

## HYDROCRACKING OF GAS OIL OVER NiMo/Al<sub>2</sub>O<sub>3</sub> CATALYST

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**ABSTRAK :** *Nikel molybdenum komersial yang disokong pada pemangkin alumina (NiMo/Al<sub>2</sub>O<sub>3</sub>) digunakan untuk pemetakan gas minyak pada keadaan operasi yang berbeza, suhu tindakbalas antara 300-400°C, masa sentuh 30-120 min dan pemangkin disuap pada nisbah 0-0.08 dengan menggunakan reaktor goncang tekanan tinggi yang baru direka. Kandungan produk utama ialah cecair, gas dan kok. Jumlah penukaran pada 59.61wt% dan nilai maksimum 51.91wt% produk cecair (jumlah bahan api sulingan) didapati pada suhu 450°C, 90 minit masa sentuh dan 0.04 nisbah pemangkin yang disuap. Taburan keluaran untuk eksperimen yang dijalankan pada keadaan berbeza ditunjukkan dan dibincang.*

**ABSTRACT :** Commercial nickel molybdenum supported on alumina catalyst (NiMo/Al<sub>2</sub>O<sub>3</sub>) was used for hydrocracking of gas oil under various operating conditions, reaction temperature in range 300-450°C, contact time 30-120 min and catalyst to feed ratio 0-0.08 using newly designed high-pressure shaking reactor. The product consists mainly from liquid, gas and coke. A total conversion of 59.61wt% and a maximum value of 51.91wt% of liquid product (total distillate fuels) were obtained at temperature of 450°C, 90 minutes contact time and 0.04 catalyst to feed ratio. Product distributions under different experimental conditions were presented and discussed.

**KEYWORDS :** Petroleum gas oil, NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst, a high-pressure shaking reactor.

## INTRODUCTION

Since total crude oil demand is projected to grow and the oil reserves in the world are limited, there is a strong need to convert hydrocarbon feed stocks into lower boiling point products in greater yields and with more selectivity. In many parts of the world, light oil production is declining and heavy oil conversion, therefore, becomes increasingly important to maintain economic viability of these regions (Heinrich *et al.*, 1997). Recently, the price of crude oil has reached US \$ 72 per barrel in the international market ([www.answers.com/topic/oil-price-increases-of-2005](http://www.answers.com/topic/oil-price-increases-of-2005)) and the majority of machines and equipments being made at present are designed to run using liquid fuel. Therefore, it is important to extract much useful materials from crude oil.

Many investigators have reported the production of light fuels from cracking of heavy oils over different cracking catalysts (Sato *et al.*, 1999). The catalysts used for the hydrocracking process are formed by composting various transition metals with the solid support such as alumina, silica, alumina-silica, magnesia, carbon and zeolites Speight (1998). Tian *et al.* (1998) used batch reactor for the hydrocracking of residue oil over dispersed water-soluble Ni-Mo catalyst and alumina supported Co-Mo catalyst. The experiments were done under low operating conditions, hydrogen pressure of 7 MPa, temperature of 340°C and time 30-240 min which is suitable for this reaction. Absi-Halabi *et al.* (1998) studied the performance of a Ni-Mo-W / $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst using Kuwait vacuum residue as feed. The results revealed that the Ni-Mo-W catalyst was more active than either the Ni-Mo or Ni-W catalysts. The effect of catalyst composition on desulfurization reaction showed that both the NiMo and mixed NiMoW catalysts have nearly the same activity pattern toward desulfurization. Kaluza and Zdrail (2001) reported MoO<sub>3</sub> on activated carbon catalyst prepared by a new impregnation method for hydrodesulfurization process of thiophene. It was concluded that molybdenum trioxide was chemisorbed and highly dispersed 'monolayer' form up to loading of about 15% MoO<sub>3</sub> and then almost levelled off. Sato *et al.* (1999) carried out the hydrocracking of tetralin over NiW/USY zeolite catalysts for improvement of heavy oil upgrading catalysts using a 50-ml batch type reactor at temperature of 250-400°C, contact time of 3-180 min, catalyst load of 0.3 g and operating pressure of 2-10.2 MPa. Their results revealed that the major reaction path in the initial period was found to differ from that later in the reaction. During the initial reaction period, tetralin is hydrocracked via a bimolecular process over both USY and NiW/USY. Subsequently, hydrocracking is catalyzed without the formation of heavy compounds. Hydrocracking over NiW/USY is superior to that over USY only in the longer reactions. This difference is due to the limited role of NiW sulphide in the hydrocracking of tetralin. NiW sulphide hydrogenates aromatic compounds so that the cycloparaffinic compounds produced are easily cracked over acid sites.

The aims of this work are to investigate the effect of operating condition (temperature, reaction time and catalyst to feed ratio) on hydrocracking of petroleum gas oil over commercial NiMo/ Al<sub>2</sub>O<sub>3</sub> catalyst.

## **EXPERIMENTAL**

### **Materials**

Desulphurized petroleum gas oil (DS-GO) derived from sweet Far-East crude oil with density of 0.8260 kg/l at 15°C was used in this investigation. This sample was obtained from Shell Refinery Company Bhd., Port Dickson, Malaysia. The analyses of the gas oil are given in Tables 1-2. The high purity gases nitrogen (99.999%) and hydrogen (99.999%) were obtained from Gas Pantai Timur Sdn. Bhd, Malaysia. A mixture of 5% H<sub>2</sub>S in H<sub>2</sub> balance was supplied by BOC, UK.

**Table 1.** Distillation analysis of the gas oil

| <b>Temperature, °C</b> | <b>Volume, %</b> |
|------------------------|------------------|
| 240                    | IBP              |
| 253                    | 5                |
| 256                    | 10               |
| 263                    | 20               |
| 267                    | 30               |
| 273                    | 40               |
| 279                    | 50               |
| 286                    | 60               |
| 294                    | 70               |
| 306                    | 80               |
| 323                    | 90               |
| 334                    | 95               |
| 346                    | FBP              |

**Table 2.** Elemental composition analysis, wt% of the gas oil

|                  |       |
|------------------|-------|
| C                | 85.17 |
| H                | 14.74 |
| N                | 0.087 |
| S                | 0.003 |
| H/C atomic ratio | 2.077 |

### Catalyst

Commercial NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst was provided by Sud-Chemie AG Germany. The chemical composition and physical properties of the NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst are listed in Table 3-4. The catalyst was supplied in 1.3 mm size and crushed to the size range of 6/ 125 μm. Prior to the reaction tests, the catalyst was pre-treated to increase its performance. About 2 g of the catalyst was placed in a stainless steel tubular reactor of 9 mm inside diameter and 130 mm length placed vertically inside tubular programmable temperature furnace. Nitrogen gas was introduced to the system to purge the air completely out of the system. During this purging operation the programmable temperature furnace was set to give a heating rate of 10°C/min. when the temperature of the reactor reached the desired temperature (360°C), 5% H<sub>2</sub>S balance hydrogen gas was allowed to pass through the system at 40 cm<sup>3</sup>/min for 3 h. On completion of the run, the furnace was switched off and the gas flow was turned off, allowing the nitrogen gas to again purge the system (Ferrari *et al.*, 2001; Farag *et al.*, 1999).

**Table 3.** Chemical composition and physical properties of the NiMo / Al<sub>2</sub>O<sub>3</sub> catalyst (Sud-Chemie AG Germany)

| Property                                  | Value    |
|---|----------|
| I. Chemical Composition (nominal)         |          |
| NiO, wt%                                  | 5.2 0.5  |
| MoO <sub>3</sub> , wt%                    | 23.0 1.0 |
| Na <sub>2</sub> O, wt%                    | <0.05    |
| Al <sub>2</sub> O <sub>3</sub> , wt%      | balance  |
| II. Physical Properties (typical)         |          |
| Particle Shape, TRIAX - Shaped Extrusions |          |
| Particle Size, mm                         | 1.3      |
| Bulk Density, kg/m <sup>3</sup>           | 790      |
| Surface Area, m <sup>2</sup> /g           | 175      |
| Pore Volume, 1/kg                         | 0.43     |
| Side Crush Strength, N/kg                 | 32       |
| Loss of Attrition, wt. %                  | <5       |

\*Supplied by manufacturer

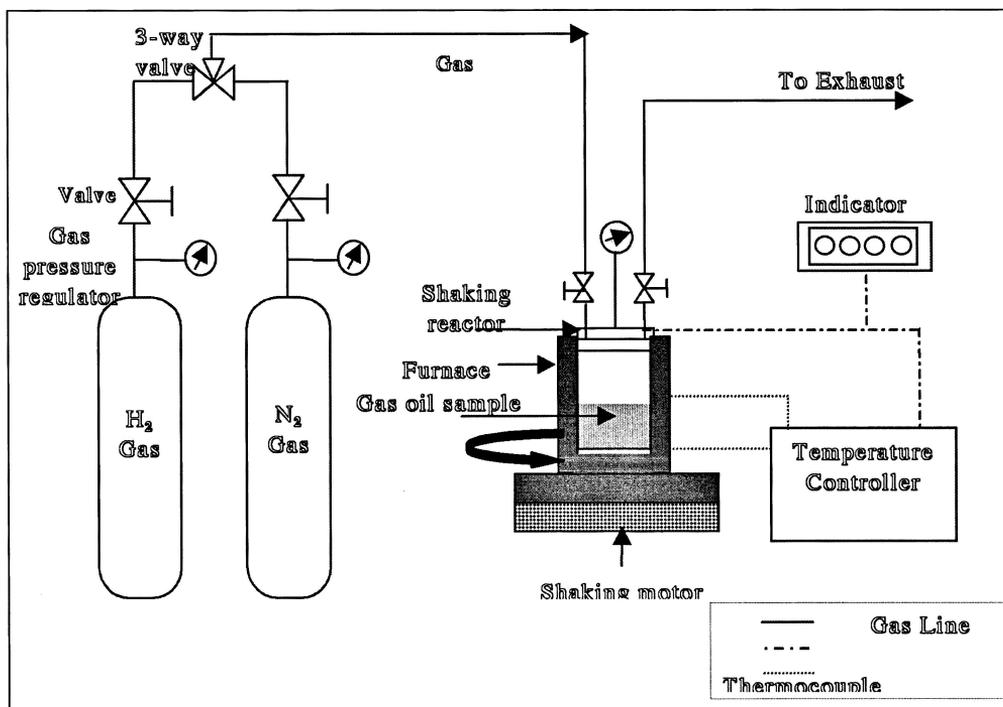
**Table 4.** BET surface area, pore volume, average pore diameter and acidity of commercial NiMo / Al<sub>2</sub>O<sub>3</sub> catalyst

|                                     |        |
|-------------------------------------|--------|
| BET surface area, m <sup>2</sup> /g | 175    |
| Pore volume. cm <sup>3</sup> /g     | 0.43   |
| Average pore diameter, nm           | 9.8    |
| Acidity, mmol / g <sub>Cat</sub>    | 0.4228 |
| Weak acidity, %                     | 33.30  |
| Strong acidity, %                   | 66.70  |

### The experimental set up

The 70-ml stainless steel high-pressure shaking reactor was manufactured with 15.24 cm long and 2.21cm inside diameter. The reactor was equipped with a vertical tubular furnace of 15 cm length and 5 cm diameter and used as heating source. This furnace was supplied by Watlow, USA, with maximum temperature of 1000°C. Type K thermocouples were placed outside and inside the reactor wall and were capable of monitoring temperature up to 1100 °C.

About 30 g of desulphurized petroleum gas oil (DS-GO) sample was firstly poured into the reactor, and then the catalyst was added in different ratios from 0 to 0.08. Hydrogen valve was opened to develop a total hydrogen atmosphere after purging with nitrogen. The reactor was then heated to reaction temperature in the range 300-450°C. The reaction was carried out for a fixed period of time in the range 30-120 minutes after the reactor working temperature and pressure were attained. At the end of the run the reactor was cooled down to room temperature and the product was collected for analysis. The reactor was washed with dichloromethane. The schematic diagram of the experimental set up using a high-pressure shaking reactor is shown in Figure 1.



**Figure 1.** Schematic diagram of the experimental set up for hydrocracking of petroleum gas oil using a high-pressure reactor

The conversion, product yield, and catalyst to oil ratio were obtained using the following equations:

$$\% \text{ Conversion} = \frac{(W_{GO} - W_R)}{W_{GO}} \times 100 \quad (1)$$

where  $W_{GO}$ ,  $W_R$  are weight of gas oil feed and weight of unconverted fraction remaining in the liquid product after distillation, respectively.

$$\% Y_I = \frac{W_I}{W_{GO}} \times 100 \quad (2)$$

where  $Y_I$  is the yield of the product (wt%),  $I$  is the distillate fraction (gasoline, kerosene, diesel),  $W_I$  is weight of the distillate fraction.

$$\text{Catalyst to gas oil ratio} = \frac{W_{CA}}{W_{GO}} \quad (3)$$

where  $W_{CA}$  is weight of catalyst loaded.

### ASTM distillation analysis

ASTM method D 86 was used to determine the product boiling range distribution and to investigate the yield of the lighter products after hydrocracking reaction. The distillation curve of the liquid products indicates the quantities of useful fractions to the refiner. The ASTM distillation unit was supplied by Hotech Instruments Corp. About 25 ml of sample was poured into the distillation flask. The heater was started and the temperature at the neck of the distillation flask was recorded when the first drop of condensate was collected. The volume of condensate was taken down at the temperature 160, 200 and 240°C (Ooi *et al.*, 2004, Tian *et al.*, 1998).

### Gas Chromatograph (GC)

The gaseous products were analyzed using a gas chromatograph (Hewlett Packard, model No. 5890 series II) equipped with Porapak Q, 270 cm-length x 3.15 mm stainless steel column (Supelco). The GC was equipped with flame ionization detector (FID). The flame ionization detector (FID) was used to find out the hydrocarbons components present in gaseous product. The gases detected were hydrocarbons  $C_1$ - $C_5$ . The identity of resulting GC peaks was defined by injecting standard gases to FID detector.

## Nitrogen Adsorption

Pore volume, surface area and average pore diameter of synthesized catalysts were measured using Autosorb1, Quantachrome Autosorb Automated Gas Sorption System supplied by Quantachrome. The samples were degassed for 3 h under vacuum at temperature of 300°C using Autosorb1 instrument before measurements were performed (Zhu *et al.*, 1999).

## Scanning electron microscopy (SEM)

SEM studies were performed using Leica Cambridge Stereoscan 360, UK and Polaron for the coating system (sputter coating). SEM revealed quickly the normal size and shape of the particles, providing a representative micrograph of the surface of supports and catalysts, and also to show the effect of metal on the particle size of supports. Before the scanning, the powder samples were spread onto the double-side carbon tape, and coated with gold (20-30 nm thickness) in order to increase the conductivity and therefore the quality of the results.

## Thermogravimetric analyzer (TGA)

Thermogravimetric analyzer (TGA) supplied by Perkin-Elmer, USA was used to study the thermal stability of the catalysts. About 5 mg of sample were loaded into a platinum pan and heated under nitrogen gas stream of 20 cm<sup>3</sup>/min from ambient temperature to 900°C with a control heating rate of 20°C/min.

TGA-TPD (temperature-programmed desorption) was conducted on the same TGA instruments. About 5 mg of the sample was placed in a platinum pan and heated under nitrogen gas stream of 20 cm<sup>3</sup>/min from ambient temperature to 500°C with a control heating rate of 20°C/min and hold at this temperature for 30 minutes. Then the temperature was lowered to 100°C followed by injecting isopropylamine for 10 min. The desorption of physisorbed base molecules was allowed to continue at 100°C for about one hour (until the mass nearly constant). The sample was heated to 700°C at 20°C/min to desorb the chemisorbed isopropylamine. The chemisorption curve reveals the density and acid strength of the catalyst sample. The acidity was calculated by the following formula and reported in units of millimoles of acid sites per gram of catalyst.

$$\text{Acidity} = \frac{W \left[ \frac{1}{Mb} \right] \left[ \frac{1000mg}{1g} \right]}{W_z} \quad (4)$$

where  $W$  is the mass loss due to the desorption of base in the temperature of interest ( $g$ ),  $W_z$  is the mass of zeolite-based catalyst after pre-treatment ( $g$ ), and  $M_b$  is the molecular weight of base (isopropyl amine).

### Elemental analyzer (EA)

The PE 2400 Series II CHNS Elemental Analyzer supplied by M/S Perkin Company, USA was used to determine H/C ratio and percentage of carbon, hydrogen, nitrogen and sulphur in the feed. About 1.5-2.5 mg of sample was put in a tin capsule unit. The maximum and minimum furnace temperatures were set at 975 and 500°C. The required gases are highly purified helium, oxygen and compressed air.

## RESULTS AND DISCUSSION

### Catalyst characterization

The commercial NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst was characterized using different techniques. The BET surface area, pore volume and average pore diameter are given in Table 2 and the pore size distribution of this catalyst is shown in Figure 2. As evident from Figure 2, alumina-based catalyst has mesopores which are desirable for the hydrocracking of heavy compounds.

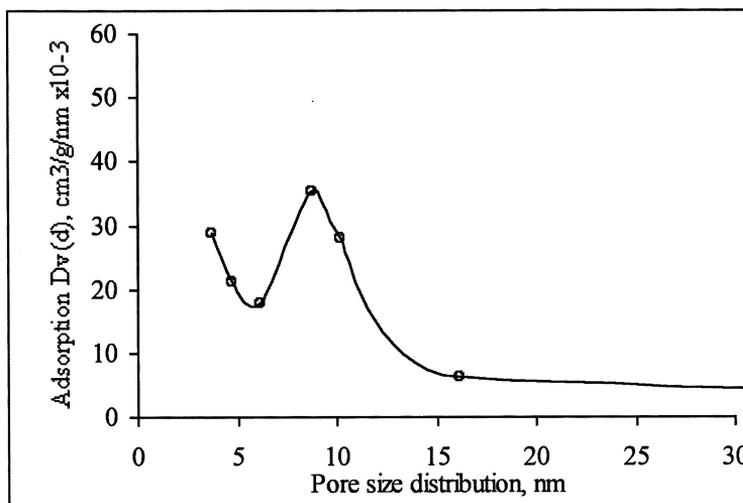
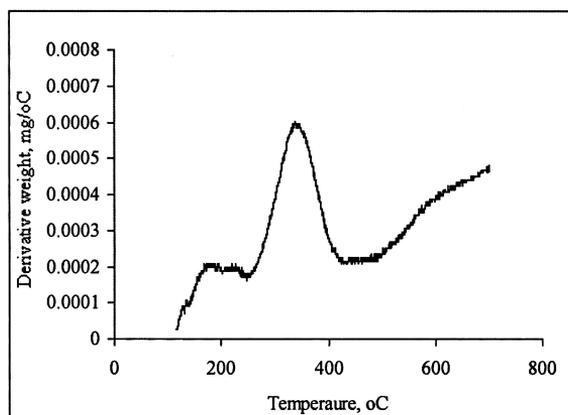


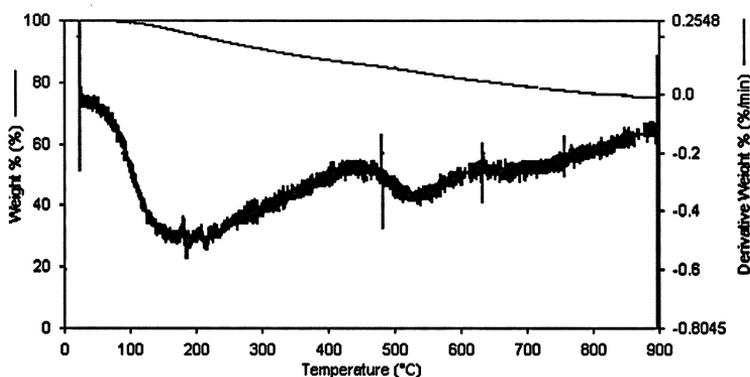
Figure 2. Pore size distribution of NiMo / Al<sub>2</sub>O<sub>3</sub> catalyst

The acid sites of commercial NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst was carried out using TGA-TPD (temperature-programmed desorption). The number of weak and strong acid sites is shown in Table 2. The total number of acid sites, measured by the amount of isopropylamine, was 0.4228 mmol/g. The TGA-TPD profile is shown in Figure 3. The TGA-TPD measurements show that there are two acid sites, the peak in temperature range of 100-200°C is associated to the weak acid site (weak Lewis type) and the second peak found in temperature range of 300-400°C represents strong acid sites (strong Lewis type).



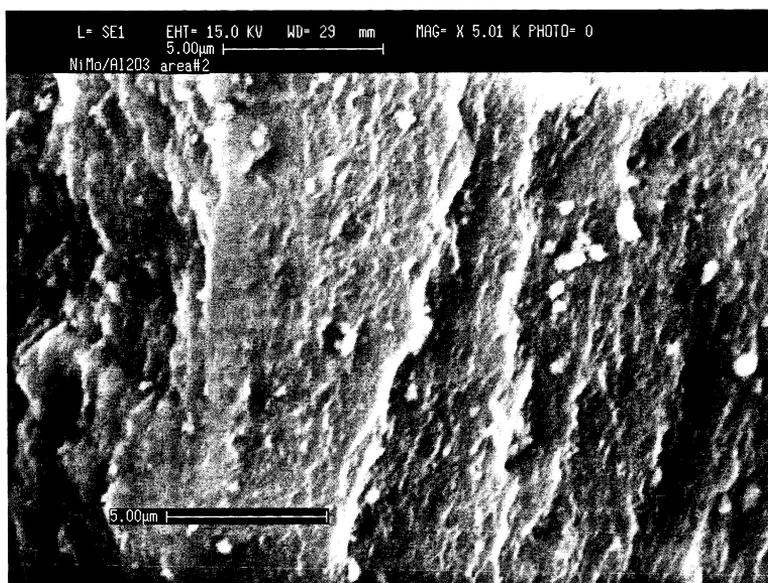
**Figure 3.** TGA - TPD acidity for NiMo / Al<sub>2</sub>O<sub>3</sub> catalyst

Thermal gravity experiment was carried out to study the stability of the catalyst. Figure 4 shows the weight loss (TG) and DTG curves of commercial NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst. Two stages of thermal decomposition behaviour of the catalyst are seen : a plateau from 30 to 120°C with a little weight loss due to the moisture release and a main weight of catalyst in the last stage. That means the catalyst showed high thermal stability in the temperature range of 400-500°C. This stability of the catalyst is favourable to prevent thermal decomposition of the catalyst during the reactions and regeneration processes.



**Figure 4.** TGA result for commercial NiMo / Al<sub>2</sub>O<sub>3</sub> catalyst

Figure 5 shows scanning electron microscopy of commercial NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts. It can be clearly seen the metals appear to be primarily randomly distributed although some aggregation could be detected.



**Figure 5.** SEM images for NiMo / Al<sub>2</sub>O<sub>3</sub> catalyst, magnification is 5000 : 1

### Effect of reaction temperature

The analyses of the gas oil feed are given in Tables 1-2. Table 5 shows effect of reaction temperature on the total conversion and products distribution over NiMo/Al<sub>2</sub>O<sub>3</sub> at 120 minutes time and 0.04 catalyst to feed ratio. A total conversion of 58.24 wt% was obtained at temperature of 450°C, while a minimum value of 14.50 wt% conversion was noticed at temperature of 300°C. A maximum value of 47.54 wt% of liquid product (total distillate fuels) was obtained at 450°C. The liquid product consists of gasoline, kerosene and diesel, where the yields of these products were 14.55, 14.42 and 18.57 wt%, respectively. Higher reaction temperature favours the hydrocracking reactions, which lead to formation of gas, coke and liquid consisting of higher percentage of the distillate fuels. At higher temperature, heavier compounds are cracked to product with lower boiling point. Usually at higher temperature more energy is provided to break the carbon-carbon bonds into shorter chains besides the action of the active catalyst that provide the active sites necessary for the cracking. Thus, the total conversion, distillate fuels increased with increasing temperature. However, 10.70-wt% of both gas and coke were obtained under this temperature. Hence, the carbon-carbon bonds in liquid phase are cleaved to produce distillate fuels, gas and coke products, so these products and total conversion were found to increase with increasing reaction temperature.

**Table 5.** Gas oil conversion in the investigation of role of temperature range (Conditions : Reaction time = 120 min, Catalyst to oil ratio = 0.04)

| Temperature, °C       | 300   | 350   | 400   | 450   |
|-----------------------|-------|-------|-------|-------|
| Conversion (%)        | 14.50 | 20.00 | 28.80 | 58.24 |
| Total distilled fuels | 11.20 | 17.00 | 22.70 | 47.54 |
| Gasoline              | -     | -     | 0.86  | 14.55 |
| Kerosene              | -     | 0.98  | 2.54  | 14.42 |
| Diesel                | 11.20 | 16.02 | 19.30 | 18.57 |
| Gas + Coke            | 3.30  | 3.00  | 6.10  | 10.70 |

**Effect of contact time**

Table 6 presents effect of contact time on total conversion and yield of products at 450°C temperature and 0.04 catalyst to feed ratio. It can be seen that total distillate products and diesel yield were increased with time until 90 minutes then decreased, while conversion and other wt% of distillate fuels were increased with reaction time. At lower reaction time, the complex compounds in gas oil were not completely cracked. The initial step in the hydrocracking of gas oil to lighter products involves free radical cracking (Gray, 1994). The free radicals and olefins resulting from this cracking are very reactive and can recombine to form heavy products. Stable oil and gas products resulting from primary cracking can also undergo free radical cracking and thus generate additional free radicals and olefins. These can further react to produce light and heavy products. The gas and coke products were constant with time until 90 minutes then increase. This increment of other wt% of distillate fuels at time above 90 minutes was happened because part of diesel product cracked to produce gasoline, kerosene, gas and coke products.

**Table 6.** Gas oil conversion in the investigation of role of contact time range (Conditions : Reaction temperature = 450°C, Catalyst to oil ratio = 0.04)

| Time, min             | 30    | 60    | 90    | 120   |
|-----------------------|-------|-------|-------|-------|
| Conversion (%)        | 33.26 | 52.25 | 59.61 | 58.24 |
| Total distilled fuels | 31.26 | 49.95 | 51.91 | 47.54 |
| Gasoline              | 6.33  | 8.54  | 10.00 | 14.55 |
| Kerosene              | 4.84  | 5.48  | 8.47  | 14.42 |
| Diesel                | 20.09 | 35.93 | 33.44 | 18.57 |
| Gas + Coke            | 2.00  | 2.30  | 7.70  | 10.70 |

### Effect of catalyst to feed ratio

Table 7 shows total conversion and yield of products as a function of catalyst to feed ratio at 450°C reaction temperature and 90 minutes contact time. The total conversion was increased with catalyst to feed ratio and the optimum value of diesel and total distilled fuels was obtained at 0.04 ratio. The conversion and formation of distillate products are dominated by thermal cracking and the main role of catalyst is to enhance the uptake of hydrogen and prevent condensation and coking reactions (Gray, 1994). The hydrocracking reactions require significant breaking of carbon-carbon bonds. Breaking of C-C bonds relies on carbenium ion intermediates, promoted by the acid sites on the NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst surface.

**Table 7.** Gas oil conversion in the investigation of role of catalyst to feed ratio (Conditions : Reaction temperature = 450°C, Contact time = 90 minutes)

| Catalyst to feed ratio | 0     | 0.02  | 0.04  | 0.06  | 0.08  |
|------------------------|-------|-------|-------|-------|-------|
| Conversion (%)         | 36.70 | 39.15 | 59.61 | 58.91 | 59.65 |
| Total distilled fuels  | 28.10 | 32.25 | 51.91 | 52.61 | 51.85 |
| Gasoline               | 6.13  | 8.78  | 10.00 | 10.70 | 11.85 |
| Kerosene               | 7.60  | 6.73  | 8.47  | 9.34  | 8.48  |
| Diesel                 | 14.37 | 16.74 | 33.44 | 32.57 | 31.42 |
| Gas + Coke             | 8.60  | 6.90  | 7.70  | 6.30  | 7.80  |

### CONCLUSIONS

The hydrocracking of petroleum gas oil at reaction temperature in range 300-450°C, contact time 30-120 min and catalyst to feed ratio 0-0.08 was studied in high-pressure shaking reactor. Petroleum gas oil was converted to transportation fuels (gasoline, kerosene and diesel), gas and coke by hydrocracking over commercial NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst with total conversion of 59.61 wt% at temperature of 450°C, 90 minutes contact time and 0.04 catalyst to feed ratio. The effect of different operating conditions on hydrocracking reaction over commercial NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst was studied and found that 450°C reaction temperature, 90 min contact time and 0.04 catalyst to feed ratio are the most suitable operating conditions. Alumina-based catalyst showed very high thermal stability and has mesopores which are desirable for the hydrocracking of heavy compounds.

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