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Extraction of bitumen with sub- and supercritical water

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Abstract−The sub- and supercritical water extractions of Athabasca oil sand bitumens were studied using a micro reactor. The experiments were carried out in the temperature range of 360-380 °C, pressure 15-30 MPa and water density 0.07-0.65 g/cm^3 for 0-2 hrs. The extraction conversion of bitumens increased with solvent power and temperature. A maximum conversion of 24% was obtained after 90 min extraction at the supercritical condition. Hydrogen and carbon mono-oxide were not detected in sub-critical region but in the supercritical region. The supercritical condition was favorable to the hydrogen formation for bitumen extraction. The extraction products were upgraded relative to the original bitumens due to direct hydrolysis of low-energy linkage and H_2 formed by water gas shift reaction in supercritical condition. 18% of initial sulfur in bitumen can be removed at maximum conversion condition. The asphaltene contents of the residue were significantly higher than that of original bitumen due to preferential extraction of aromatic compounds in supercritical condition.

Key words: Bitumen, Supercritical Water, Sulfur Removal, Asphaltenes, Upgrading

INTRODUCTION

The current energetic crisis is mainly due to the energy increasing demand (India, China etc.) and the depletion of conventional crude oil reserves. Petroleum dependence could be avoided by exploiting alternate fossil sources of fuel as coal, oil shales and oil sands. Oil sand bitumens have higher concentrations of asphaltenes, resins and hetero atomic species containing nitrogen, sulfur and heavy metals than conventional crude oils. Especially asphaltenes, the toluene-soluble and hexane insoluble fraction were responsible for coking tendency of the oil and deactivation of hydroprocessing catalyst [1,2]. Hence, bitumens must be upgraded through the prior removal of these contaminants (asphaltenes, sulfur, metals, etc.). The bitumen from oil sands can be recovered using surface recovery and in-situ thermal processes. The mining recovery methods involve the mining of oil sands and the subsequent physical separation to recover the bitumen from the sand reservoir by a hot water process [3]. In oil sand industry such as the steam assisted gravity drainage (SAGD) process [4] and hot water extraction process [5,6], the hot steam is continuously injected into an oil sand reservoir and the heated oil with steam condensate is obtained in the form of water-in-bitumen emulsions. After the lighter components from the bitumen are removed, the heavier components of the bitumen can be upgraded as feedstock by solvent deasphalting extraction [7] and supercritical fluid extraction [8,9]. The ROSE (residuum oil supercritical extraction) process developed by Kerr-McGee Refining Corp. [10] has been commercially used to remove the asphaltenes from bitumen residue by paraffin solvent under severe conditions and is also unsuitable for bitumen emulsion type feedstock containing a significant amount of water and solid [11].

Since the mid-1970s, considerable interest has been focused on extraction with supercritical fluid. Several publications have reported supercritical extraction of coal [12,13] and heavy oil [8,14,15] with common organic solvent or water. This work reported here was prompted by an earlier result [16] in which we evaluated extraction of Alaska low rank coals with sub- and supercritical water. Supercritical water extraction has some advantage in view of the availability of hydrogen from water gas shift reaction. The objective of this study is to understand the removal of sulfur and asphaltene in bitumen by sub- and supercritical water treatment. The effects of operation variables are investigated to determine some optimal factors associated with the process and to confirm the upgrading of bitumen by means of supercritical water.

EXPERIMENTAL

1. Materials

The bitumen used in the experiments was extracted from Canada's Athabasca oil sands. Table 1 shows the physical and chemical properties of the bitumen and measuring methods. Solvents used were toluene (Junsei Chemical Company, Japan, purity 99.5%), hexane (Junsei Chemical Company, Japan, purity 96%) dichloromethane (Junsei Chemical Company, Japan, purity 99%), methanol (Oriental Chemical Industries, Korea, purity 99.6%) and deionized water prepared by pure water fabricator (S. A. 67120, Millipore Co., USA).

2. Apparatus

The schematic diagram of experimental apparatus and micro reactor is shown in Fig. 1. A micro vessel of 42.3 ml was used as pressurized reactor, which was connected with a pressure gauge and outlet gas port through an on-off valve. In each experiment, the reactor was charged with ca. 2 g of bitumen and 2-30 g of deionized water which was calculated by water density according to reaction temperature and pressure condition. After pressurized flushing with helium into the reactor, the reactor was sealed. The reactor was placed

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Table 1. Physical and chemical properties of Athabasca oils and bitumen

Property	Bitumen	Method/Equipment
Kinematic viscosity (mm^2/s @ 40 °C)	294.89	DVUltra Rheometer, Brookfield, USA
API specific gravity (°API)	8.31	ASTM D 287/DMA 4500, Anton Paar., Austria
Boiling point distribution (°C)	114-612	ASTM D 2887/ACG 2123A, Agilent Technolgy, USA
Density (g/cm^3 @ 15°C)	1.0112	
Elemental analysis		Truspec CHN and SC-432 DR, LECO Co., USA
C (wt%)	81.86	
H (wt%)	10.32	
N (wt%)	1.53	
S (wt%)	4.87	ASTM D 3176
O (wt%)	1.41	
SARA analysis		IATROSCAN MK-6s, Mitsubishi, Japan
Saturates (wt%)	6.82	
Aromatics (wt%)	53.36	
Resins (wt%)	25.40	
Asphaltenes (wt%)	14.42	

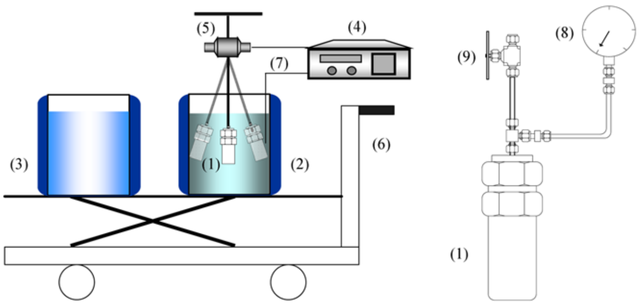

Fig. 1. Schematic diagram of experimental apparatus.

1. Micro reactor
2. Molten salt bath
3. Water bath
4. Controller
5. Shaker
6. Mover
7. Thermocouple
8. Pressure gauge
9. On-off valve

into a molten salt bath heated to a designed temperature and shaken for homogeneous mixing. Though around 2-10 min is required to reach reaction temperature and pressure when a micro reactor is put into molten salt bath, the reaction time is defined as the residence time in molten salt bath because the reaction can occur during heating time. After reaction time, the micro reactor was taken out of the molten salt bath to terminate reaction and suddenly cooled to room temperature by placing it in a water bath.

Temperature of molten salt bath and shaking speed of the reactor were controlled by PID controllers connected with a K-type thermocouple and a speed gauge, respectively.

3. Analysis

Bitumen was extracted in the temperature range of 360 and 380 °C, pressure 15-30 MPa and water density 0-0.65 g/cm^3 for 0-120 min. After the extraction of bitumen, the unreacted residue was collected from the reactor and filtered to separate the water through 1.2 μm glass filter. Residue obtained after final filtration was dried in an oven at 80 °C overnight and its weight was measured for total conversion calculation. The total conversion is given by Eq. (1).

$$\text{Conversion}\ (\%) = 100 - \left(\frac{\text{wt of residue}}{\text{wt of bitumen}}\right) \times 100 \tag{1}$$

CO, CO_2, CH_4 and H_2 as gas products were detected by gas chromatograph (Acme 6000, YoungLin, Korea) with a packed column of carbosphere (80/100), and the total sulfur was analyzed using sulfur analyzer (9000NS, ANTEK, USA). The weight of gas product was calculated from molecular weight and the volume of gas at standard temperature and pressure. The yield of gas product and the sulfur removal in gaseous effluent from original bitumen were defined as Eqs. (2) and (3).

$$\text{Yield (wt \%)} = \left(\frac{\text{wt of gas product}}{\text{wt of bitumen}}\right) \times 100 \tag{2}$$

$$\text{Sulfur gas removal (wt \%)} = \left(\frac{\text{wt of sulfur in gas product}}{\text{wt of sulfur in bitumen}}\right) \times 100 \tag{3}$$

The saturates, aromatics, resins and asphaltene contents of the bitumen and residue were determined by a modified SARA analysis (the modified SARA analysis was described in detail elsewhere [17]). The sulfur contents in the bitumen and residual solids were determined by using a sulfur analyzer (SC-432DR, LECO Co., USA) in accordance with ASTM method D3176. The sulfur contents in residue were defined as sulfur remains of residue. The total sulfur removal was obtained from sulfur remain through Eq. (4).

$$\text{Total sulfur removal (wt \%)} = 100 - \left(\frac{\text{wt of sulfur in residue}}{\text{wt of sulfur in bitumen}}\right) \times 100 \tag{4}$$

The procedure of analysis explained above and the equipment and method to analyze bitumen are summarized in Fig. 2 and Table 1, respectively.

RESULTS AND DISCUSSION

1. Effect of Reaction Time

Fig. 3 shows total conversion and pressure change at 380 °C and

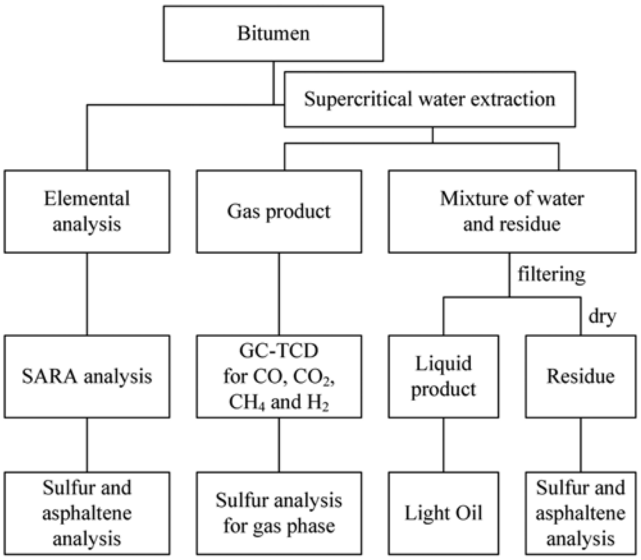

Fig. 2. The procedure of product analysis.

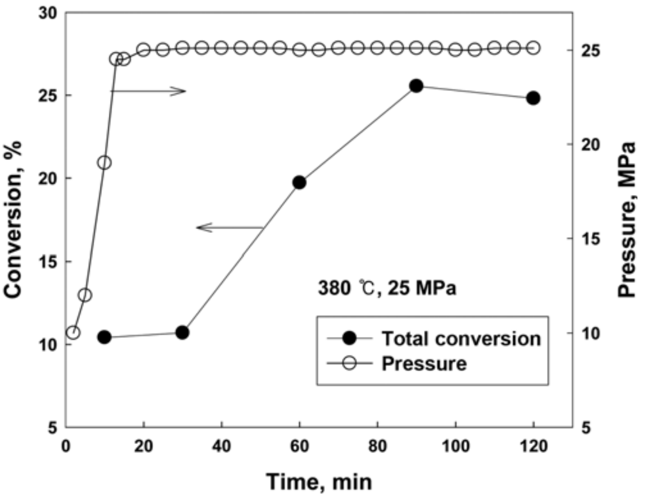

Fig. 3. Total conversion of bitumen and pressure change at 380 °C and 25 MPa according to reaction time.

25 MPa according to various reaction times, respectively. As shown in Fig. 3, the total conversion of bitumen increased with increasing reaction time up to 90 min. The presence of only minor discrepancy, i.e., –2.8% in error level (conversion 25.5% at 90 min, 24.8%, 120 min) indicated that the total conversion reached to almost constant value over 90 min. While, the vessel pressure with only water reached a constant value within 10 min. It indicates that the supercritical reaction between water and bitumen begins after 10 min and proceeds until 90 min.

This result about reaction time is in good agreement with a previous study for Chinese Datong coal [18]. In the report, reaction time for supercritical water treatment using micro reactor was fixed on 90 min for each run because total conversion increased sharply within 30 min and then the increasing rate was very low in the range of 60-90 min at 380 °C and 25 MPa. In this work, reaction time was fixed similarly on 90 min to obtain higher conversion under the same condition.

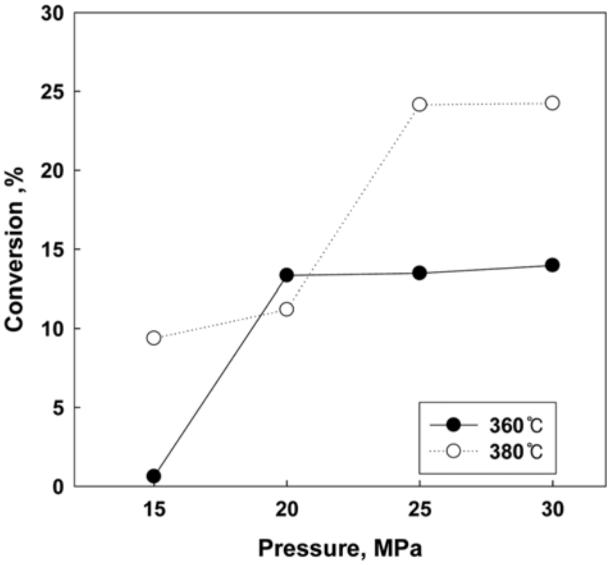

Fig. 4. Total conversion of bitumen according to reaction temperature and pressure.

2. Effect of Reaction Temperature and Pressure

Fig. 4 shows total conversion according to pressure at 360 °C and 380 °C, respectively. Total conversion at 380 °C increased with increasing reaction pressure. In addition, it is known that total conversion increased dramatically over two times when the reaction condition moved from sub-critical to supercritical region at 380 °C. On the contrary, in the sub-critical condition of 360 °C, total conversion increased up to 20 MPa and reached a constant value (14%). These results are thought to be related with the solvent power of a water solvent. The solvent power of sub- and supercritical water depends on its density, which at a given temperature is most affected by pressure. A higher conversion can probably be obtained with higher water density, because generally the solvent power increases with increase of its density and hydrolysis is promoted under high water density. In the region of 20-30 MPa, as the density of the water was held almost constant (ρ=0.55-0.61 g/cm^3), the effect of pressure was considerably reduced at 360 °C. The reason that the conversion at 15 MPa and 380 °C (ρ=0.0739 g/cm^3) is higher than that at 15 MPa and 360 °C (ρ=0.0885 g/cm^3) is because the temperature effect is dominant at lower value of similar density. While in the case of 20 MPa, the conversion at 360 °C is higher than that of 380 °C, because the effect of density is more dominant (ρ=0.1211 g/cm^3 at 380 °C and 20 MPa, ρ=0.5480 g/cm^3 at 360 °C and 20 MPa). Therefore, the solvent power is a more important factor for increasing the conversion in sub-critical condition. However, the most significant factor to increase the conversion is phase transition from sub-critical to supercritical condition. Though the densities over 25 MPa at 380 °C were lower than those over 25 MPa at 360 °C, higher conversion was obtained as shown in Fig. 4. Since supercritical water reacts with the low-energy linkage in bitumen, such as -O-CH$_3$, and -O-R by direct hydrolysis, a higher extraction can be achieved in supercritical condition.

The effects of temperature and pressure on the gas composition are shown in Table 2 and Fig. 5. The results shown in the figure

Table 2. Effect of pressure on composition of gas products at 360 °C and 380 °C

Condition		Component				
Temperature	Pressure	H_2, %	C_1, %	H_2S, %	Others, %	Total gas, ml
360 °C	15 MPa	-	2.50	0.89	96.61	1.0
	20 MPa	-	5.74	1.18	93.07	1.4
	25 MPa	-	6.71	1.48	91.82	2.0
	30 MPa	-	6.74	1.68	91.58	2.2
380 °C	15 MPa	-	7.36	2.07	90.57	7.0
	20 MPa	-	8.48	2.99	88.53	7.5
	25 MPa	10.08	15.33	4.08	70.50	10.2
	30 MPa	11.98	20.16	4.13	63.72	11.0

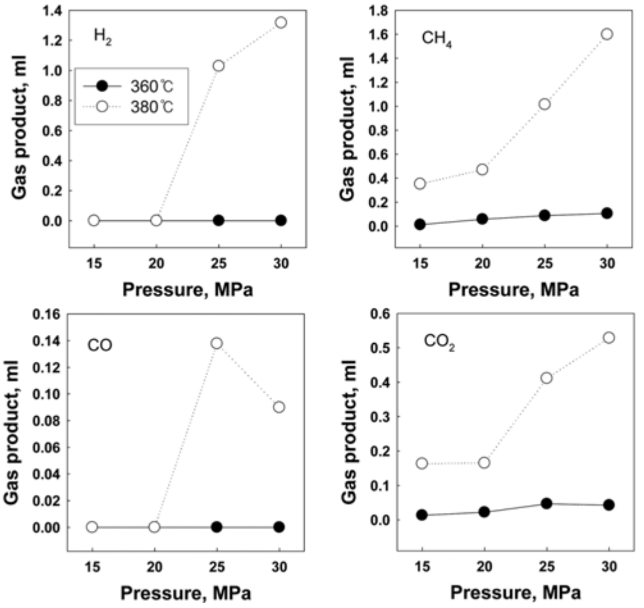

Fig. 5. Gas products according to reaction temperature and pressure.

and table are the average of two or more runs. Total volume of gas product increased with the increase of pressure and temperature. The interesting observation was that the product gas volume in sub critical region of 360 °C increased a little linearly with pressure, but the volume at 380 °C jumped up over 10 ml in the region of supercritical condition. In addition, total gas volume at 380 °C and 20 MPa was much larger than that of 360 °C and 20 MPa in contrast to total conversion. It seems that the effect of reaction temperature is more dominant than that of solvent power for gas formation. However, the effect of gas product on total conversion was only slight level and the yield of liquid product was much greater than that of gas product.

In Table 2, other gases consisted of higher hydrocarbon over C_1, the percentage of which was higher than 91% of total gas formation in sub-critical condition. However, higher hydrocarbon decreased into 64% in supercritical condition because of hydrolysis ability of supercritical water. Simultaneously, Fig. 5 shows that the volumes of H_2, CO_2 and CH_4 increased dramatically in supercritical region. The results indicate that supercritical condition is more effective than sub-critical condition to form the gas products such as C_1 gases and hydrogen from Bitumen.

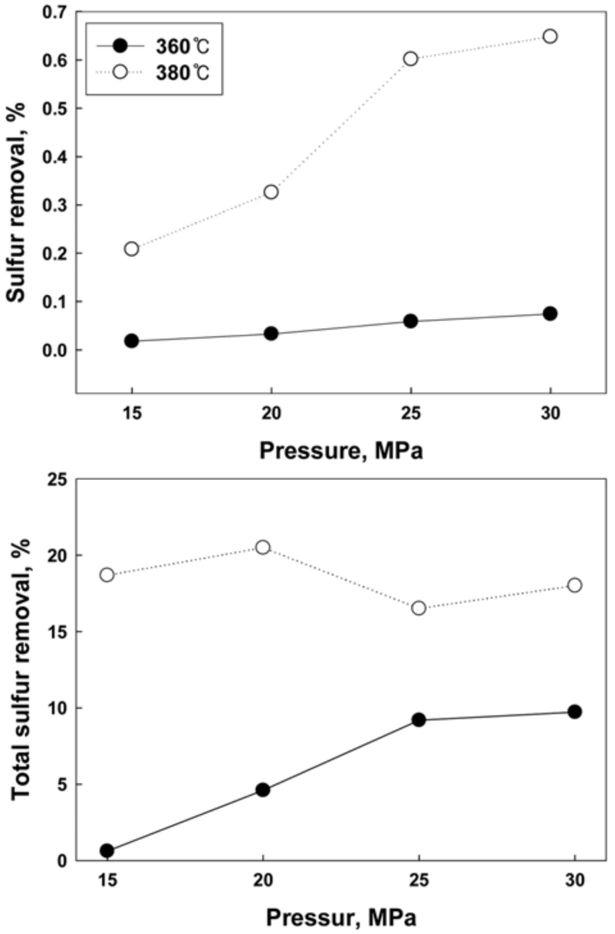

Fig. 6. Total sulfur removal and sulfur removal through gas effluent according to reaction temperature and pressure.

In the case of supercritical treatment for coal, the main gas product among C_1 gases was CO_2 irrespective of reaction temperature and pressure, due to decomposition of the carboxyl group in the coal matrix [16], while the main gas product for bitumen was CH_4 in all conditions. In addition, hydrogen was not detected in sub-critical region but in the supercritical region and amount of CO gas decreased at 30 MPa after increasing by 25 MPa at 380 °C. It means that water gas shift reaction occurs in supercritical region as following Eq. (5). Therefore, it is thought that supercritical condition is favorable to the hydrogen formation for bitumen extraction.

$$CO+H_2O \rightarrow H_2+CO_2 \qquad (5)$$

In the subcritical region of 360 °C, we cannot exclude the possibility of hydrogen formation. If hydrogen formation occurred, the hydrogen was formed not by water gas shift reaction but by hydrolysis because CO_2 gas was scarcely produced in the subcritical region of 360 °C.

3. Sulfur Removal

Fig. 6 shows sulfur removal through gas effluent and sulfur remains in residue of filtrate. The volume of sulfur removed through gas phase effluent was less than 0.45 ml (0.65%, sulfur removal) even at supercritical conditions. Moreover, in sub-critical region, sulfur removal showed just a trace. On the other hand, the total sulfur removals from bitumen were about 16-20% at 380 °C and below 10% at 360 °C. It indicates that the majority of sulfur is removed not through gas effluent but through liquid extract. In addition, as shown in Fig. 6, it is known that the effect of pressure on total sulfur removal in supercritical region is less dominant than that in sub-critical region.

4. Asphaltene Removal

The residual fractions of the bitumens after supercritical water extraction were mixed with proper amounts of n-hexane to yield hexane insolubles, i.e. asphaltenes. The asphaltene content of the residual fractions was examined to determine the effect of operation variables on the removal or rejection of the asphaltenes. The measured asphaltene content of the residual fractions was compared with the asphaltene content of the original bitumen. Fig. 7 shows the results of SARA analysis for residue after extraction at 360 and 380 °C. The asphaltene contents at 360 °C were almost constant (14.4-15.5%) irrespective of reaction pressures, and these values were similar to the asphaltene content (14.4%) of the original bitumen. It also means that the asphaltene contents of extractions under sub-critical reaction of 360 °C are almost the same value of initial asphaltene content in bitumen feed stock. In contrast to residue at 360 °C, the asphaltene contents of the residue under supercritical condition at 380 °C were much higher than those of the bitumen and the residues after sub-critical extraction. On the basis of mass balance for asphaltenes, it is expected that liquid extractions obtained after supercritical reaction have no asphaltene. Therefore, it is possible to remove most asphaltene in bitumen feed through supercritical extraction.

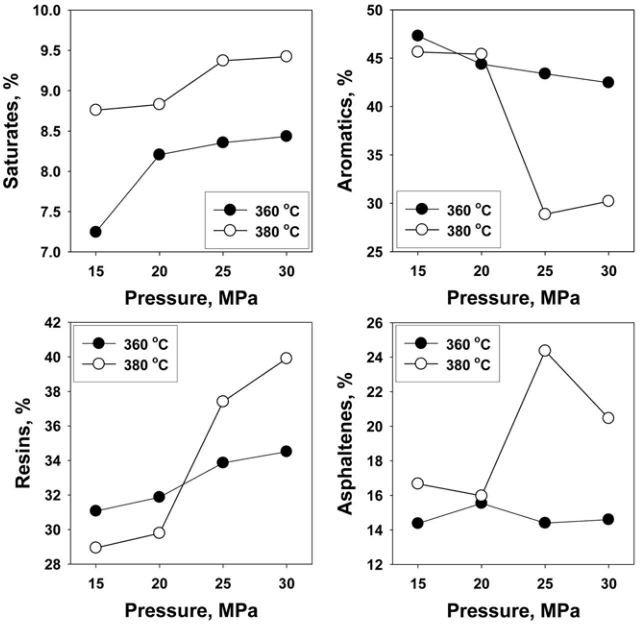

Fig. 7. The results of SARA analysis for residue after extraction at 360 °C and 380 °C according to reaction pressure.

The resin and asphaltene contents of the residual fractions increased sharply from sub-critical to supercritical condition at 380 °C, while the aromatic contents decreased considerably under supercritical condition. It is assumed that the aromatic compounds were preferentially extracted compared to resins and asphaltenes. On the point of view, the extract samples after supercritical reaction were significantly upgraded due to relative lower extraction of asphaltene from the original bitumen. Moreover, Berkowitz et al. [8] explained that in supercritical condition (24.5 MPa, 400 °C), precursor asphaltenes react with hydrogen to form hydrocarbon in bitumen+heavy oil fraction and it is tempting to ascribe this to introduction of some H from $CO+H_2O \rightarrow H_2+CO_2$ into the extract. Because in our observation, hydrogen is formed in supercritical condition, it is thought that the hydrogen reacts with precursor asphaltenes, resulting in lower asphaltene in the extraction.

CONCLUSION

The role of supercritical water and the effects of operating variables such as reaction temperature, pressure, and water density on the extraction of bitumens from Canada's Athabasca oil sands were investigated in a batch type micro reactor. The sub-critical extraction yields of bitumens increased with increase in solvent density. Compared with sub-critical condition, the extraction of bitumen in supercritical condition was accelerated through direct hydrolysis of low-energy linkage and H_2 formed by water gas shift reaction. Total volume of gas product increased with increasing temperature and pressure and CO and H_2 formed especially at only supercritical condition. It was seen that supercritical condition was favorable to the hydrogen formation via water gas shift reaction. With the increase of temperature and pressure, the sulfur in bitumen released into the gas effluents, but the sulfur removal through liquid effluents was much greater than that through gas effluents. The aromatic compounds were preferentially extracted in comparison with resins and asphaltenes under supercritical treatment. The asphaltene contents of the residual fractions in supercritical region were higher compared to that of original bitumen, indicating significant upgrading of the extract samples after the supercritical treatment.

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