

Comparison Study of Heptylbenzene and Hexylbenzene Decomposition under Supercritical Water

Pradip C. Mandal, Sujan Chowdhury, and Mitsuru Sasaki

Abstract—The world reserves of conventional light oils are decreasing and being replaced by an increasing amount of heavy oils. Heptylbenzene (HPB) and hexylbenzene (HXB) are compounds that are also present in heavy oils. This study is aimed at comparing the supercritical hydrolysis reaction of HPB and HXB producing low molecular weight hydrocarbons. The dramatic change in the ionic product and the dielectric constant of water under supercritical conditions makes it an acid or a base catalyst. In this study, water was used without any catalyst. The reaction was carried out in an 8.8 mL batch type reactor fabricated from Hastelloy C-276 whose respective design temperature and pressure was 500°C and 50 MPa. The comparison study on the ability of supercritical water (SCW) to decompose HPB and HXB were studied at temperatures of 450-475°C and water partial pressure (WPP) of 35 MPa. The experimental results show that conversion as well as production of low molecular weight compounds was high at water to oil ratio of 10, a reaction time of 60 min and a temperature of 475°C. The supercritical water was found to be potential to convert the heavy oils into the lighter oils without the addition of any catalyst.

Index Terms—Batch reactor, heavy oil, heptylbenzene, hexylbenzene, supercritical water.

I. INTRODUCTION

The upgrading of heavy oils will continue to increase in importance as changes in crude oil availability cause a shift toward heavier crudes [1]-[8]. The coking process and catalytic hydrogenation process are the traditionally used upgrading process [1], [9]. Catalytic pyrolysis of heavy oil has attracted great interests to produce low molecular weight hydrocarbons. In catalytic pyrolysis, the reactions are coupled catalytically and thermally [10]. The heavy oil contains significant quantities of metals, sulfur and nitrogen heteroatoms. The main obstacle to use catalytic process is that metals and asphaltenic molecules accumulate on catalysts surface during the process causing permanent catalyst deactivation [11]. In addition, high molecular-weight compounds, which are difficult to crack, and char formation are also observed during cracking making the process non-profitable [9]. Traditional cracking can be probably replaced by supercritical hydrothermal cracking to overcome the difficulties of pyrolysis.

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Supercritical water (SCW), water whose temperature and pressure is above the critical point (374°C, and 22.1 MPa), is a highly diffusive steam and can be miscible with gases and hydrocarbons to form a homogeneous mixture [12]. The supercritical water oxidation (SCWO) processes have successful evidence for treating organic wastes [13] using solubility effect of SCW. Literature revealed that the ion product of water increases significantly at high temperatures and pressures. The dielectric constant of SCW varies between 2 and 30. This range includes the dielectric constants of nonpolar solvents, such as, hexane whose dielectric constant is close to 1.8 and those of polar solvents, such as, methanol whose dielectric constant is close to 32.6. Due to this dramatic variability in the ion product and dielectric constant, SCW possesses acidic or base effects on chemical reactions [14] and has attracted much attention as a clean and efficient reaction medium [15] for conversion of organic compounds. It also inhibits the cracking of bitumen to lower molecular weight substance [16]. SCW also acts as a hydrogen donor [1] and water molecules often take part as collision partners [12]. Because of its special properties, subcritical water and SCW has in recent years been considered an effective reaction medium in organic synthesis, fuel processing, biomass conversion, hydrogen production, upgrading of heavy oils and so on [3].

Very recently, SCWO [9], [13], [17] was introduced as an important application of reactions in hydrothermal system, water at high temperature and pressure. Previous studies on SCWO have focused only on heteroatom-containing organic compounds [9]. Sato *et al.* in 2003 [12] discovered that SCW is favorable for the decomposition of alkylphenols in water. Very few studies have been conducted on the pyrolysis of hydrocarbons in SCW by Houser *et al.* [18] in 1986, Hirth and Franck [19] in 1993, Arai and Adschiri [20] in 1999, Ederer *et al.* [21] in 1999, Savage [22] in 1999, Ding *et al.* [23] in 2006 and Mandal *et al.* [9] in 2011. These studies showed that water had no significant effect on the pyrolysis of alkylbenzenes. Nevertheless, the cage effect (the manner in which the properties of a molecule are affected by its surroundings), water attack on the molecular species or thermolysis, and the change in the phase behavior would decide the role of SCW on the alkylbenzenes decomposition reaction [9]. Mandal *et al.* conducted kinetic and simulation study of heptylbenzene (HPB) decomposition in SCW [9], [24]. Their study shows that HPB decomposed under SCW producing low molecular weight hydrocarbons and suppressing coke formation.

The reactions of alkylbenzene both in neat pyrolysis and in SCW are essential to understand the effect of water on the decomposition of alkylbenzene [9]. Long chain n-alkylbenzenes present in heavy crude oil or oil sands are

the dimplest chemical models of alkylaromatic moieties. In this paper, comparison reactions of HPB and hexylbenzene (HXB) both in the absence and in the presence of SCW are carried out to understand the effect of SCW on hydrolysis reaction.

II. EXPERIMENTAL SECTION

A. Materials and Equipment

Commercially available HPB (purity: 99.7% by GC), HXB (purity: 99.9% by GC), and acetone were purchased FROM Wako Pure Chemicals Ltd. and used as received without further treatment.

B. Materials and Equipment

All experiments were carried out in an 8.8 mL batch reactor fabricated from hastelloy C-276. The reactor was designed and tested by AKICO (Tokyo, Japan) for a maximum temperature of 500°C and maximum pressure of 50 MPa. An electric furnace also made by AKICO was used to heat up the reactor isothermally during potential experiments.

C. Experimental Procedure

Approximately 2.0 mL HPB or HXB and 0 - 2.0 mL distilled water were taken in the batch type reactor for pyrolysis and hydrolysis reactions. The amount of water loaded into the reactor was moderated to control water partial pressure (WPP) at constant temperature and reactor volume. The software, Water I, v.3.3, produced by Summit Research Corporation (1996) was used to calculate the amount of water required by fixing the temperature and WPP. The reactor was reassembled and argon gas was used to purge the reactor to remove gaseous portion from the reactor. Then the reactor was loaded into an electric furnace made by AKICO (Tokyo, Japan), that was pre-heated to the reaction operating temperature, to heat up. During each run, the reactor was shaken by front and back motion at approximately 70 cycles per minute, a rate sufficient to cause the reactor interior temperature to increase quickly. After a specific reaction period, the furnace was stopped, and quenched in water bath for an hour. The reactor was then open and water was separated using a separating funnel. Finally, the reaction products were collected by washing with acetone.

D. Analytical Procedure

Qualitative analysis of the reaction liquid mixture was done using the GC/MS method and quantitative analysis was carried out by GC-FID. The GC/MS column was a non-polar HP-1MS capillary column, 30 m long by 0.32 mm diameter. The GC-FID measurement was carried out using Shimadzu GC 2014 instrument using the same temperature program used in GC/MS. The samples were diluted by adding acetone for GC/MS and GC-FID analysis. Conversion was defined as the amount of reactant reacted divided by the amount of reactant loaded.

III. RESULTS AND DISCUSSION

HPB is a colorless liquid that contain seven carbon atoms in its side chain. HXB containing six carbon atoms in its side

chain is also a colorless liquid. The color of liquid product obtained by pyrolysis and supercritical hydrolysis turned from yellowish to reddish over increasing reaction time and temperature. Though HPB and HXB were immiscible with water, they dissolved in SCW by decomposition. Reaction liquid products and gaseous products were obtained at the end of specific reaction time both in HPB and HXB decomposition. Reaction liquid products were analyzed which comprise light hydrocarbons and heavy hydrocarbons. Productions of light hydrocarbons dominated in the yield of products. The reaction of HPB and HXB both in the absence and in the presence of SCW involved decomposition to short chain alkylbenzenes by continuous specific scission, the fragmentation of terminal peripheral alkyl substituent, and random scission, the fragmentation of alkyl substituent at different parts of side chain, phenomena. In addition, naphthalene produced by ring formation reaction and heavier molecular compounds produced by addition reaction in side chain of benzene via secondary reactions of scission products.

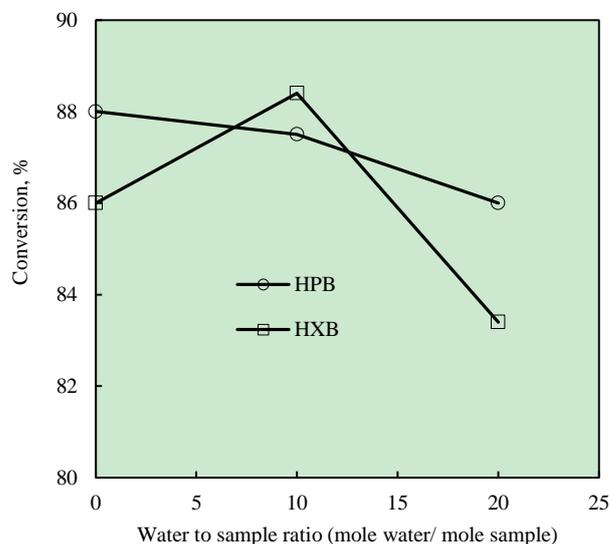
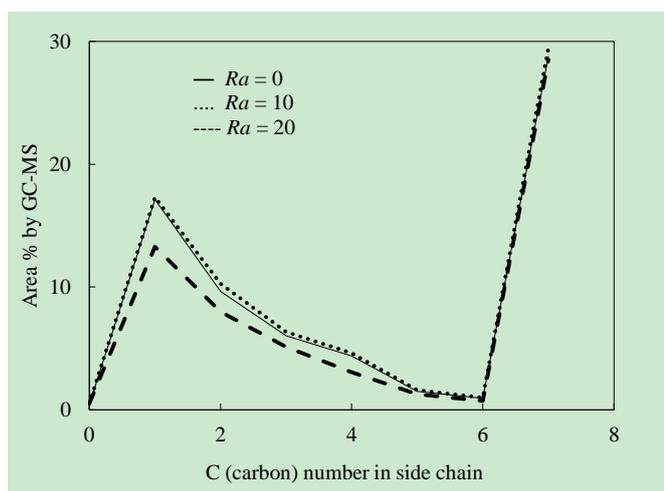
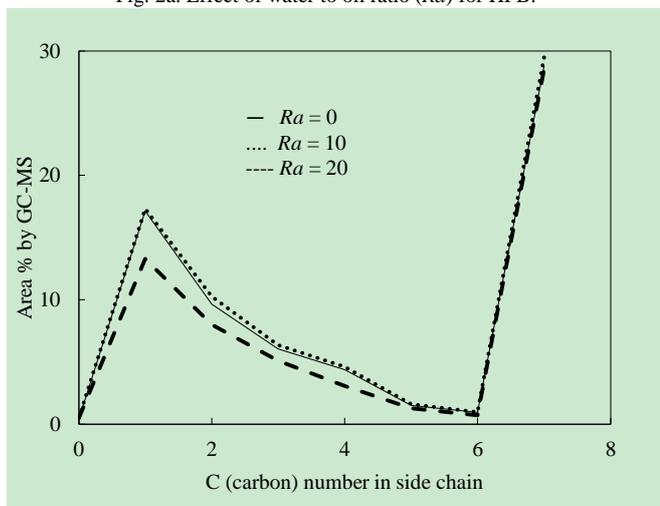


Fig. 1. Conversion of HPB and HXB.

The conversion versus water to sample (HPB or HXB) ratio plot of HPB and HXB supercritical hydrolysis is displayed in Fig. 1. It was found that average HPB conversion was high compared to HXB conversion. In addition, conversion of HPB and HXB depends on molar ratio of water to sample at a constant temperature of 450°C. Experimental results show that HXB conversion was high at water to HXB ratio of 10. On the other hand, HPB conversion slowly decreased by the action of SCW. Mandal *et al.* [9] revealed that HPB conversions are affected very slightly at supercritical condition. Similar results were observed during the reaction with HXB. Mandal *et al.* in their study of HPB conversion in SCW discovered that SCW had a negligible influence on the reaction pathways; but it can accelerate phenylolefin and toluene formation path by suppressing the other paths compare to pyrolysis without water. During the HXB conversion in SCW, SCW could suppress precipitation or char formation and the side reactions that produced high molecular weight compounds at high temperatures. This was the good agreement with HPB conversion in SCW.

Golombak and Ineke [25] in 2013 disclosed that the hot

water can pyrolytically crack the long molecular weight hydrocarbon structures. Literature review revealed that the hydrothermal reaction mechanism depends on water density: the reaction is controlled by the ionic reaction mechanism at high water density and low temperature; whereas the free radical reaction mechanism is prevalent at low water density and high temperature [26], [27]. Thus, reactions of heavy oil with subcritical water can be described by free radical reaction mechanism as presented by Mandal *et al.* [9]. Weingartner and Franck [28] disclosed that ionic product falls by orders of magnitude at SCW condition, thus is able to produce H and OH radicals under experimental conditions.

Fig. 2a. Effect of water to oil ratio (R_a) for HPB.Fig. 2b. Effect of water to oil ratio (R_a) for HXB.

Heteroatom containing organics present in the body can react with water via hydrolysis [14], [17], [18]. Moriya and Enomoto [29], Arai and Adschiri [20] and Mandal *et al.* [9] reported that the effect of SCW on the pure hydrocarbon decomposition is insignificant. Fig. 2a and 2b illustrate the effect of water to oil ratio on HPB and HXB decomposition at a temperature of 450°C, a pressure of 35 MPa and a reaction time of 60 min respectively. Toluene was the most abundant product throughout the course of the reaction both in HPB and HXB decomposition. But production of toluene was high in HPB decomposition indicating the increasing of ring scission reactions. Water to oil ratio 10 had a high capability to produce low molecular weight compound compare to pyrolysis and supercritical hydrolysis at ratio 20 indicating that low ratios can favor the production of low molecular

weight compounds.

Fig. 3a and 3b depict the reaction time effect on decomposition of HPB and HXB at a temperature of 450°C, a pressure of 35 MPa and reaction time of 60 min respectively. Scission on long chain alkylbenzenes increased to produce short chain alkylbenzenes with increasing reaction time. Conversion was low at lower reaction time, but it increased with time. Toluene was the dominating liquid products at all reaction time. On the other hand, HPB produced more toluene than HXB indicating the probability of HXB to produce more gaseous products.

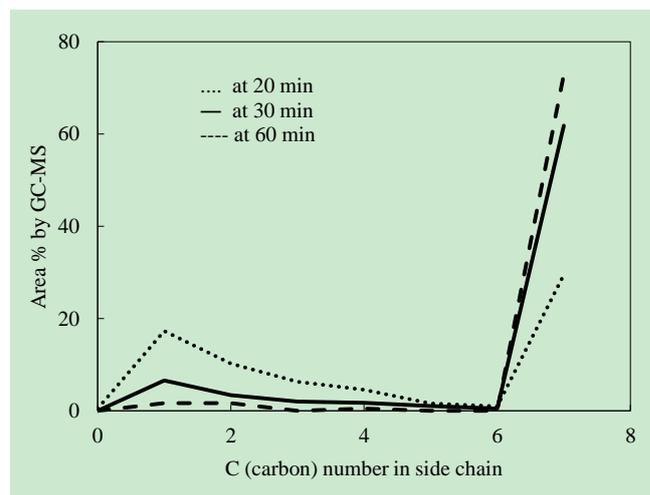


Fig. 3a. Effect of reaction time for HPB.

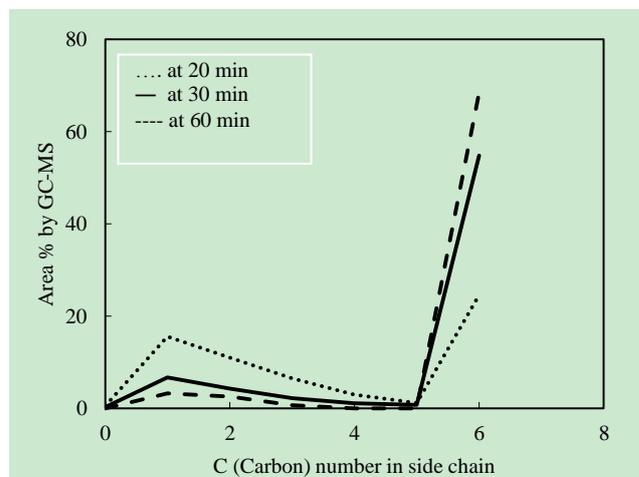


Fig. 3b. Effect of reaction time for HXB.

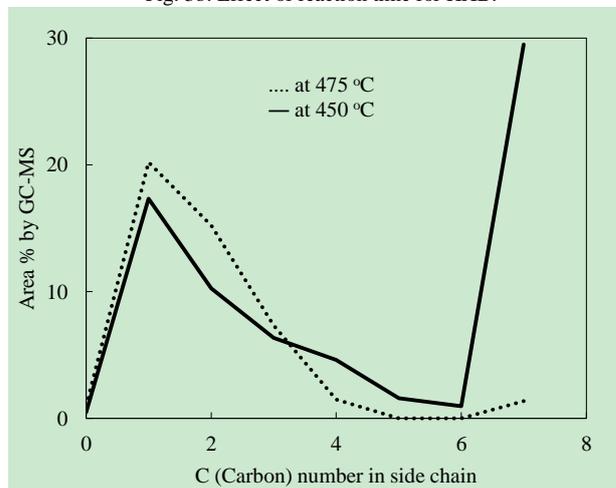


Fig. 4a. Effect of temperature for HPB.

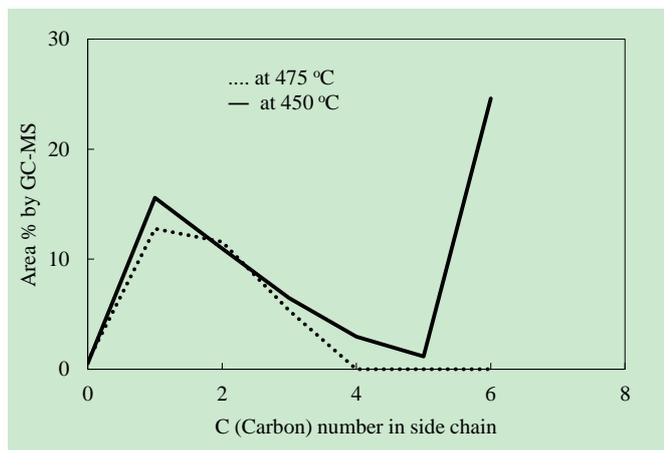


Fig. 4b. Effect of temperature for HXB.

Fig. 4a and 4b show the effect of temperature on decomposition of HPB and HXB at a pressure of 35 MPa and a reaction time of 60 min. During HXB decomposition, productions of short chain containing compounds were decreased by the action of heat indicating the high production of gases. Thus, short chain alkylbenzene produced more gaseous products than long chain alkylbenzene at extreme reaction conditions. Toluene was found to be a stable compound during the course of reactions.

IV. CONCLUSIONS

This study has shown that both HPB and HXB decomposed into light hydrocarbons; heavy hydrocarbons and gases. The basic reaction mechanisms of both HPB and HXB decomposition were shortening and rearranging side chain of benzene, ring formation and addition reaction in side chain of benzene. The average HPB conversion was high compared to the average HXB conversion though the product distribution was sensitive to water to oil ratios. But, low water to oil ratio favored the production of low molecular weight compounds. Conversion as well as production of low molecular weight compounds was high at a reaction time of 60 min and a temperature of 475°C. Nevertheless, HPB and HXB decomposed successfully under SCW without catalyst at temperatures of 450-475°C and a pressure of 35 MPa producing low molecular weight hydrocarbons.

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