



Hydrocracking of atmospheric distillable residue of Mongolian oil

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Abstract: Many catalytic processes to refine heavy part of crude oil have attracted much interest due to declining reserves of light crude oils. This study focused on hydrocracking process of atmospheric distillable residue of Mongolian crude oil in the first time compared to those of other countries. Residue samples were hydrocracked with a commercial catalyst at 450⁰C, 460⁰C, 470⁰C for 2 h under hydrogen pressure of 10 MPa. The amount of residual fraction (350⁰C<BP) decreased to 9.4wt% by the hydrocracking of atmospheric distillable residue from Tamsagbulag crude oil. When the ME-AR was hydrocracked, the high consumption of hydrogen was related to the lowest H/C atomic ratio of feed atmospheric residue. The amount of liquid fractions (BP<350⁰C) including gaseous products increased from 45.4wt% to 89.2wt%, when the reaction temperature increased from 450⁰C to 470⁰C. The highest yield of the middle fraction for each sample was observed at temperature of 460⁰C. On the other hand, the effect of temperature on the yield of middle fraction was not so high as compared with the yields of other fractions. The contents of n-paraffins on middle and heavy fractions of TB-AR, DQ-AR were similar, but ME-AR's was around 2 times lower than other after hydrocracking runs.

Keywords: Hydrocracking, atmospheric residue, Tamsagbulag crude oil, commercial catalyst, middle fraction

Introduction

In recent years, considerable attention has been paid to the research on refining process of heavy part of Mongolian crude oils. Mongolian crude oils have small amounts of sulfur [1] and heavy metals [2], which make some troubles to the refining processes of crude oil. Therefore, it is considered that there is a possibility to refine Mongolian crude oil by cheap and efficient technology. On the other hand, Mongolian crude oils contain a large amount of atmospheric residual (52.9 - 69.8 wt%), which should be converted into light and

middle oils in order to produce motor fuels and chemicals [3,4].

The current study has focused on the catalytic hydrocracking process in the atmospheric distillable residue of Mongolian crude oil comparing with those of Chinese and Arabian crude oils at different temperatures under hydrogen pressure of 10 MPa using a commercial cracking catalyst. Our experiments have been carried out at the Hydrocracking Catalyst Laboratory of Advanced Fuel Group, Energy Technology Research Institute (ETRI), National Institute

Experimental

Materials. Three atmospheric distillable residues were used in this work. Mongolian Tamsagbulag crude oil's is coded as TB-AR; Chinese Daqing oil's - as DQ-AR; mixed Middle East crude oil's - as ME-AR. The TB oil sample was supplied by "Daqing Tamsag" Company, which is doing a mining operation in Mongolia. Atmospheric distillable residues of DQ-AR and ME-AR were obtained from Japanese refinery. Elemental analysis results of the atmospheric distillable residues are shown in Table 1.

Table 1. Elemental analysis of the atmospheric residues

Samples	C, %	H, %	S, %	N, %	H/C
TB-AR	86.54	13.12	0.18	0.16	1.82
DQ-AR	86.59	13.13	0.12	0.16	1.82
ME-AR	85.55	11.85	2.47	0.13	1.66

Hydrocracking test. An atmospheric residue sample was hydrocracked at 450⁰C, 460⁰C and 470⁰C for 2 hours using a fixed bed reactor that was inserted into an electric furnace with vertically shaking type. The dates in table 2 show the conditions of hydrocracking experiments. About 4 g of atmospheric distillable 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 for every run [5].

Table 2. The condition of hydrocracking test

Sample	Name	TB-AR, DQ-AR, ME-AR
	Weight	4.0g
Catalyst	Type	NiMo/Al ₂ O ₃
	Weight	0.2g
Pressure of hydrogen		10 MPa
Inner volume of reactor		50 ml
Temperature		450 ⁰ C, 460 ⁰ C, 470 ⁰ C
Reaction time		2 hours

Analysis. After the reaction, gaseous 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. Initially, atmospheric distillable residue was separated using by a distillation method to examine quantitatively its fractional composition. The Gas chromatography system coupled with a sulfur chemiluminescence detector (GC-SCD; Agilent 6890) was used to determine the sulfur content. 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 [5,6].

AR - Atmospheric distillable residue of crude oil, Boiling point is over than 350⁰C

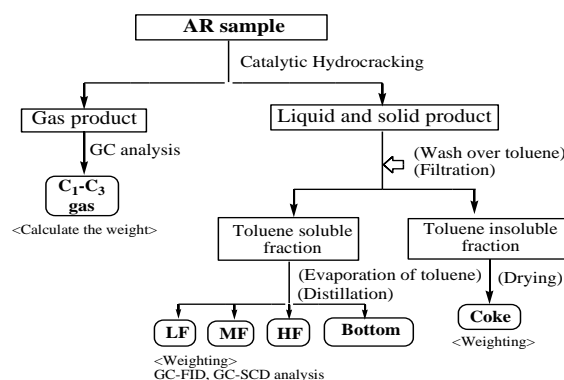
LF - Light fraction, <220⁰C

MF - Middle fraction, 220⁰C–350⁰C

HF - Heavy fraction, 350⁰C – 500⁰C

Bottom – Residue 500⁰C<

Figure 1. Flow chart showing the handling of the products for experimental hydrocracking



The liquid product was handled as shown in Figure 1. At first, the toluene insoluble fraction (TIF) was extracted from hydrocracking products. The toluene soluble fraction (TS) was recovered after solvent evaporation, and was then divided into four sub fractions by a distillation method: light fraction (LF), middle fraction (MF), heavy

fraction (HF) and bottom. The separated distinct fractions were weighed to check a material balance including the content of gaseous products.

Results and Discussion

Table 3 shows the product distribution after the hydrocracking of atmospheric residue at different temperatures for 2 h under hydrogen pressure of 10 MPa using a fixed bed reactor.

Table 3. The products content after catalytic hydrocracking of the atmospheric residue at different temperatures

Samples	Temperature, °C	Consumption hydrogen, wt%	Conversion, wt%	Content of products (wt %)					
				C ₁ -C ₃ Gas	LF	MF	HF	Bottom	Coke
TB-AR	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
DQ-AR	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
ME-AR	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

The yield of light fraction reached about 60 wt%, the yield of liquid fractions (BP<350°C) reached approximately 80 wt% in the hydrocracking for ME-AR. In the case of TB-AR, the amount of residual fraction (BP>350°C), was decreased from 43.3wt% to 9.4 wt%, when the hydrocracking temperature increased. This result was effectively.

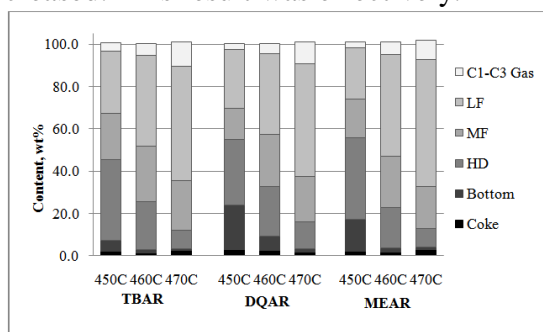


Figure 2. The change of distribution for products after the run of hydrocracking.

Hydrocracking reactions of all AR samples at the highest temperature of 470°C in the present study provided the largest amount of

consumed hydrogen and the yield of light fraction, consequently, and the lowest yield of heavy, bottom and residual fractions. In particular, the consumption amount of hydrogen gas for hydrocracking conversion was the highest for the atmospheric residue of Middle East oil (ME-AR). It should be explained by the lowest H/C atomic ratio of corresponding feedstock. The H/C ratio of ME-AR was the lowest (1.66) as shown in Table 1.

Figure 2 illustrated the change of distribution for products after this hydrocracking series. It was evident that in increasing the temperature, was lightened the products. The distribution of liquid fraction (<350°C) including gaseous product, changed from 45.4-55.0 wt% to 84.9-89.2 wt%, when temperature increase from 450°C to 470°C. The excess of 100 wt% provided a consumption amount of hydrogen.

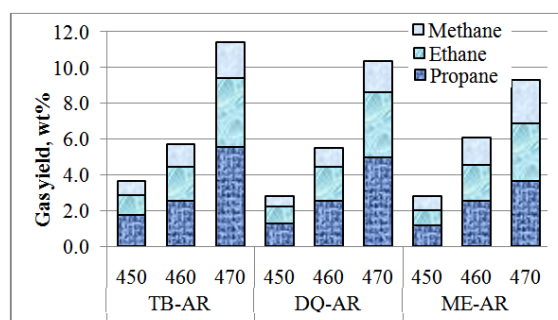


Figure 3. The yield of C₁-C₃ gases after hydrocracking

Yields of gaseous products after catalytic hydrocracking are illustrated in Figure 3. With the atmospheric distillable residue of Tamsagbulag crude oil (TB-AR), the highest yield of gaseous products was obtained after the run of catalytic hydrocracking at the temperatures of 450°C and 470°C. It was evident that with increasing temperature the yield of total C₁ - C₃ gases increased for all AR samples. Also the methane content in gaseous products was the lowest, but the propane content was the highest after every run of catalytic hydrocracking.

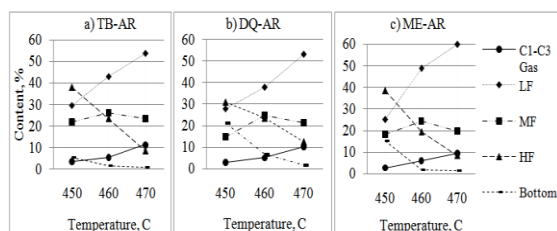


Figure 4. Relationship between content of products and hydrocracking temperature

Figure 4 summarizes a dependence of total product distribution on hydrocracking temperature for TB-AR, DQ-AR and ME-AR samples. As reaction temperature increased, a yield of light fraction (LF) increased, but yields of heavy fractions (HF) and bottom decreased respectively in all runs. Also a formation of gaseous products occurred significantly with increasing temperature. However, a change in the yield of middle fraction was not clearly observed when a reaction temperature increased. It is suggested that an effect of temperature on cracking reactivity of larger molecules (in particular, heavy fraction) was higher compared to that of smaller molecules (MF).

Table 4. Content of fractions and n-paraffins, in hydrocracking products, analyzed by GC-FID [wt%]

Samples	TB-AR			DQ-AR			ME-AR		
	450°C	460°C	470°C	450°C	460°C	470°C	450°C	460°C	470°C
on middle distillate of hydrocracking product									
<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
n.paraffins	46.3	46.1	45.9	46.7	46.5	45.0	21.2	26.1	25.9
on heavy distillate of hydrocracking product									
<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
n.paraffins	41.1	37.3	29.4	40.4	37.7	32.4	18.6	20.5	14.8

The content of subfractions and n-paraffin on middle and heavy distillates of hydrocracking product were shown in Table 4. The contents of n-paraffins for TB-AR, DQ-AR were similar, but ME-AR's was around 2 times lower than others, after hydrocracking series. This result related from hydrocarbons structure of feedstock.

Conclusions

Atmospheric residue of Tamsagbulag crude oil (TB-AR) was tested for catalytic hydro cracking in the first time. In order to compare a cracking reactivity of Mongolian crude oil, the Chinese Daqing (DQ-AR) and Middle East (ME-AR) samples were tested under the following conditions: over 200 mg of commercial NiMo/Al₂O₃ catalyst at the temperature of 450°C -470°C for 2 hours under hydrogen pressure of 10 MPa. Some conclusions can be drawn as follows:

- (1) In the hydrocracking of atmospheric residue from Tamsagbulag crude oil (TB-AR) the yield of the gas and liquid products (BP<350°C) increased sharply at 460°C.
- (2) The consumption amount of hydrogen gas for hydro cracking conversion was the highest for the atmospheric residue of Middle East oil (ME-AR). It should be explained by the lowest H/C atomic ratio of corresponding feedstock.
- (3) The contents of n-paraffins for TB-AR, DQ-AR were similar, but ME-AR's was around 2 times lower than others, after hydrocracking series. This result related to there's hydrocarbons structure.

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