

## Development of a Recycling Process for Waste Polyethylene: Pyrolysis of Model Hydrocarbons in the Presence of Supercritical Water

Masaru Watanabe, Tadafumi Adschiri, and Kunio Arai\*.

Department of Chemical Engineering, Tohoku University, Sendai, Japan, 980-8579

E-mail: karai@arai.che.tohoku.ac.jp Fax: +81-22-217-7246

A basic study was conducted on n-hexadecane (n-C<sub>16</sub>) pyrolysis in supercritical water (SCW) to investigate hydrocarbon pyrolysis for recycling waste polyethylene. In the absence of water at 673 K - 723 K and 10 min - 60 min reaction time, the pyrolysis reaction rate of n-C<sub>16</sub> in Ar (without water) increased to a maximum and then decreased with increasing n-C<sub>16</sub> concentration and the yield of n-alkanes from n-C<sub>16</sub> pyrolysis in Ar increased with increasing n-C<sub>16</sub> concentration. A mathematical model of n-C<sub>16</sub> pyrolysis was developed. The model could accurately describe the product distribution and the overall rate of n-C<sub>16</sub> pyrolysis over a wide range of condition (temperatures ranging from 600 K to 900 K, initial n-C<sub>16</sub> concentrations ranging from  $7 \times 10^{-3}$  mol/l to 2 mol/l) [1]. In the presence of SCW at 0.17 g/cm<sup>3</sup> - 0.5 g/cm<sup>3</sup> loading density, 673 K, and 60 min reaction time, the 1-alkene/n-alkane ratio of n-C<sub>16</sub> pyrolysis in SCW increased to a maximum and then decreased with increasing water density. The reaction rate of n-C<sub>16</sub> pyrolysis in SCW (0.5 g/cm<sup>3</sup>) was lower than that in Ar or in SCW at the lower water densities. Using the model, the effect of SCW on pyrolysis of n-C<sub>16</sub> can be interpreted as a process in which H abstraction is suppressed at lower water densities and promoted at higher water densities.

### Introduction

One process for recycling plastics is pyrolysis. Control of the product distribution for the oils to be used widely is considered to be an important technical requirement. However, for the case of pyrolysis, control of the reaction is difficult. The use of a solvent during the pyrolysis may be one idea for controlling pyrolysis product distribution. Since the reaction temperature is generally above 673 K, most organic solvents will be vapor at these conditions. Only a few studies exist on the effect of supercritical fluid (SCF) on the pyrolysis of heavy oils or its model compounds have been reported [2-4].

In general, the use of an SCF as a reaction solvent changes reaction rate, equilibrium, and

the overall reaction pathway, specifically around of a critical point, because of the significant variation of solvent properties. We focus on supercritical water (SCW) as a solvent, which can dissolve hydrocarbons [5] and whose dielectric constant is widely variable, and started research for the development of a new process for the conversion of waste plastics in SCW, where control of product distribution is emphasized.

For understanding the pyrolysis reactions in that process, a fundamental study was conducted for n-C<sub>16</sub> pyrolysis in SCW and in Argon (Ar). The effects of SCW on the pyrolysis can clearly be seen through its influence on the product distribution.

## Experimental

Experiments were conducted with stainless steel (SUS 316) tube bomb reactors (6 cm<sup>3</sup>) in the presence and in the absence of water. The hydrocarbon n-hexadecane (n-C<sub>16</sub>) (98.5 % purity) was used as a model compound.

For the experiments without water, 0.1 g to 2 g of n-C<sub>16</sub> (0.07 mol/l to 1.47 mol/l of n-C<sub>16</sub> concentration) was loaded into the reactor. For this case, the reactor was pressurized with 1.0 MPa of Argon (Ar). The experiments were carried out at temperatures ranging from 673 K or 723 K and reaction times ranging from 10 min to 60 min.

For SCW experiments, a 0.1 to 2.0 g of sample was loaded into the reactor. The amount of water loaded ranged from 1.0 g (0.17 g/cm<sup>3</sup> of water density) to 3.0 g (0.5 g/cm<sup>3</sup> of water density). Reaction temperature was 673 K and reaction time was 60 min. Detailed experimental apparatus and procedure can be found elsewhere [1].

Conversion of n-C<sub>16</sub> ( $X_{n-C_{16}}$ ) was evaluated as

$$X_{n-C_{16}} = \left( 1 - \frac{[n-C_{16}]_f(\text{mol})}{[n-C_{16}]_0(\text{mol})} \right) \times 100 \text{ [\%]} \quad (1)$$

where  $[n-C_{16}]_0$  is amount of n-C<sub>16</sub> loaded and  $[n-C_{16}]_f$  is amount of n-C<sub>16</sub> recovered. The apparent first order rate constant ( $k_{(16)}$ ) was evaluated by

$$k_{(16)} = - \frac{\ln(1 - X_{n-C_{16}} / 100)}{\tau} \quad (2)$$

where  $\tau$  is the reaction time. Molar selectivity was evaluated as

$$\text{Molar Selectivity} = \frac{[n-C_i]}{\sum_{j=1}^{15} \{ [n-C_j] + [OI_j] \}} \times 100 \text{ (\%)} \quad \text{or} \quad = \frac{[OI_i]}{\sum_{j=1}^{15} \{ [n-C_j] + [OI_j] \}} \times 100 \text{ (\%)} \quad (3)$$

where  $[n-C_i]$  is the amount of n-alkane,  $n-C_i$ , where  $i$  is a carbon number, and  $[Ol_i]$  is produced amount of 1-alkene,  $Ol_i$ , where  $i$  is also a carbon number. The 1-alkene/n-alkane ratio ( $\theta_i$ ) at carbon number of  $i$  was defined by:

$$\theta_i = \frac{[Ol_i]}{[n-C_i]} \quad (4)$$

## Results and Discussion

### 1. Pyrolysis of pure n-hexadecane

Products of  $n-C_{16}$  pyrolysis were  $C_1 \sim C_{15}$  n-alkanes, and  $C_2 \sim C_{15}$  1-alkenes. The yield of longer chain n-alkane in the products increased with increasing  $n-C_{16}$  concentration. The overall rate of  $n-C_{16}$  pyrolysis increased up to its maximum and then decreased with increasing  $n-C_{16}$  concentration.

Based on the results of the  $n-C_{16}$  pyrolysis, a model was developed [1]. The model was based on KR theory [6]. For H abstraction, the rate constant of this reaction is inversely proportional to a carbon number of a radical. For termination, the rate constant of this reaction depends on the carbon number of a radical that has the same functional form as the rate constant of H abstraction. In the model, we employed the kinetic parameters reported by Doue and Guiochon [7]. According to the model, the overall rate of  $n-C_{16}$  pyrolysis constant is evaluated by

$$k_{(16)} = \frac{k_{H0}k_{\beta(16)}\sqrt{\frac{2k_{init}[n-C_{16}]}{k_{term0}}}}{k_{\beta(16)} + k_{H0}(1/16)[n-C_{16}]} \quad (5)$$

where  $k_{H0}$ ,  $k_{\beta(16)}$ ,  $k_{init}$ , and  $k_{term0}$  are rate constant of H abstraction,  $\beta$ -scission, initiation, and termination, respectively.

The model gives quantitative description for product distribution and for reaction rate over a wide range of conditions (temperatures ranging from 600 K to 900 K, initial  $n-C_{16}$  concentrations ranging from  $7 \times 10^{-3}$  mol/l to 2 mol/l) [1].

### 2. n-Hexadecane pyrolysis in SCW

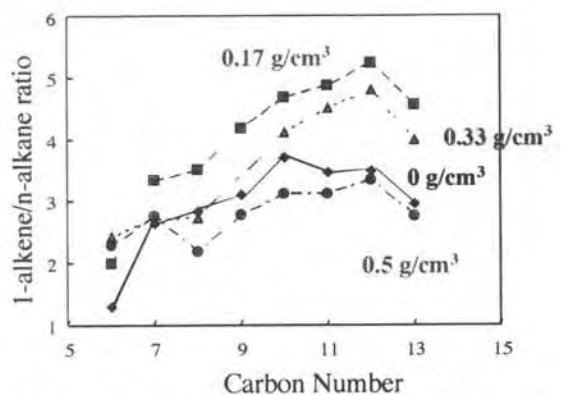
The main products were 1-alkenes and n-alkanes for all cases. No compounds having oxygen, such as carbon oxides or alcohol, were detected in the products.

Figure 1 shows the ratio of 1-alkene to n-alkane at 673 K of temperature and 0.07 mol/l of  $n-C_{16}$  (0.1 g of loaded amount of  $n-C_{16}$ ) in Ar (0 g/cm<sup>3</sup> of water density) and in SCW (0.17

$\text{g/cm}^3$  to  $0.5 \text{ g/cm}^3$  of water density). As shown in Fig. 1, the 1-alkene / n-alkane ratio increased up to  $0.17 \text{ g/cm}^3$  of water density and then decreased with increasing water density. At all n-C<sub>16</sub> concentrations (0.07 mol/l to 1.47 mol/l), the 1-alkene / n-alkane ratio of the product of n-C<sub>16</sub> pyrolysis in Ar and in SCW increased and then decreased with water density such as shown in Fig. 1.

Conversion of n-C<sub>16</sub> was the lowest in dense SCW ( $0.5 \text{ g/cm}^3$  of water density) over all n-C<sub>16</sub> concentration ranges (0.07 mol/l to 1.47 mol/l).

By comparing the experimentally obtained results for product distribution and conversion with the model estimation, the rate of H abstraction could be interpreted to be suppressed and then promoted with increasing water density. Our explanation for this change of H abstraction rate is a change of conformation of the alkyl radical which affects the rate for H abstraction and termination.



T = 673 K, [n-C<sub>16</sub>] = 0.07 mol/l, Conversion = 1 ~ 6 %

Figure 1 Ratio of 1-alkene to n-alkane

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