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THERMAL AND CATALYTIC CRACKING OF PETROLEUM RESIDUE OIL

Y. Syamsuddin, B. H. Hameed, R. Zakaria, and A.R. Mohamed
School of Chemical Engineering, Engineering Campus,
University Science Malaysia, 14300 Nibong Tebal, Penang, Malaysia
e-mail: chbassim@eng.usm.my

ABSTRACT

Thermal and catalytic cracking over synthesized nickel-molybdenum supported on aluminum borate (NiMo/AB) catalysts were studied. A series of aluminum borate supports with various aluminum borate (A/B) weight ratios were prepared by precipitation method. NiMo/AB catalysts were prepared by impregnation of nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) and ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}.4H_2O$) solution. These samples have been characterized with respect to surface areas, average pore diameters, pore size distribution, and acidity strengths. Thermal and catalytic cracking of atmospheric petroleum residue oil were carried out in a high pressure batch reactor at 340°C, 3 h reaction time and 0.5 g catalyst loading. The results revealed that catalytic cracking gave better product conversion and yield compared to thermal reaction. The conversion was 51.43 wt% from thermal reaction compared to 60-65 wt% from catalytic cracking. The yield of gasoline was 6.25 wt% and 11.5-13.37 wt% from thermal and catalytic cracking, respectively.

Keywords: Residue oil, Catalytic cracking, Synthesized catalyst, Thermal cracking

I. INTRODUCTION

The demand of gasoline and middle distillates as transportation fuels are increasing. As the reserves of lighter crude oils continue to decline, there is an increasing need to upgrade the residue oil into more value-added products. The emphasis on the conversion of less valuable products into transportation fuels continues to grow, while the environmental demands on the processes and products become more stringent.

Petroleum residue oil usually contains a high proportion of sulfur and metal contaminants, which contribute the problem of air pollution and cause catalyst deactivation in most refining processes. Hydrocracking is one of the dominant residue conversion processes. It is a catalytic petroleum refining process that is commonly applied to upgrade the heavier fractions obtained from the distillation of crude oils [1]. It is a flexible process, where it allows the conversion of a wide range of feedstock to a variety of products. The two main goals are to increase the distillates output of the refinery and to improve the quality of the residual fuels. This process is one of hydrogen addition route processes that using active hydrodesulfurization (HDS) catalyst. The most common catalyst used has included nickel-molybdenum (Ni-Mo) and cobalt-molybdenum (Co-Mo) supported on alumina oxide [2]. Besides alumina, other supports such as silica, zirconia, and zeolite have been used to prepare the catalyst [3]. Zeolite as a catalyst has been widely used for numerous processes throughout the chemical and petroleum processing industries [4]. CoMo catalyst supported on aluminum borate was found to be useful and can be used for HDS and hydrodemetallization (HDM) process of residue oil [5] and CoMo dispersed on the aluminum borate support was reported to be well suited for HDS reactions of atmospheric gas oil [3].

Hydrocracking is not the only process that is utilized to process heavy oils. Thermal cracking is also in use but catalytic hydrocracking has many advantages, such as: higher gasoline yield, better gasoline octane quality, improved balance of gasoline and distillate production and higher yield of isobutene in the butane fraction [6].

The objective of this research is to compare the thermal and catalytic reaction of petroleum residue oil and to examine the performance of the synthesized Nickel-Molybdenum supported on Aluminum Borate (NiMo/AB) catalyst for hydrocracking of atmospheric petroleum residue oil.

II. EXPERIMENTAL

1. Sample of Petroleum Residue Oil

The sample used in this research was Atmospheric Petroleum Residue Oil provided by Shell Refining Company, Port Dickson, Malaysia. The analysis of the residue oil is presented in Table 1.

Table 1: Analysis of Residue Oil

Elemental Composition Analysis	
Component	wt. %
C	85.28
H	12.11
N	1.11
S	1.50
H/C	1.70
ASTM Distillation Analysis	
Fraction, °C	wt. %
< 170	-
< 190	0.2
< 220	1.2
< 250	3.2
> 250	95.4
Viscosity at 50°C	
Speed (rpm)	Viscosity (mPas)
10	80.0
20	80.0
30	80.0
40	90.0
50	88.0
60	80.0
70	85.7

Sample: Atmospheric Petroleum Residue Oil
Source: Shell Refining Company, Port Dickson, Malaysia

2. Preparation of the Catalysts

The catalytic cracking reaction of petroleum residue oil has been conducted using synthesized nickel-molybdenum supported on aluminum borate (NiMo/AB) catalysts. The AB supports were prepared by the precipitation method using aluminum nitrate and boric acid solutions. By altering the amount of aluminum nitrate and boric acid, a desired AB supports could be obtained. The resulting AB precipitates were filtered, washed with distilled water, dried overnight at 100°C and calcined at 550°C for 5 hours. NiMo/AB catalysts were prepared by impregnation method using ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}.4H_2O$) and nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) solution. The impregnated catalyst was dried at 100°C for 12 hours and calcined at 550°C for 5 hours. The sample was denoted as NiMo/ABx, where x represent the A/B weight ratio.

In order to promote the activity of catalyst, presulfiding treatment was necessary. The sulfidation process was done by using 5% hydrogen sulfide balance hydrogen at 300°C for 2 hours.

3. Characterization of the Catalysts

The catalysts were characterized for their surface area and average pore diameter using a nitrogen adsorption method. The equipment used for the analysis was Autosorb I from Quantachrome, USA [7]

The acidity strength of the catalysts was determined by temperature-programmed desorption of ammonia. The equipment was Chembet 3000 from Quantachrome, USA [8]. About 0.1 g of powdered sample was placed in a quartz sample cell and was pretreated to 500 °C at a rate of 30°C/min for 1 h. Ammonia was adsorbed at 150°C (to avoid excessive physical adsorption) for 1 h. Thermal desorption of ammonia was then conducted using helium as a carrier gas and raising the temperature up to 600°C at a rate of 10°C/min.

4. Reaction System

Thermal and catalytic cracking reactions of petroleum residue oil have been performed in 300 ml high pressure batch reactor. Schematic diagram of the experimental set up is shown in Figure 1. About 80 g of residue oil was mixed with 0.5 g catalyst and poured into the reactor. After purging with nitrogen, the reactor was pressurized with 10 bar hydrogen pressure. The reactor was then heated to the temperature of 340°C and the reaction is carried out for 3 hours. The zero reaction time was defined when the required reactor working temperature was attained. The gas and liquid products were collected for analysis. The bomb and stirrer assembly were washed with diesel oil.

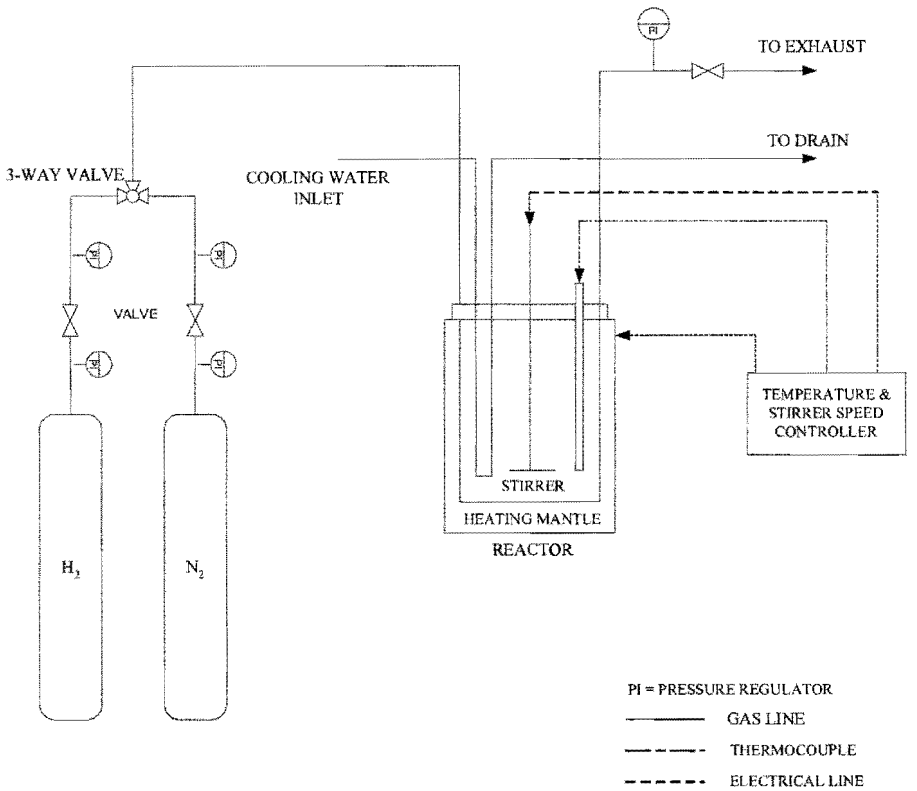

Figure 1: Schematic Diagram of the Experimental Setup

5. Analysis of Products

The composition of gas products were determined by Hewlett Packard model no. 5890 Series II Gas Chromatography equipped with FID detector and Porapak Q, 90 cm x 3.15 mm stainless steel column. The detection of the separated components was performed using a flame ionization detector (FID).

Distillation of the liquid products were carried out using ASTM D 86 [9] Distillation Unit model Analis from Belgium to determine the boiling range of the product and yield of lighter products after the process. In addition to this, Brookfield LV-III Rheometer has been used. This analysis was performed to determine the viscosity changes

of the product as compared to the feed at a constant temperature of 50°C. This parameter is used as a guide to investigate the effect of catalyst on visbreaking. In order to analyze the composition of the residue oil in terms of carbon, hydrogen, nitrogen and sulfur weight percentages, they were also analyzed using Perkin Elmer 2400 Series II CHNS Analyzer.

The definition of terms used in the analysis of the products is as follow:

5.1 Yield

The yield of the desired product is defined as the amount of the particular product obtained from the residue oil feed after reaction divided by the amount of residue oil feed.

$$\%Yield = \frac{D}{F} \times 100\% \quad (1)$$

where

D = amount of desired product (gasoline, kerosene, etc), g
F = amount of residue oil feed, g

5.2 Conversion

Conversion is defined as the amount of converted product divided by the amount of residue oil feed.

$$\%Conversion = \frac{F - U}{F} \times 100\% \quad (2)$$

where

U = amount of unconverted material, g

The unconverted material was assumed to be the weight of the liquid remained after distillation process.

III. RESULTS AND DISCUSSION

1. Catalysts Characterization

1.1 Surface Area and Average Pore Diameter

Surface area and average pore diameter of Aluminum Borate supports and nickel molybdenum supported on aluminum borate (NiMo/AB) catalysts are presented in Tables 2 and 3, respectively. As shown in Table 2, the incorporation of a small amount of boron into the alumina resulted in an increase in surface area. Further incorporation of boron into the alumina structure resulted in a high decrease in surface area. Table 3 demonstrates that both the surface area and average pore diameter of aluminum borate supports were reduced after being impregnated by the nickel and molybdenum metal species. This was due to the plugging of small pores by impregnation.

Although hydroprocessing reactions occur on the active sites of the catalyst, a suitable pore size distribution is required to ensure the access of reactant molecules to the active sites. The micropore dimensions can have a significant bearing on diffusion of reactants to the active sites, particularly for heavy feeds [10]. The range of pore dimension of < 20 Å, 20 < dp < 500 Å, > 500 Å are attributed to micropore, mesopore and macropore, respectively. The pore size distribution of synthesized NiMo/AB catalysts of various A/B ratios is presented in Figure 2. From this figure, it can be seen that the pore dimension of NiMo/AB catalysts are mostly in the range of 20-250 Å, which is categorized as mesoporous material.

Table 2: Surface Area and Average Pore Diameter of Aluminum Borate Supports

Support	Surface Area, m^2/g	Average Pore Diameter, Å
AB1	26.64	40.44
AB3.5	137.30	70.15
AB5	285.80	82.45
AB10	342.10	69.15
AB20	284.80	65.81

Table 3: Surface Area and Average Pore Diameter of NiMo/Aluminum Borate

Catalyst	Surface Area, m^2/g	Average Pore Diameter, Å
NiMo/AB1	8.58	88.62
NiMo/AB3.5	60.70	43.49
NiMo/AB5	48.07	49.68
NiMo/AB10	174.90	33.98
NiMo/AB20	149.80	42.37

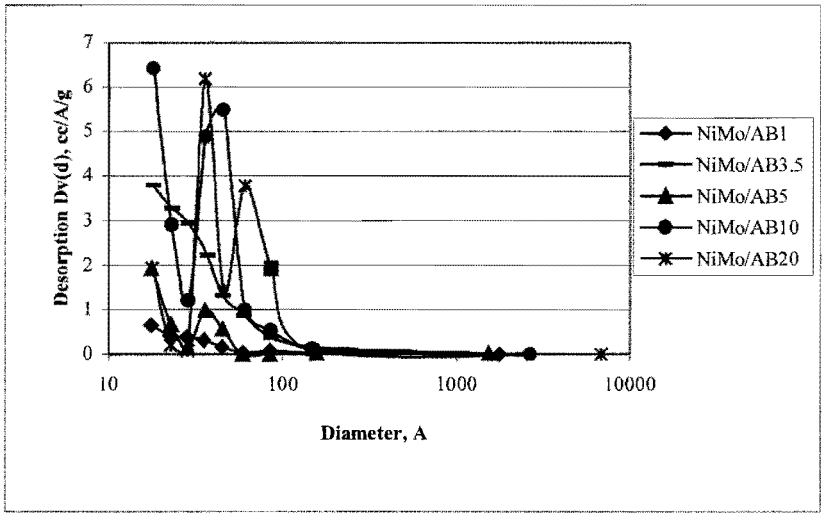

Figure 2: Pore Size Distribution of NiMo/AB Catalysts at Different A/B Ratio

1.2 Acidity Strength

The synthesized catalyst was characterized for the acidity strength using NH_3-TPD method [8]. The results are given in Figure 3. It was found that the maximum desorption temperature of ammonia of NiMo/AB3.5 is 350.6°C, indicating that this catalyst is categorized in between the medium and strong acid sites.

2. Cracking Activity

Products of the hydrocracking reaction were gaseous, liquids and solids. Figure 4 shows the conversion and product distribution over thermal cracking and hydrocracking over synthesized catalysts.

The total gaseous product from reaction with NiMo/AB catalysts is slightly higher than that of thermal reaction. This is because of the presence of metal Ni which led to over cracking (produce more gas). This result is in agreement with the result reported previously [11].

The gaseous products from the reaction are methane, ethane, propylene, propane, butane and pentane. Methane was the major gaseous product.

The viscosity of liquid product from thermal reaction at 50°C is 2.18 MPas, which is equivalent to 97.5% viscosity reduction. The viscosity of liquid products from hydrocracking over synthesized catalysts are in the range of 2.94-4.22 MPas, which is equivalent to 95.2-96 % viscosity reduction. This results show that both the reactions promote high visbreaking activity. Actually, the viscosity is strongly dependent on size of residue molecules [12].

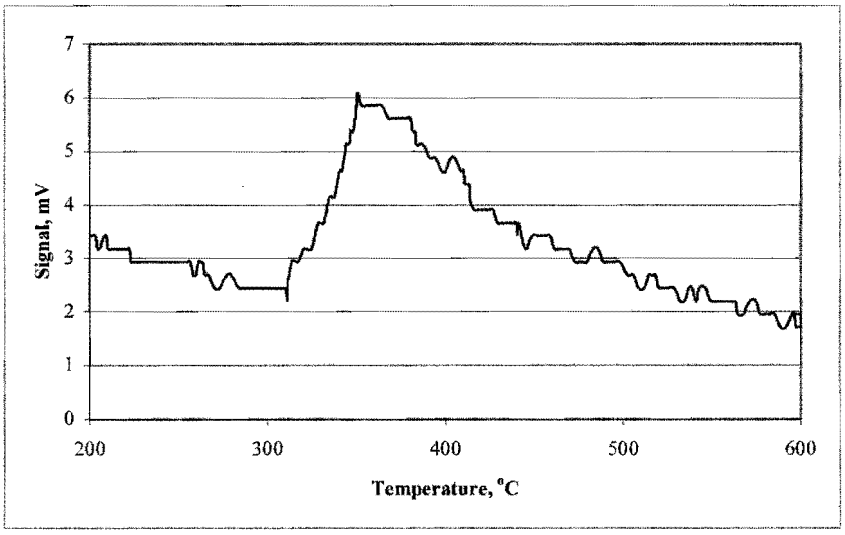

Figure 3: NH_3-TPD Profile of Synthesized NiMo/AB3.5 Catalysts

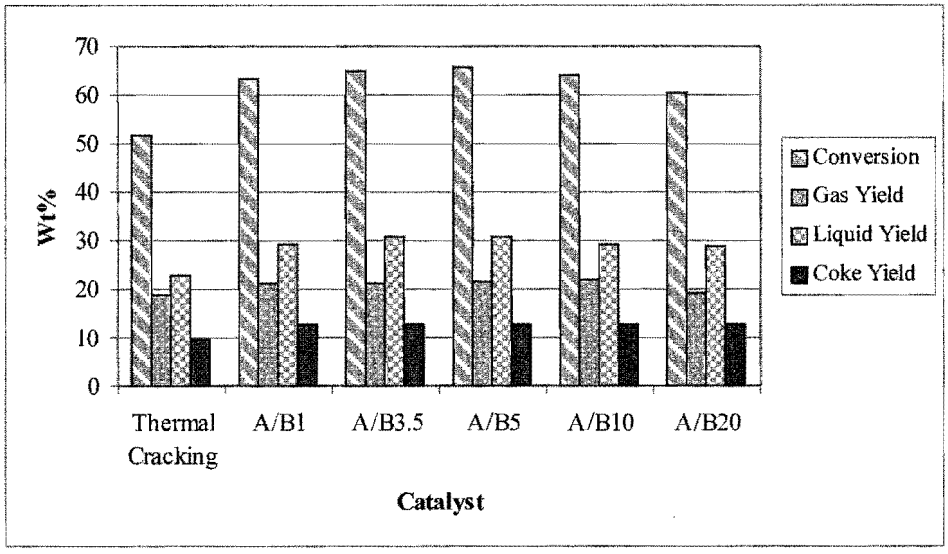

Figure 4: Conversion and Product Distribution over Thermal Cracking and Hydrocracking over Synthesized NiMo/AB Catalysts

Non-catalytic thermal reaction caused a 12.35% increment of H/C ratio, compared to 15.88-20% for catalytic cracking reaction, as shown in Figure 5.

In the presence of catalyst, H/C ratio is higher than reaction without catalyst. This is caused by the presence of acid sites of catalyst, where cracking reaction takes place on the acid sites of catalyst [2]. Gasoline product, as the most desired liquid product obtained from thermal reaction was 6.25 wt%, compared to 11.5-13.37 wt% for catalytic cracking reaction, as shown in Figure 6.

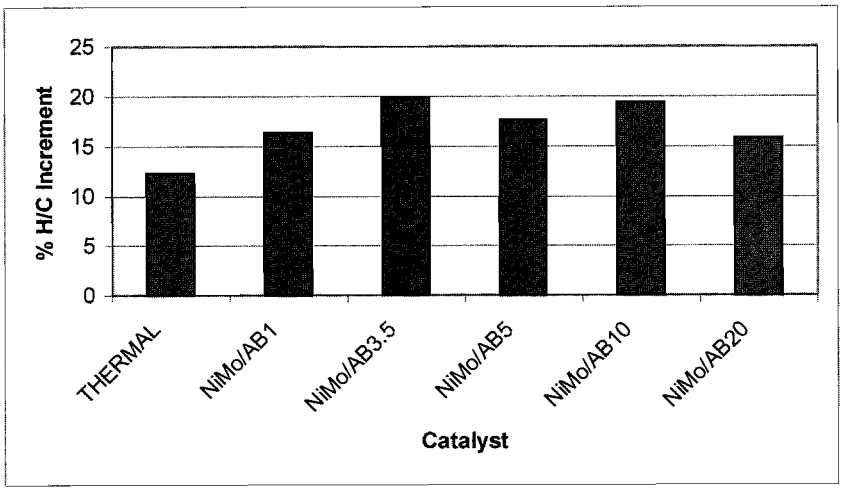

Figure 5: Increment of H/C Ratio from Thermal Reaction and Catalytic Cracking over Various A/B Ratio Catalysts

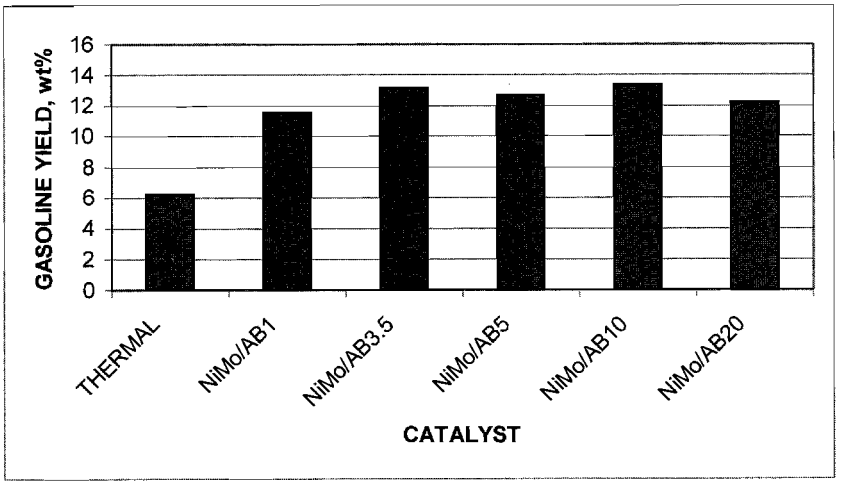

Figure 6: Gasoline Product Obtained over Thermal and Synthesized NiMo/AB Catalysts

IV. CONCLUSIONS

Petroleum residue oil can be converted to lighter liquid products by hydrocracking process with conversion of 51.43 wt% from thermal reaction and 60-65 wt% over synthesized NiMo/AB catalysts. The total gaseous product from reaction with NiMo/AB catalysts is slightly higher than that of thermal reaction, because of the presence of

metal Ni which led to over cracking (produce more gas). Gasoline, as the most desired liquid product, obtained from reaction over NiMo/AB catalysts are more than that obtained from thermal reaction, because of the acidity of NiMo/AB catalysts. The conversion of residue oil and yield of products were affected by the catalyst activity and strong acidity.

Nomenclature

D Amount of desired product (gasoline, kerosene, etc), g
F Amount of residue oil feed, g
U Amount of unconverted material, g

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REFERENCES

1. Speight, J.G., Petroleum Chemistry and Refining, Applied Energy Technology Series, Taylor and Francis, (1998).
2. Williams, P.T., and Chishti, H.M., Reaction of Nitrogen and Sulphur Compounds During Catalytic Hydrotreatment of Shale Oil, Fuel, 80, pp 957-963 (2001).
3. Li, C., Chen, Y.W., Yang, S.J., and Wu, J.C., Hydrodesulfurization Reactions of Atmospheric Gas Oil over CoMo/Aluminum Borate Catalysts, Ind. Eng. Chem. Res., 32, pp 1573-1578 (1993).
4. Bhatia, S., Zeolite Catalysis: Principles and Application, CRC Press, Inc., (1990).
5. Tsai, M.C., Chen, Y.W., Kang, B.C., Wu, J.C., and Leu, L.J., Hydrodesulfurization Reactions of Residue Oils over CoMo/Aluminum Borate Catalysts in a Trickle Bed Reactor, Ind. Eng. Chem. Res., 30, pp 1801-1810 (1991).
6. Adwani, H.A., and Anthony, R.G., Upgrading of Heavy Oils by Catalytic Hydrocracking: A Basic Review. The Arabian J. Sci. and Eng., 21(4B), pp 653-661.(1996).
7. Gregg, S.J., Sing, K.S.W, Adsorption Surface Area and Porosity, Academic Press, London, 1982, p. 90.
8. Hassan, A., Ahmed, S.., Ali, M.A., Hamid, H., Inui, T., A Comparison Between β-and USY-Zeolite-Based Hydrocracking Catalysts, Appl. Catal. A: General, 220 pp 59-68 (2001)
9. ASTM D 86
10. Furimsky, E. and Massoth, F.E., Deactivation of Hydroprocessing Catalysts, Catal. Today, 52, pp 381-495 (1999).
11. Karagoz, S., Yanik, J., Ucar, S., Saglam, M., and Song, C., Catalytic and Thermal Degradation of High-Density Polyethylene in Vacuum Gas Oil over Non-acidic and Acidic Catalysts, Appl. Catal. A: Gen., 6371, pp 1-12 (2002).
12. Shih, S.S., Residue Upgrading by Hydrovisbreaking and Hydrotreating, Marcel Dekker, Inc., 1994.