Propylene hydration in high-temperature water

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Abstract

The hydration of propylene with sulfuric acid catalyst in high-temperature water was investigated using a flow reaction system. The major product was isopropyl alcohol (IPA). Diisopropyl ether, n-propyl alcohol and C6 olefins were produced as byproducts. The temperature dependency of reaction rate for propylene disappearance was measured in the range of 280-400   at a fixed pressure of 30 MPa. The apparent pseudo-first-order rate constant increased with increasing temperature at 280-340   , reaching a maximum around 340   , while sharply decreased above 360   .

Introduction

IPA is one of the most important chemicals for solvent applications, chemical derivatives and cosmetics. Most of them are produced by hydration reaction using propylene and water as raw materials. There are two representative processes for the synthesis of IPA. The first method consists of indirect hydration, in which propylene reacts with highly concentrated sulfuric acid to form sulfuric ester, followed by hydrolysis to form IPA. The second method involves direct hydration of propylene with an acid catalyst, such as acidic ion-exchange resin[1] or solid phosphorous acid[2]. Although the bulk of IPA is manufactured by indirect processes, direct processes are simpler and technically newer, and have become of much interest in chemical industry.

Chemical reactions of organic compounds in high-temperature water have attracted much attention and have thoroughly been investigated[3-6]. Basic advantages of these applications using high-temperature water are found on its inexpensiveness and benignity. From the engineering standpoint, high-temperature water has attractive properties. For example, the dielectric constant of water at supercritical conditions ranges from 5 to 25. The values correspond to the dielectric properties of polar organic solvent under normal conditions[7]. Therefore, organic compounds and gases are soluble in high-temperature water. It might be thus expected to conduct chemical reactions with a faster rate.

Additionally, water density, dielectric constant[7], ion product[8] and others can be widely changed with pressure and temperature so that solvent properties could be adjusted to desired reaction conditions.

Our interest in the use of high-temperature water in IPA production process is originated from the background described above. Although hydration reaction is thermodynamically not favored at high temperatures and rather less attention has been paid, a new production process might be adjusted through a high pressure reaction in combination with a proper pressure operation. We have exhibited that propylene reacted with water at subcritical or supercritical conditions of water in the absence of any acid catalyst or in the presence of very small amount of acid catalyst to form IPA, and showed the possibilities of new IPA production process using high-temperature water[10,11]. The purpose of this study is to explore the kinetic analysis of propylene hydration and to find suitable conditions for industrial applications.

Experimental

Four flow reactors that have different volumes respectively were used in this study. These were 2 ml tube (0.99 mm ID, 1.59 mm OD, 2680 mm), 10 ml tube (2.18 mm ID, 3.18 mm OD, 2680 mm), 20 ml tube (2.18 mm ID, 3.18 mm OD, 5360 mm) and 50 ml tube (2.18 mm ID, 3.18 mm OD, 13500 mm) made of Inconel 625.

Liquid propylene (99.8% purity) obtained from Takachiho Chemicals Co. was used as a reactant. A dilute solution of sulfuric acid (5.1×10^{4} mol/kg) was prepared from 1 N sulfuric acid obtained from Wako Pure Chemical Industries and degassed, distilled water.

Figure 1 displays a schematic diagram of a flow reaction system for the hydration of propylene. Aqueous dilute solution of sulfuric acid was first preheated through a preheater. Fresh liquid propylene was separately pumped and introduced into the entrance of the reactor. After the reaction, IPA and unreacted reactants were then discharged through a condenser and a back-pressure regulator, and then flowed into a separator. At each operating condition, at least triplicate samples of the reactor effluent were collected for analysis. The composition of samples was analyzed by a gas chromatograph equipped with a mass selective detector (GC-MS, Agilent technology model 5973N). A capillary column (liquid phase: HP-5, 60 m$\times$ 0.25 mm$\times$ 0.25 μm, J&W) was employed to separate the products. The calibration standards were used to quantify the yield of each product. The composition of the gas stream was calculated on the basis of the GC area percentage.

Propylene and water flow rates were calculated from the average density of a mixture of propylene and water at each reaction condition. Propylene density was calculated by SRK equation[9], while that of water was available in the steam table[12].

Results and Discussion

Table 1 shows the results of experiments. Reactions were conducted at 30 MPa,

temperatures of 280 400 and water-to-propylene molar ratio of 10 with 5.1×10^4 mol/kg sulfuric acid catalyst.

Hydration of propylene yielded IPA as a primary product. Diisopropyl ether, C6 olefins and trace amount of n-propyl alcohol were usually produced as byproducts. Judged from these analytical results, we can deduce several possible pathways for the reaction of propylene. Major pathway involves the hydration reaction of propylene to form IPA.

$$C_3H_6 + H_2O \underset{k_b}{\overset{k_f}{\rightleftharpoons}} i\text{-}C_3H_7OH \tag{1}$$
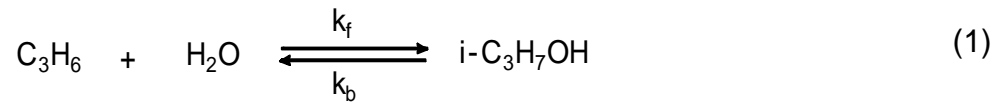
Pathways toward the byproducts involve the dimerization reactions of IPA or propylene to form diisopropyl ether or C6 olefins.

$$2\,i\text{-}C_3H_7OH \rightleftharpoons (i\text{-}C_3H_7)_2O + H_2O \tag{2}$$

$$2\,C_3H_6 \longrightarrow C_6H_{12} \tag{3}$$
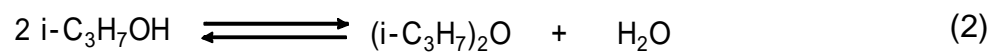
Because our goal in this study is to explore reactivity of propylene in high-temperature water, the overall rates of propylene disappearance are determined at temperatures of 280-400 at 30 MPa, in which we treat the conversion of propylene as a reversible reaction. The apparent pseudo-first-order rate constants, k_f, in propylene can be described as follows;

$$k_f t = X_e \ln \frac{X_e}{X_e - X} \tag{4}$$

where X_e and X represent equilibrium conversion and conversion at time t, respectively. The rate of propylene disappearance is shown in Figure 3 as a plot of $X_e\ln(X_e/(X_e-X))$ versus time. An approximately linear relationship indicates that the reaction follows kinetically the first order in propylene. Therefore, the rate constant k_f can be estimated from the slope of the best-fit line.

A plot of $\ln k_f$ versus $1/T$ in Figure 4 shows that the rate constant increased as the temperature increased from 280 to 340 , reaching a maximum at 340 , followed by a sharp drop above the critical temperature of water. One possible explanation for this behavior is that at least two different factor contribute to the overall reaction rate. At temperatures of 280-340 acceleration of reaction rate is considered to be due to heat energy, following a typical Arrhenius-type expression. On the other hand, around and above 360 another factor dominantly affects. Because the hydration reaction is a acid-catalyzed reaction with $k_f = k_H[H^+]$, significant decrease in reaction rate near and above the critical temperature would be caused by the decrease in proton concentration. As a result, it has been suggested that the better conditions for the hydration of propylene are

located in the subcritical region of water. It would seem, moreover, that further investigations are needed in order to clarify the pressure effect on the propylene hydration.

Conclusion

The hydration of propylene with 5.1×10^{4} mol/kg sulfuric acid catalyst at 30 MPa was conducted at the temperatures of 280-400 and provided IPA, n-propyl alcohol, diisopropyl ether and C6 olefins as products.

The apparent pseudo-first-order rate constants for propylene disappearance were measured. The temperature dependence showed a typical Arrehnius-type at temperatures of 280-340 , reaching a maximum around 340 , while significantly decreased above the critical temperature.

Acknowledgements

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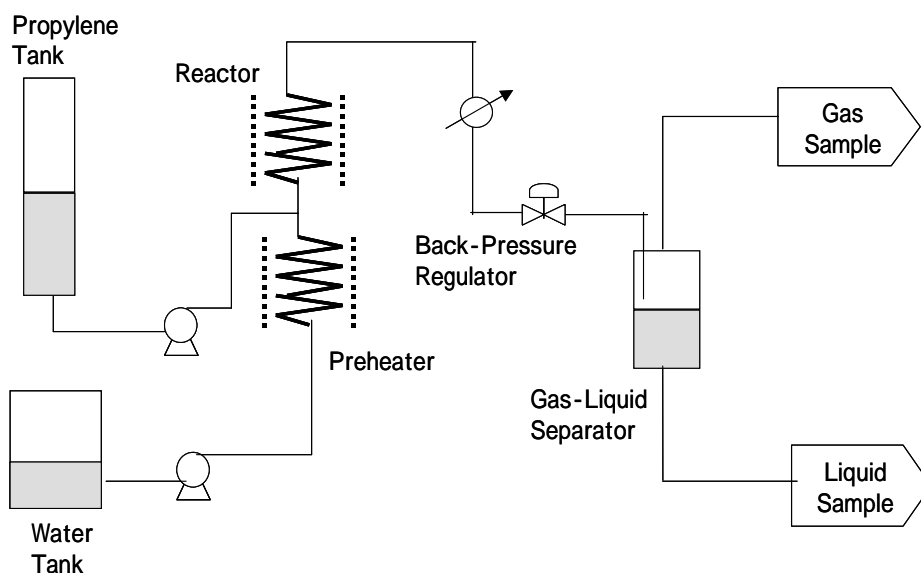[12] The Japan Society of Mechanical Engineers, Steam Tables, **1981**

Figure 1

A schematic diagram of a flow reaction system for the hydration of propylene in high-temperature water.

Table 1

Propylene hydration at 30 MPa and water-to-propylene molar ratio of 10 with 5.1×10^{-4} mol/kg sulfuric acid catalyst. NPA: n-propyl alcohol, IPE: diisopropyl ether.

| Expt. No.	Temp. ( )	Reaction Time (min)	Conversion (%)	IPA	Product Yield (%) NPA	IPE	C_6H_{12}
1	280	1.0	1.9	1.8	0.0	0.0	0.0
2		1.5	6.3	6.2	0.0	0.0	0.1
3		2.0	8.0	7.7	0.0	0.1	0.2
4		10.0	26.6	23.9	0.0	1.6	1.1
5	310	0.4	6.2	6.0	0.0	0.1	0.1
6		1.0	13.8	13.1	0.0	0.3	0.4
7		1.6	17.2	16.0	0.0	0.6	0.6
8		1.8	21.1	19.7	0.0	0.7	0.6
9		2.0	19.5	17.6	0.0	0.9	1.0
10		10.0	33.6	27.8	0.1	2.3	3.4
11		15.0	36.4	29.6	0.1	2.6	4.1
12	340	0.2	9.8	9.4	0.0	0.1	0.3
13		1.0	19.4	17.3	0.1	0.7	1.3
14		2.0	20.6	18.2	0.1	1.0	1.3
15		10.0	19.2	15.9	0.1	0.5	2.5
16	360	0.2	5.6	5.3	0.0	0.1	0.2
17		1.0	14.0	12.8	0.0	0.4	0.8
18		2.0	14.7	13.0	0.1	0.5	1.2
19	380	0.2	1.6	1.5	0.0	0.0	0.2
20		1.0	4.9	4.3	0.0	0.1	0.5
21		2.0	6.9	6.3	0.0	0.1	0.4
22		10.0	8.2	4.8	0.0	0.0	2.5
23	400	0.2	0.5	0.2	0.0	0.0	0.2
24		1.0	0.8	0.3	0.0	0.0	0.4
25		2.0	0.7	0.3	0.0	0.0	0.4
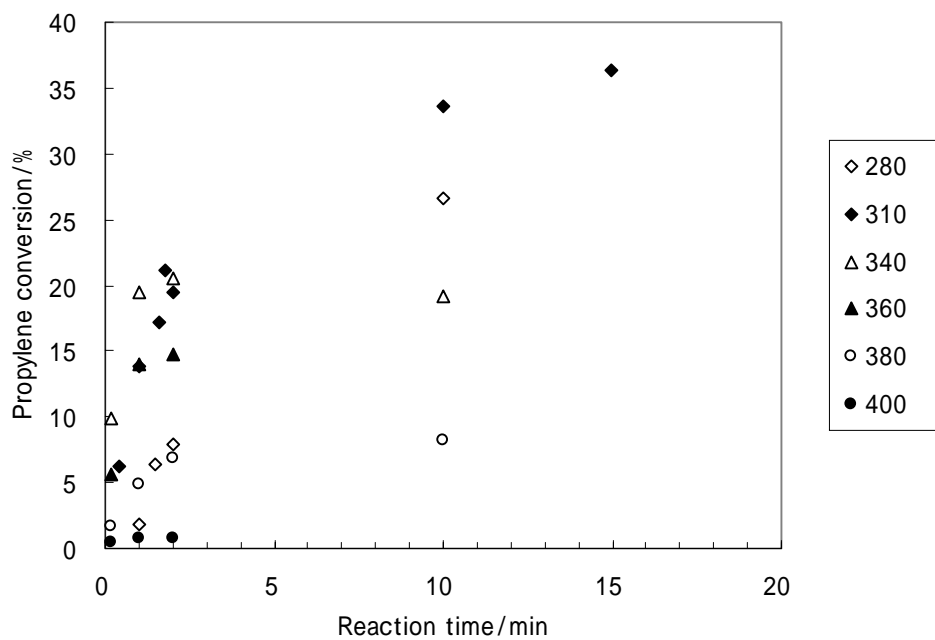
Figure 2

Conversion of propylene at 30 MPa.
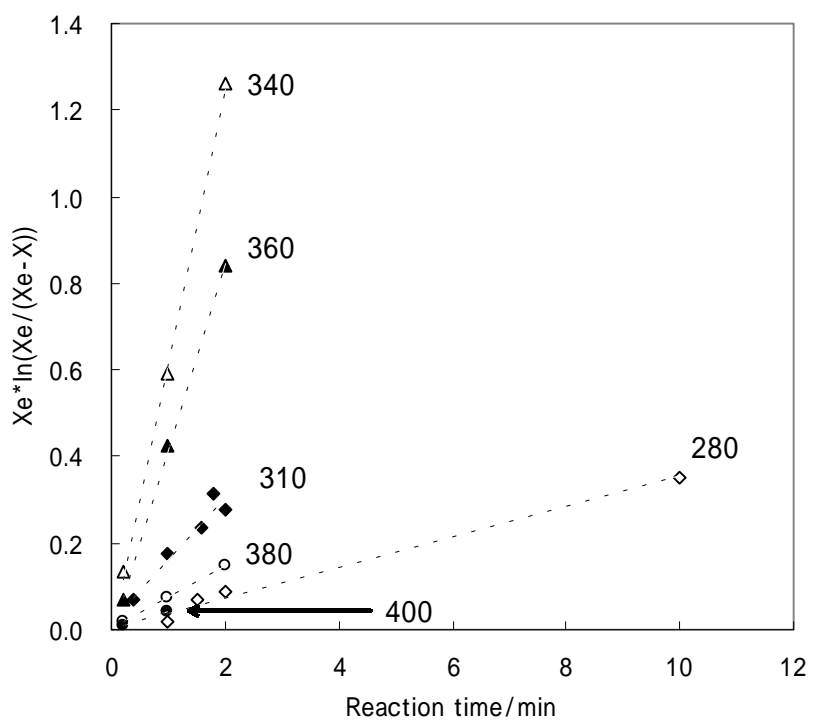
Figure 3

A plot of Xe ln (Xe/(Xe-X)) versus reaction time at temperatures of 280-400 . Xe: equilibrium conversion, X: conversion at time t.
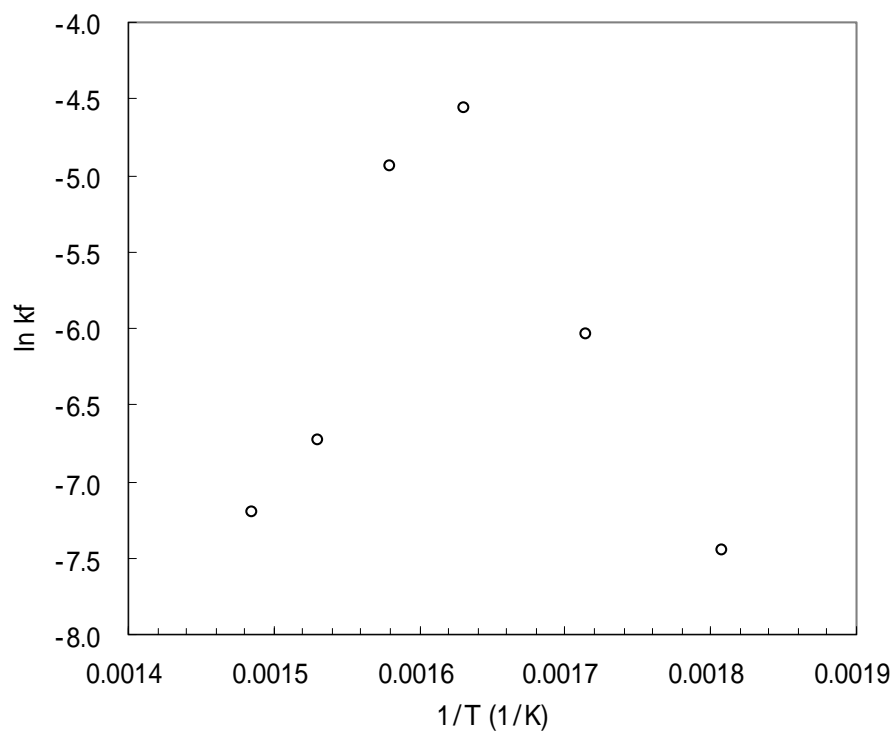
Figure 4
Arrhenius plot with apparent pseudo-first-order rate constant k_f for the disappearance of propylene at 30 MPa.