

Studies on Paraldehyde Depolymerization for Chemical Heat Pump

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The paraldehyde/acetaldehyde (Pa/A) chemical heat pump has been investigated for the generation of low-temperature energy. The purpose of this work is to investigate the depolymerization of paraldehyde for the chemical heat pump cycle. The depolymerization rate of paraldehyde has been measured at the range from 13 °C to 30 °C with acid resin catalyst in the two-component system of paraldehyde and acetaldehyde without other liquid. The cooling power was estimated from the depolymerization rate of paraldehyde. The high cooling power and the high Coefficient Of Performance (COP) are required. The high concentration of acetaldehyde leads to the high COP. The cooling power, however, decreases with an increase in the concentration of acetaldehyde.

Keywords : chemical heat pump, depolymerization of paraldehyde, reaction rate

INTRODUCTION

Chemical heat pump (CHP) utilizes endothermic/exothermic reaction such as the adsorption/desorption, hydrogenation/dehydrogenation and hydrolysis/dehydrolysis. The many CHP systems are using inorganic reaction such as $\text{CaCl}_2/\text{CH}_3\text{NH}_2$ [1] and $\text{CaO}/\text{H}_2\text{O}/\text{Ca}(\text{OH})_2$ [2]. The CHP system using organic reaction has been proposed as following system: 2-propanol/acetone [3], cyclohexane/benzene [4] and 2-methyl-2-propane/2-methyl-2-propanol [5]. The CHP using organic reaction is suitable to arrange continuous cycle, because both the reactant and the product are fluid.

The paraldehyde/acetaldehyde (Pa/A) system has been proposed to utilize the CHP cycle for the generation of low-temperature thermal energy. The cycle consists of two kinds of working fluid; paraldehyde (1,3,5-trimethyl-2,4,6-trioxane) and acetaldehyde. The reactions are the reversible

couple; depolymerization of paraldehyde and polymerization of acetaldehyde. The interesting points of this system are as follows; each reaction produces only one product, and the separation of acetaldehyde from paraldehyde is easy because of large difference in the boiling point between paraldehyde and acetaldehyde.

The cycle is shown in Fig. 1. Liquid paraldehyde is depolymerized in an endothermic reactor at low temperature and at low pressure. The liquid paraldehyde, then, is turned into acetaldehyde vapor. The acetaldehyde vapor is compressed and transferred to an exothermic reactor. The acetaldehyde is trimerized over the acid catalyst to form the liquid paraldehyde in the exothermic reactor. The liquid is returned to the endothermic reactor through an expansion valve to complete the cycle.

The purpose of this work is to investigate the depolymerization of paraldehyde for the CHP cycle. The cooling power of the Pa/A system

depends on the depolymerization rate of paraldehyde. The depolymerization of paraldehyde has been studied at high temperature in gas phase [6] or in dilute organic solution [7]. The depolymerization of liquid paraldehyde has been performed in the two-component system of paraldehyde and acetaldehyde without other liquid at low temperature in this study.

EXPERIMENTAL

The experimental apparatus is shown in Fig. 2. Paraldehyde was purified by reflux with active carbon. Feed paraldehyde was mixed with acetaldehyde. The concentration of acetaldehyde in the feed paraldehyde varied from $7.8 \times 10^{-2} \text{ mol}\cdot\text{kg}^{-1}$ to $2.0 \text{ mol}\cdot\text{kg}^{-1}$. The reactor temperature was set at 13, 20 or 30 °C. The minimum setting temperature was limited by the melting point of paraldehyde (12.6 °C). The reactor temperature was controlled within the range of $\pm 0.3 \text{ °C}$ by a water jacket heat exchanger.

The catalyst was the strongly acidic cation exchange resin (Amberlyst15 E). The catalyst was mixed with aluminum particles to minimize the temperature distribution in the catalyst bed. The temperatures at the inlet reactor and at the catalyst bed were measured by the K-type thermocouples. The temperature difference between the catalyst bed and the reactor temperature was kept within the range of $\pm 0.3 \text{ °C}$. The mixed catalyst was packed at the middle of the aluminum pipe reactor and supported by stainless steel wire gauze. The weight of the catalyst was 0.25 g and that of aluminum was 2.5 g. The average diameter of the catalyst was 0.5 mm. The diameter of the aluminum pipe was 6.0 mm.

The feed flow rate of the paraldehyde was $12.4 \text{ ml}\cdot\text{min}^{-1}$. The liquid product was sampled by a cooling syringe to avoid the vaporization of the sample, owing to the low boiling point of acetaldehyde. The product compositions were analyzed by gas chromatography.

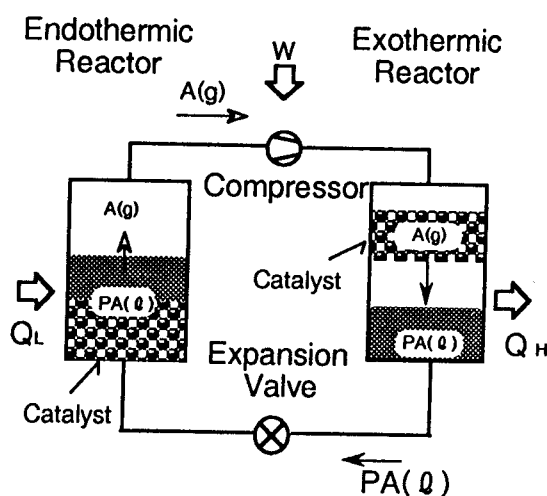


Fig. 1. The heat pump cycle of paraldehyde /acetaldehyde.

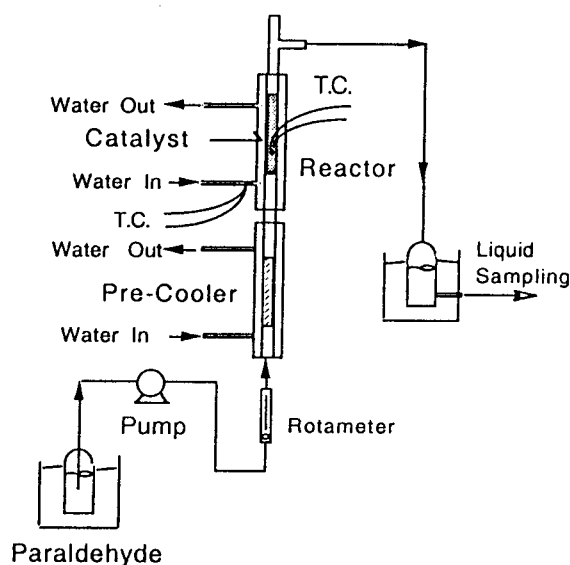


Fig. 2. Experimental apparatus.

REACTION MECHANISM

The kinetic model of the depolymerization of gas paraldehyde on mordenite was proposed by Chong and Curthoys [6] at high temperature as shown in Fig. 3. The same mechanism has been assumed in this work. The depolymerization of paraldehyde consists of the 4 steps of the elementary processes. The step 1 is the adsorption of paraldehyde and the transfer of proton from the H-bonding of acid catalyst site to the oxygen atoms in the paraldehyde molecule. The step 2 is as follows: the C-O bond in paraldehyde is broken, the ring of paraldehyde is opened and the vicinal bond electrons are rearranged. Then acetaldehyde and the unstable species (a di-radical) are produced. The step 3 is the decomposition of the unstable species. The step 4 is the desorption of acetaldehyde. The depolymerization mechanism of paraldehyde can be described by the Langmuir-Hinshelwood kinetic model. The reaction rate at each step is given by the following equation.

$$R1 = k1 C_{Pa}C\theta - k-1 C_{Pa}\theta \tag{1}$$

$$R2 = k2 C_{Pa}\theta - k-2 C_{AA}\theta C_A \tag{2}$$

$$R3 = k3 C_{AA}\theta - k-3 C_{A}\theta C_A \tag{3}$$

$$R4 = k4 C_{A}\theta - k-4 C_A C\theta \tag{4}$$

According to the previous paper [6,7], the ring opening process (the step 2) is the rate determining. The step 2 and step 3 are simplified to eq.(2)* in this study. The process is assumed to be the rate determining step.

$$R2^* = k_2^* C_{Pa}\theta - k_{-2}^* C_{A}\theta C_A^2 \tag{2}^*$$

The relationship between the concentration of vacant active sites on the catalyst and the concentration of adsorbed active sites was given by

$$C_{Pa}\theta + C_{A}\theta + C\theta = 1 \tag{5}$$

The rate equation of the depolymerization is written by

$$R_{Pa} = \frac{k_2^* K_1 C_{Pa}}{K_4^{-1} C_A + K_1 C_{Pa} + 1} \tag{6}$$

The concentration of acetaldehyde and that of paraldehyde have a following relationship owing to two-component system.

$$M_{AC}A + M_{Pa}C_{Pa} = 1 \tag{7}$$

The relationship between the inverse of the depolymerization rate and that of the concentration of paraldehyde is expressed as

$$R_{Pa}^{-1} = K_A C_{Pa}^{-1} + K_B \tag{8}$$

where

$$K_A = \frac{1}{k_2^* K_1} \left(\frac{K_1}{M_{Pa}} + 1 \right)$$

$$K_B = \frac{1}{k_2^* K_1} \left(K_1 - \frac{M_{Pa}}{M_A} K_4^{-1} \right)$$

The constants of K_A and K_B are independent of the concentration of paraldehyde and acetaldehyde. The constants of K_A and K_B depend on temperature and on the characteristic of the catalyst.

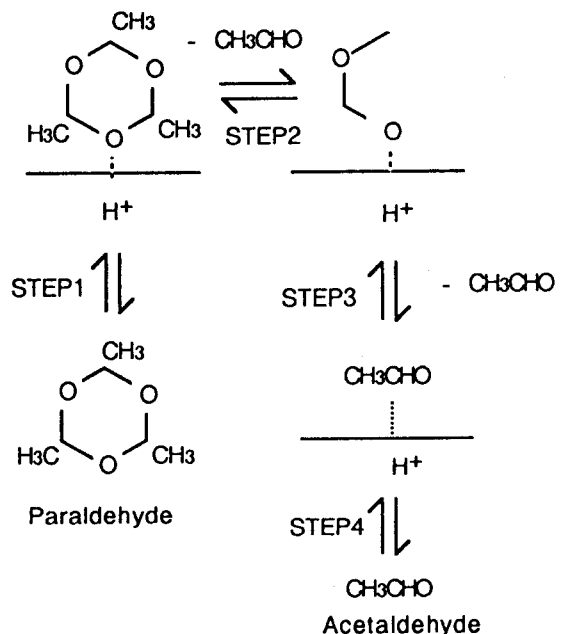


Fig. 3. Mechanism of the paraldehyde depolymerization over acidic catalyst.

RESULTS

The results of the measurement of the depolymerization rate are shown as Fig. 4. The depolymerization rate decreases with the concentration of acetaldehyde. The depolymerization rate increases with the reaction temperature. The depolymerization rate was estimated from the residence time at the reactor and from the concentration change from the inlet and the outlet of the reactor.

The relationship between inverse of the concentration of paraldehyde and that of the depolymerization rate is plotted as shown in Fig. 5. This figure shows that the relationship has a straight line. The relationship of the straight line indicates that the assumption of the rate determining step is reasonable.

The constant of K_A in eq.(8) is evaluated from the slope of the straight line. The constant of K_B in eq.(8) is evaluated from the intercept when the inverse of concentration of paraldehyde equals zero. The relationship between the inverse of temperature and logarithm of K_A and K_B is shown in Fig. 6, and the following equation is obtained.

$$R_{Pa} = \left(\frac{2.92 \times 10^{22} C_{Pa}}{1 - 0.132 C_{Pa}} \right) \exp \left(- \frac{1.80 \times 10^4}{T} \right) \quad (9)$$

The cooling power can be evaluated from the depolymerization rate. The rate equation is indispensable for the evaluation of performance of the Pa/A heat pump cycle.

DISCUSSION

The high cooling power and the high Coefficient Of Performance (COP) are required for the CHP cycle. The cooling power has been evaluated from the paraldehyde depolymerization

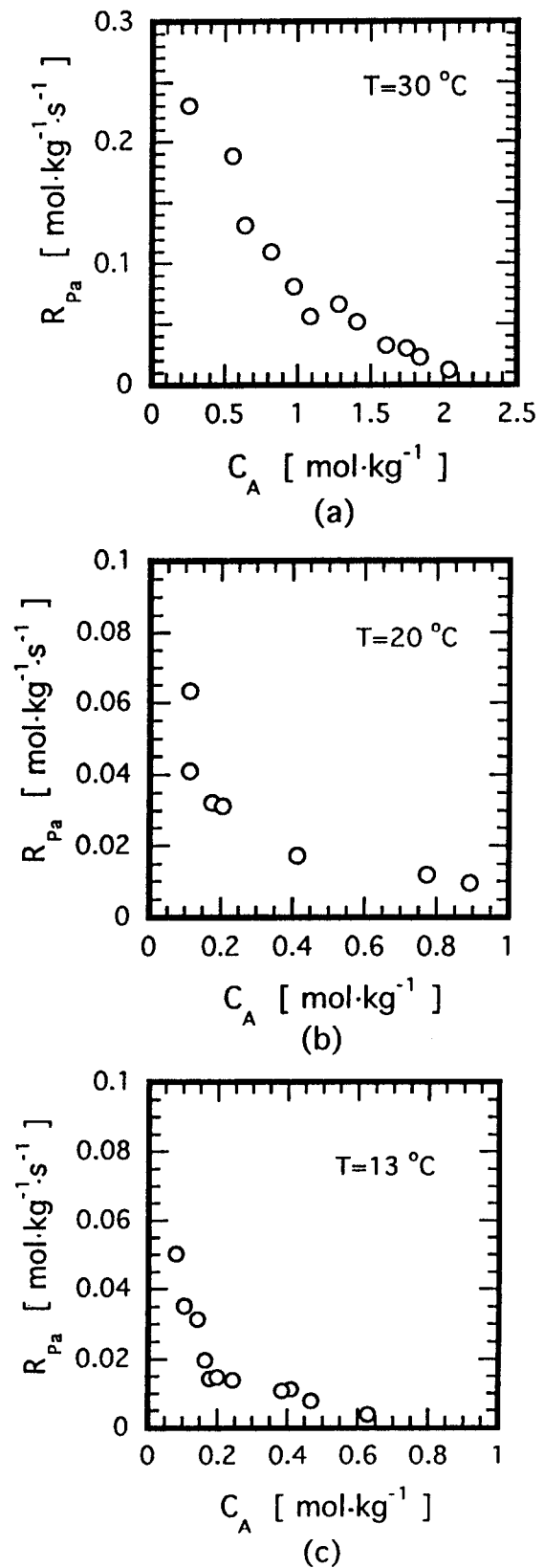
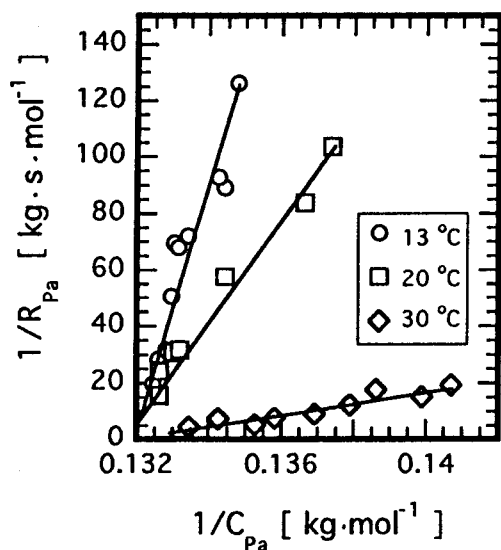
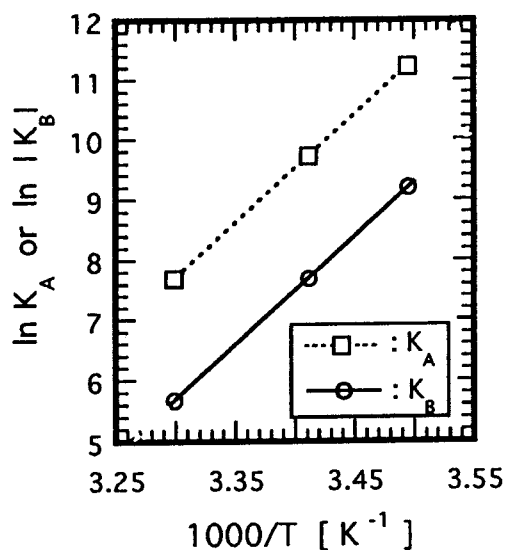


Fig. 4. Effects of the reaction rate on the concentration of acetaldehyde; (a) 30 °C ; (b) 20 °C ; (c) 13 °C.

Fig. 5. $1/CP_a$ vs. $1/RP_a$.Fig. 6. Effects of the temperature on K_A and K_B .

rate which is affected by the concentration of acetaldehyde. The concentration of acetaldehyde is controlled by the pressure of the endothermic reactor owing to enough fast rate of the vaporization than the depolymerization rate. The

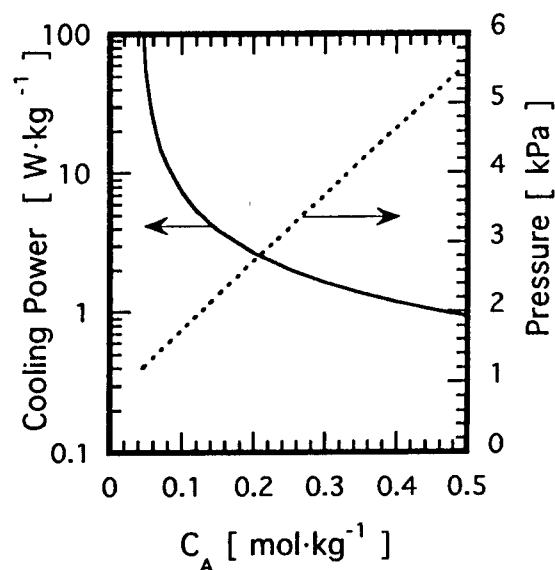


Fig. 7. Effects of the concentration of acetaldehyde on the cooling power and the pressure at 13 °C.

COP is the ratio of the endothermic energy to the compressor work. The compressor work is evaluated from the pressure ratio of the exothermic reactor to the endothermic reactor.

The effects of the concentration of acetaldehyde on the cooling power and on the pressure at 13 °C are shown in Fig. 7. The high concentration of acetaldehyde leads to the high COP because the high concentration of acetaldehyde results in the low compressor work owing to the low pressure of the endothermic reactor. The cooling power, however, decreases with an increase in the concentration of acetaldehyde.

The high cooling power is required at high concentration of acetaldehyde. The depolymerization rate depends on the characteristic of the catalyst. The depolymerization rate and the cooling power can be improved by the development of the capability of the catalyst.

CONCLUSION

The high cooling power and the high COP is required for the CHP cycle. The rate equation of the depolymerization of paraldehyde has been obtained. The cooling power of the CHP with Pa/A system was estimated from the depolymerization rate of paraldehyde. The high concentration of acetaldehyde leads to the high COP owing to a decrease in the compressor work. However the cooling power decreases at the high concentration of acetaldehyde. The cooling power depends on the characteristic of catalyst. The development of catalyst is required for the CHP with Pa/A system.

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NOMENCLATURE

C_A = concentration of acetaldehyde	[mol·kg ⁻¹]
C_{Pa} = concentration of paraldehyde	[mol·kg ⁻¹]
C_θ = concentration of vacant sites of catalyst	[mol·kg ⁻¹]
$C_{A\theta}$ = concentration of active sites of catalyst adsorbed by acetaldehyde	[mol·kg ⁻¹]
$C_{AA\theta}$ = concentration of active sites of catalyst adsorbed by intermediate product	[mol·kg ⁻¹]
$C_{Pa\theta}$ = concentration of active sites of catalyst adsorbed by paraldehyde	[mol·kg ⁻¹]
k_i = rate coefficient of forward reaction at step i	[kg·mol ⁻¹ ·s ⁻¹]
k_{-i} = rate coefficient of reverse reaction at step i	[kg·mol ⁻¹ ·s ⁻¹]
K_A = constant	[s]

K_B = constant	[kg·s·mol ⁻¹]
K_i = reaction equilibrium constant at step i	[-]
M_A = molecular weight of acetaldehyde	[kg·mol ⁻¹]
M_{Pa} = molecular weight of paraldehyde	[kg·mol ⁻¹]
R_{Pa} = reaction rate of depolymerization of paraldehyde	[mol·kg ⁻¹ s ⁻¹]
R_i = reaction rate of step i	[mol·kg ⁻¹ s ⁻¹]
T = temperature	[K]

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