Paraldehyde Depolymerization for
Chemical Heat Pump Application

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ABSTRACT

Chemical heat pump is using the reversible chemical reaction. The reversible reaction of paraldehyde/acetaldehyde system has been expected to be applied to the chemical heat pump. The purpose of this work is to investigate the endothermic depolymerization of paraldehyde with the acidic resin catalyst for cooling system application. The rate equation, the rate constant of depolymerization and the cooling power have been evaluated under 13-40 °C and at 1 atm. The bubble of acetaldehyde generated at the reactor. The produced bubble inhibits the depolymerization. The cooling power is 1.0 W/kg at 13 °C. The cooling power is almost same as that of conventional air conditioning system. The COP can be improved by the separation of the unreacted substance.

1. INTRODUCTION

Chemical heat pump (CHP) is the chemical process which is applied to change the temperature level of the thermal energy. The advantages of the CHP are the high energy-density storage, the environmental safety without CFCs, and the high potential for air conditioning application and upgrading the heat source. The system can be operated by many conditions; temperature change, pressure change and concentration change.

The CHP system is using endothermic/exothermic chemical reaction such as the dehydrogenation/hydrogenation reaction, and the depolymerization/polymerization reaction. The dehydrogenation/hydrogenation system of i -propanol/acetone with catalyst is one of example[1]. The paraldehyde/acetaldehyde system has been proposed by the authors. The paraldehyde/acetaldehyde system is one of the depolymerization/polymerization system. The reactions are performed over the solid acid catalyst.

The purpose of this work is to investigate the depolymerization and evaluate the cooling power of the cooling cycle for the kinetics evaluations and the performance of the CHP for the equilibrium evaluations. The cooling power and the performance of the CHP are necessary for the application of paraldehyde/acetaldehyde system. The cooling power of the paraldehyde/acetaldehyde system depends on the rate of the depolymerization. The depolymerization of paraldehyde has been studied at high temperature [2,3]. The kinetics of the depolymerization of paraldehyde was required at low temperature for the cooling system. The depolymerization of paraldehyde has been measured and the cooling power

has been estimated from experimental result, and the performance of cooling system has been evaluated.

2. CYCLE EXPLANATION

The paraldehyde/acetaldehyde system has high possibility to use 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 cycle are as follows; this system can be applied for air conditioning system, each reaction produces only one product, and the separation of acetaldehyde from paraldehyde is easy because of large difference in boiling point between paraldehyde and acetaldehyde.

The cycle is shown in Fig. 1. The liquid paraldehyde is depolymerized in the endothermic reactor at low temperature and at low pressure. The liquid paraldehyde, then, is turned into acetaldehyde vapor. Acetaldehyde vapor is compressed and transferred to the 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 the expansion valve to complete the cycle.

3. EXPERIMENTAL PROCEDURE

The experimental apparatus is shown in Fig. 2. The feed paraldehyde contained some acetaldehyde. The concentration of acetaldehyde in the feed paraldehyde was varied. The reaction temperature was set at 13, 20, 30 and 40 °C. The minimum setting temperature was limited by the melting point of paraldehyde (12.6 °C). The maximum setting temperature was limited by the side reaction. The side reaction can not be neglected above 50 °C. The temperature was controlled by the water jacket heat exchanger, and
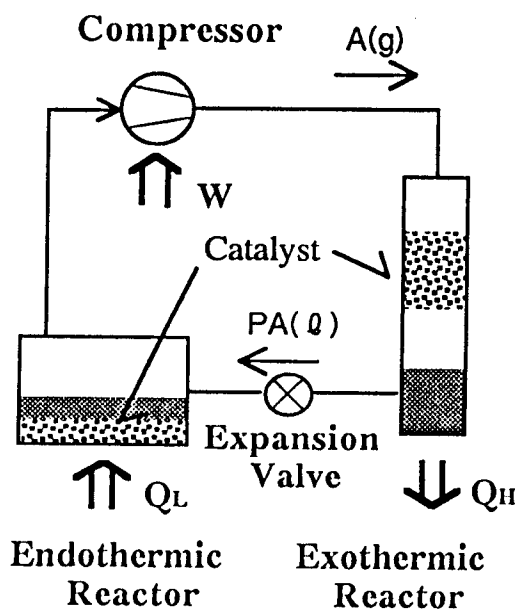

FIGURE 1. The heat pump cycle of
paraldehyde / acetaldehyde;
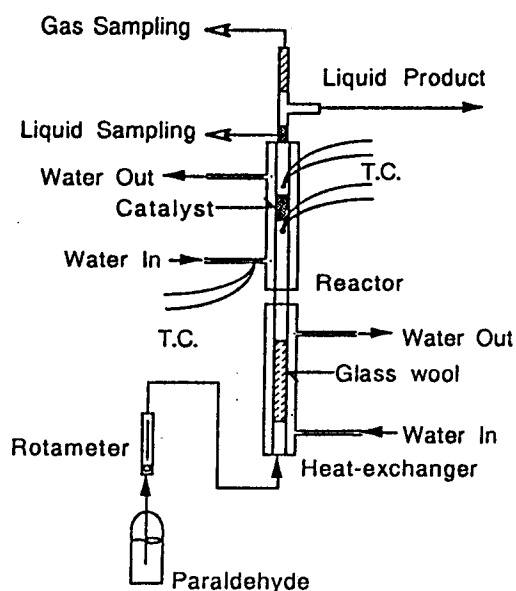A: acetaldehyde, Pa: paraldehyde.

FIGURE 2. Experimental apparatus.

measured by the K-type thermocouples. The error of controlling reaction temperature was maintained within ±0.40 °C.

The catalyst was the strongly acidic cation exchange resin (Amberlyst 15 E). The catalyst was packed at the middle position of the aluminum pipe reactor and supported by stainless steel wire gauze. The weight of catalyst was 0.15 g, and that of catalyst at the reaction temperature of 40 °C is set 0.15 or 2.80 g.

The feed flow rate of the paraldehyde was among 2.3-18.0 ml / min. The liquid product was sampled by the cool syringe, in order to avoid vaporization of the sample; the boiling point of acetaldehyde is 21 °C. The gas product was sampled by warm syringe to prevent condensation of vapor. The product compositions were analyzed by the gas chromatography.

4. RESULTS AND DISCUSSION

The results at 13 °C and 40 °C are shown in Figs. 3 and 4, respectively. The concentration of acetaldehyde increases with the contact time. The rate of the depolymerization decreases with an increase in the initial concentration of acetaldehyde.

The depolymerization rate is affected by the concentration of acetaldehyde in the liquid. The rate of depolymerization is fast at low concentration of acetaldehyde. The rate is zero at equilibrium. The rate depends on the difference between the concentration of acetaldehyde in liquid and that of acetaldehyde at the equilibrium. The rate of the depolymerization; R is assumed as first order reaction in the difference concentration. The rate of the depolymerization at the concentration of acetaldehyde; C_A, can be expressed as

$$R = dC_A/dt = k(Ce-C_A)$$
$$-kt = log(1-C_A/Ce)$$

where Ce is concentration at the reaction equilibrium, k is the rate constant, and t is the contact time. The equilibrium concentration and the equilibrium pressure have been measured and calculated. The effects of temperature on the equilibrium pressure and equilibrium mole fraction are shown in Fig. 5.
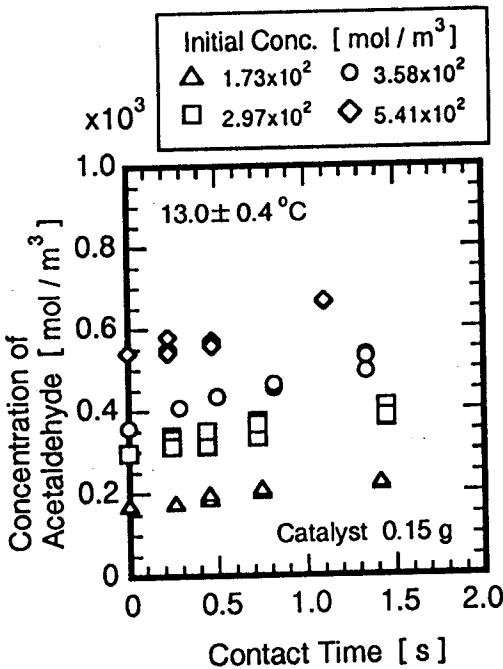

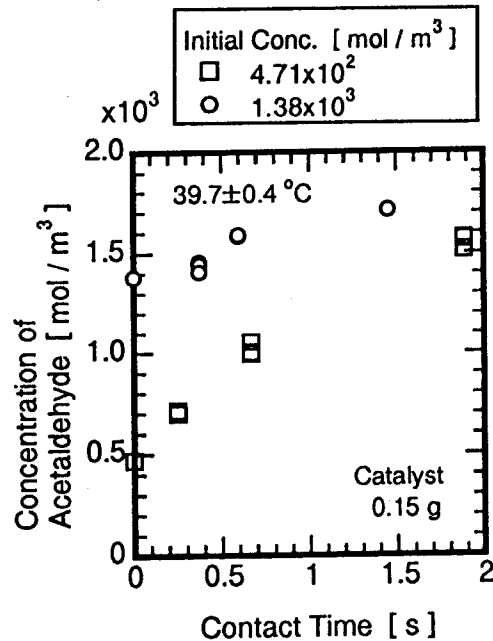FIGURE 3. Relationship between outlet concentration of acetaldehyde and contact time.

FIGURE 4. Relationship between outlet concentration of acetaldehyde and contact time.

The relationship between the bubble generation rate and the contact time is shown in Fig. 9. The bubble generation increases with the contact time. The outlet concentration of the gas and that of the liquid are shown in Fig. 10. The outlet concentration of acetaldehyde in liquid increases and approaches the equilibrium level, with the contact time. The concentration of the gas is almost steady. The reaction rate decreases at the bubble generating as compared with no bubble generation, as shown in Fig. 8. The produced bubble inhibits the depolymerization of paraldehyde. The produced bubble forms the gas holdup around the catalyst, and inhibits the mass transfer.

The pressure of the reactor was atmospheric; 101.3 kPa and higher than the equilibrium, then the generation of the bubble should be not occur. The equilibrium pressure is 84.8 kPa at 40 °C, as shown in Fig. 5. The bubble, however, has been observed at the reaction temperature of 40 °C. The bubble is generated on the catalyst surface. The bubble generation is due to the local concentration on the catalyst surface. The acetaldehyde concentration on the catalyst surface is higher than the bulk concentration.
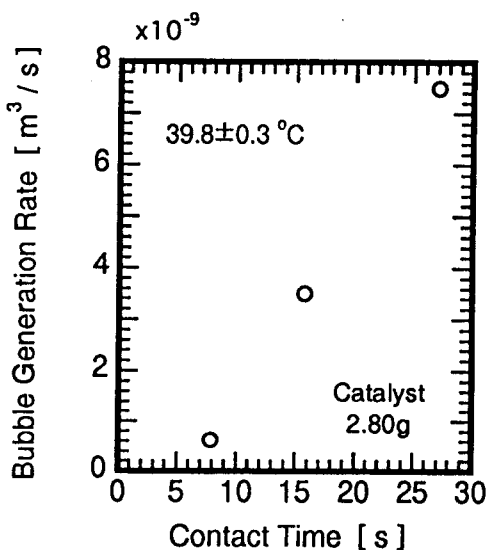

FIGURE 8. Effects of temperature on reaction rate constant .

FIGURE 9. Relationship between bubble generation rate and contact time.
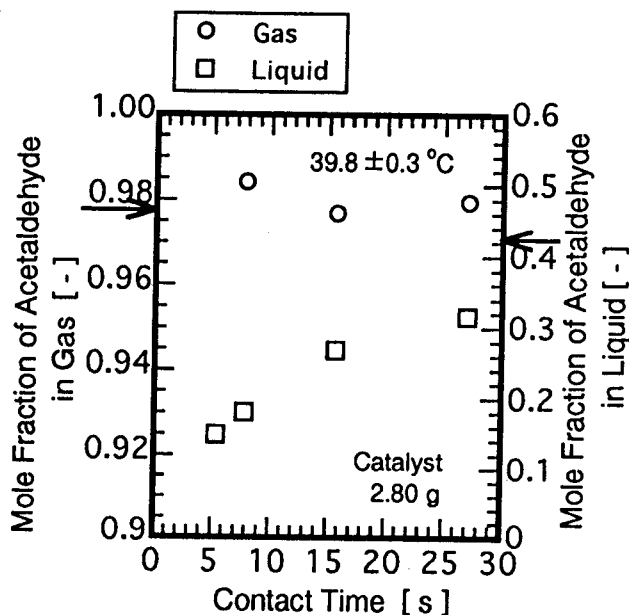
FIGURE 10. Effects of contact time on mole fraction of acetaldehyde in gas and in liquid ; arrows indicate equilibrium at 40 °C.

5. CHEMICAL HEAT PUMP APPLICATION

The cooling power at the endothermic reactor has been estimated. The relationship between the cooling power and the concentration in the reactor is shown in Fig. 11. The cooling power consists of the heat of reaction and the latent heat of vaporization. The

The modified contact time and the concentration data are plotted in semilogarithmic coordinates in Figs. 6 and 7. The contact time in Figs. 3 and 4 was converted to the modified contact time, since the initial concentration of acetaldehyde was varied. Figures 6 and 7 indicate that the reaction rate decreases with an increase in the modified contact time. The straight lines should be obtained from the relationship between $log(1-C_A/Ce)$ and the modified contact time. The slope of the straight line corresponds to the rate constant.

The relationship between the rate constant and the reaction temperature is shown in Fig. 8. The rate constant increases with an increase in the reaction temperature. The increase in the rate constant results in the endothermic reaction. The reaction constant at 13 °C is almost same as that of 20 °C. It is an unsettled question.

The endothermic reactor of the CHP system is operated under low pressure. The bubble of acetaldehyde is generated at the catalyst bed of the endothermic reactor. The bubble may affect the rate of depolymerization. The bubble effect has been considered at 40 °C with the long catalyst bed; the catalyst weight was 2.80 g.
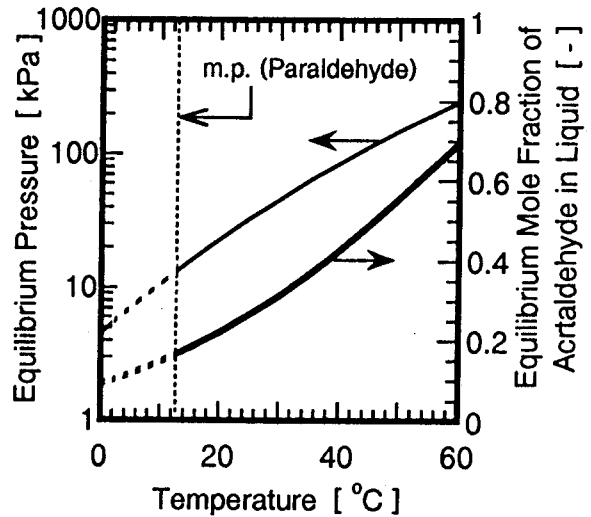

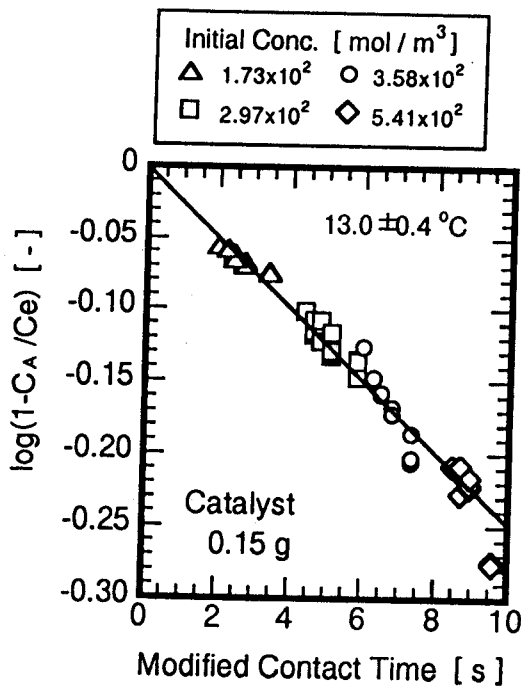**FIGURE 5.** Effects of temperature on equilibrium pressure and equilibrium mole fraction.

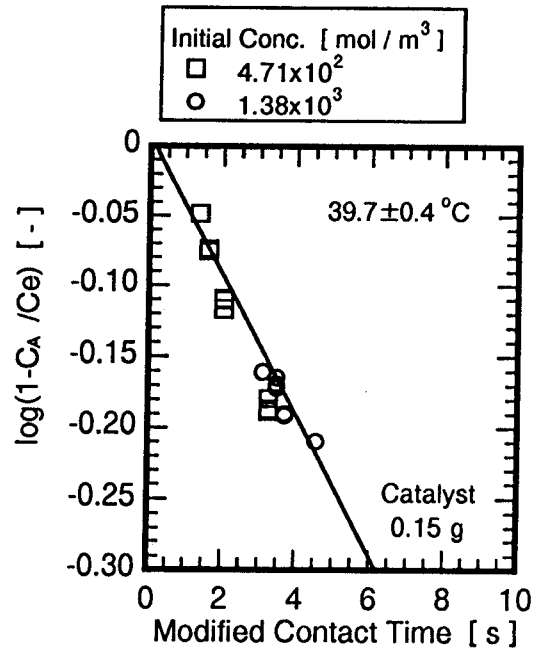**FIGURE 6.** Relationship between $log(1-C_A/Ce)$ and contact time.

FIGURE 7. Relationship between $log(1-C_A/Ce)$ and contact time.

cooling power is 1.0 kW/kg at 13 °C, when the concentration is 8×10^2 mol/m^3. The cooling power of the paraldehyde/acetaldehyde system is almost same as that of a conventional mechanical heat pump with R-22. The cooling power of the mechanical heat pump with R-22 is about 0.8-2.0 kW/kg. The cooling power of the paraldehyde/acetaldehyde system is dependent on the characteristic of the catalyst. The cooling power can be improved by the development of the capability of the catalyst.

The paraldehyde/acetaldehyde system has been evaluated by the coefficient of performance (COP). The COP is defined as the ratio of the endothermic heat energy to the work of the compressor. The COP has been calculated with the equilibrium data as shown in Fig. 5. The compression process at the compressor is adiabatic. The COP is 8.33, when the temperature of endothermic reactor and that of the exothermic reactor are 13 °C and 40 °C, respectively.

The effects of the separation of the unreacted substance have been evaluated by the COP. The unreacted substance is included in the outlet fluid of each reactor. The unreacted substance is separated and returned to each reactor. The liquid acetaldehyde is the unreacted substance at the outlet of exothermic reactor (A). The bubble paraldehyde is the unreacted substance at the outlet of the endothermic reactor (B). The work of separation is neglected in the evaluation. The results are presented in table 1. The COP can be improved by the separation. The separation at (A) is slightly effective than the separation at (B).
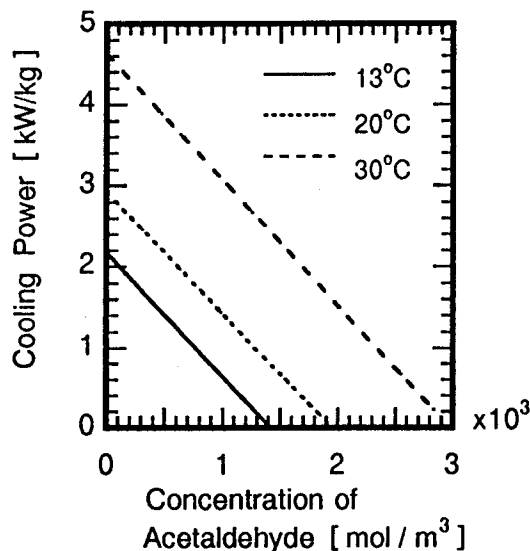

FIGURE 11. Relationship between cooling power and concentration of acetaldehyde.

TABLE 1. Comparison of COP; separation point; A: outlet of the exothermic reactor; B: outlet of the endothermic reaction, endothermic reactor: 13 °C; exothermic reactor: 40 °C

Separation Point	COP
no separation	8.33
A	9.55
B	9.36
A+B	10.58

ACKNOWLEDGMENTS

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