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Study of pyrolysis kinetics of Alberta oil sand by thermogravimetric analysis

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Abstract−The kinetics of the thermal decomposition of Alberta oil sand has been investigated by thermogravimetric analysis (TGA) for the study of oil sand pyrolysis characteristics. The TGA experiments were carried out at four different heating rates of 10, 20, 30, 40 °C/min up to 900 °C to verify weight variation and reaction temperature. The activation energy of the thermal decomposition of Alberta oil sand obtained from the kinetic analysis was similar to that of the previous researches. Also, bitumen was extracted by solvent (toluene, THF (tetrahydrofuran)) and analyzed. Extracted bitumen was analyzed by using proximate analysis, ultimate analysis, heavy metal analysis, heating value, asphaltenes, API, SIMDIS, density, TLC, and molecular weight. The analyses of the extracted bitumen were similar to those of heavy residue.

Key words: Kinetics, Oil Sand, Pyrolysis, Thermogravimetric Analysis, Bitumen

INTRODUCTION

Oil sand, which is also known as tar sand and bituminous sand, is a stratum of sand or sandstone containing viscous petroleum [1]. The crude bitumen extracted from the oil sand has large molecular nature, making it difficult and expensive to process into gasoline, diesel fuel, jet fuel and other products. In spite of difficulty and cost, the oil sand has recently been considered to be a part of the world's oil resources because of high oil prices and new technologies which enable it to be profitably extracted and upgraded to usable products.

The Alberta oil sand deposits contain about 1.6 trillion barrels of oil, which cover an area of approximately 40,000 km^2 and about 20% of oil sand can be recoverable using open-pit mining [2]. After oil sand is mined, the bitumen has to be recovered from the oil sand in order to upgrade and transport to refineries. At present, several methods may be applied to recover bitumen from the oil sand, such as water-based extraction [1], solvent extraction [3,4], pyrolysis [2, 5-9], etc.

Pyrolysis is an excellent process to generate char, oil, and gaseous products from coal, biomass, and oil shale, etc. There have been many researches which adopted thermogravimetric methods to investigate reaction kinetics of thermal decomposition by pyrolysis from oil shale [10-18]. Many studies on oil sand pyrolysis using thermogravimetric analyzer have also been carried out [7-9,19,20]. The pyrolysis reactivity and kinetic characteristics of the oil sand depend strongly on both the oil sand itself which, in general, consists of inorganic materials of 75-85%, water of 3-5%, and bitumen of 1-18% and bitumen characteristics. Hence, in this study, to verify the content of bitumen, we first extracted bitumen from the Alberta oil sand using toluene [3] and THF (tetrahydrofuran) [21] and performed proximate analysis, ultimate analysis, heavy metal analysis, asphaltenes, SIMDIS, TLC, API gravity, molecular weight, and viscosity to analyze bitumen characteristics. Then, we performed non-isothermal thermogravimetric analysis in order to investigate pyrolysis characteristics and kinetic parameters of the Alberta oil sand. The results will be effectively applied to the fixed-bed or fluidized-bed pyrolysis.

EXPERIMENTAL

1. Apparatus

Fig. 1 shows a schematic diagram of the experimental apparatus for extracting bitumen from the oil sand using toluene and THF. The apparatus consists of a water heating bath, water condenser, water cooling bath, pressure valve, rotary equipment, and sample bag. Fig. 2 shows a schematic diagram of the thermogravimetric analyzer apparatus (TGA 2950, TA Instrument) [22]. The tempera-

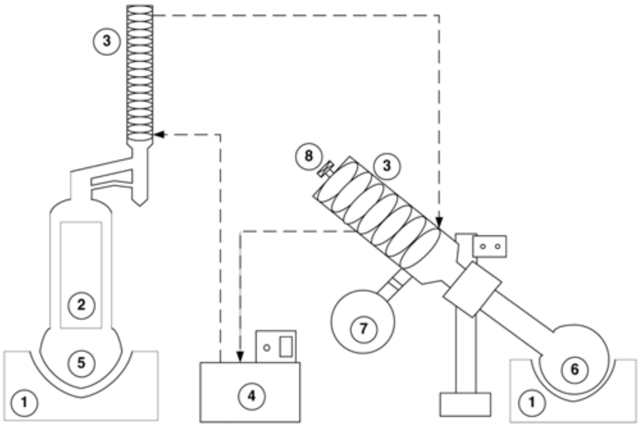

Fig. 1. Schematic diagram of the experimental apparatus for extracting bitumen from the oil sand (① Water heater bath, ② Sample bag, ③ Water condenser, ④ Water cooler bath, ⑤⑥ Toluen, THF & extracted bitumen, ⑦ Pure bitumen, ⑧ Pressure valve, ⑨ Rotary equipment).

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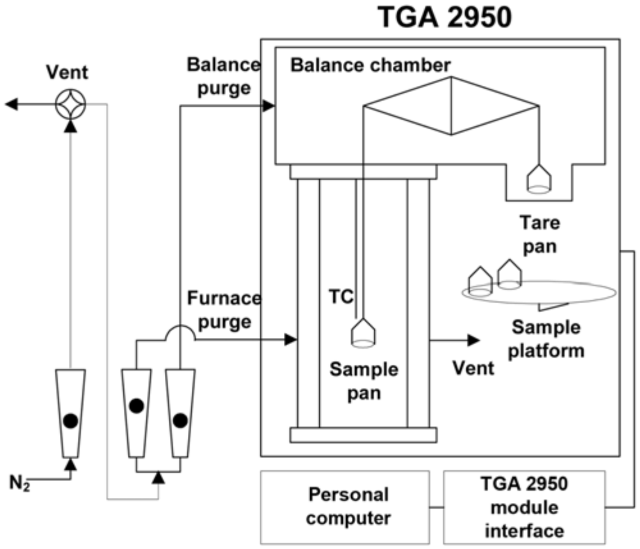

Fig. 2. Schematic diagram of TGA 2950.

ture range, heating rate range, maximum gas flow rate, and weighing range of TGA 2950 were 25-1,000 °C, 0.1-100 °C/min, 100 ml/min, 0.1 g-100 mg or 0.1 g-1,000 mg, respectively. The mass differentiation according to the temperature (time) differentiation, which is measured by TGA-2950, was saved to the PC through TGA-2950 module interface.

2. Procedure

The bitumen was extracted by using highly-soluble and easy-handling organic solvents (toluene, THF) in order to look into the characteristics of bitumen which was extracted from the oil sand. The measured amount of oil sand was loaded in a porous fabric pouch, then the pouch was located in a modified Soxhlet extractor. The solvent was boiled in the boiling flask at the bottom of the extractor and the evaporated solvent was again condensed at the condenser section and poured into the oil sand pouch washing the bitumen into the boiling flask. The extraction process was maintained for 24 hours. After the extraction the bitumen-solvent mixture was filtered to remove fine particles which could be introduced during the extraction. The filtered mixture was loaded in a rotary evaporator and condensed at 343 K bath for 12 hours.

To investigate pyrolysis characteristics and kinetic parameters of the Alberta oil sand, thermogravimetric analysis was performed. During the experiment, about 10 mg of the oil sand sample was placed on a sample pan situated on the sample arm of the balance and pyrolyzed under 100 ml/min of air flow up to 900 °C at heating rate of 10, 20, 30, 40 °C/min, respectively, in order to verify weight variation and reaction temperature.

RESULTS AND DISCUSSION

1. Bitumen Analysis

Table 1 summarizes the physical and chemical properties of bitumen which was extracted by toluene and THF and reported at several

Table 1. Physical and chemical properties of bitumens and heavy residue

	Bitumen by toluene	Bitumen by THF	Heavy residue	[2]	[6]	[8]	[9]
Oil sand [g]	402	466.6					
Bitumen [g]	53.5	63.09					
Bitumen yield [wt%]	13.31	13.52		14.8	6.0-7.6	10.4	13.55
Proximate analysis [wt%]							
H_2O	2.55	4.47					
Volatile	85.96	83.94					
Ash	0	0					
F. Carbon	11.49	11.59					
Ultimate analysis [wt%]							
C	85.75	85.00	82.26	82.6	83-86	83.1	79.16
H	13.30	13.10	11.65	10.2	11.0-11.6	10.1	10.65
N	0.66	0.64	0.61	0.6	1.1-1.4	0.4	0.35
S	5.46	5.20	5.55	5.2	0.3-0.6	4.8	9.84
O				1.4	N.D.-4.1	1.1	
Heating value [kcal/kg]	9,970	9,930	9,510		9,775-9,823		
Asphaltenes [%]	12.69	12.56	11.79	26.4	8.5-16.9		
API gravity	8.25	-		7	11.9-13.5		
Density [g/cm^3]	0.9994	-					
TLC analysis [%]							
Peak 1 Saturated	9.073		4.33			22.0	55.81
Peak 2 Aromatic	45.501		59.70			21.0	16.68
Peak 3 Resin	29.205		21.16			39.0	12.86
Peak 4 Asphaltene	16.222		14.81			18.0	14.65
Molecular weight [g/mol]	506	489			402-678		

* N.D.: Not Detected

references. The yield of bitumen which was extracted from Alberta oil sand by the above methodology was about more than 13%. Throughout the proximate and ultimate analysis it was composed mostly of volatiles and fixed carbons, with more than 85% and 5% of carbon and sulfur components, respectively. The composition was similar to the heavy residue, the bitumen of Alberta oil sand which was extracted by dichloromethane [2], and the bitumen in Athabasca oil sand [8], but the content of sulfur was different from the bitumens in Whiterocks oil sand [6]. The molecular weight of extracted bitumen by toluene and THF was 506 and 489 g/mol, respectively. And the heating value of extracted bitumen by toluene as a solvent was similar to that by THF as a solvent, with 9,900 kcal/kg, which was greater than that of heavy residue. The molecular weight and heating value of extracted bitumen in this study were consistent with those of bitumens in Whiterocks oil sand. By thin layer chromatography (TLC) analysis, saturates, aromatics, resins, and asphaltenes of the extracted bitumen by toluene were 9, 45.5, 29.2, and 16.2%, respectively. It was similar to heavy residue, but different from bitumens in Athabasca oil sand and in Whiterocks oil sand, which had aromatics about 21% and 16.7%, respectively.

Table 2 summarizes the heavy metal content in bitumens extracted by toluene and THF. Arsenic was not detected from the extracted bitumen, while large amounts of vanadium, nickel, copper, etc., were detected. The extracted bitumen by toluene as a solvent contained Ca, Fe and Mg more than three times compared with that by THF as a solvent. The heavy metal content in bitumen of SUNCOR oil sand [23] is also summarized in Table 2. The amounts of arsenic, vanadium, iron were similar to the bitumen in SUNCOR oil sand, while the amount of sodium was different. Compared with the bitumen in SUNCOR oil sand, heavy metal content was analogous to bitumen extracted by toluene.

2. Kinetic Analysis

Since previous researches for kinetic parameters indicated that the activation energy was calculated based on the first-order reaction [7-9,19,20], the pyrolysis of the Alberta oil sand was also assumed as a first-order reaction in this study. To calculate the activation energy based on the TGA experiments, the direct Arrhenius plot method [17] was used. The extent of conversion, X, was defined by as follows:

$$X=\frac{w_0-w_t}{w_0-w_\infty} \tag{1}$$

where w_0 is the initial weight, w_t is the weight after t minutes and w_∞ is the weight after complete pyrolysis. Thus, the rate of oil sand decomposition is given by:

$$\frac{dX}{dt}=A\exp\left(\frac{-E}{RT}\right)(1-X) \tag{2}$$

where A is the frequency factor (min^{-1}), E is the activation energy (J/mol), R is the gas constant (J/mol K), and T is the temperature (K). By introducing the heating rate, Eq. (2) can be modified by:

$$\frac{dX}{dT}=\left(\frac{A}{b}\right)\exp\left(\frac{-E}{RT}\right)(1-X) \tag{3}$$

where b gives dT/dt. Eq. (3) was rearranged as follows:

$$\ln\left[\frac{1}{(1-X)}\frac{dX}{dT}\right]=\ln\left(\frac{A}{b}\right)-\frac{E}{RT} \tag{4}$$

Table 2. Heavy metal contents in bitumens

	Bitumen by toluene	Bitumen by THF	Bitumen [23] (SUNCOR oil sand)
Heavy metal analysis [ppm]			
Arsenic	N.D.	N.D.	0.2-0.6
Vanadium	203.0	195.5	145-200
Nickel	71.7	70.2	
Calcium	25.3	8.26	
Cobalt	0.80	0.53	
Copper	0.73	0.63	
Iron	139.2	33.8	100-600
Magnesium	26.2	8.1	
Manganese	3.2	1.0	2.4-14
Molybdenum	10.0	9.4	
Sodium	15.1	9.3	30-120
Zinc	1.0	0.7	

* N.D.: Not Detected

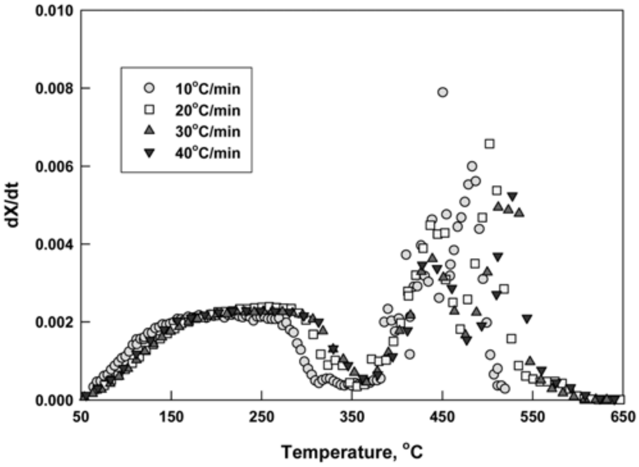

Fig. 3. DTG curves of Alberta oil sand at different heating rates.

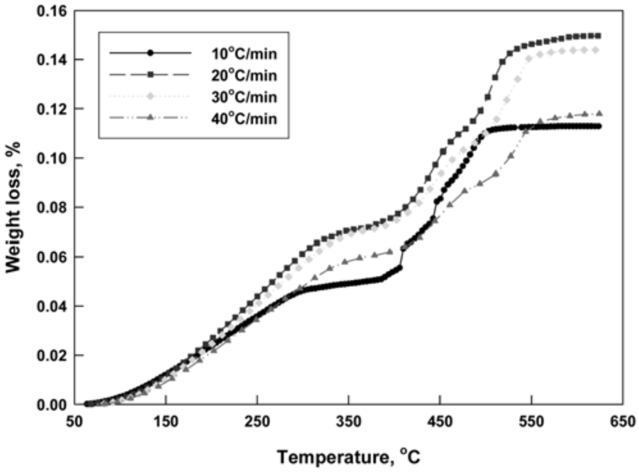

Fig. 4. TG curves of Alberta oil sand at different heating rates.

The values of E and A were calculated by using Eq. (4) by plotting the experimental values of ln[(dX/dT)/(1−X)] versus 1/T.

Figs. 3 and 4 show the differential thermogravimetric (DTG) and the thermogravimetric (TG) curves of Alberta oil sand at different heating rates. From those figures, the weight loss process of oil sand can be divided into two steps, such as devolatilization of light organics from 50 to 350 °C and carbonaceous decomposition of heavy organics between 350 and 600 °C [9,20]. The reaction region and peak temperatures were shifted to higher temperature with increasing heating rates as has been reported by others [9,20].

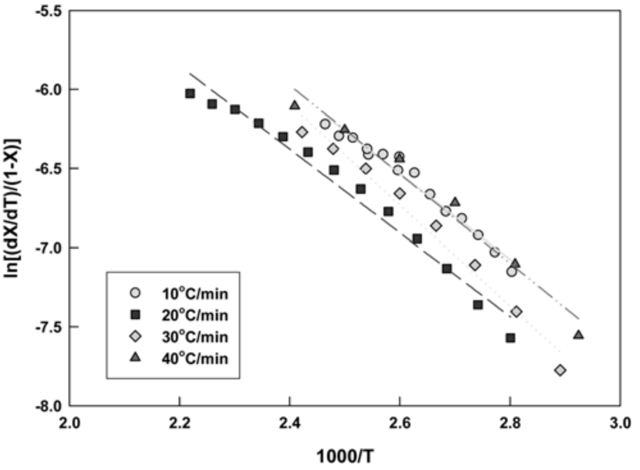

Fig. 5. Plot of ln[(dX/dT)/(1−X)] versus 1,000/T for devolatilization.

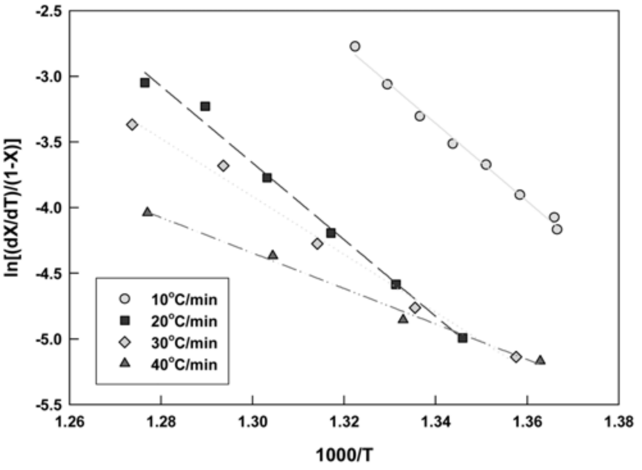

Fig. 6. Plot of ln[(dX/dT)/(1−X)] versus 1,000/T for carbonaceous decomposition.

Figs. 5 and 6 show a typical plot of ln[(dX/dT)/(1−X)] versus 1,000/T for the devolatilization and the carbonaceous decomposition, respectively, pointing to the reaction of oil sand pyrolysis which was described by a first-order reaction in the studied temperature region. From the slope and intercept of the line, the values of E and A can be obtained. Table 3 shows the kinetic parameters of Alberta oil sand pyrolysis at different heating rates. The coefficient of determination R^2 was close to unity for both the devolatilization and the carbonaceous decomposition, so the first-order reaction model was suitable [13]. The activation energy increased from 19 kJ/mol to 23 kJ/mol with the increase of the heating rate in the devolatilization, while it decreased from 246 kJ/mol to 146 kJ/mol with the increase of the heating rate in the carbonaceous decomposition. Li et al. [8] reported that the activation energy of Athabasca oil sand was 166 kJ/mol, that of Karamay oil sand was 207 kJ/mol, and that of Erlian oil sand was 122 kJ/mol. Khraisha [7] reported the activation energy of Jordan oil sand was 138 kJ/mol. Meng et al. [9] reported the activation energy of Tumuji oil sand was 176 kJ/mol. Sonibare et al. [20] reported that the activation energy of Ilubinrin oil sand was 324 kJ/mol and that of Oloda oil sand was 287 kJ/mol. All data from literature were calculated at the heating rate of 10 °C/min. At the same heating rate, the activation energy of Alberta oil sand was 246 kJ/mol, which was less than that of Ilubinrin and Oloda oil sands, but more than that of Athabasca, Karamay, Erlian, Jordan, and Tumuji oil sands. This may be attributed to the different properties of different oil sand.

CONCLUSIONS

Alberta oil sand extraction using modified Soxhlet extractor and pyrolysis kinetics using TGA have been performed. The composition of the extracted bitumen is similar to that of heavy residue and bitumen in Athabasca oil sand. By TLC analyses, however, the contents of saturates, aromatics, resins, and asphaltenes of the extracted bitumen are different from those of bitumens in Athabasca oil sand. By heavy metal analyses heavy metal contents were analogous with the extracted bitumen, compared with the bitumen in SUNCOR oil sand. By TGA analysis, the weight loss process of Alberta oil sand can be divided into two steps, such as devolatilization of light organics from 50 to 350 °C and carbonaceous decomposition of heavy organics between 350 and 600 °C. The activation energy in the devolatilization region is 19-23 kJ/mol and that in the carbonaceous decomposition region is 146-246 kJ/mol. At the same heating rate, the activation energy of the Alberta oil sand is similar to that of different oil sands. The results will be effectively applied to the fixed-bed or fluidized-bed pyrolysis.

Table 3. Kinetic parameters of Alberta oil sand pyrolysis at different heating rates

Heating rate (°C/min)	Devolatilization			Carbonaceous decomposition		
	E (kJ/mol)	A (min^{-1})	R^2	E (kJ/mol)	A (min^{-1})	R^2
10	19.54	1.6	0.9716	246.44	6.2×10^{15}	0.9930
20	21.96	1.0	0.9747	242.93	8.1×10^{14}	0.9916
30	22.30	1.2	0.9789	188.64	1.3×10^{11}	0.9914
40	23.38	2.2	0.9724	146.48	1.4×10^{8}	0.9912

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