Effect of decalin as a hydrogen donor in cracking of atmospheric residue from Tamsagbulag oil, Mongolia

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ABSTRACT

In this work, we studied the thermal cracking of atmospheric residue from Tamsagbulag crude oil in the presence of hydrogen donor-decalin. The oil is highly paraffinic and has high a viscosity and low yield of distillate fraction. Therefore, deep processing is necessary to increase the yield of distillate fractions. The cracking experiments were carried out using decalin at two different concentrations (5% and 10 wt.% of feed) under a hydrogen pressure of 5 MPa. Additionally, a control experiment was conducted without the use of decalin under a nitrogen pressure of 0.4 MPa. The experimental temperature was 450°C and the duration varied from 60 to 180 minutes. The cracking process resulted in the formation of gaseous, liquid products, and coke from the atmospheric residue. The yield of liquid products was found to be two times less without decalin (49.0%) compared to decalin at 5% (82.42 wt.%) and 10% (86.67 wt.%) for 120 minutes. From these results, we have concluded that the optimal condition of the cracking process to obtain higher fuel fraction and lower gaseous and coke is the cracking process with 10% decalin for 120 min under a hydrogen pressure of 5 Mpa at 450°C.

Keywords: *atmospheric residue, cracking, hydrogen donor, fraction, decalin*

1. INTRODUCTION

Cracking is a process of converting high hydrocarbons of heavy crude oil to small hydrocarbon fractions and more useful petroleum products. Nowadays, the hydrocracking process is extensively used to upgrade heavy crude oil. A considerable amount of hydrogen is required for this process. Generally, cyclic compounds such as decalin, tetralin, and naphthalene are considered efficient solvents for hydrogen donation in the hydrocracking process. The inclusion of hydrogen donor molecules promotes hydrogen addition to the cracking products. Hydrogen donor molecules are dehydrated in the reaction system. This improves product quality and reduces the polymerization of heavy molecules through free radicals. [1-5]. There are 3 large deposits of crude oil in the east and southeast of Mongolia with the total proven reserves amounting to 332.7 million tons, while the total proven recoverable reserves are 42 million tons (Fig. 1).

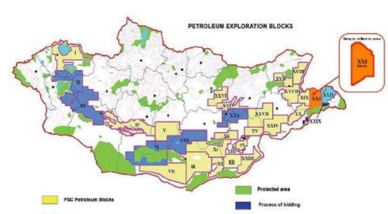

Figure 1. Oil exploration blocks of Mongolia

In our previous research efforts, we studied the physicochemical properties and hydrocarbon composition of Mongolian oil. From the results, Mongolian crude oil is characterized as heavy oil with high viscosity, and low content of distillate fraction, and the properties of the oils are almost similar [8-9]. In this

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study, we aimed to increase the yield of the distillate fraction of Mongolian oil using cracking with and without decalin as a hydrogen donor. In recent years, researchers focused on the development of liquefaction technology for the production of heavy hydrocarbons, such as heavy oils, natural bitumens, and unconventional oil [9,10]. However, the studies on liquefaction and thermal cracking of high-paraffinic and viscous oils are very few. Therefore, the study of cracking to increase the yield of fuel fraction of high paraffinic Mongolian oil is very novelty and has practical importance.

2. EXPERIMENTAL

2.1 Materials

The atmospheric residue (>350ºC) used in this study was obtained from crude oil of XXI block of Tamsagbulag deposit at 2300-2600 m depth, which is in Dornod province, Mongolia.

2.2 Experimental procedures.

Physical and chemical properties such as specific gravity, kinematic viscosity, freezing point, and fractional composition were determined by standard methods of Petroleum Analysis [11]. Hydrocarbon group composition (asphaltene, resin, saturates+aromatics) was determined by the SARA methods [4,12]. The hydrocarbon compounds of the obtained liquid products were studied by gas chromatography-mass spectrometer using Thermo Scientific-Trace 1310 GC with the TSQ8000-triple Quadrupole MS equipment. The type of capillary column was DB5MS 30m x 0.25mm (D=0.25 µm). Helium with a flow rate of 1.5 ml/min was used as carrier gas [13]. The elemental analysis (carbon, hydrogen, nitrogen, and sulfur) was done by using FlashSmart/Flash 2000 instrument with a TCD detector. The cracking experiment was carried out in a batch reactor with a 50 ml volume. Reaction conditions; hydrogen donor-decalin under a hydrogen pressure of 5MPa and without decalin under nitrogen pressure of 0.4 MPa at 450°C for 60-180 min. The mass of feedstock charged into the reactor was approximately 10 g. Decalin ($C_{10}H_{18}$, purity 99%) was used as a hydrogen donor solvent. The amount of decalin was 5 and 10 % by the weight of the feedstock. The scheme of the experiments is shown in Fig. 2. The obtained liquid product after cracking was distilled to light, middle, and residue by vacuum distillation equipment. The coke in the cracking product was extracted by toluene.

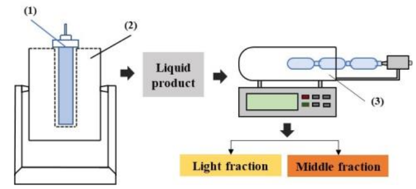

Figure 2. The scheme of the experiments; (1)- reactor, (2)-furnace (3)- vacuum distillation equipment

3. RESULTS AND DISCUSSION

The physiochemical properties, hydrocarbon content, elemental analysis, and fractional composition of the Tamsagbulag oil and its atmospheric residue (>350°C) were studied. The physicochemical properties of the samples are shown in Table 1.

Tamsagbulag crude oil has a high content of saturated and aromatic hydrocarbons, therefore it has higher values of viscosity, specific gravity, flash point, and freezing temperature, and the oil was classified as high-paraffinic crude oil. The result of fractional composition shows the low yield of light and middle distillates and high content of atmospheric residue (63.19%) from the oil. Therefore, a deep-processing technology is very important to increasing the yield of fuel fractions. The atmospheric residue is rich in saturated and aromatic hydrocarbons and paraffin hydrocarbons. Therefore, it was expected that the residue can be easily decomposed into lower molecular hydrocarbons. According to the results of elemental composition, the content of heteroatomic compounds (nitrogen, sulfur) in the residue is low. It will affect positively on the quality of distillate products. The material balance of cracking products of atmospheric residue from Tamsagbulag oil is shown in Table 2.

As a result of the cracking of the atmospheric residue formed gaseous, liquid products, and coke. We have studied the effect of decalin in the heavy residue upgrading process. It is shown that the yield of liquid products after cracking in the presence of decalin of 5 and 10% is almost two times more than without a donor. The results show that decalin is effective for cracking high paraffinic crude oil. A high-yield gaseous product was produced during cracking without a donor for 120 min at 450°C. In this condition, gaseous products cannot be converted to liquid products. The amount of coke after cracking for 60 and 120 min with 10% of decalin was decreased by 10 wt. % compared with cracking for 180 min. It is shown that the amount of coke increases as the reaction temperature increases.

Table 1. Physicochemical properties of Tamsagbulag crude oil and its atmospheric residue

Characteristics of crude oil	Tamsagbulag oil (XXI)	The atmospheric residue (AR)
Appearance	black and thick	black and thick
Specific gravity, 20°C, кg/m^3	0.869	0.906
Kinematic viscosity, mm^2/sec, 40°C	45.25	not flow
Flashpoint, in the open cup, °C	67.7	184
Freezing point, °C	21	20.6
SARA, wt %:		
Saturates+Aromatics	72.60	80.45
Paraffin in the saturates+aromatics	-	44.86
Resins	26.3	18.06
Asphaltenes	1.01	1.39
Fractional composition, wt%:		-
Boiling point, °C	30	
Light (start boiling to – 220°C)	21.43	
Middle (220–350°C)	15.38	
Heavy (Lub) fraction (350-450°C)	20.92	
Vacuum residue (>450°C)	42.27	
Elemental composition, wt %		
Carbon	85.75	84.55
Hydrogen	12.95	11.31
Nitrogen	0.10	1.68
Sulfur	0.36	0.84
Oxygen	0.84	1.61
H/C	1.81	1.6

Table 2. The yield of cracking products of atmospheric residue from Tamsagbulag oil

№	Products wt.%	Condition of experiments, (at 450°C)					
		Non-hydrogen donor	Hydrogen donor-decalin				
			5%		10%		
		Reaction time, min					
		120		180	60	120	180
1	Gas	41.93	11.47	18.09	5.34	11.18	14.21
2	Liquid products	49.04	82.42	74.60	92.26	86.67	73.04
3	Coke	9.03	6.11	7.31	2.40	2.15	12.75

To determine the yield of distillate fractions, the cracking product from the residual oil was distilled by vacuum distillation equipment at temperatures from boiling point to 220 °C (light fraction-gasoline) and from 220 to 350 °C (middle fraction-diesel fuel). The fractional composition of cracking products is shown in Fig. 3.

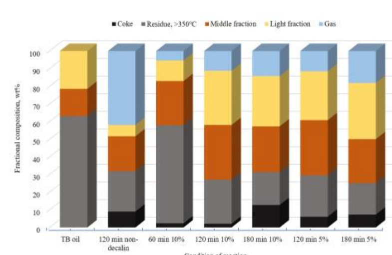

Figure 3. Fractional composition of cracking products of Tamsagbulag atmospheric residues

The effect of the addition of decalin was tested in the experiments of the cracking with decalin, the yield of light fraction increased 2-5 times in comparison with the experiment without decalin. Fig. 3 shows that the results of cracking of the oil residue formed a diesel fraction from 19.79 to 31.28 wt.% and in the case of the addition of decalin, the yield of diesel increased to 11.5 wt.% compared with non-decalin. However, a higher liquid fraction (92.26%) was produced when oil residue was cracked with 10% decalin for 60 min at 450 ºC, the yield of gasoline in the liquid fraction was very low, and the yield of distillate residue above 350 ºC was higher (55.54%). This is due to the fact that the hydrocarbons of liquefied part have not completely broken down into the fuel fraction for 60 min. It is shown that the reaction time plays a more important role during the cracking process. The experiments have shown that the optimal condition of the cracking process to obtain higher fuel (light and middle) fraction and lower gaseous and coke is the cracking process with 10% decalin for 120 min under a hydrogen pressure of 5 MPa at 450°C. Fig. 4 shows the group composition (SARA) of liquid products produced by cracking of Tamsagbulag atmospheric residue (AR). The content of asphaltene, resin, and saturates+aromatics hydrocarbons in the cracking products were compared to that of atmospheric residue. After cracking without decalin, the content of hydrocarbons (saturates+aromatic) decreased from 80.45 to 67.68% and the content of resin increased from 18.06% to 30.55%.

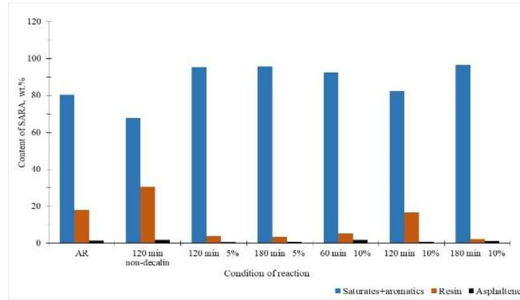

Figure 4. The group composition (SARA) of cracking products

This is a result of the conversion of aromatic hydrocarbons in the atmospheric residue into resinous compounds during the heat treatment. The series of experiments in the presence of decalin showed that the content of saturated and aromatics hydrocarbon increased, and the resin content strongly decreased. The high-molecular hydrocarbons in the residue are degraded into low-molecular compounds in this condition, thus increasing fuel yield [6,14]. It is possible to determine how the hydrocarbons are converted during the cracking process of the atmospheric residue by studying the conversion of group composition [15]. The study has shown that cracking at 450 °C with decalin can liquefy asphalt-resin compounds into low-molecular-weight compounds, increasing the output of gasoline and diesel fractions. The content and distribution of n-paraffins in atmospheric residue and its cracking products were determined by GC-FID and are shown in Fig. 5.

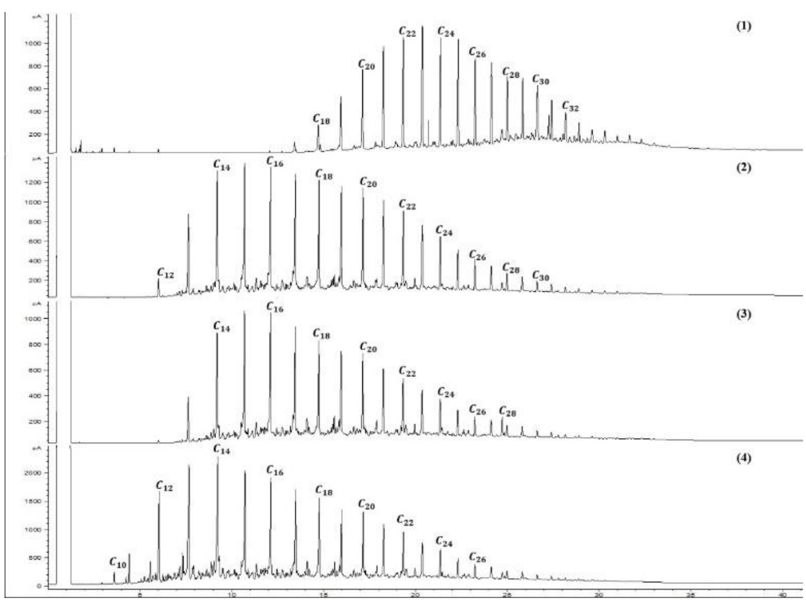

Figure 5. GC-FID chromatogram of atmospheric residue and cracking products; (1)-AR; (2) -120 min 5% decalin; (3)-180 min, 5% decalin; (4)-180min, 10% decalin

Fig. 5 (1) shows that the atmospheric residue contains n-paraffin with carbon atoms from C17 to C34 and after the cracking process (Fig. 5.(2-4)) decreased n-paraffin with high molecular atoms, was formed n-paraffin with low molecular atoms. As a result of cracking, long-chain paraffins are converted to low molecular weight paraffin. The content of n-paraffin and its distribution in the cracking products are shown in Fig. 6, 7.

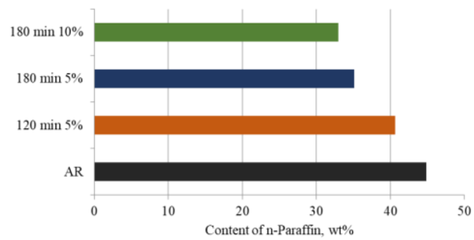

Figure 6. Content of n-paraffins in the atmospheric residue and cracking products

Fig. 6 shows that the content of n-paraffins of obtained products after cracking was decreased compared with the content of oil residue and the maximum conversion of paraffin is shown in the experiment with 10% decalin for 180 min.

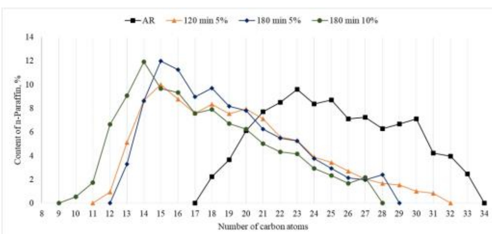

Figure 7. Molecular mass distribution of n-paraffins in the atmospheric residue and the cracking products

The atmospheric residue contains 44.86% n-paraffin with carbon atoms ranging from C_{17} to C_{34}, and n-paraffin with carbon atoms from C_{21} to C_{30} being predominant. During the cracking of the oil residue, the paraffins with carbon atoms C_{23}-C_{34} are converted into low molecular n-paraffins, resulting in a low molecular n-paraffin with carbon atoms ranging from C_{12} to C_{17}. The products after cracking contains n-paraffin of 32-40 wt% with carbon atoms C_{10}-C_{32} (Fig. 7). It is found that during the cracking, long-chain paraffins are broken down into low molecular paraffins, resulting in higher yields of liquid product [4, 16].

4. CONCLUSION

We have investigated the physical and chemical properties and hydrocarbon composition of Tamsagbulag oil of Mongolia (XXI block) and its atmospheric residue (>350°C). Crude oil has a low yield of light and medium fractions and a high content of atmospheric residue (63.19%). Therefore, a deep-processing technology is very important to increase the yield of light and middle distillate fractions. According to the results, the cracking process was found to be most effective when carried out for 120 minutes under a hydrogen pressure of 5 MPa at 450°C and with the addition of 10 wt.% decalin. Furthermore, the study showed that the cracking process of high paraffinic atmospheric residue was highly efficient with decalin, which increased the yield of distillate fractions. These results suggest that the use of decalin as an additive in the cracking process can be a viable strategy to increase the yield of fuel fractions and reduce the yield of less desirable end products such as gases and coke.

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