

Liquefaction of Heavy Oil and Its Model Compounds in Supercritical Water

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An upgrading process for heavy oil and its model compounds were investigated in supercritical water using batch reactor. Bitumen was mainly obtained as a residue of the petroleum refining process. In fact, bitumen is of great importance to the chemical industry because of its great variety of special properties, which has favored the development of a wide field of applications. The development of process has been proposed to recover chemical resources from bitumen that can accomplish the destruction of the bitumen into harmless to produce useful compounds. Water at hydrothermal condition is considered a promising and an environmentally acceptable solvent for a wide variety of chemical reactions such as organic syntheses and decomposition of hazardous waste into harmless compounds. In these works, water at supercritical conditions was applied as a solvent for degradation of swelled biomass resources and solid waste polymers or upgrading of bitumen and its model compounds. The experiments were conducted at temperature of 673 K and at various reaction pressures. The chemical species in the aqueous products were analyzed by gas chromatography mass spectrometry. The effect of pressure and reaction time on the decomposition process was presented. Ultimate analysis of solid residue was also conducted using a CHN analyzer. Moreover, this method could become an efficient method for upgrading bitumen into harmless and high yield of valuable chemical intermediates on the basis of the experimental results.

INTRODUCTION

The bitumen as a part of heavy oils is one of the world's largest petroleum resources. But, bitumen was an under-utilized resource because of its inherently poor quality. Generally, bitumen industrial application only concerned the road pavement and recently has been more dedicated to the inerting of waste. The utilization of bitumen is very interesting and the development process has been proposed to recover chemical compounds from bitumen. Hydrocracking is one of the current routes for upgrading bitumen. In this process, bitumen was characterized by the conversion of the higher molecular weight constituents in feedstocks to lower boiling products. This process is also used for the purpose of improving product quality without appreciable alteration of the boiling range. However, hydrogen supply is a major cost in hydrocracking. Therefore, alternative upgrading processes that do not use externally supplied hydrogen are desirable.

Supercritical water ($T_c = 647$ K; $P_c = 22.1$ MPa) is an environmentally acceptable solvent for a wide variety of chemical reactions and it was not only participates in a reaction as a solvent but also as a reactant [1,2]. Supercritical water is a dense steam and can be miscible with light gases and hydrocarbons to form a homogeneous phase by the proper choice of temperature and pressure [1]. C-C and C-O bonds, such as those found in ethers and esters, and the aliphatic C-H and C-S bonds are easily broken in supercritical water [1,3,4]. The thermal reaction of heavy oil is of considerable practical interest and it has been studied in supercritical water. Under supercritical conditions, two major reactions occur: oxidation and hydrolysis [5-7]. Because of these reactions, tar could be decomposed successfully into useful chemical compounds in supercritical water [8,9]. Hu et al. [10] treated oil shale with supercritical water and resulted in a higher conversion and a larger oil recovery than that obtained from toluene extraction. Supercritical water gave also more facile decomposition of the polar components in oil shale compared with supercritical toluene [11]. These results indicated that supercritical water can be an effective solvent for the extraction and decomposition of heavy hydrocarbons.

In these works, supercritical water will be used in the upgrading of bitumen. Water might be a cheaper source for hydrogen that is required in upgrading bitumen and provides the incentive for this investigation. The process of upgrading bitumen in supercritical water can be considered to proceed in two steps: bitumen dissolution in solvent and transformation of the initially formed primary decomposition products into light liquids. The extent of either process depends on the nature of the bitumen and the reaction conditions, such as the presence or absence of donor solvents. When bitumen is heated, numerous radicals are obtained as a result of thermal cleavage. These radicals can be stabilized by the addition of hydrogen, provided from a donor solvent. The aim of this work was to determine the reaction mechanism of bitumen in supercritical water without catalyst. The effects of water and reaction time on the conversion of bitumen using a batch reactor will be discussed.

MATERIALS AND METHODS

Bitumen was obtained from the industrial oil distillation process (Shell Canada) and used as a starting material. The chemicals used were almost purchased from Wako Pure Chemicals Industries Ltd. (Osaka, Japan) and had purity >95.0%. Others, they are purchased from Sigma-Aldrich Corp. (SIGMA-ALDRICH Japan K.K.) and received from company. All chemicals were used as received.

Experiments were conducted using a Hastelloy C-276 tube reactor (AKICO Co., Ltd., Tokyo, Japan). The reactor was loaded with 0.3 g of bitumen and pure water. Argon gas was used to purge the reactor before it was sealed. The reactor was placed into an electric furnace (ISUZU Co. Ltd., model NMF-13AD) and heated up. The time required to heat up the reactor from room temperature to desired temperature was 4 min and after that the reactor temperature was the same as the furnace temperature. After a given amount of time (5, 15, 30, 60, and 120 min), inclusive of heat up time of about 4 min, the reactor was removed from the electric furnace and quickly quenched in a water bath at atmospheric conditions. After cooling, the liquid and solid fractions were collected. In this study, the gaseous fraction was not collected. The liquid products were analyzed by gas chromatography mass spectrometry (GC-MS) and matrix-assisted laser desorption ionization time of flight mass spectroscopy (MALDI-TOF-MS). The solid products were defined as asphaltenes and dried in vacuum

evaporator then cooled in desiccator for 1 day at room temperature and then weighed. On the other hand, asphaltene at each operating temperature was analyzed by a spectrum one fourier transform infrared spectroscopy (FT-IR) spectrophotometer and a CHN analyzer (Yanaco, CORDER MT-6). The same method was used for the bitumen model compounds experiments as the starting materials.

RESULTS

In order to understand the solubility of bitumen in aliphatic and aromatic solvents, n-hexane, chloroform, tetrahydrofuran (THF), and toluene were applied as solvents. Bitumen was dissolved in these solvents at room temperature. The amounts of the solvent are 40 times of bitumen in volume. They were mixed and shaken. After 6 hours, they were removed from shaker mechanical device and kept overnight. The results showed that bitumen can dissolve completely in chloroform, THF, and toluene.

In n-hexane, the precipitation occurred. Next, to determine the content of asphaltene in bitumen, the aliphatic solvents (alkanes) derived from petroleum were used as solvents. They are n-pentane, n-hexane, n-heptane, and n-dodecane. Ultrasonic was applied at each sample. The collected solution (bitumen and solvent) was filtered using a membrane filter paper. The insoluble product was defined as asphaltene and dried for 1 day at room temperature and then weighed. Toluene is also used

as a solvent for determination of coke. The weight of the asphaltene can be determined by subtracting the weight of the filter papers from total weight. As shown in **Figure 1**, the solubility of bitumen could approach to 88.40 (g of bitumen/40 g of solvent) and took place at 15 min of ultrasonic with solvent n-dodecane. The solubility of bitumen in n-pentane and n-hexane was almost similar. In this work, based on these results, n-hexane was decided as a solvent extraction. On the other hand, n-hexane has many uses as a special-purpose solvent

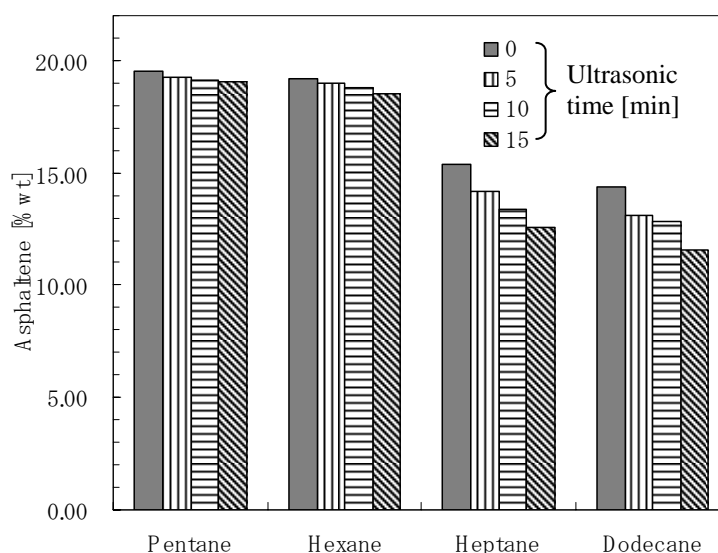


Figure 1. The content of asphaltene in bitumen.

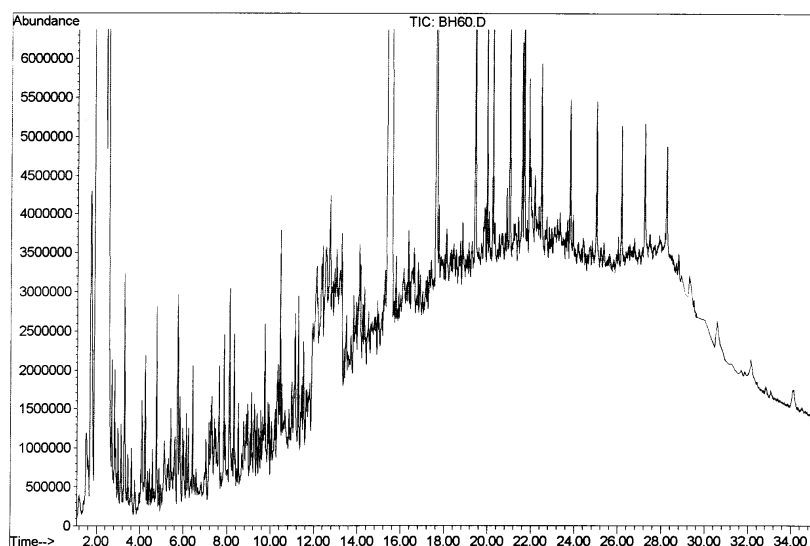


Figure 2. GC-MS chromatogram of bitumen after treatment by supercritical water.

and oil extractant. In a highly purified form, n-hexane is used in chemical laboratories as an extractant for a wide range of hydrocarbons and non-polar organic compounds. It is also a minor constituent of crude oil and natural gas and had boiling point higher n-pentane and lower n-heptane.

A variety of processes are available for converting the petroleum into more valuable products. The upgrading of bitumen by supercritical water is one of thermal techniques to study the nature of the volatile thermal fragments from bitumen. This thermal technique has produced strong evidence for the presence of lower or small aliphatic or aromatic systems. Regarding of this purpose, the analysis of products in n-hexane soluble was performed by GC-MS. It was well known that GC-MS is a powerful tool or method for identified the aromatic and aliphatic compounds. The identities of these compounds determined through a match of mass spectra in the GC-MS computer library are reliable. They contained a wide range of organic compounds. The results of the bitumen product compositional analysis after treatment by supercritical water appear in **Figure 2**. Among these, the aromatic compounds, i.e. benzene, toluene, alkylbenzene, anthracene, phenanthrene, carbazole and xylenes. The aliphatics compound such as alkanes and alkene were detected. The compounds had higher boiling point such as eicosane, benzopyrene, picene, coronene, and pyranthrene were not detected by GC-MS due to their high boiling point. Aromatic compounds have dominated as the degradation products of bitumen at these conditions. Thus, it is reasonable to assume that these products are derived from the cleavage of ether and ester linkages of bitumen.

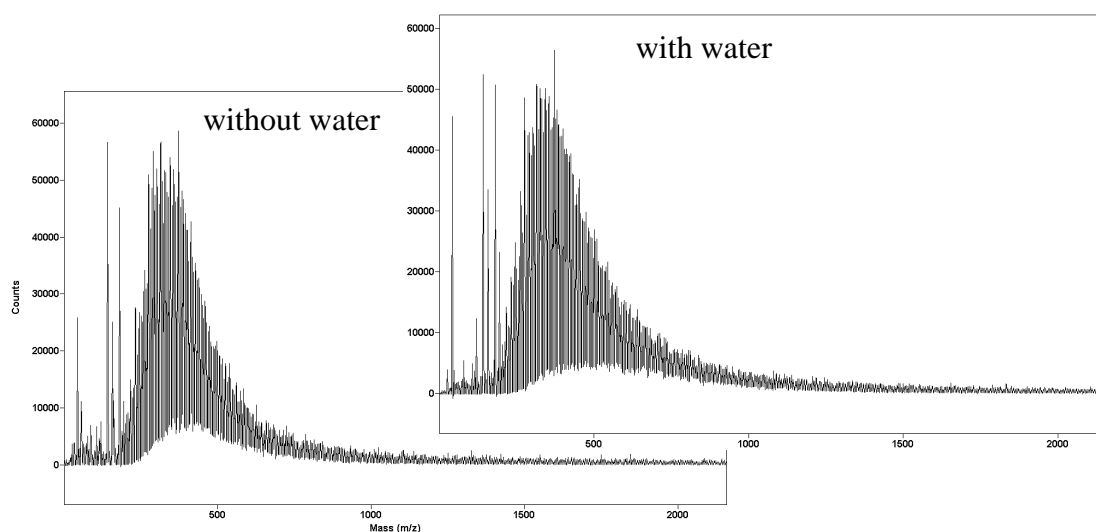


Figure 3. MALDI-TOF MS chromatogram for bitumen after treatment at 673 K.

It is well known that the thermal decomposition technique products were separated into gases, liquid products and solid residue. In this work, the gas product was not be recovered. Most of the thermal decomposition technique products of bitumen in liquid phase can be classified as aromatic compounds. **Figure 3** shows the molecular weight of bitumen-derived compounds in n-hexane soluble was measured by MALDI-TOF-MS associated with m/z numbers, which is considered to give highly reliable information on polymer molecular weights. This figure shows that the decomposition of bitumen is almost completed under supercritical conditions, forming species of low molecular weight (200 to 700 amu). This result suggested that water had high influence to the decomposition of bitumen, which is probably because the degree of ionic dissociation of water at the same temperature.

The thermal decomposition of bitumen supercritical water can be considered to proceed in two steps: bitumen liquefaction in solvent and transformation of the initially formed primary liquefaction products into light liquids. This mechanism is very complex resulting in the formation of numerous compounds. A better understanding of thermal decomposition of bitumen pathways can be achieved by identifying the main intermediate compounds that formed during bitumen decomposition. In this study, dodecylbenzene (DDB), phenanthrene, and pyrene have been chosen as bitumen model compounds.

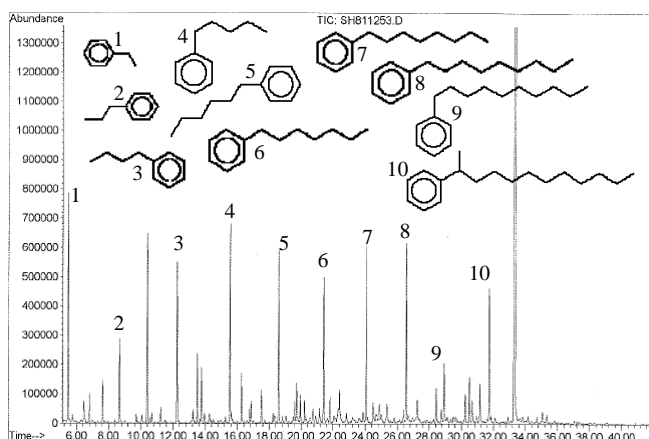


Figure 4. GC MS chromatogram of DDB, showing its derived compounds.

The amount of organic compounds from decomposition of DDB in the liquid portion was determined qualitatively. **Figure 4** shows GC-MS identification of the compounds contained in the liquid portion recovered after treatment at 723 K; 60 min. The large peaks were ethylbenzene (1), propylbenzene (2), butylbenzene (3), pentylbenzene (4), hexylbenzene (5), heptylbenzene (6), octylbenzene (7), nonylbenzene (8), decylbenzene (9), and 1-methylundecylbenzene (10).

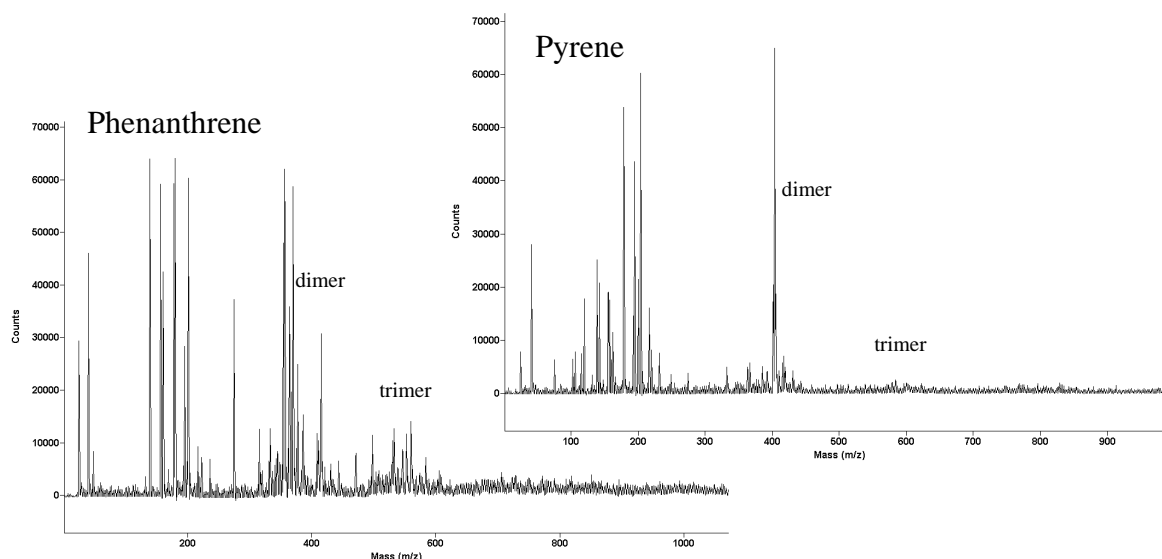


Figure 5. MALDI-TOF MS of phenanthrene and pyrene after treatment at 773 K; 60 min reaction time, respectively.

The characteristics of phenanthrene and pyrene after treatment by supercritical water was performed by MALDI TOF-MS. **Figure 5** shows a typical MALDI spectrum of them. These figures show that the products consist of oligomers clearly shown such as dimer and trimer. Dimers were defined as the molecular weight around 360 and 400 amu for phenanthrene and pyrene, respectively. Trimers from phenanthrene derived compounds appeared clearly at 430-450 amu. The degradation and polymerization reactions have led to the formation of numerous ringed structures of similar molecular weight. Although MALDI can be used to accurately determine the molecular weight, the technique has yet to be established as a

quantitative method of analysis. Therefore, in this work, the relationship between the intensity of a MALDI peak and the mass of that species in the liquid phase product is unknown.

CONCLUSION

The liquefaction of bitumen and the decomposition of its model compounds were carried out at 673 K and 723-773 K. These processes constitute a powerful technology for the transformation of hazardous which had high-molecular-weight into useful chemical compounds. These results suggest that supercritical water can be an effective solvent for the extraction and decomposition of them. With increasing reaction time, the amounts of bitumen-derived compounds formed were increased. The process was accelerated with increasing water density at the same temperature. MALDI spectrum shows that oligomers formed by degradation and polymerization reactions of phenanthrene and pyrene.

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