

# STUDY ON SUPERCRITICAL WATER BEHAVIOR OF BITUMEN

Wahyudiono<sup>1</sup>, Mitsuru Sasaki<sup>2,\*</sup>, Motonobu Goto<sup>1</sup>

<sup>1</sup>Bioelectrics Research Center, Kumamoto University, Japan

<sup>2</sup>Graduate School of Science and Technology, Kumamoto University, Japan

Phone: +81-96-342-3666; Fax: +81-96-342-3679; E-mail: msasaki@kumamoto-u.ac.jp

## Abstract

Bitumens were mainly obtained as a residue of the petroleum refining process and generally they are used for paving roads, roofing, coating, insulation, etc. In fact, bitumens are of great importance to the chemical industry because of their great variety of special properties, which has favored the development of a wide field of applications. They can be considered as colloidal systems in which micelles of high-molecular-weight organic molecules (asphaltenes) are dispersed in an oily phase (maltenes) consisting of low-molecular-weight saturated and aromatic hydrocarbons together with resins. The development of process has been proposed to recover chemical resources from bitumens that can accomplish the destruction of the bitumens into harmless to produce useful compounds. It was well known that 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 without catalyst. The experiments were conducted using a batch-type reactor at temperature of 673 K. The chemical species in the aqueous products were analyzed by gas chromatography mass spectrometry and gas chromatography flame ionization detector. 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 [5-9]. Because of these reactions, tar could be decomposed successfully into useful chemical compounds in supercritical water [10,11]. Hu et al. [12] 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 [13]. 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.

## Experimental

### *Materials*

Bitumen was obtained from the industrial oil distillation process (Shell Canada) and used as a starting material. First, the crude oil is distilled under atmospheric pressure in order to separate the volatile fractions from the heavy products. Then, the heavy products are submitted to a vacuum distillation. The residue obtained after this second distillation constitutes the bitumen. At room temperature, the bitumen is soluble in toluene, chloroform, and tetrahydrofuran. 2,5-dihydroxybenzoic acid (DHB) were purchased from Wako Pure Chemicals Industries, Ltd. (Osaka, Japan) and had purities of more than 98.0%. The analytical reagents used were *n*-pentane (98.0%), *n*-hexane (96.0%), *n*-heptane (99.0%), *n*-dodecane (99.0%), toluene (99.5%), chloroform (99.7%), and tetrahydrofuran (99.8%) from Wako Pure Chemicals Industries Ltd. (Osaka, Japan). All chemicals were used as received.

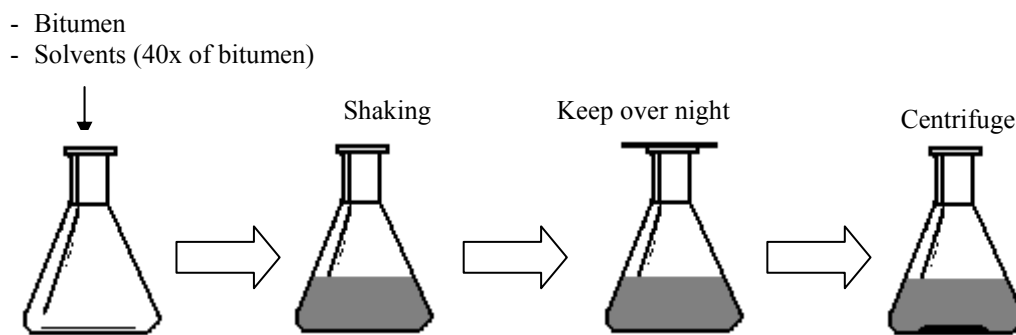
### *Experimental Procedure*

Experiments were conducted using a Hastelloy C-276 tube reactor (AKICO Co., Ltd., Tokyo, Japan; with internal volume 8.8 cm<sup>3</sup>). The reactor was loaded with 0.3 g of bitumen without any treatments and amounts of pure water were added corresponding to 0.10-0.40 g.cm<sup>-3</sup> water density. Pressures were calculated from the steam tables. 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 quickly heated to 673 K. 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 temperature and pressure. After cooling, the liquid and solid fractions were collected by washing the inside of the reactor with pure hexane was 15 mL. The collected product solution was separated using a

centrifuge and vacuum evaporation. Each experiment was conducted in duplicate/triplicate and reported as mean standard deviation. In this study, the gaseous fraction was not collected. Furthermore, the gas products were negligible in the yield calculation. The liquid products were analyzed by gas chromatography mass spectrometry/ flame ionization detector (GC-MS/FID) after extraction with hexane. 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. Matrix-assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF-MS) analysis was also conducted for liquid product with DHB as a matrix. On the other hand, asphaltenes 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).

## Results and Discussion

In this work, in order to understand the solubility of bitumen in aromatic and aliphatic solvents, *n*-hexane, chloroform, tetrahydrofuran (THF), and toluene were applied as solvents. Bitumen was dissolved in these solvents at room temperature. The amount of bitumen is about 0.10924~0.11034 g and the amounts of the solvent are 40 times of bitumen. They were mixed and shaken (see Figure 1). After 6 hours, they were removed from shaker mechanical device and kept over night. The results showed that bitumen can dissolve completely in chloroform, THF, and toluene (see Table 1). In *n*-hexane, the precipitation occurred.



**Fig. 1.** Scheme of solubility experiment.

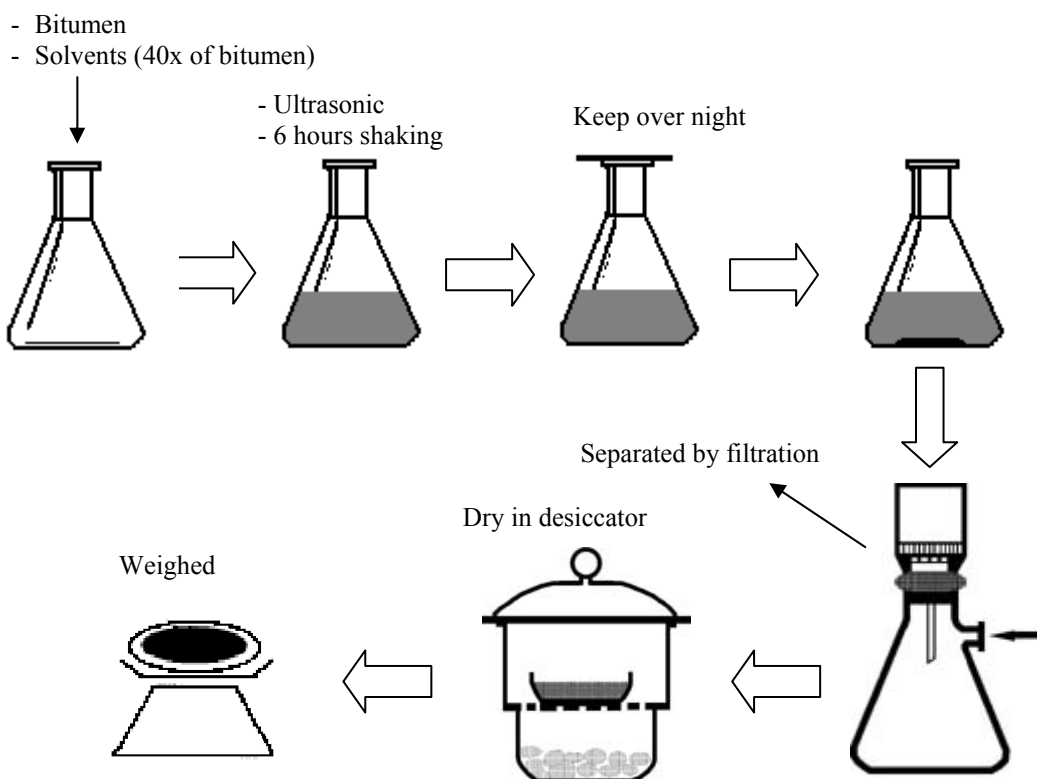
**Table 1.** The solubility of bitumen

Conditions	Solvent	Solubility of bitumen
	<i>n</i> -Hexane	Incompletely
- Room temperature	Chloroform	Completely
- Shaken	THF	Completely
	Toluene	Completely

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. According to the standard procedure for separating asphaltene from bitumen, the volume of each solvents that is 40 times the volume of the aliquot bitumen. Experiments were performed at room temperature. Ultrasonic was applied at each sample at 0, 5, 10, and 15 min. Then they were shaken using mechanical device about 6 hours and kept over night. The collected solution (bitumen and solvent) was filtered using a

membrane filter paper. The insoluble product was defined as asphaltene and dried in a desiccator for 1 day at room temperature and then weighed. In order to understand the content of coke in bitumen, toluene 40 times of weight of asphaltene was added at each asphaltene dried (see Figure 2). Then the same procedure was performed. The weight of the asphaltene can be determined by subtracting the weight of the filter papers from total weight. The asphaltene content is calculated by:

$$\text{Asphaltene [wt \%]} = \frac{\text{Weight of dried asphaltene (g)}}{\text{Weight of bitumen (g)}} \times 100 \quad (1)$$

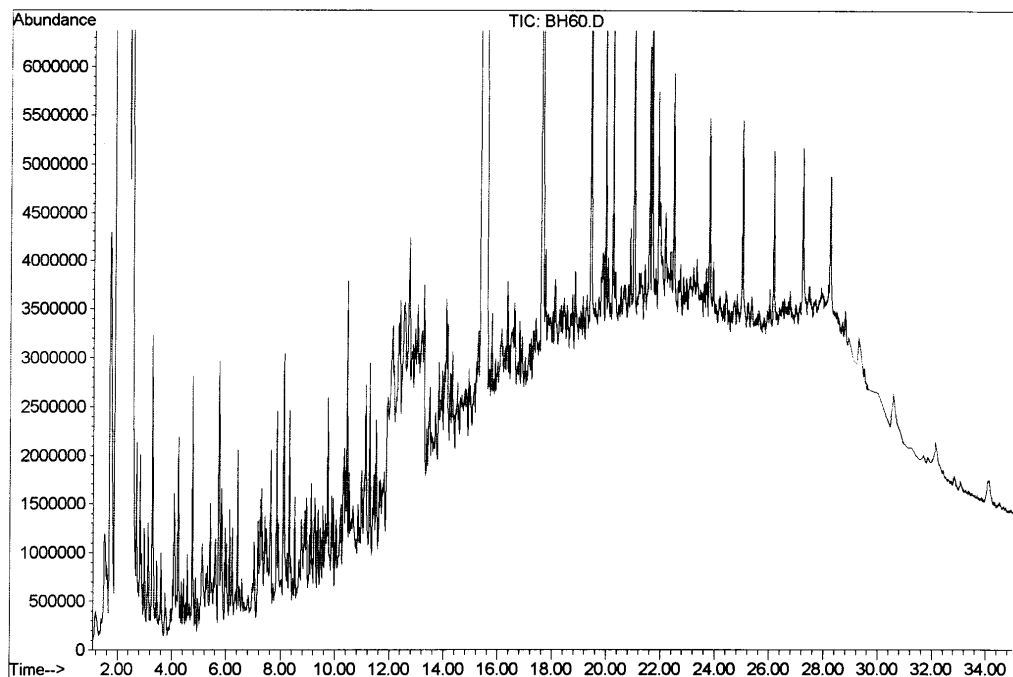


**Fig. 2.** Scheme of asphaltene determination.

Based on the results, *n*-hexane was decided as a solvent extraction for upgrading of bitumen at supercritical water. Because it was well known that *n*-hexane has many uses as a special-purpose solvent 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.

Petroleum is not a uniform material. 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 (see Figure 3). It was well known that GC-MS is a powerful tool or method for identified the aromatic and aliphatic compounds. Mass spectrometry, used as a detection method, gives the molecular weight and, with fragmenting ionization, the compound type of each peak. On the other hand, GC-FID was also

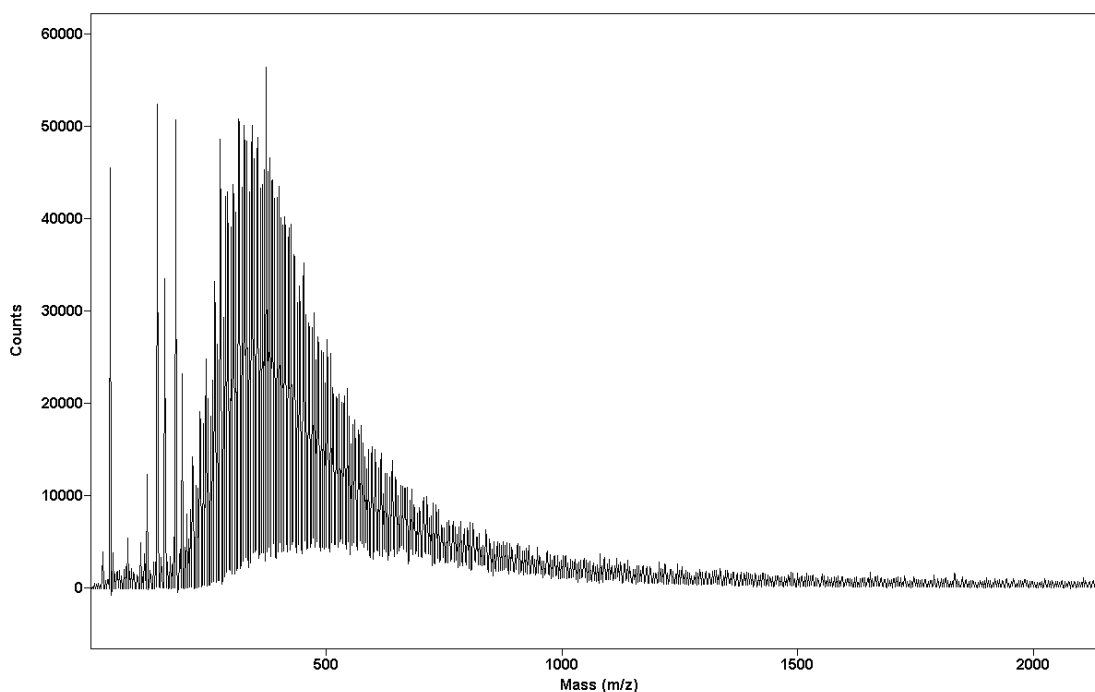
applied as a comparison results. The identities of these compounds determined through a match of mass spectra in the GC-MS computer library are reliable. They contained a wide range of organic compounds. Among these, the monocyclic volatile-aromatic compounds, i.e. benzene, toluene, ethylbenzene and xylenes. The aliphatics compound such as alkanes (pentane, heptane, dodecane) and alkene (pentene, isopentene) were detected. Unfortunately the compounds had higher boiling point such as eicosane, benzopyrene, picene, coronene, and pyranthrene were not detected by GC-MS/FID due to their high boiling point. Also, the NIST (National Institute of Standards and Technology) mass spectral library was used for identification of compounds in the liquid phase products both of them. 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.



**Fig. 3.** GC-MS chromatogram of upgrading bitumen at 673 K; 1.76g of water; 60 min.

In general the thermal decomposition technique products were separated into gases, liquid products and solide residue. Unfortunately the gas product could not be recovered. Most of the thermal decomposition technique products of bitumen in liquid phase can be classified as aromatic compounds. Figure 4 show 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. The difference in the peak intensity qualitatively corresponds to the amounts of dissolved bitumen derived compounds in *n*-hexane; nevertheless, the non homogenous spread of the sample on the target spots could not render a quantitative precise of the analysis. Therefore, molecular weight distributions can be clearly observed. This figure shows that the decomposition of bitumen is almost completed under supercritical conditions, forming species of low molecular weight (200 to 700 amu). Quantitatively, the peaks intensities bitumen obtained by decomposition in lower water density or shorter reaction time was higher than those in high water density or longer reaction time.

Judging from these results, higher water density or longer reaction time decreased the amount of the higher molecular weight compounds and increased that of lower molecular weight compounds.



**Fig. 4.** MALDI-TOF MS chromatogram for bitumen after treatment at 673 K; 1.76 g of water; 60 min.

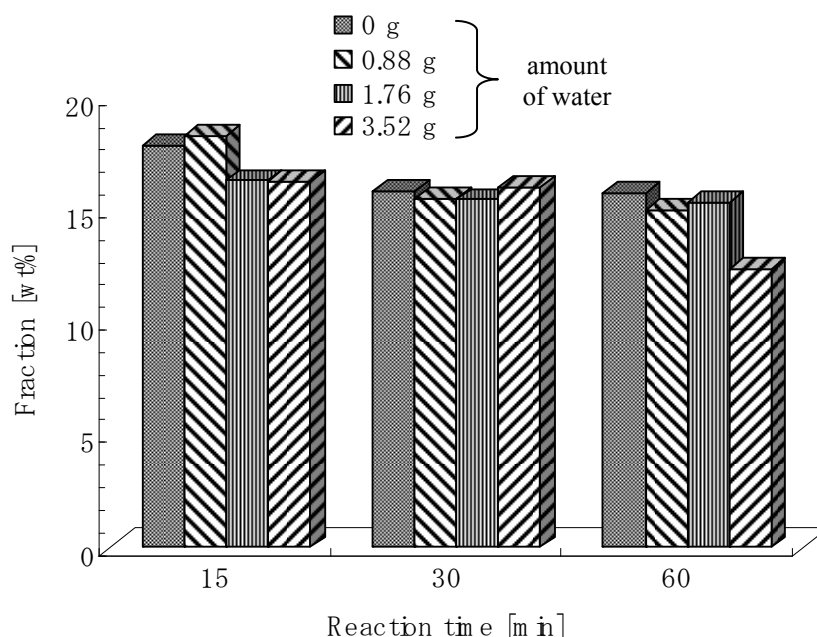
Ultimate analysis of solid residue was also conducted using a CHN analyzer (Yanaco, CORDER MT-6). This analysis was performed to determine the amount (typically a weight percent) of an element in a compound. The most common type of elemental analysis is for carbon, hydrogen, and nitrogen (CHN analysis). This type of analysis is especially useful for organic compounds (compounds containing carbon-carbon bonds). Table 2 shows the ultimate analysis of solid residue content in weight % dry and ash free material (wt% DAF). The concentration of carbon increased gradually with increasing reaction time. The loss of hydrogen in the solid residue is reflected in the decrease in hydrogen content during the thermal decomposition process at these conditions. These results also showed that dehydrogenation occurred.

**Table 2.** Elemental analysis of solid residue by CHN analyzer.

Temp. [K]	Time [min]	Ultimate analysis [wt. %, DAF]				Atomic ratio [-]	
		C	H	N	O*	H/C	O/C
Room <sup>+</sup>	-	80.45	8.36	1.40	9.79	0.104	0.122
673	30	81.55	8.61	1.00	8.84	0.106	0.108
(1.76 of	60	82.19	7.76	1.73	8.32	0.094	0.101
water)	120	82.56	7.01	1.31	9.12	0.085	0.110

It is known that the thermal decomposition of compounds was promoted by increasing water density, which implies that the transition state of the rate-determining step was stabilized compared to the

corresponding reactants. Figure 5 showed the time-evolution profile on bitumen decomposition in supercritical water at 673 K at various water densities, respectively. It shows that bitumen decomposition was enhanced gradually by increasing water density. This phenomenon can be explained by considering electrostatic effects, which are described in terms of the solvent dielectric constant. If the transition state is more polar than the reactants, an increase in the dielectric constant causes the liquefaction process to increase. However, the trend of bitumen decomposition with respect to the reaction time appears quite different. At lower water density, the degree of bitumen decomposition was enhanced gradually by increasing reaction time. When the water density was high, it was unpredictable. In that range, due to the proximity of the critical point, water properties differ from the supercritical ranges and are very sensible to small changes in the operation conditions, leading to a great scatter in experimental data. It is clear that the liquefaction of bitumen in general increases with increase in temperature reaction.



**Fig. 5.** The asphaltene content in bitumen after treatment by supercritical water at 673 K.

## Conclusions

The hydrothermal upgrading of bitumen was carried out using a batch-type reactor at 673 K and various pressures. 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 bitumen. With increasing reaction time, the amounts of bitumen-derived compounds formed were increased. The decomposition process of bitumen was accelerated with increasing water density at the same temperature. Based on these results, it is proposed that supercritical water treatments could become a benign technology for upgrading bitumen to recover useful chemical compounds.

## Acknowledgments

This work was conducted through the Kumamoto University 21<sup>st</sup> COE Program “Pulsed Power Science”. It was also supported by the Japan Petroleum Energy Center (JPEC) as a technological development project supported financially by the Ministry of Economy, Trade and Industry, Japan.

## References

1. Savage, PE. (1999), “Organic chemical reactions in supercritical water,” *Chem Rev*, pp. 603–621.
2. Akiya, N, Savage, PE. (2002), “Roles of water for chemical reactions in high-temperature water,” *Chemical Reviews*, pp. 2725–2750.
3. Tagaya H, Suzuki Y, Kadokawa J, Karasu M, Chiba K. (1997), “Decomposition of model compounds of phenol resin waste with supercritical water,” *Chem Lett*, pp. 47–48.
4. Lachance R, Paschkewitz J, DiNaro J, Tester JW. (1999), “Thiodiglycol hydrolysis and oxidation in sub- and supercritical water,” *J Supercrit Fluids*, pp. 133–147
5. Goto M, Nada T, Kawajiri S, Kodama A, Hirose T. (1997), “Decomposition of municipal sludge by supercritical water oxidation,” *J Chem Eng Jpn*, pp. 813-881.
6. Goto M, Nada T, Ogata A, Kodama A, Hirose T. (1998), “Supercritical water oxidation for the destruction of municipal excess sludge and alcohol distillery wastewater of molasses,” *J Supercrit Fluids*, pp. 277-282.
7. Sasaki M, Kabyemela B, Malaluan R, Hirose S, Takeda N, Adschiri T. (1998), “Cellulose hydrolysis in subcritical and supercritical water,” *J Supercrit Fluids*, pp. 261-268.
8. Sasaki M, Fang Z, Fukushima Y, Adschiri T, Arai K. (2000), “Dissolution and hydrolysis of cellulose in subcritical and supercritical water,” *Ind Eng Chem Res*, pp. 2883-2890.
9. Adschiri T, Shibata R, Arai K. (1997), “Phenol recovery by BPA tar hydrolysis in supercritical water,” *Sekiyu Gakkaishi*, pp. 291-297.
10. Wahyudiono, Fujinaga S, Sasaki M, Goto M. (2006), “Recovery of phenol through the decomposition of tar under hydrothermal alkaline conditions,” *Chem Eng Technol*, pp. 882-889.
11. Wahyudiono, Sasaki M, Goto M. (2007), “Noncatalytic liquefaction of tar with low-temperature hydrothermal treatment,” *J Mater Cycles Waste Manage*, pp. 173-181.
12. Hu H, Zhang J, Guo S, Chen G. (1999), “Extraction of Huadian oil shale with water in sub- and supercritical states,” *Fuel*, pp. 645–651.
13. Funazukuri T, Yokoi S, Wakao N. (1988), “Supercritical fluid extraction of Chinese Maoming oil shale with water and toluene,” *Fuel*, pp. 10–14.