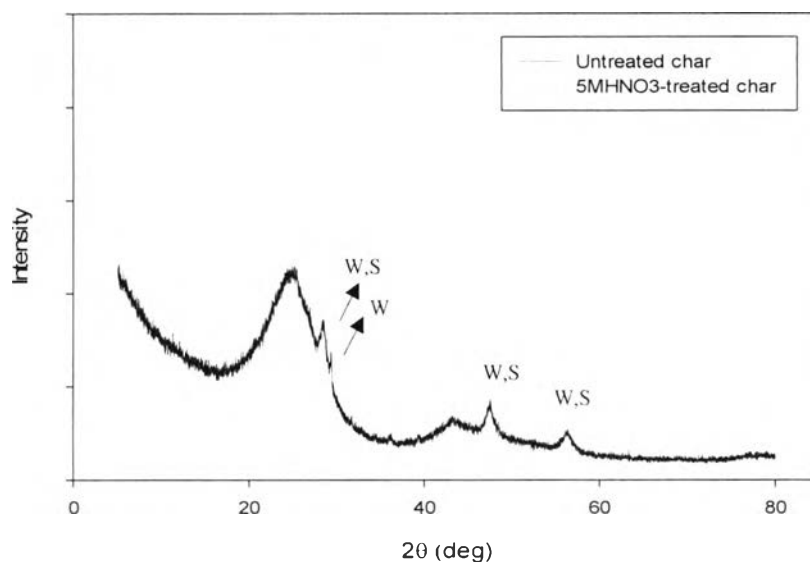


Figure 7.3 XRD patterns of untreated and 5 M HNO₃-treated chars (W = wurtzite (α -ZnS), S = sphalerite (β -ZnS)) (López *et al.*, 2013b).

The untreated and 5 M HNO₃-treated chars are mainly composed of carbon at 74.60 wt% and 79.05 wt%, respectively, and their mineral contents are approximately 14.71-6.79 wt%. The increase of carbon concentration in 5 M HNO₃-treated char well indicates that the other volatile matters are leached by using nitric acid, especially the reduction of sulfur compound by 38.2 %. As compared between untreated and treated chars on the change in concentration of inorganic species, the demineralization of Si, Al, Zn, Mg, Ca, Na, Fe, Cl, K, and P is observed using nitric treatment. Agreed well with the FE-SEM images as shown in Figures 7.4a-7.4b, it is clearly seen that nitric treatment has a corrosive effect on pyrolysis char surface, causing the removal of volatile and mineral in chars.

Table 7.3 Major elements and mineral contents in TDC before and after nitric acid treatment

	Untreated char	5 M HNO ₃ -treated Char
Mineral content (mean ± s.d., wt%)		
Si	5.83±0.42	2.72±0.13
Al	2.63±0.02	2.51±0.15
Zn	1.26±0.07	0.28±0.03
Mg	0.15±0.02	0.03±0.04
Ca	0.26±0.05	0.13±0.02
Na	0.55±0.02	0.47±0.07
Fe	0.29±0.01	0.08±0.01
Cl	0.52±0.01	0.42±0.02
K	0.22±0.01	0.16±0.01
P	0.09±0.01	0.00±0.00
Others	85.29±0.62	93.21±0.32
Main element (mean ± s.d., wt%)		
C	74.60±0.28	79.05±0.07
H	1.06±0.01	0.74±0.02
N	0.49±0.00	0.80±0.00
S	2.46±0.01	1.52±0.01

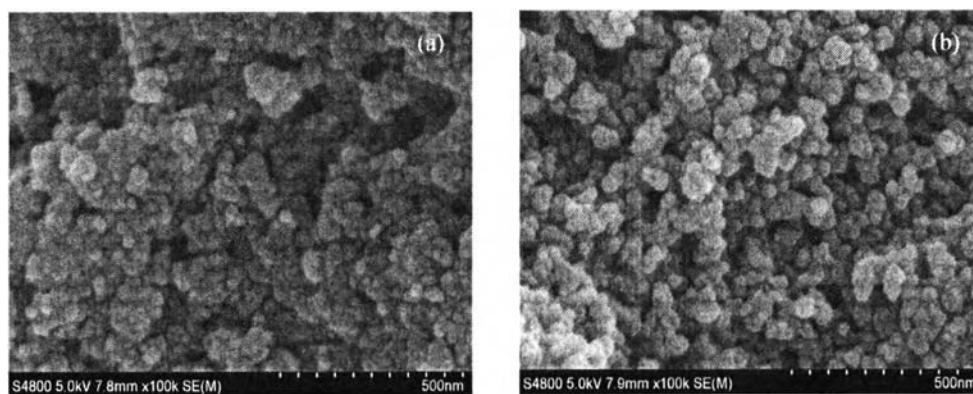


Figure 7.4 FE-SEM images of (a) untreated and (b) 5 M HNO₃-treated chars.

7.4.2 Catalytic Pyrolysis

The distributions of products, obtained from untreated and 5 M HNO₃-treated chars, are illustrated in Figure 7.5a. The 5 M HNO₃-treated char tended to increase gas fraction due to higher acidity, higher surface area, and larger

pore size, causing the greater cracking activity and then converting liquid into the gas phase. Using the untreated char results in the same product distribution as in the non-catalyst case. Additionally, untreated and 5 M HNO₃-treated chars give similar gas composition as seen in Figure 7.5b.

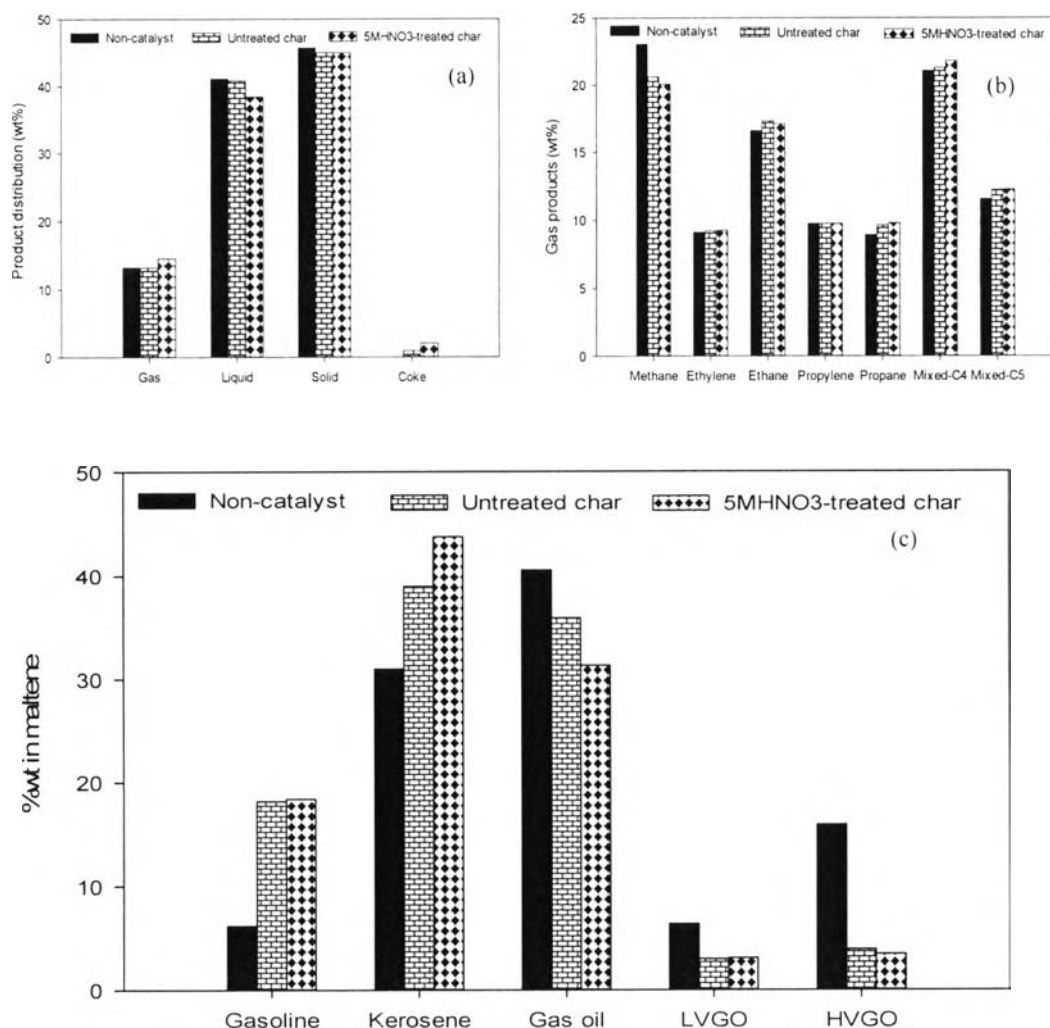


Figure 7.5 (a) Product distribution, (b) gas products and (c) petroleum fractions from using pyrolysis char as catalyst.

The petroleum fractions from using untreated and 5 M HNO₃-treated chars are displayed in Figure 7.5c. As compared with thermal decomposition, both untreated and 5 M HNO₃-treated chars dramatically decrease heavy fractions (LVGO, and HVGO) in oil by roughly three times. Also, gas oil is reduced using both chars by 11.4 % and 22.7 %, respectively, which therefore drastically enhances

gasoline content by approximately three times, and increases kerosene content by 25 % untreated char and 41.3 % treated char.

Figures 7.6a-7.6f show the contour plots and surface plots of total ion chromatogram (TIC) of maltenes from non-catalyst, untreated and treated char cases. These figures indicate that the condition, used to analyze the tire-derived oils, were satisfied to separate the complex components. These compounds can be classified into 3 main categories; that are aliphatics, alicyclics, and aromatics as seen in Figures 7.6a-7.6b. Additionally, these categories can be classified into 8 sub-groups; that are, saturated hydrocarbon (SATs), olefins (OLEs), naphthenes (NAPs), terpenes (TERs), mono-aromatics (MAHs), poly-aromatics (PAHs) and polar-aromatics (PPAHs). Using the 5 M HNO₃-treated char, DAHs, PAHs, PPAHs, are cracked via ring opening reaction, causing the increases in MAHs, TERs, NAPs, and OLEs greater than the untreated char as seen in Figures 7.6e-7.6f and 7.7. These results indicate that the decrease in gas oil, LVGO, and HVGO concentrations may be caused by the reduction of large-size aromatics (DAHs, PAHs, and PPAHs).

As a result, it can be picturized in Figure 7.8 that since the pyrolysis chars are unassociated carbon structure with wide-range of pore sizes, the large pore size of untreated and treated chars may allow the higher amount of bulky molecules to pass through the pore, and their smaller pores may provide the molecules to stay inside the channel with a longer residence time, leading to a higher thermal cracking activity. However, the treated char is likely to perform on catalytic cracking better than the untreated one since it more greatly converts gas oil. This is due to treated char may provide more molecular adsorption on surface due to its higher surface area, and then the molecules are stabilized in carbenium ion form that subsequently undergo further secondary reactions.

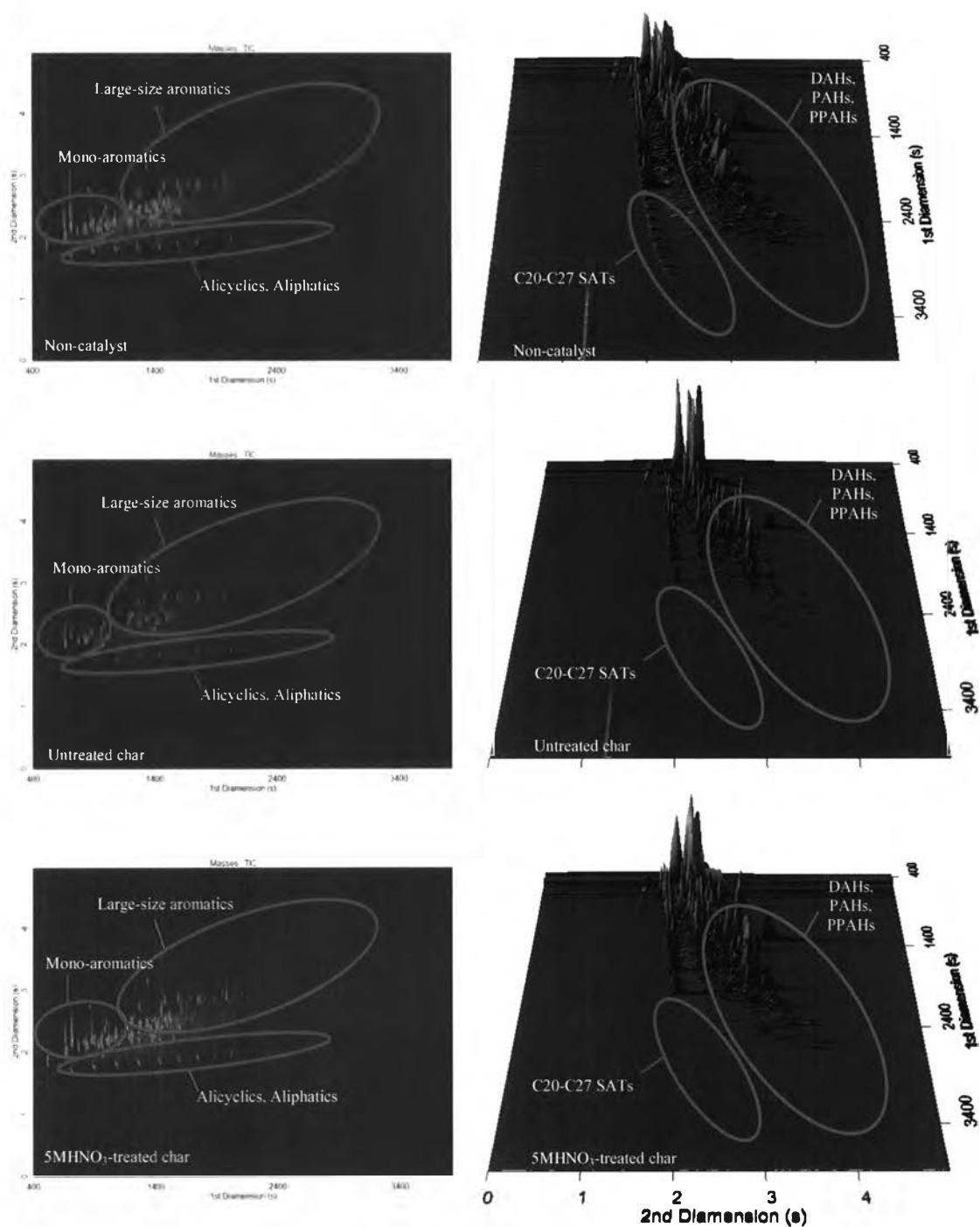


Figure 7.6 Total Ion Chromatograms of maltenes: contour plots (2D) in cases of (a) non-catalyst, (b) untreated char, and (c) 5 M HNO₃-treated char and surface plots (3D) in cases of (d) non-catalyst, (e) untreated char, and (f) 5 M HNO₃-treated char.

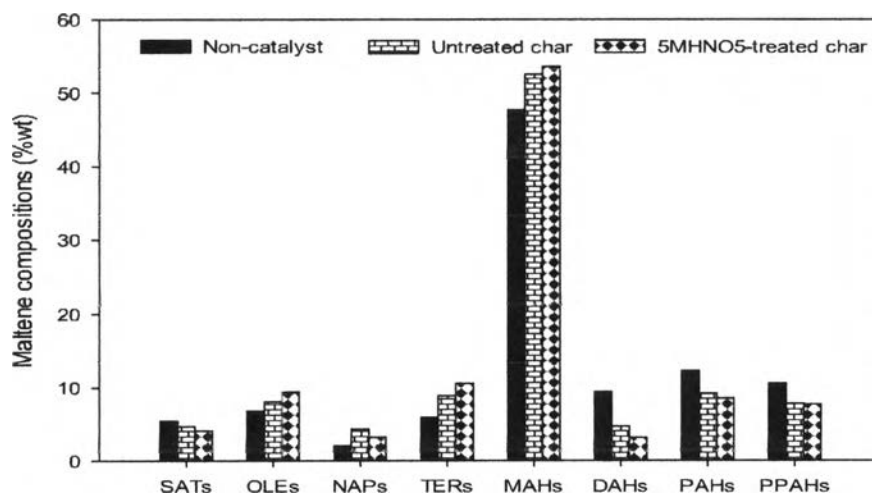


Figure 7.7 Maltene compositions from using pyrolysis chars as catalysts.

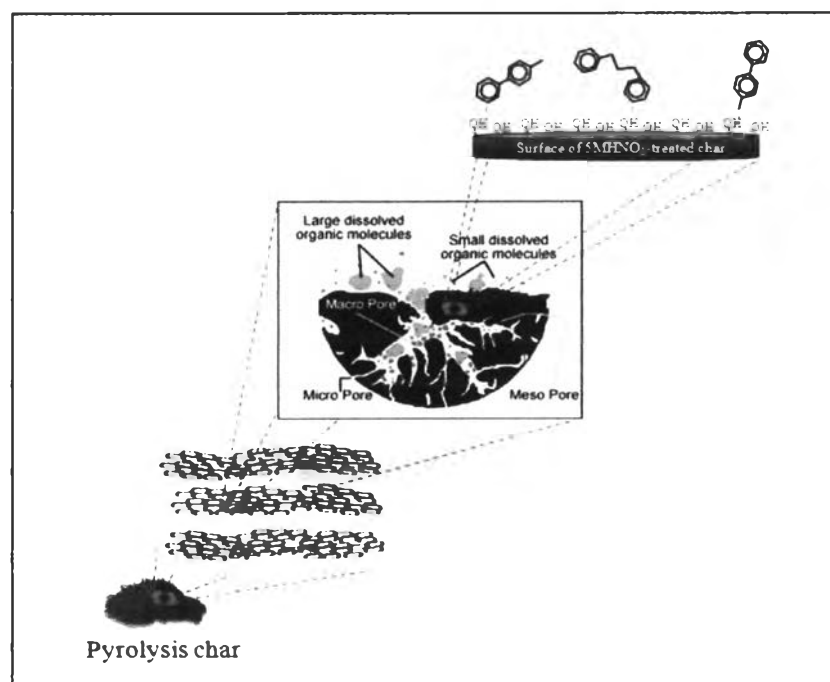


Figure 7.8 Visualized surfaces of untreated and 5 M HNO₃-treated chars.

7.4.3 Hetero-atom Removal from Tire-derived Oil

Originally added as additives in tire production, hetero-atoms such as nitrogen and sulfur can be formed compounds in tire-derived oil. Table 7.4 reports the elemental contents in the TDOs. The results illustrates that the TDO obtained from non-catalyst is mainly composed of carbon (69.1 wt%), hydrogen (9.62 wt%), and hetero-atoms (1.67 wt%).

Table 7.4 Elemental contents in TDOs (wt%)

Element	Non-catalyst	Untreated Char	5 M HNO ₃ -treated Char
C	69.10±0.42	66.90±0.57	64.40±0.57
H	9.62±0.15	9.60±0.07	9.69±0.05
N	0.40±0.04	0.38±0.04	0.54±0.02
S	1.27±0.00	0.93±0.02	0.92±0.00

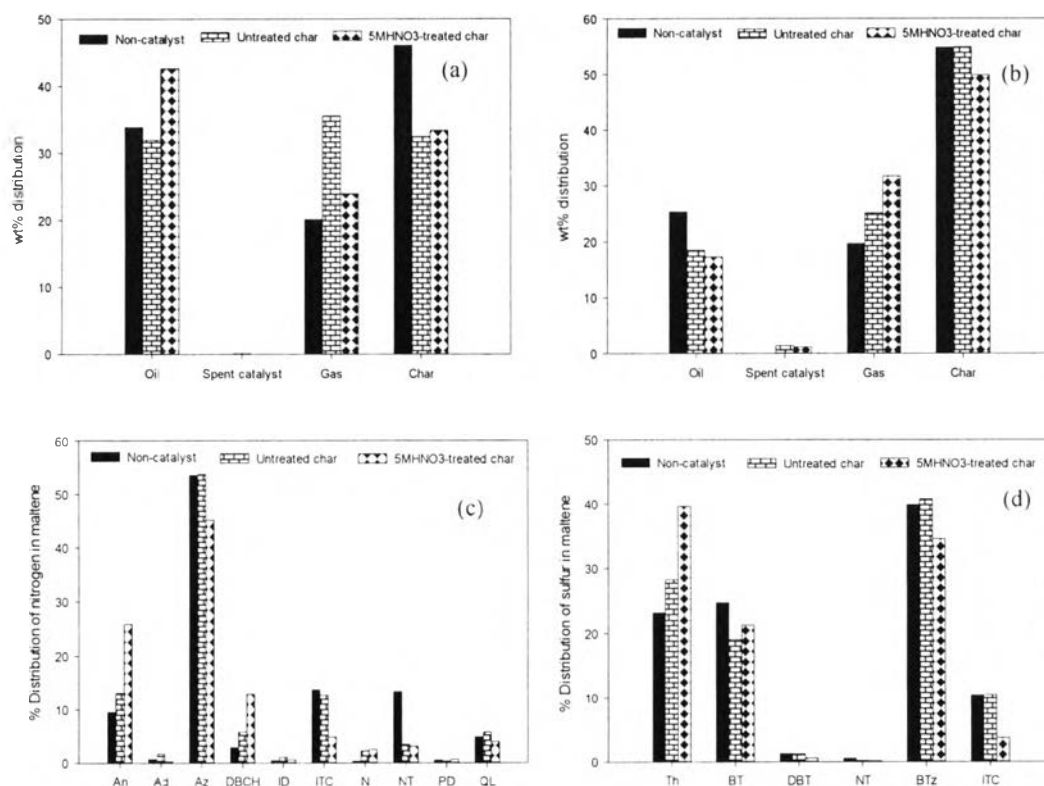


Figure 7.9 Distribution of (a) nitrogen and (b) sulfur contents in overall products and (c) nitrogen and (d) sulfur groups in maltenes obtained from using untreated and 5 M HNO₃-treated chars.

Figures 7.7a and 7.7c illustrate the distribution of nitrogen content in overall products and nitrogen groups in oils, respectively. Nitrogen compounds in the TDOs are classified into 10 groups; that are, amines (An), amides (Ad), azo compounds (Az), diazabicycloheptenes (DBCH), indoles (ID), isothiocyanates (ITC), nitro compounds (N), nitriles (NT), pyridines (PD), and quinolines (QL). The main nitrogen compounds in untreated and treated char cases are azo compounds and amines. It can be observed that untreated char shows the performance on the reduction of nitrogen content in TDO (from 0.40 wt% to 0.38 wt%) as seen in Table 7.4, causing a high distribution of nitrogen in the gas phase. This result can be explained that nitriles may be reformed to gas species since they are drastically decreased. On the other hand, even though treated char cannot remove nitrogen content in TDO (with 0.54 wt% detection), it can greatly convert azo compounds, isothiocyanates, and nitriles, forming amines, diazabicycloheptenes, and nitro compounds.

Figures 7.7b and 7.7d illustrate the distribution of sulfur content in overall products and sulfur groups in oils, respectively. Sulfur compounds in the TDOs are divided into 6 groups; that are, thiophenes (Th), benzothiophenes (BT), dibenzothiophenes (DBT), naphthothiophenes (NT), benzothiazoles (BTz), and isothiocyanates (ITC). Interestingly, both untreated and treated chars show the impressive decrease in sulfur contents in TDOs by approximately 26.6-27.3 % as seen in Table 7.4, causing a high distribution in gas phase as seen in Figure 7.7b. However, sulfur species in TDOs obtained from these two catalysts are different, possibly due to the differences in surface area, pore size, and total acidity. The main sulfur compound group in the untreated char case is benzothiazoles whereas that of treated char is thiophenes. The untreated char better removes benzothiophenes whereas the treated char more greatly decreases benzothiazoles and isothiocyanate.

7.5 Conclusions

The solid char from thermolysis of scrap tire rubber was treated with 5 M HNO_3 and characterized for their properties. Both treated and untreated chars were

consequently tested in waste tire pyrolysis, aiming to investigate their potential as a catalyst from the product distribution and oil quality. It was found that the treatment using HNO_3 enhanced the acidity and surface area of char, while the pore structure was not significantly destroyed. Furthermore, it also eliminated inorganic substances, especially ZnS. The untreated and 5 M HNO_3 -treated chars can convert heavy proportions (gas oil, LVGO, and HVGO) in tire-derived oils into lighter fractions (gasoline and kerosene). Moreover, aromatics (DAHs, PAHs, and PPAHs) in oils were also converted via ring opening into other hydrocarbon groups. However, the 5 M HNO_3 -treated char gave the higher performance on catalytic cracking than the untreated char due to higher acidity, higher surface area, and larger pore size. Additionally, the untreated and treated chars did not only remove large-size aromatics and heavy fractions in TDOs but also sulfur content.

7.6 Acknowledgements

The authors would like to thank The Petroleum and Petrochemical College, Chulalongkorn University, Thailand, Center of Excellence on Petrochemical and Materials Technology, and Thailand Research Fund (TRF: RSA5680021) for all supports.

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