

A Comparative Study on the Hydrocracking for Atmospheric Residue of Mongolian Tamsagbulag Crude Oil and Other Crude Oils

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ABSTRACT

Upgrading heavy and residual oils into valuable lighter fuels has attracted much attention due to growing worldwide demand for light petroleum product. This study focused on hydrocracking process for atmospheric residue (AR) of Mongolian crude oil in the first time compared to those of other countries. Residue samples were hydrocracked with a commercial catalyst at 450°C, 460°C, 470°C for 2 hours under hydrogen pressure of 10 MPa. The AR conversion and yield of light fraction (LF) reached to 90.6 wt% and 53.9 wt%, at 470°C by the hydrocracking for atmospheric residue of Tamsagbulag crude oil (TBAR). In each sample, the yield of MF was the highest at 460°C temperature, which is valuable lighter fuel product. The polyaromatic, polar hydrocarbons and sulfur compounds were concentrated in the MF and HF because the large amount of light hydrocarbons produced from TBAR as the increasing of the hydrocracking temperature. The content of n-paraffinic hydrocarbons was decreased in HF of TBAR, on effect of hydrocracking temperature. This result suggests the longer molecules of n-paraffin (C₂₀-C₃₂) in HF were reacted better, than middle molecules of n-paraffin (C₁₂-C₂₀) in MF during the hydrocracking reaction. Because the hydrocarbon components of feed crude oils were various, the contents of n-paraffinic hydrocarbons in MF and HF of TBAR and DQAR were similar, but MEAR's was around 2 times lower and the hydrogen consumption was the highest for the MEAR after hydrocracking.

Keywords: Tamsagbulag Crude Oil; Hydrocracking; Atmospheric Residue; Sulfur Compound; N-Paraffinic Hydrocarbon

1. Introduction

Upgrading heavy and residual oils into valuable lighter fuels has attracted much attention due to growing worldwide demand for light petroleum product from declining reserves of sweet crude oils. Although there are large quantities of heavy oils such as atmospheric- and vacuum-distilled residual oils generated as byproducts in the refinery process, it is not easy to convert these residual oils into useful hydrocarbons [1-3]. Various methods, such as thermal cracking, catalytic cracking and hydrocracking are used to produce lighter fuels from heavy oils. In these methods, large hydrocarbon molecules of residual oil have broken up into smaller and more useful hydrocarbons by cracking reaction. Cracking process is called the hydrocracking, which is reacted under the hydrogen atmosphere, with a catalyst at high temperature and pressure [4].

Even though Mongolian Zuunbayan's petroleum refinery had been closed off in 1969, geological and chemical study of Mongolian crude oils has revived in the

last 2 decades. Mongolian oils are paraffinic [5-7] and have low amounts of sulfur [8], heavy metals [9], which make some troubles to the refining processes of petroleum. However Mongolian crude oils contain a large amount of atmospheric residue, which should be converted into light and middle oils in order to produce motor fuel and chemicals [10]. Although the cracking process is important for refining of heavy residue, there is no research of cracking process for the atmospheric residue of Mongolian crude oils [11]. The present research has focused on the hydrocracking for the atmospheric residue of Tamsagbulag crude oil at different temperatures, with a commercial catalyst. On comparison with those of Chinese Daqing oil and Arabian mixed Middle East oil at same conditions.

2. Experimental

2.1. Materials

Three atmospheric residues (AR) were used in this study.

AR of Mongolian Tamsagbulag crude oil is coded as TBAR; Chinese Daqing—as DQAR; Arabian mixed Middle East—as MEAR. The TB oil sample was supplied by “Daqing Tamsag” Company, which is doing a mining operation in Mongolia. DQAR and MEAR were obtained from Japanese petroleum refinery. The properties of atmospheric residues are shown in **Table 1**.

2.2. Hydrocracking Test

Hydrocracking of AR was carried out at 450°C, 460°C and 470°C for 2 h using a fixed bed reactor that was inserted into an electric furnace with vertically shaking type. About 4 g of atmospheric residue with 200 mg of commercial catalyst was charged into the reactor, the inner volume of which was 50 ml. The reactor was pressurized by hydrogen gas up to 10 MPa at ambient temperature, and then was heated to the prescribed temperature. Reaction temperature was maintained for 2 hours in every run, and all runs were repeated two times. **Table 2** shows the conditions of the hydrocracking tests.

2.3. Analysis

Initially, atmospheric residue was separated using by a

Table 1. The properties of the atmospheric residues.

Properties	Unit	TBAR	DQAR	MEAR
C	wt%	86.2	86.3	86.0
H	wt%	13.1	13.1	11.9
S	wt%	0.18	0.12	2.47
N	wt%	0.16	0.16	0.13
H/C	atom/atom	1.82	1.82	1.66
Saturate	wt%	57	59	44
Aromatic	wt%	29	33	45
Resin	wt%	9.5	5.8	7.2
C ₅ Asphaltene	wt%	2.6	1.5	1.5
C ₇ Asphaltene	wt%	1.4	0.3	2.6
Ni/V ^a	atom/atom	5/<1	6/1	4/10
CCR	wt%	3.3	4.6	6.4

^aReferred to an article, which is noted on reference [9].

Table 2. The condition of hydrocracking test.

Sample	Name	TBAR, DQAR, MEAR
	Weight	4.0 g
Catalyst	Type	NiMo/Al ₂ O ₃
	Weight	0.2 g
H ₂ Gas	Pressure	10 MPa
	Temperature	450°C, 460°C, 470°C
	Retention time	2 hours

distillation method to examine quantitatively its fractional composition. The hydrocracking product was handled as shown in **Figure 1**. At first, the toluene insoluble fraction was extracted from the hydrocracking products.

The toluene soluble fraction was recovered after solvent evaporation, then divided into four fractions by a distillation method: light fraction (LF) boiling point less than 220°C, middle fraction (MF) boiling point of 220°C - 350°C, heavy fraction (HF) boiling point of 350°C - 500°C and bottom boiling point over than 500°C. The separated distinct fractions were weighed to check a material balance including the yield of gases products.

After the reaction, gases products were subjected to Gas chromatography coupled with thermal conductivity detector (GC-TCD; Agilent, 6890) to estimate its composition. Then, contents of methane, ethane and propane gases were calculated using a calibration of standard gas samples. The Gas chromatography system coupled with a sulfur chemiluminescence detector (GC-SCD; Agilent 6890) was used to determine the sulfur content in liquid products from hydrocracking. The distillation curve of the liquid product was examined using a GC-FID system (Agilent, model 6890GC) that was equipped with a fused silica column 5 m long.

2.4. Equations

We used the following equations to calculate the conversion of AR (1), hydrogen consumption (2) and the yield of light fraction (3).

$$C_{AR} = \frac{W^0 - W^1}{W^0} \times 100\% \quad (1)$$

C_{AR} —Conversion of AR, wt%;

W^0 —Initial weight of atmospheric residue, g;

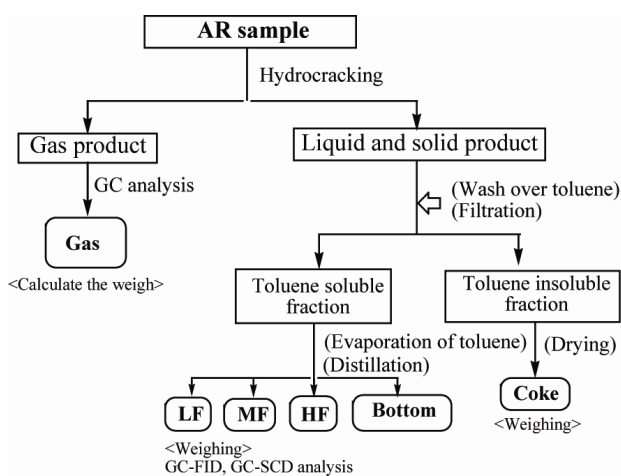


Figure 1. Product separation method of AR hydrocracking test (AR-Atmospheric residue of crude oil, LF-Light fraction, <220°C, MF-Middle fraction, 220°C - 350°C, HF-Heavy fraction, 350°C - 500°C, Bottom-Residue, >500°C).

W^1 —Weight of atmospheric residue after the reaction, g;

$$W_{H_2} = \frac{W_{H_2}^0 - W_{H_2}^1}{W^0} \times 100\% \quad (2)$$

W_{H_2} —Hydrogen consumption, wt%;

$W_{H_2}^0$ —Weight of hydrogen, which was charged into reactor, g;

$W_{H_2}^1$ —Weight of hydrogen after the reaction, g;

W^0 —Initial weight of atmospheric residue, g.

$$W_{LF} = (W_{AR} + W_{H_2}) - (W_{Gas} + W_{MF} + W_{HF} + W_{Bot} + W_{Coke}) \quad (3)$$

According to the feature of the product separation method we calculated the yield of LF (3) from the material balance, which was limited from 100.4 wt% to 101.9 wt%. The excess of 100 wt% was provided by the amount of hydrogen consumption [12].

3. Results and Discussions

Table 3 shows the product distribution after the hydrocracking of AR samples at different temperatures for 2 hours under hydrogen pressure of 10 MPa, using a fixed bed reactor.

The yield of LF reached to 53.9 wt%, the yield of liq-

uid fractions (<350°C) including gas product reached to 88.9 wt% in the hydrocracking for TBAR at the highest temperature of 470°C. Also the AR conversion was increased from 56.7 wt% to 90.6 wt%, when the hydrocracking temperature increased from 450°C to 470°C. The amount of hydrogen consumption was the highest for MEAR. It should be explained by the lowest H/C atomic ratio of corresponding feedstock. The H/C ratio of MEAR was the lowest (1.66) as shown in **Table 1**.

Figure 2 summarized a dependence of each product yield on reaction temperature for AR samples. It was evident that the hydrocracking product was lightened as the increasing of reaction temperature. Hydrocracking reaction of all AR samples used in this research at the temperature of 470°C provided the largest amount of gas and LF, consequently the lowest yield of HF and bottom. The yield of MF was the highest at temperature of 460°C in all of AR samples, however the variation for yield of MF was not so high compared to the yields of the other products, by the increasing of reaction temperature.

The yields of gas products after the catalytic hydrocracking of the AR samples are illustrated in **Figure 3**. With the TBAR the highest yield of gases product was produced after the run of hydrocracking at the temperatures of 450°C and 470°C. Also the methane content in

Table 3. The product distribution after hydrocracking of atmospheric residue samples at different temperatures.

Samples	Initial fractional composition (wt%)		Temperature (°C)	Hydrogen consumption (wt%)	AR conversion (wt%)	Content of products (wt%)					
	HF	Vacuum residue				Gas	LF	MF	HF	Bottom	Coke
TBAR	55.8	44.2	450	0.5	56.7	3.7	29.3	22.0	38.0	5.3	2.2
			460	0.4	74.9	5.7	43.0	26.1	23.6	1.5	0.5
			470	0.9	90.6	11.4	53.9	23.6	8.6	0.8	2.6
DQAR	31.7	68.3	450	0.4	47.9	2.8	27.9	14.8	30.8	21.3	2.8
			460	0.4	69.9	5.0	37.9	24.8	23.4	6.7	2.6
			470	0.9	85.8	10.3	53.2	21.4	12.5	1.7	1.8
MEAR	33.6	66.4	450	1.2	46.2	2.8	24.3	18.3	38.5	15.3	2.0
			460	1.1	79.0	6.1	47.9	24.2	19.3	1.7	1.9
			470	1.9	90.2	9.3	60.0	19.9	8.5	1.3	2.9

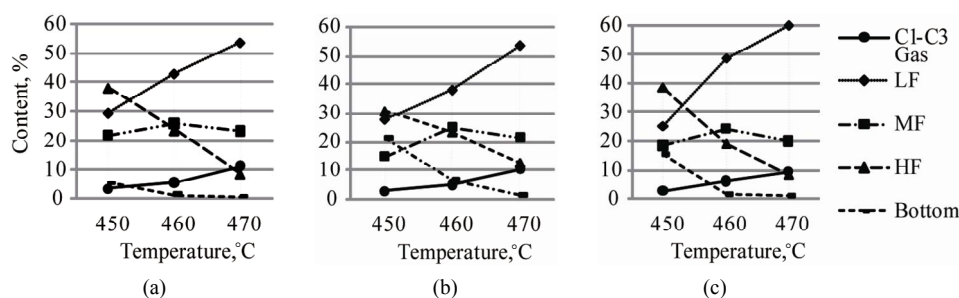


Figure 2. Relationship between the content of products and the temperature of hydrocracking. (a) TBAR; (b) DQAR; (c) MEAR.

gases products was the lowest, but the propane content was the highest after every run of the hydrocracking for AR samples. The ratio of the contents of C₁-C₃ gases was nearly constant for the all of AR [13].

The contents of subfractions, hydrocarbons and the amount of sulfur in MF and HF after the hydrocracking of AR samples were shown in **Table 4**. The content of (<254°C) subfraction was decreased, in place of it, the contents of (<344°C), (>344°C) subfractions in MF were

expanded as the increasing of reaction temperature of the hydrocracking. Also the content of (<344°C) subfraction was decreased, in place of it, the contents of (<496°C) subfraction in HF was expanded as the increasing of reaction temperature. It means that the hydrocarbons component became heavier in the MF and HF after the hydrocracking of all of AR samples as the increasing of reaction temperature.

The content of saturate hydrocarbons was decreased,

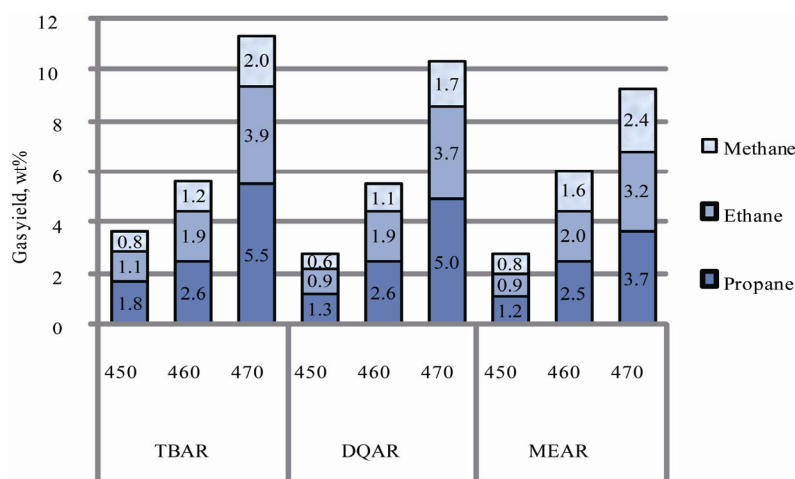


Figure 3. The yield of C₁-C₃ gases after the hydrocracking.

Table 4. Contents of subfractions, hydrocarbons and the amount of sulfur in hydrocracking products of AR samples (wt%).

Sample Temperature Properties	TBAR			DQAR			MEAR		
	450°C	460°C	470°C	450°C	460°C	470°C	450°C	460°C	470°C
<i>Subfractions</i>	<i>In middle fraction (MF)</i>								
<151°C	-	-	-	-	0.1	0.1	0.1	0.2	0.2
<254°C	42.8	32.6	29.7	46.8	40.9	35.4	36.0	33.4	27.9
<344°C	53.9	60.1	61.9	48.1	54.9	59.6	59.5	60.1	63.6
>344°C	3.3	7.3	8.4	5.1	4.1	4.9	4.4	6.3	8.3
<i>Content of hydrocarbons</i>									
Saturates	78.7	76.3	69.1	79.1	79.3	74.6	66.2	62.7	51.5
Monoaromatics	18.3	17.5	19.7	16.9	17.0	18.0	28.9	29.3	32.4
Polyaromatics	2.8	5.5	9.9	2.0	3.0	6.3	4.8	7.8	15.7
Polar	0.2	0.7	1.3	0.7	1.1	2.0	0.1	0.2	0.3
<i>n-paraffins</i>	46.3	46.1	45.9	46.7	46.5	45.0	21.2	26.1	25.9
<i>Sulfur</i>	19	29	35	9	14	21	180	330	750
<i>Subfractions</i>	<i>In heavy fraction (HF)</i>								
<254°C	0.2	1.2	0.5	0.2	1.7	1.5	1.4	0.9	4.7
<344°C	34.3	21.3	13.4	27.3	30.3	14.4	22.3	23.4	15.1
<496°C	63.4	71.3	81.0	70.8	65.4	78.3	72.4	72.6	76.6
>496°C	2.1	6.2	5.1	1.7	2.6	5.8	3.9	3.1	3.6
<i>n-paraffins</i>	41.1	37.3	29.4	40.4	37.7	32.4	18.6	20.5	14.8
<i>Sulfur</i>	22	125	200	36	120	140	980	1160	2320

but the contents of polyaromatic, polar hydrocarbons and the amount of sulfur compound were expanded in MF of TBAR as the increasing of temperature for hydrocracking. Also the amount of sulfur in HF was increased, by dependent of the reaction temperature. Summation of this result and the product distribution after hydrocracking of AR (Table 3), polyaromatic, polar hydrocarbons and sulfur compounds were concentrated in MF and HF because the large amount of light hydrocarbons produced from AR and moved to LF as an increasing of the reaction temperature [14].

The content of n-paraffinic hydrocarbons in HF was decreased by dependent of the reaction temperature. However the content of the n-paraffinic hydrocarbons was not changed in MF of TBAR. This result suggests the longer molecules of n-paraffin (C₂₀-C₃₂) in HF were reacted better, than middle molecules of n-paraffin (C₁₂-C₂₀) in MF during the hydrocracking reaction [15]. The contents of n-paraffins in MF and HF of TBAR and DQAR were similar, but MEAR's was around 2 times lower after hydrocracking because the hydrocarbon component of those AR samples and feed crude oils were the various [12,13].

4. Conclusions

Atmospheric residue of Mongolian Tamsagbulag crude oil (TBAR) was tested for hydrocracking in the first time. In order to compare a hydrocracking reactivity of TBAR sample with Chinese Daqing (DQAR) and Arabian mixed Middle East (MEAR) samples were tested with commercial NiMo/Al₂O₃ catalyst at different temperatures of 450°C - 470°C. Some conclusions can be drawn as follows:

1) In the hydrocracking of TBAR, the yield of liquid fractions including of gas product (<350°C) expanded sharply as the increasing of reaction temperature. The yield of middle fraction (MF) from TBAR was the highest at temperature of 460°C;

2) The polyaromatic, polar hydrocarbons and sulfur compounds were concentrated in MF and HF of TBAR because the large amount of light hydrocarbons produced from AR and moved to LF as the increasing of the reaction temperature;

3) With the hydrocracking of TBAR and DQAR, the content of the n-paraffinic hydrocarbons more decreased in HF than MF by dependent of the reaction temperature. This result suggests the longer molecules of n-paraffins (C₂₀-C₃₂) in HF were reacted better, than the middle molecules of n-paraffin (C₁₂-C₂₀) in MF during the hydrocracking reaction of TBAR, DQAR samples;

4) The contents of n-paraffinic hydrocarbons in MF and HF of TBAR and DQAR were similar, but MEAR's was around 2 times lower than those and the hydrogen

consumption was the highest after hydrocracking for the MEAR, because the hydrocarbon component of those AR samples and feed crude oils were various.

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