

UPGRADING OF BITUMEN WITH SUPERCRITICAL WATER FOR A SYSTEM COMBINED WITH SAGD.

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INTRODUCTION

Recent development of Steam Assisted Gravity Drainage (SAGD), which is believed to be an economically feasible recovery method of bitumen from oil sand deposits, is now asking for a new upgrading technology. In the operation of SAGD, mixture of bitumen and hot water at the temperature above 500 K is continuously recovered, so that the mixture recovered can be fed into a ground reactor. Then, the on-site upgrading by hydrothermal reaction could be a new technology as a combined system with SAGD.

Functions of water in hydrothermal reactions have been studied, and it was found by NMR analysis that hetero-atoms contained in low molecular compounds were easily substituted by hydrolysis and polymers were easily cracked to useful low molecular compounds with the supply of hydrogen from water [1].

On the basis of these fundamental studies, studies on the upgrading of bitumen in supercritical water were carried out.

EXPERIMENTAL

Batch-type autoclaves of 45 cm³ in volume were used. The autoclave and the induction furnace used for heating are shown in Fig.1. Experimental conditions of hydrothermal treatment are shown in Table 1. The sample oil was prepared by extraction from athabasca oil sands with toluene and subsequent evaporation of toluene. The viscosity of original oil (bitumen) is over 10⁵ mPa·s at 303 K.

In each experiment, 5 g of the bitumen was put into an autoclave with a certain amount of alkali aqueous solution and a stirring ball made of the same alloy as that of inner vessel of the autoclaves (Inconel 600). The autoclave was inserted horizontally at the center of the furnace and was heated up to a reaction temperature at the heating rate of 40°C/min. The content of autoclave was stirred with the stirring ball by rocking the furnace. After keeping the temperature for a certain time, the autoclave was taken out of the furnace and was cooled down to the room temperature at the similar cooling rate to the heating rate. Then the oil product was separated from water with separation funnel, but when the fractions of product were measured, toluene was used to wash the inner wall of the autoclave to ensure the recovery.

A rotational viscometer was used for measuring the viscosity of oil products at 303 K. Molecular weight distribution of oils was obtained with HPLC, which was calibrated with standard polystyrenes. Sulfur content was analyzed by CNS analyzer. Light oil components were analyzed with GC/MS and GC/AED (Atomic Emission Detector).

RESULTS AND DISCUSSION

Products

In all cases of hydrothermal treatment, bitumen was converted to much lighter oil. Fig.2 shows that the viscosity of oil products decreases with increasing temperature, and the reaction condition of 703 K for reaction temperature and 15min for reaction time is enough to produce sufficiently light oils for pipeline transportation.

Figure 3 shows the viscosity reduction with the reaction time as well as the water loading which is the ratio of the volume of water loaded into the reaction chamber to that of the reaction chamber. Drastic reduction was achieved in first 5 min. And the effect of water loading, that is water density, is also seen.

Figure 4 shows the influence of KOH concentration. As the KOH concentration increased, the viscosity of oil product slightly decreased, but when the KOH concentration is more than 5 mol/dm³ (M), the viscosity reduction is less. The viscosity

of oil product in case of without alkali is slightly lower than those with around 1 M alkali. In kinds of alkali, KOH was most effective.

Figure 5 shows normalized molecular weight distributions of oil products and original oil. Because of the characteristics of the separation column used, the distribution in the region of molecular weight less than 100 ($\text{LogMw}=2$) is not accurate. But, it is seen that the heavy components are diminished as the reaction proceeds.

Figure 6 shows the fraction of products by weight at different temperatures. Fractions of coke (toluene-insoluble), and gas and water-soluble organic compounds are increased with increasing temperature. But, the fraction of gas and water-soluble organic compounds is obtained as difference, and about a half of it is estimated to be lighter oil components which are evacuated in evaporating toluene used as the extractant. Therefore, it can be said that the fraction of asphaltene (n-pentane-insoluble but toluene-soluble) for the original oil is roughly equal to the sum of those of others than malten (n-pentane-soluble), that is to say, the fraction of malten does not change much.

Fraction of coke produced at 703 K is ca. 5%, which is much less than that in the thermal cracking. This may imply that hydrogen is supplied from water and/or the water prevents polymerization. The original vanadium content of 160 ppm was reduced to 12 ppm by the 15 min reaction at 703 K.

As to the gas composition, H_2 and CH_4 were produced, but CO_2 and H_2S gases did not exist when alkali solution was used. However, when pure water was used instead of alkali solution, CO_2 and H_2S as well as H_2 and CH_4 were produced.

Desulfurization

Figure 7 shows the desulfurization at various temperatures. The sulfur content of oil product at 703 K decreased to 2.0% from 4.5% (original). Fig.8 shows the variation of sulfur content with the reaction time. The sulfur content decreased to a half of the original value in first 5 min in all cases of water loading. After first 5 min, influence of water loading appears, but 30% of sulfur still remains even in the case of 40% water loading. In the case of thermal cracking without water, sulfur removal was less.

Figure 9 shows the GC/MS total ion chromatogram of oil product after 100 min reaction. The parent peaks of a series of paraffin and low molecular aromatic compounds were mainly detected. Fig.10(A) shows a S atom chromatogram of the oil product obtained with GC/AED. These peaks are grouped as C_1 to C_3 alkyl benzothiophenes and dibenzothiophenes with the help of GC/MS selected ion chromatograms. As examples, selected m/e number chromatograms corresponding to the parent peaks of C_1 to C_3 alkyl dibenzothiophenes are shown in Fig.10(B) to (D). The parent peaks of benzothiophene and dibenzothiophene were not detected.

As shown in Fig.8, it was difficult to decrease the sulfur content of oil products further by increasing the reaction time. Table 2 shows results of GC/MS and GC/AED analysis of oil products in long time reactions. It is seen that the concentrations of benzothiophenes (BTs) and dibenzothiophenes (DBTs) increased with reaction time and/or reaction temperature, though the total sulfur content changes little. This means that these BTs and DBTs are produced by breaking aliphatic C-C bonds in high molecular aromatic sulfur compounds and these aromatic compounds are hardly decomposed. Table 2 also shows the effect of water loading, which implies more breakage of C-S bonds with high water loading, probably in aromatic structures.

Decomposition of benzothiophenes and dibenzothiophenes

Figures 11 and 12 show results of hydrothermal decomposition of BT and DBT. BT was easily decomposed in the region of subcritical water. 5-Methyl BT is less reactive than BT but it was decomposed in the subcritical region. DBT was hardly decomposed in the near-critical region of water but was decomposed in the supercritical region of water as shown in Fig.12. However, only 50% of 2,8-dimethyl DBT was decomposed at the reaction condition of 703 K, 120 min, 40% water loading and 5 M KOH, at which 96% of DBT was decomposed.

These results show that low molecular aromatic sulfur compounds themselves, at least BTs, can be decomposed by hydrothermal reaction in the supercritical region of water, but they are hardly decomposed when mixed with other oil products.

DISCUSSION ON THE HYDROTHERMAL CRACKING

From the results so far described, it may be summarized that the viscosity reduction occurs simultaneously with desulfurization, but the dominant mechanisms in the first 5 min and subsequent reactions are different each other. In the first 5 min reaction, the thermal cracking may be dominant and the breakage of C-S bonds in aliphatic structures may occur. In this process, increase of water loading may cause hindering the thermal cracking, which proceeds by radical reactions, because of the enhancement of ionic character of water. At the next stage of cracking, the slow thermal cracking of C-C bonds and the hydrothermal cracking of C-S bonds probably in aromatic structures may lead to the reduction of viscosity and sulfur content. Through the whole process of cracking, water acts to suppress the production of coke. Data are not shown here, but experimental results of hydrothermal cracking of polymers show that hydrogen is supplied from water, which may prevent coking, where oxygen goes mostly into water-soluble compounds and some form CO_2 . Similar mechanisms may act in the hydrothermal cracking of bitumen, but it does not accelerate the reaction.

CONCLUSIONS

Fundamental studies on the hydrothermal cracking of oil sands in the region of supercritical water were carried out to clarify the reaction condition for developing a new on-site upgrading method. Reaction conditions of temperature of 700K reaction time of 5-15min, water loading of 20% (pressure \approx 3.1MPa) and 0.1-1 M KOH give us upgraded oils of viscosity of 10-20 mPa·s, sulfur content of less than a half and vanadium content of less than 10%, with less coke. It should be also emphasized that neither hydrogen gas nor catalyst was used, and neither CO_2 nor H_2S was issued. A combined system with SAGD can utilize the waste water to generate steam for injection.

ACKNOWLEDGMENT

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REFERENCE

[1] Nakahara, M., Tenuh, T., Wakai, C., Fujita, E., and Enomoto, H., ^{13}C -NMR Evidence for Hydrogen Supply by Water for Polymer Cracking in Supercritical Water. *Chemistry Letters* 1997, 163-164.

Table 1 Experimental Conditions.

water loading (%)	20-40
temperature (K)	673-723
time (min)	0-30
KOH (M)	1-10

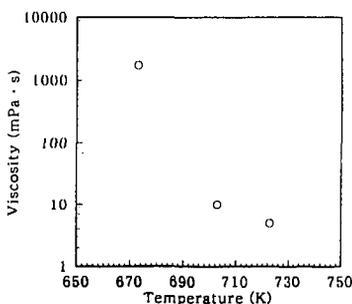


Fig. 2 Viscosity of oil products. (1M KOH, 20% water loading)

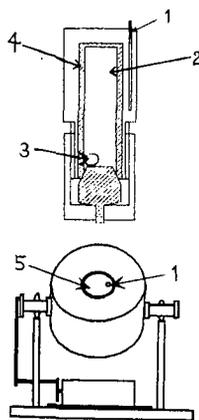


Fig. 1 A batch type autoclave (top) and the induction furnace (bottom).
1: thermocouple, 2: chamber
3: stirring ball, 4: inner vessel,
5: autoclave

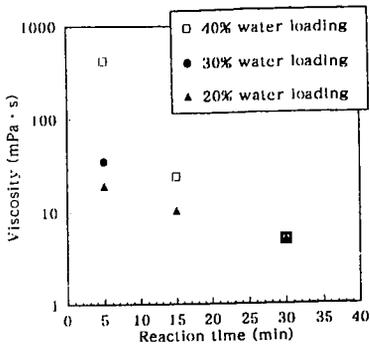


Fig.3 Viscosity of oil products with reaction time.

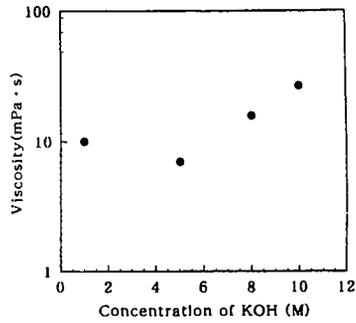


Fig.4 Influence of KOH concentration on the Viscosity of oil products. (Reaction temperature: 703K, Reaction time:15min, 20% water loading,)

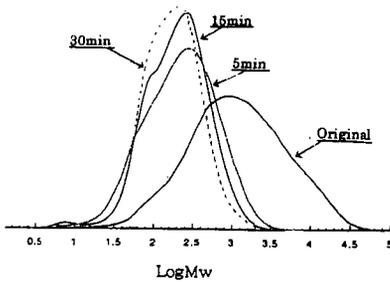


Fig.5 Comparison of molecular weight distribution. (Reaction temperature: 703K, 1M KOH, 20% water loading)

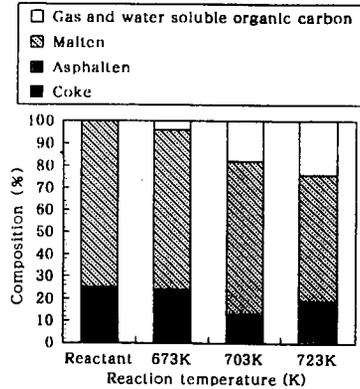


Fig.6 Fraction of products. (Reaction time: 15min, 1M KOH)

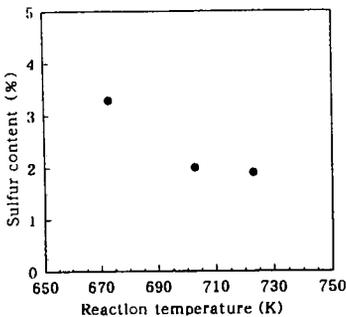


Fig.7 Sulfur content of oil products. (Reaction time:15min, 1M KOH 20% water loading)

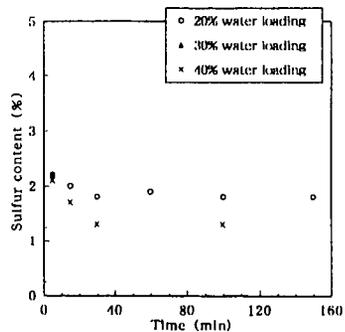


Fig.8 Influence of reaction time on sulfur contents of oil products. (1M KOH)

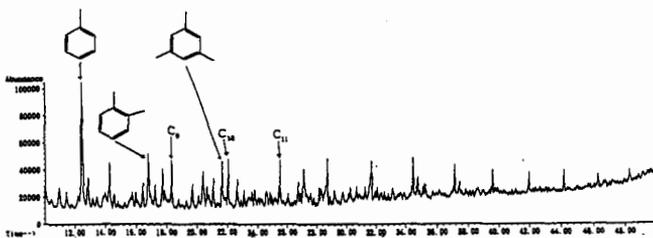


Fig.9 GC/MS chromatogram of n-hexane soluble oil products.
(Reaction temperature: 703K, Reaction time: 100min,
1M KOH, 20% water loading)

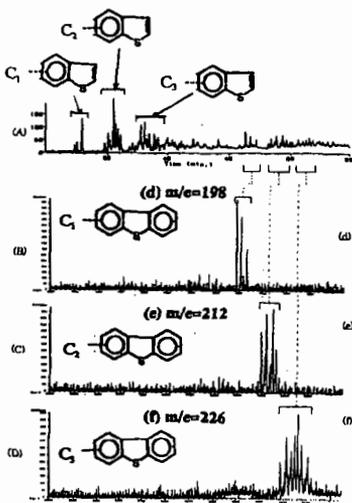


Table 2 Concentration of sulfur compounds.

No.	1	2	3	4	5	6
Temperature(K)	430	430	430	450	430	430
Time(min)	60	100	150	100	100	100
KOH (M)	1	1	1	1	1	5
Water Loading(%)	20	20	20	20	40	20
Sulfur content(%)	1.9	1.8	1.8	1.7	1.3	1.5
C ₁ -BT(wt%)	0.03	0.05	0.06	0.10	0.02	0.02
C ₂ -BT	0.06	0.10	0.12	0.17	0.06	0.07
C ₃ -BT	0.07	0.11	0.12	0.15	0.08	0.11
C ₁ -DBT	0.02	0.03	0.04	0.06	0.02	0.02
C ₂ -DBT	0.04	0.07	0.08	0.10	0.03	0.04
C ₃ -DBT	0.03	0.07	0.08	0.10	0.03	0.02
SUM	0.25	0.43	0.50	0.68	0.24	0.28

Fig.10 Chromatograms of low molecular sulfur compounds.

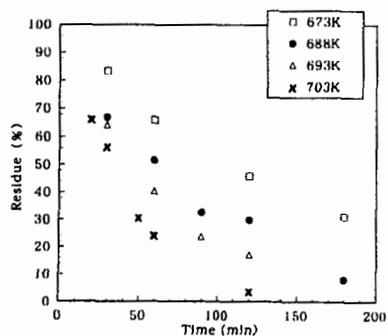


Fig.12 Decomposition of Dibenzothophene by hydrothermal reaction.
(5M KOH)

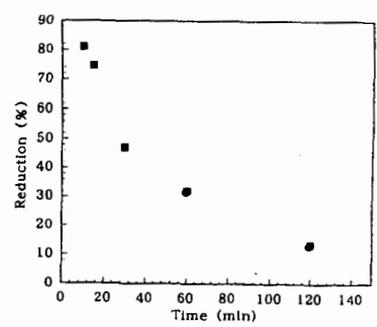


Fig.11 Decomposition of Benzothophene by hydrothermal reaction.
(Reaction Temperature:573K,5M NaOH)