CHEMICAL ENGINEERING TRANSACTIONS

VOL. 35, 2013

A publication of
AIDIC
The Italian Association of Chemical Engineering
www.aidic.it/cet

Guest Editors: Petar Varbanov, Jiří Klemeš, Panos Seferlis, Athanasios I. Papadopoulos, Spyros Voutetakis

ISBN 978-88-95608-26-6; **ISSN** 1974-9791

DOI: 10.3303/CET1335223

An Attempt on Using a Regenerated Commercial $NiMoS/Al_2O_3$ as a Catalyst for Waste Tyre Pyrolysis

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A used commercial sulfided $NiMoS/Al_2O_3$ catalyst from the hydrodesulfurization unit of a refinery in Thailand was employed as a catalyst for waste tire pyrolysis since it contains both acid and metal sulphide functions that could potentially benefit cracking and sulphur removal simultaneously. It was regenerated prior to use in a catalytic zone operated at 350 °C of the pyrolysis reactor. As a result, as compared to the non-catalytic case, the catalyst gave less long residue with a higher amount of full range naphtha in the tire-derived oil that contained a higher amount of mono-aromatics. Moreover, the oil contained a fewer amount of polar-aromatics as well as less sulphur content. Furthermore, the oils were analyzed for sulphur species by using GC-TOF. The results showed that the oil obtained from sulphided $NiMoS/Al_2O_3$ had a higher amount of sulphur-containing molecules in the range of gasoline than the non-catalytic oil. Most of the sulphur-containing molecules found in gasoline, kerosene and gas oil ranges were benzothiophene derivatives such as 3-methybenzothiophene (C_9H_8S), benzo[b]thiophene, 2,5-dimethyl- ($C_{10}H_{10}S$), and dibenzothiophene derivatives such as naphtho[2,3-b]thiophene, 4,9-dimethyl- ($C_{14}H_{12}S$).

1. Introduction

Tire pyrolysis has been generally known as a feasible and economical method because it allows the valuable substances to be recovered. The products are regained in three main phases comprised of char, oil and gas, which have different applications. Char can be used as a blending, carbon black, or converted to activated carbon. The derived oil can be the source of chemicals in chemical industry since it contains a high concentration of benzene, toluene, xylene and other aromatic derivatives. It is also added to petroleum refinery feedstock due to the gross calorific value of about 40.0 MJ/kg similarly to light fuel oils (Cunliffe and Williams, 1998). The gas products are mainly composed of light hydrocarbons such as olefins and C_1-C_4 paraffins that are also useful as a fuel. Due to the valcanization of tire, large network between sulphidic crosslinks and rubber chains are formed, which can be monosulphidic (-S-), disulphidic (-S-S-) and polysulphidic ($-S-S_x-S-$) (Bilgili et al., 2001). The release of sulphur from the tire structure during pyrolysis affects to the quality of oil products. In consequence, it is expected to be removed to obtain the light oil with less sulphur. Therefore, the cracking and desulphurization abilities of a pyrolysis catalyst are needed simultaneously. A hydrodesulphurization (HDS) catalyst is a commercial catalyst used for removing sulphur compounds from oils to produce the clean fuel. After the regular operation, the activity of the catalyst continuously decreases; however, the spent catalyst can be regenerated for reuse. In exclusive of the economic benefit, a spent commercial $NiMoS/Al_2O_3$ catalyst has the potential to be used as a tire pyrolysis catalyst because it has both acid and metal sulphide functions that can simultaneously promote the ability of cracking and desulphurization. H_2 required in desulphurization reaction can be supplied from cracking of waste tire. However, the activity on removal of sulphur-containing compounds during pyrolysis is highly acquired from the commercial HDS catalyst. It has been reported that the hydrogenation ability of NiMo sulphide catalyst resulted in high activity in HDS of 4,6-di-methyl-dibenzothiophene (Kim et al., 2003). From the work of Rodríguez-Castellón et al. (2008), a presulphided Ni5-Mo11 catalyst (using 90/10 % of N_2 /H_2S at atmospheric pressure) gave the highest dibenzothiophene (DBT) conversion at 3.0 MPa and 300-340 °C as compared to the conventional sulphided Co(Ni)Mo(W)

Please cite this article as: Saeng-arayakul P., Jitkarnka S., 2013, An attempt on using a regenerated commercial nimos/al2o3 as a catalyst for waste tyre pyrolysis, Chemical Engineering Transactions, 35, 1339-1344 DOI:10.3303/CET1335223

catalyst. They also concluded that Ni-promoted catalysts had greater performance than Co-promoted catalysts at high temperatures because of high hydrogenation ability, similar to the result of Li-hua et al. (2011), They found that the sulphided catalyst containing 18% of Mo and 4% of Ni showed high HDS activity, hydrogenation selectivity, and favoured the hydrogenation of phenyl ring in the DBT molecule due to the high stacking number of MoS_2 which is the active site facilitating the adsorption of sulphur-containing reactants and desorption of hydrogen sulphide products (Villarroel et al., 2008). Since a regenerated $NiMoS/Al_2O_3$ catalyst is comprised of acid (Al_2O_3) and metal sulphide (NiMoS), the objective of this work was to investigate the ability of the catalyst in waste tire pyrolysis and desulphurization, aiming to improve the quality and quantity of pyrolysis oil that have a lower sulphur level. Sulphur species and sulphur distribution in products are also reported in this work.

2. Experiment

2.1 Material and Preparation

A regenerated commercial $NiMoS/Al_2O_3$ obtained from a refinery in Thailand was first screened for the clean pellets, then crushed, and sieved into the size range of 400-425 μm by using 40-60 mesh sizes of sieves. To prepare a waste tire sample, the side wall of a used tire sample, Bridgestone TURANZA GR-80, was scraped and then sieved into a particle size range of 8-18 mesh.

2.2 Pyrolysis Process

The tire sample was pyrolyzed in the lower zone (thermal pyrolysis zone) of reactor from room temperature to the final temperature of 500 ^oC with the heating rate of 10 $^oC/min$, and then the pyrolytic effluent with ~30 vol% H_2 (Aylón et al., 2007) carried by nitrogen flow to the upper zone packed with a catalyst. The catalytic zone was controlled at 350 ^oC. The system was held for 90 mins to ensure the complete conversion of tire. The tire pyrolysis experiments were performed according to the procedure written in Dũng et al. (2009). The product effluent carried by nitrogen was condensed to liquid products by using ice-salt condensers. The incondensable product was passed to the condensers and collected by a gas sampling bag.

2.3 Catalyst characterization

The element composition of a catalyst sample was characterized by X-ray fluorescence spectrometry (XRF). Thermo Finnigan/Sorptomatic 1990 was used to determine the specific surface area and total pore volume of the catalyst using Brunauer-Emmet-Teller (BET) method. The sample was out-gassed at 150 ^oC, overnight, to primarily clean up the impurity, and then was in a helium environment at 300 °C for 4 hours prior to the adsorption of nitrogen gas. The acidity of catalyst was analyzed by Temperature Programmed Desorption of isopropylamine (IPA-TPD) via manual injection. 0.05 g of sample was firstly purged by He flow to eliminate the moisture until no peak of water was observed. The IPA-TPD was conducted form room temperature to 800 °C with a heating rate of 20 $^oC/min$ under the He flow. The desorpton of isopropylamine (m/e = 44), ammonia (m/e =17) and propylene (m/e = 41) were detected by a mass spectrometer (Kresnawahjuesa et al., 2000) and previously Farneth and Gorte (1995). Besides the polar-aromatic content in oil as reported previously (Manchantrarat and Jitkarnka, 2012), the used catalyst was also characterized by LECO® Elemental Analyzer, TruSpec®S at the furnace temperature of 1,350 °C to determine the amount of sulphur in the catalyst. The amount of coke on the spent catalyst was analyzed by Thermogravimetric/Differential Thermal Analysis (TG/DTA), heated from room temperature to 700 °C (10 °C/min) with oxygen gas (50 mL/min).

2.4 Product analysis

The liquid and solid products were weighed to determine the product distribution. The amount of gas was then determined by mass balance. An incondensable product in the gas sampling bag was analyzed by using a Gas Chromatograph (GC), Agilent Technologies 6890 Network system, using HP-PLOT Q column with FID detector with He as a carrier gas. Asphaltene was first separated from the liquid products by dissolving in n-pentane with the ratio of 1:40 (oil: n-pentane). Saturated hydrocarbons, mono-, di-, poly- and polar-aromatics were fractionated from the obtained maltenes by specific solvents (Šebor et al., 1999) using liquid adsorption chromatography, then further analyzed for the true boiling point curves (TPBs) by using a Varian CP-3800 stimulated distillation gas chromatography (SIMDIST GC), equipped with an FID according to the ASTM D2887 method. The TBPs of liquid hydrocarbons were cut to petroleum fractions, which are 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 oils were also analysed for the sulphur content by using elemental analysis (LECO, US). Finally, a Gas Chromatograph-Mass Spectrometer (Time of Flight), GC-MS (TOF), with 2D dimension mode was used to identify sulphur-containing compounds in the oil by using helium and nitrogen as a carrier and cooling gas, respectively.

3. Results and Discussion

3.1 Effect of spent NiMoS/Al$_2$O$_3$ to catalytic pyrolysis of waste tire

The results of pyrolysis with and without the catalyst including the product yield, liquid composition, petroleum cuts and light gas yield are given Figure 1. The results from product yield in Figure 1a indicate that the spent NiMoS/Al$_2$O$_3$ decreases the yield of liquid products from ~42 wt% to ~32 wt% in accordance with the increasing amount of gas products and coke formation while the solid yield remains constant. It means that using a catalyst promotes the decomposition of tire-derived product evolved from the thermal pyrolysis zone, resulting in a higher amount of lighter product (gases) that indicates high reaction activity of the catalyst. It is not surprised that coke is formed on the spent catalyst. The amount of coke per gram of the catalyst is also shown in Table 1. Figure 1b presents the chemical composition in the maltene fractions. It is observed that the spent NiMoS/Al$_2$O$_3$ catalyst can reduce polar-aromatics, but it shows low performance in poly-aromatics reduction, resulted in the shortage of saturated hydrocarbons. The remarkable result is found on the increase in mono-aromatics in the catalytic case. The TBP of maltene oil was cut into petroleum fractions that are shown in Figure 1c. The amount of the lightest fraction, full range naphtha, is increased from the expense of heavy fractions in the experiment using spent NiMoS/Al$_2$O$_3$ catalyst. Nevertheless, the minor decrease of gas oils and long residue is possibly due to the mild acidity of Al$_2$O$_3$ support. It is interesting that using the spent NiMoS/Al$_2$O$_3$ shows high selectivity in alkane gas products (Figure 1d), possibly because of the hydrogenation ability (Li-hua et al., 2011). It is known that an alkane is a saturated hydrocarbon, so alkane was easily formed by hydrogenation. Hence, the spent NiMoS/Al$_2$O$_3$ is a good catalyst for producing light alkane gas products from waste tire pyrolysis if compared with the non-catalytic experiment.

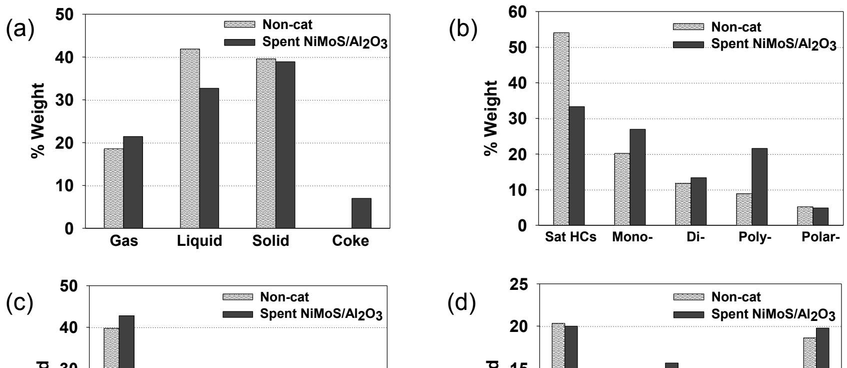

Figure 1: Effects of spent NiMoS/Al$_2$O$_3$ on the pyrolysis products: (A) product distribution, (B) liquid composition, (C) petroleum cuts, and (D) light gas yield.

The shift of pyrolysis products from using the spent NiMoS/Al$_2$O$_3$ catalyst can be explained by IPA-TPD results. The TPD profiles in Figure 2 present the MS signal of isopropylamine (m/e = 44), ammonia (m/e = 17) and propylene (m/e = 41) from mass spectrometer. The maximum desorption of unreacted isopropylamine was observed at 120 ^{o}C, associated to weak acid sites on the surface of the spent NiMoS/Al$_2$O$_3$ catalyst while the maximum desorptions of propylene and ammonia around 300 - 400 ^{o}C represent brønsted acid sites due to the fact that isopropylamine is decomposed on brønsted acid sites (not Lewis acid sites), producing propylene and ammonia. The catalyst has both weak and brønsted acid sites; however, weak acid sites are dominant, meaning that the catalyst has mild acidity or fewer amounts of strong brønsted acid sites. It can be explained that the slight changes on heavy to light products are caused by the mild cracking ability of the spent $NiMoS/Al_2O_3$ acid catalyst.

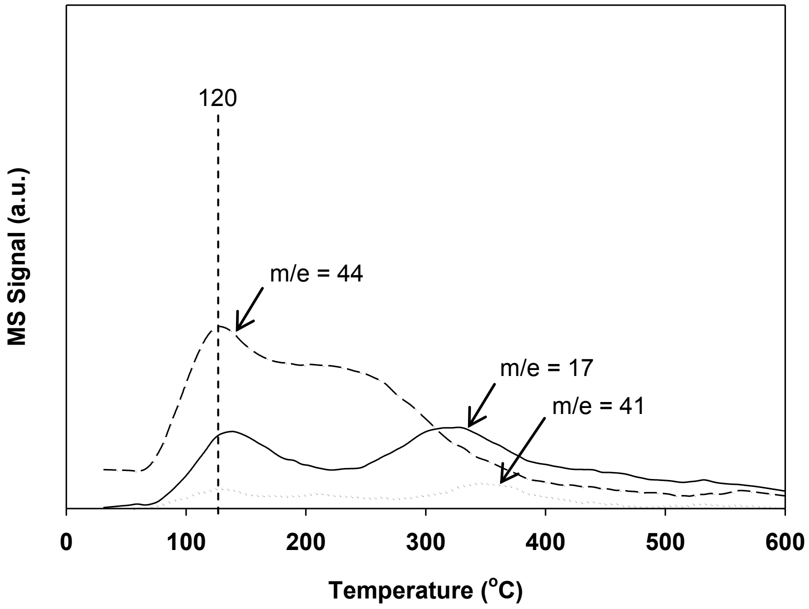

Figure 2: IPA-TPD profiles of isopropylamine (m/e = 44) desorption, ammonia (m/e =17) and propylene (m/e = 41) formations on the spent $NiMoS/Al_2O_3$ catalyst.

It is possible that the reactions occur mostly in the pore of catalyst, so it can be suggested that coke is formed in the pore of acid catalyst. The physical properties of catalyst and the amount of coke in the used catalyst are shown in Table 1.

Table 1: Physical properties of spent $NiMoS/Al_2O_3$ and the amount of coke in the used catalyst

Catalyst	Specific surface area (m^2/g)	Pore specific volume (cm^3/g)	Median pore width (Å)	Coke (g/g cat)
$NiMoS/Al_2O_3$	198.75	0.42	8.86	0.36

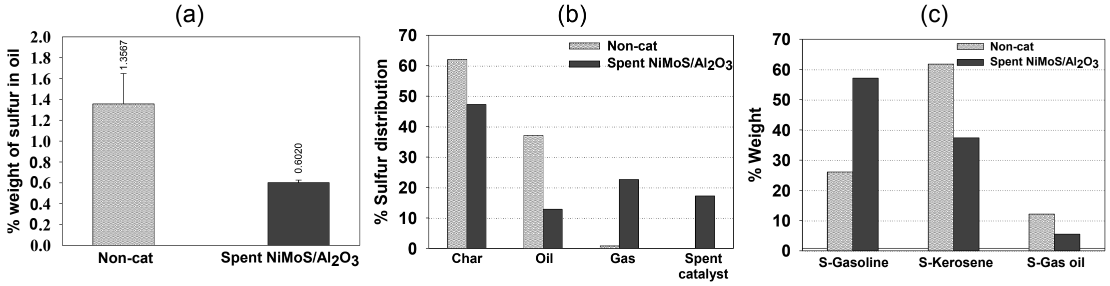

Figure 3: Effect of spent $NiMoS/Al_2O_3$ on the sulphur contents: (a) sulphur in oil, (b) sulphur distribution in products, and (c) petroleum cuts.

3.2 Sulphur removal ability

The sulphur contents in pyrolysis oil obtained from the elemental analyzer are given in Figure 3a. A high amount of sulphur content was found in the non-catalytic case; however, it can be reduced from 1.36 to 0.60 wt% by using the catalyst. The disappearance of the sulphur in oil occurs in conjunction with a higher distribution of sulphur in the gas product and the used catalyst as indicated by the sulphur balance (Figure 3b). The high amount of sulphur in the gas fraction is possibly in the form of H_2S (Lin et al., 1997).

It has been reported that H2S can be adsorbed on the active site catalyst (Sidhpuria et al., 2008), resulting in a high deposition of sulphur on the spent catalyst. By using the GC-MS (TOF), the distribution of sulphur in light petroleum cuts illustrated in Figure 3C indicates that the spent NiMoS/Al2O3 catalyst can change the high distribution of sulphur, which is formerly in kerosene (C10-C13) and gas oil (C14-C20), to in gasoline (C5-C9). It can be concluded that the catalyst had the ability in both cracking and desulphurization simultaneously.

Table 2: Prominent C, H, S-containing molecules found in gasoline (C5-C9), kerosene (C10-C13) and gas oil (C14-C20) ranges of the oil

Petroleum cuts	Compounds	Formula	Area (%)*	
			Non-cat.	Cat.
Gasoline	Thiophene, 2-ethyl-5-methyl-	$C_7H_{10}S$	-	0.0523
	Thiophene, 3-(1,1-dimethylethyl)-	$C_8H_{12}S$	-	0.0470
	Benzo[b]thiophene	C_8H_6S	0.0283	0.0613
	3-Methylbenzothiophene ^{I}	C_9H_8S	0.0499	0.1657
Kerosene	Benzo[b]thiophene, 2,7-dimethyl- ^{II}	$C_{10}H_{10}S$	0.1138	0.0279
	5-Ethylbenzo[b]thiophene	$C_{10}H_{10}S$	0.0137	0.0529
	Benzo[b]thiophene, 2,5-dimethyl-	$C_{10}H_{10}S$	0.0409	0.0897
	Benzo[b]thiophene, 7-ethyl-2-methyl-	$C_{11}H_{12}S$	0.0077	0.0547
Gas oil	2,8-Dimethyldibenzo(b,d)thiophene	$C_{14}H_{12}S$	0.0062	0.0059
	3,7-Dimethyldibenzothiophene	$C_{14}H_{12}S$	0.0091	0.0067
	Naphtho[2,3-b]thiophene, 4,9-dimethyl-	$C_{14}H_{12}S$	-	0.0140

*% Area of C,H,S-containing molecules in maltene fraction determined by GC-MS (TOF)

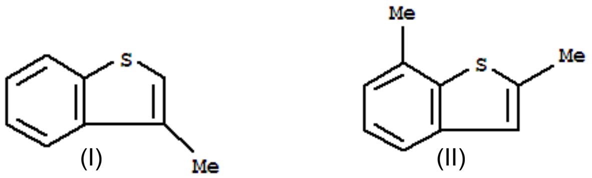

Figure 4: Examples of sulphur-containing compounds found in pyrolysis oils.

Table 2 shows the prominent C, H, S-containing molecules in each petroleum cuts. It is observed that sulphur species obtained in the highest amount from the non-catalytic case are benzo[b]thiophene, 2,7-dimethyl- in kerosene (C_{10}-C_{13}) fraction whereas those observed from the spent NiMoS/Al_2O_3 case is 3-methylbenzothiophene in gasoline fraction (C_5-C_9), which contains less number of alkyl groups than the non-catalytic case as shown in Figure 4. Most of the sulphur-containing molecules found in gasoline, kerosene and gas oil ranges are benzothiophene derivatives such as 3-methybenzothiophene (C_9H_8S), benzo[b]thiophene, 2,5-dimethyl- ($C_{10}H_{10}S$), and dibenzothiophene derivatives such as naphtho[2,3-b]thiophene, 4,9-dimethyl- ($C_{14}H_{12}S$). However, the sulphur species found the most in this study are benzothiophene derivatives, which is different from Williams and Bottrill (1995) who found dibenzothiophene derivatives in majority.

4. Conclusions

The roles of a commercial hydrodesulphurization catalyst in the catalytic pyrolysis of waste tire and sulphur removal was proven in this study. The spent commercial NiMoS/Al_2O_3 catalyst can reduce the amount of sulphur in oil from 1.36 to 0.60 wt%, and can help cracking waste tyre to lighter products. Nevertheless, the cracking activity was not considerably high due to its mild acidity. Therefore, it can be concluded that the spent HDS catalyst can be used as a catalyst for the waste tyre pyrolysis since it can produce the better quality of pyrolysis oil containing a lower sulphur level because of its acid and sulphide functions.

Acknowledgements

The authors would like to thank the Petroleum and Petrochemicals College, Chulalongkorn University, the Center of Excellence on Petrochemical and Materials Technology, Thailand Research Fund, and the Commission on Higher Education for the mutual financial support.

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