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Effect of supercritical water on upgrading reaction of oil sand bitumen

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ABSTRACT

The advantages of supercritical water (SCW) as a reaction medium for upgrading oil sand bitumen were investigated through a comprehensive analysis of the output product, which includes gaseous products, middle distillate, distillation residue, and coke. Canadian oil sand bitumen mined by the steam assisted gravity drainage method was treated in an autoclave at 420–450 °C and 20–30 MPa for up to 120 min with three kinds of reaction media: SCW, high-pressure nitrogen, and supercritical toluene. The yields of gaseous products indicated that a very small amount of water was involved in the upgrading reaction. The analytical results of the middle distillate fractions were almost the same using water and nitrogen at 450 °C. The distillation residues produced in SCW had lower molecular weight distributions, lower H/C atomic ratios, higher aromaticities, and consequently more condensed structures compared to those produced in nitrogen. The coke produced using SCW also had lower H/C values and higher aromaticities. Judging from all the analytical results, the upgrading of bitumen by SCW reaction was primarily considered to be physical in nature. As a result, it is possible to highly disperse the heavy fractions by SCW. This dispersion effect of SCW led to intramolecular dehydrogenation of the heavier component and prevention of recombination reactions, and consequently gave the highest conversion.

1. Introduction

Oil sand bitumen is an important energy resource because of its abundant supply. The proven reserve in Canada is estimated to be about 170 billion barrels [1]. Steam assisted gravity drainage (SAGD) is a mining method that enables recovery of the bitumen in deep layers by injection of steam into the ground. Because the amount of bitumen minable by conventional surface mining methods is estimated to be only about 20% of the total reserve, in situ methods such as SAGD are increasingly important. The viscosity of bitumen mined using SAGD is not sufficiently low to transport by pipeline without some treatment. Therefore, development of an effective on-site upgrading process for bitumen is essential. Because hot bitumen and high-pressure water are already available at SAGD mine sites, treatment of the bitumen using supercritical water (SCW) could be a viable solution [2].

Researchers have subjected several types of heavy crude such as oil sand bitumen [2–4], vacuum residue [5,6], asphalt [7], heavy oil [8], and coal tar [9] to SCW treatment. They reported that SCW treatment resulted in greater yields of the light fraction and smaller amount of coke compared to treatment without SCW. However, the reaction mechanisms used in these previous research efforts were not the same. Kishita et al. showed that product distributions in the early stage of bitumen upgrading were not significantly different with or without SCW according to the gas chromatography/mass spectrometry spectra of the upgraded oils obtained, even when an alkali agent was added [4]. This indicated that SCW did not affect the reaction mechanism chemically. Zhao et al. proposed reaction passes for the treatment of vacuum residue with SCW in which the SCW acted as a hydrogen transfer agent via the OH radical [5]. Cheng et al. explained that the effect of water was mainly physical [6]. Sato et al. noted that the yield of maltene increased because hydrogen atoms were provided by SCW, and capped radicals were produced during the decomposition of asphalt [7]. They referred to a report by Moriya et al., who proposed a mechanism in which hydrogen was supplied to the system via hydration of low molecular weight olefin during the treatment of high-density polyethylene with SCW [10]. Han et al. proposed that some of the free radicals produced during the decomposition of coal tar might be quenched by H or OH radicals from SCW to produce light products [9].

The underlying question in the previous research was whether hydrogen atoms in water behave as a radical capping agent. Larger amounts of light oil could be produced if water could in fact be used as a hydrogen source. Even so, the chemical effects of water have yet to be demonstrated because of lack of detailed analyses of the overall output products. Although some researchers have compared the yields of maltenes and asphaltenes separated from product oil using a solvent such as hexane or pentane [7,9], this was not sufficient to

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evaluate the overall composition. The solvent separation method is not suitable for evaluating the differences in output composition because maltene can contain large amounts of heavy components including both output products and original components that may have suffered degradation during the upgrading reaction. In fact, bitumen mined by SAGD contains as much as 89 wt% maltene and 11 wt% asphaltene when using heptane as a solvent, and as much as half of the maltene is made up of heavy compounds whose boiling points are higher than 500 °C.

The objective of this work was to clarify the effect of SCW, especially its radical capping effect, during bitumen upgrading. We treated the bitumen in an autoclave with water, nitrogen, and toluene at temperatures in the range 420–450 °C. Nitrogen was selected as an inert medium, and toluene was used mainly to make products formed with a reactive medium, for comparison with water. Instead of solvent separation, we prepared the light and heavy fractions using distillation. First, we determined a good set of conditions with water that gave a higher yield of light fraction and lower yield of coke than with nitrogen. Then, we conducted comprehensive analyses and comparisons of the products produced under those conditions.

2. Experimental

2.1. Experimental procedure

Canadian bitumen (C: 83.5, H: 10.6, N: 0.5, S: 4.2, O: 1.0, others: 0.3 wt%) mined by SAGD was used. Two steel balls, each 7.0 mm in diameter, and 4.0 g of bitumen were placed in an autoclave of 50 cm^3 with 14 mm of an inside diameter (SUS316) and surrounded with either 8.0 g of water, nitrogen at a pressure of 8.0 MPa, or 22 g of toluene. When used water and toluene, air in the autoclave was replaced by 0.1 MPa of nitrogen. The autoclave was heated to a specific temperature (420, 430, 440, or 450 °C) at a rate of 25 °C/min using a tiltable electric furnace swinging about 39 times per min. The inner pressures at 420, 430, 440, and 450 °C of water were about 27, 28, 29, and 30 MPa, respectively. Those were about 23, 23, 24, and 25 MPa for nitrogen, and 22, 23, 25, 27 MPa for toluene, respectively. The critical temperatures and pressures of water, nitrogen, and toluene were 374 °C and 22.1 MPa, −147 °C and 3.4 MPa, and 321 °C and 4.1 MPa, respectively. Therefore, all the media were in supercritical states under the experimental conditions. The autoclave was heated for a specific time (30, 40, 60, or 120 min) after setting in the furnace, then the autoclave was removed and cooled to room temperature using an electric fan. The gaseous product was then collected in a gas bag, and the product remaining in the autoclave was recovered by washing with hot toluene. The toluene-insoluble fraction (coke) was separated by filtration, and the toluene-soluble product was recovered using a rotary evaporator. The liquid product obtained in this manner was distillated using a glass tube oven at 250 °C and 0.001 MPa, which corresponds to 420 °C at 0.1 MPa. Using this distillation process, the liquid product was separated into three fractions: unrecoverable volatile matter (VM), middle distillate (MD) and distillation residue (DR). The reproducibility error in the yield of each fraction was less than 5% with three extraction experiments at 450 °C with SCW.

The products prepared at 450 °C are referred to by the experimental conditions under which they were produced: reaction medium (W for water, N for nitrogen, or T for toluene) subscript (reaction time 60 or 120 min) – product (MD, DR, or Coke). For example, W_{60}-MD is the MD prepared with water at 450 °C for 60 min, and N_{120}-DR is the DR prepared with nitrogen at 450 °C for 120 min. The MD and the DR contained in the bitumen are abbreviated as B-MD and B-DR, respectively.

2.2. Product analysis

The volume of gaseous products diluted with nitrogen was measured using a syringe, and the concentration of C_1 to C_3, CO, CO_2, and H_2 were determined using a gas chromatograph (Model 6890; Agilent). MDs were analyzed in terms of boiling point distribution, molecular weight distribution, elemental composition, hydrogen type distribution, carbon type distribution, and compound distribution. ASTM D2887 was adopted to measure boiling point distributions using a gas chromatograph (Model 6890; Agilent) and a column with an inside diameter of 0.53 mm, a length of 10,000 mm, and film thickness of 0.1 μm (forte BPX1; SGE Analytical Science Pty Ltd.). Molecular weight distributions were measured at 40 °C with tetrahydrofuran using a gel permeation chromatography (GPC) system (Gulliver series; JASCO) with columns (Mixed-D; Varian, Inc.) having an exclusive limit of 400,000 amu, as well as a refractive index detector. Elemental compositions were determined using a CHNS analyzer (EA-1110CHNS-O; Thermoquest Co. Ltd.). ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy (Lambda-500; JEOL Co. Ltd.) were performed to measure the hydrogen and carbon type distributions, respectively. The detailed procedure for the NMR measurement was described in a previous paper [11]. MDs were analyzed using the gas chromatograph equipped with three kinds of detectors (flame ionization detector (FID), sulfur chemiluminescence detector (SCD), and nitrogen phosphorus detector (NPD)) to obtain the distributions of carbon-, sulfur-, and nitrogen-containing compounds, respectively. A gas chromatograph–mass spectrometer (GC–MS, 6890GC-5973MSD; Agilent) was used to identify several components in the MD. In addition, several fractions separated from the MD were treated as measuring samples for high-performance liquid chromatography (HPLC) analysis. The amounts of saturate (SA), monocyclic aromatic (MA), polycyclic aromatic (PA), and polar (PO) compounds in the MD were determined using a HPLC system (Model 1100; Agilent) with a column having an inside diameter of 4.6 mm, a particle diameter of 5 μm, and length of 200 mm (Hypersil APS; Agilent) with hexane as a developing solvent. The MD was also separated into SA, aromatic (AR), and PO fractions using a solid phase extraction system (ASPEC XL; Gilson, Inc.) with an alumina column and hexane, dichloromethane, and a mixture of dichloromethane and methanol as extraction solvents. The fractions of SA, AR, and PO were analyzed using the gas chromatograph with a FID.

DRs were analyzed in terms of molecular weight distribution, elemental composition, hydrogen type distribution, carbon type distribution, and Conradson carbon residue (CCR). Each analytical method was the same as described above, and CCR was determined using ASTM D189. In addition, the average molecular structures of DRs were analyzed using our method [12] based on the Brown–Ladner method, the details of which are described in a previous paper [11]. In this procedure, ^{1}H and ^{13}C NMR analyses are essential for assigning the H and C atom distributions to estimate the average structural parameters for the DR. Hydrogen atoms are usually classified into four types: aromatic hydrogen (H_a), hydrogen atoms bonded to aliphatic carbon atoms in the α position of an aromatic ring (H_α), hydrogen atoms attached to methyl groups in long side chains (H_γ), and other aliphatic and naphthenic hydrogen (H_β). Polystyrenes were used in the GPC analysis as the calibration standard for molecular weights greater than 800, and decacyclene (Mw = 451) and 2, 9, 16, 23-tetra-t-butyl-29H, 31H-phtalocyanine (Mw = 739) were used for molecular weights less than 800 [13].

The coke was analyzed in terms of elemental composition and carbon aromaticity (f_a), which were determined using a solid-state ^{13}C cross-polarization magic angle spinning (MAS) NMR (CMX-300; Chemagnetics) at a ^{13}C frequency of 75.46 MHz and MAS rate of 10 kHz, with a contact time of 1 ms and a pulse repetition time of 4 s for 3600 scan times.