

## Extraction Process of Isobutylene from C<sub>4</sub>-raffinate - Absorption and Reaction of Isobutylene in Para-Toluene Sulfonic Acid -

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### C<sub>4</sub>-추진물에서의 이소부틸렌 추출공정 - 파라톨루엔 설폰산에서 이소부틸렌의 흡수 및 반응 -

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#### ABSTRACT

The optimum conditions and rates of absorption of isobutylene in aqueous para-toluene sulfonic acid(PTSA) were studied experimentally in a stirred reactor. The effects of acid concentration(30-70 wt%), acid loading (0.3-5), mixing intensity(400-1000 rpm), and temperature (20-80°C) on the absorption conditions were examined. The absorption rate of isobutylene was first order in isobutylene and variable order in PTSA concentrations. The apparent energy of activation was found to be 13 Kcal/mole.

#### INTRODUCTION

The thermal or catalytic cracking of naphtha for producing ethene yields large amounts of C<sub>4</sub>-hydrocarbons. After washing out the butadiene, the remaining C<sub>4</sub>-raffinate may contain up to 50% of isobutylene(1,2). It is necessary to be separation of isobutylene from C<sub>4</sub>-raffinate for use as the chemical feedstock. The various kinds of the isobutylene separation processes are commercially practiced or available for licence currently. A new separation technology of isobutylene from C<sub>4</sub>-raffinate has been developed and patented by Korea Institute of Science and Technology (KIST). This is the separation and recovery of isobutylene from C<sub>4</sub>-raffinate by selective absorption in the presence of para-toluene sulfonic acid(PTSA). There are some data in the literature concerning the absorption of isobutylene in aqueous solution of sulfuric acid(3,5-8). Gehlawat and Sharma(3) studied the absorption of isobutylene in a

stirred cell and a liquid jet apparatus at sulfuric acid concentration ranging from 48.5 to 71 wt%. Popovic and Deckwer(8) studied the effect of tertiary butyl alcohol (TBA) on the absorption rate of isobutylene in a bubble column. Recently Levine and Olechowski(6) were patented a process for the recovery of isobutylene as a TBA from C<sub>4</sub>-raffinate by using the 50 to 80 wt% hydrocarbyl sulfonic acid.

In spite of the numerous studies which has been reported in the literature, there are not available information concerning the design conditions prevailing in the industrial process. Therefore it was the objectives of this work to find the optimum absorption conditions and to find the kinetics of the absorption of isobutylene experimentally.

#### MATERIALS AND METHODS

Experiments were carried out in a 10cm i. d. stainless

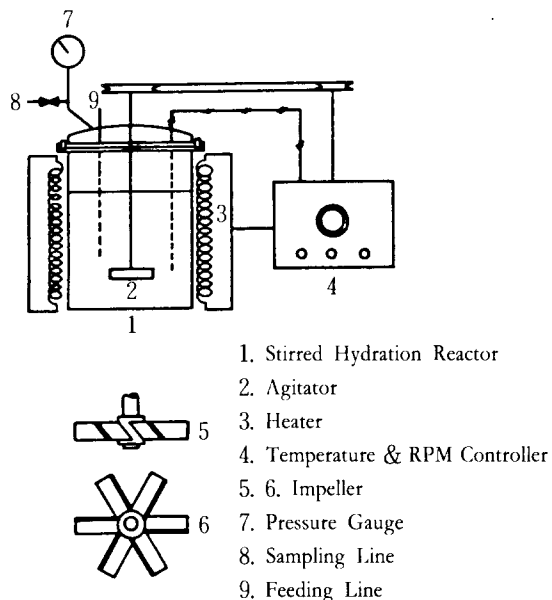


Fig. 1. Schematic diagram of stirred reactor.

steel stirred reactor of Fig. 1. The stirred reactor was kept in a desired temperature by using the band heater and temperature controller and attached the pressure gauge to record the operating pressure. The stainless steel stirrer with six pitched blade turbine, which just dipped into the liquid, was used. The  $C_4$ -raffinate used was a real mixture of  $C_4$ -hydrocarbons produced by Honam Ethylene Co.. A known amounts of the solutions of pre-fixed PTSA concentration ( $C_{PTSA}$ ) and  $C_4$ -raffinate were taken, and adjusted the desired temperature ( $T$ ), then the experiment was started. Gas phase samples were taken periodically by using a sample bottle. The gas samples were analyzed by gas chromatography using a HP5880 chromatograph with a 9m column packed with 25% benzyl cyanide and 12.5% silver nitrate on chromosorb P(60/80 mesh, A/W). A acid loading is defined as the ratio of moles of isobutyl to the moles of PTSA.

## RESULTS AND DISCUSSION

### Optimum Operating Conditions

As shown in Fig. 2, the isobutylene concentration ( $C_{IB}$ ) in the organic phase was sharply decreased until the contact time was elapsed about 10 minutes, and finally reached

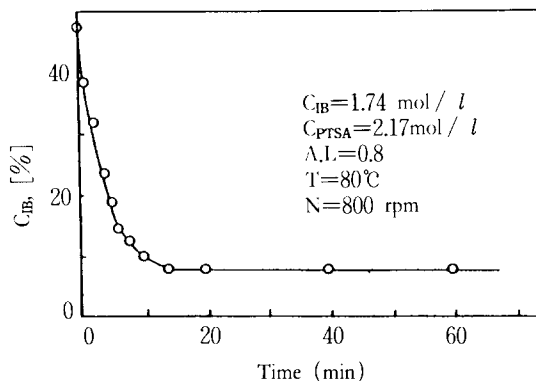


Fig. 2. The change of isobutylene concentration on the reaction time.

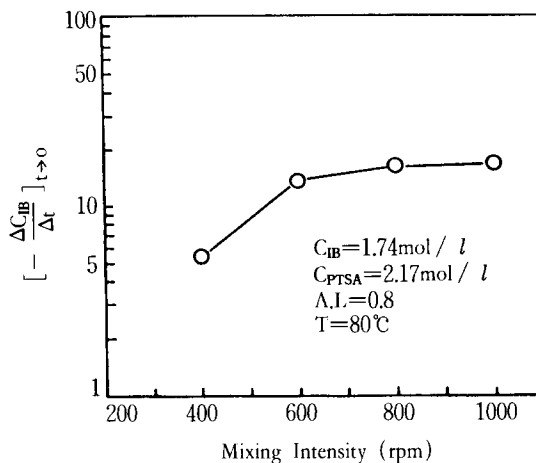


Fig. 3. The change of initial rate of absorption vs. mixing intensity.

the equilibrium state. It was indicated that the absorption and reaction of isobutylene in the PTSA solution involved the equilibrium reaction. The conversion of isobutylene ( $X_{IB}$ ) at this equilibrium state were about 85–90% in the all experiments, so the initial rate of absorption could be expressed the absorption rate of isobutylene. For the calculation of the conversion, it was assumed that the isobutylene was only absorbed in the PTSA solution. The mixing intensity affects the absorption and reaction because of the diffusional factors. Fig. 3 shows the effect of mixing intensity ( $N$ ) on the initial rate of absorption. It

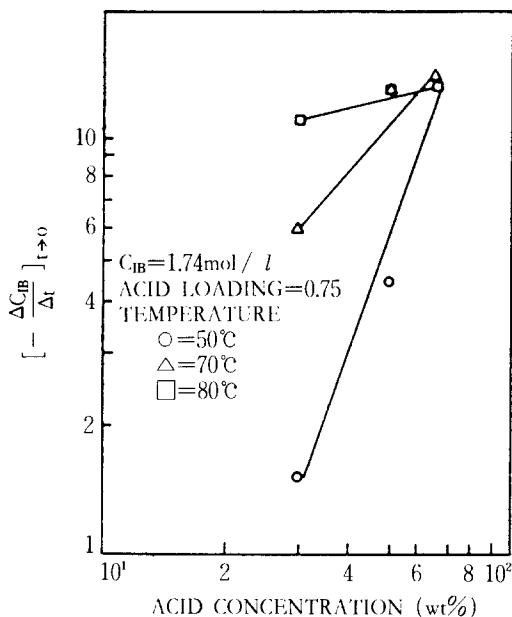


Fig. 4. Effect of acid concentration on the initial rate of absorption.

can be seen that the initial rate of absorption increase with increasing the impeller speed. However above the 600 rpm of impeller speed, the variation was not significant. It was expressed that the variation in stirring rate above the 600 rpm did not affect the absorption rates and indicated that the liquid phase mass transfer resistance was negligible.

Since the reaction of the isobutylene is the exothermic proton-catalyzed hydrolysis to TBA. The initial rate of absorption was increased with PTSA concentrations, as shown in Fig. 4. Also the higher the reaction temperature, the larger value of the initial rate of absorption was obtained. However the maximum values were obtained at the concentrations of 65 wt% regardless of the variation of the experimental conditions. Below an acid concentration of 50 wt%, the difference in reactivity between isobutylene and *n*-butenes is considerably increased, so the isobutylene is more selectively separated from the C<sub>4</sub>-raffinate. But the reaction activity fell off dramatically. Above the 70 wt% concentration, hydrate of the solid toluene sulfonic acid precipitated from the solution. Therefore the favorable condition of catalyst was about 50–65 wt% of PTSA concentration.

The rate of absorption of isobutylene was greatly effected

by the temperature. In the experiments, the higher the operating temperature, the higher the initial rate of absorption. But the conversion of isobutylene in the equilibrium state had higher value as the temperature is lower. If the temperature was increased, the reaction rate also increased, however, the solubility of the isobutylene in the system of acid/TBA/water decreased. Usually the high acid loading (A.L.) corresponding to appreciable amounts of TBA in the liquid phase may decrease the reaction rate but increase the physical solubility of isobutylene. Therefore the lower temperature at high acid loading permits a higher conversion of the isobutylene. It was observed experimentally that the effect of temperature on the initial rate of absorption above the 70°C was rarely independent on the PTSA concentration and acid loadings. Therefore the optimum temperature was about 70°C in the experimental ranges. The initial rate of absorption and the conversion of isobutylene at equilibrium state were decreased with increasing the acid loading. Also if the acid loading was greater than 1.0, it took much time to reach the equilibrium state and the hydrate of PTSA precipitated from the solution after the end of the experiment. For the absorbed isobutylene react with water in the presence of the PTSA to form TBA, the PTSA solution become supersaturation under the conditions of high acid loading.

### Kinetics of Absorption

The effect of isobutylene concentration on the rate was investigated by preparing a solution of isobutylene (from 0.47 to 1.74 mol/l), and the concentration of PTSA solution was fixed to 50 wt% (2.2 mol/l). From the experimental data, the rate ( $-dC_{IB}/dt$ ) were calculated over the interval of 10–15% conversion. The order in isobutylene was determined by the slope in graph of  $\ln(-dC_{IB}/dt)$  versus  $\ln(C_{IB})$ , with an average value of 1.10 (Fig. 5). This indicated that the rate of absorption was first order with respect to isobutylene. The same results were reported in the literature for the hydration of isobutylene by various acid catalysts (3, 8). Similar experiments to the above were carried out to establish the order of the reaction with respect to PTSA. However the order of reaction is nearly first order at the lowest concentration and fifth order at the highest. Taft (9) found that the log of the reaction rate constant for the hydration of isobutylene in nitric acid solutions vary linearly with the acidity function

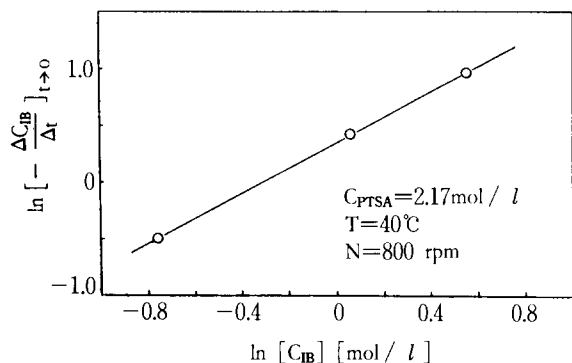


Fig. 5. Plot of  $\ln \left[ -\frac{\Delta C_{IB}}{\Delta t} \right]_{t \rightarrow 0}$  vs.  $\ln(C_{IB})$ .

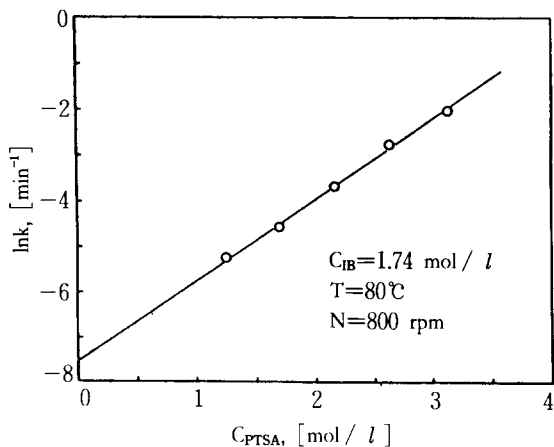


Fig. 6. Plot of  $\ln(k)$  vs. PTSA concentrations.

in solution concentration from 0.09 to 5 mol/l. Gehalwat and Sharma(3) also showed the similar results in sulfuric acid solutions.

They used the values of acidity function as the molarity of acid solutions. A plot of  $\ln(k)$  against the concentration of the aqueous solution of PTSA gave a straight line relationship (Fig. 6), and the empirical correlation was followed.  $\ln(k) = 5.6 \times 10^{-4} \exp(1.8 \times C_{PTSA})$

where  $k$  is the first order reaction rate constant.

Activation energy for the absorption of isobutylene were measured and the results are shown in Fig. 7. The Arrhenius energy is about 13 Kcal/mole for all the concentration of PTSA investigated in this work. Fig. 8 showed

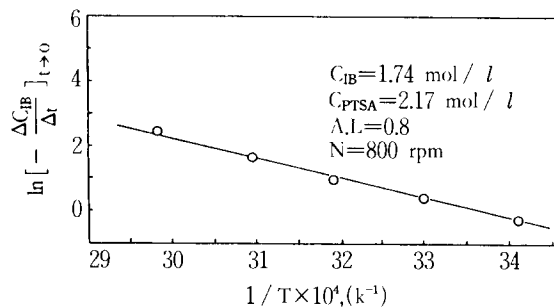


Fig. 7. Plot of initial rate of absorption vs.  $1/T$ .

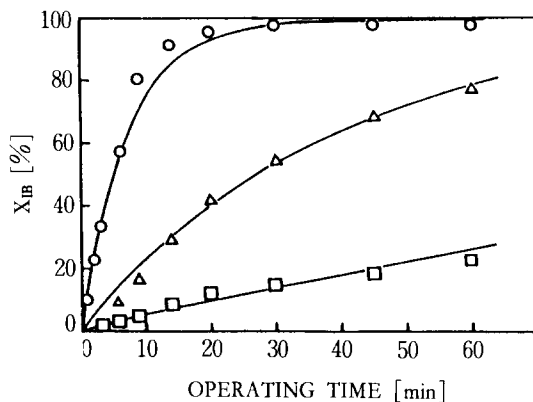


Fig. 8. The comparison between the experimental and calculated results.  
(calculated: —, experimental:  
□ = 1.3, △ = 2.2, ○ = 3.1 mol/l)

the comparison of the conversion of isobutylene between the experimental and calculated results for conditions 1. 7 mol/l of isobutylene concentration and 40°C of temperature. From the fact that the results coincide fairly well, it may be concluded that the absorption rate was predicted the experimental results very well.

## CONCLUSIONS

From the finding of this experimental study on the absorption in the stirred reactor, the conclusion can be made as follows:

1. The favorable operating conditions were 70°C of tem-

perature, 0.8 of acid loading, and 50–65 wt% of PTSA concentration.

2. The rate of absorption of isobutylene in aqueous solution of PTSA was found to be first order mechanism.
3. The first order rate constant was  $\ln(k)=5.6 \times 10^{-4} \exp(1.8 \times C_{PTSA})$  at 40°C and the activation energy was found to be 13 Kcal/mol.

### 요 약

본 연구는 혼합 반응기에서 파라-톨루엔 설펜산(PTSA) 용액으로 이소부틸렌의 최적 흡수 속도론과 최적 흡수 조건을 연구하였다.

본 실험에서 행한 실험 조건은 온도 20–80°C, 혼합속도 400–1000 rpm, 산농도 30–70 wt% 그리고 산부하(acid loading) 0.3–5 이었다.

결과적으로 최적 조건에서의 이소부틸렌의 흡수속도는 이소부틸렌 농도항에 대한 1차 반응이며 PTSA 농도항에 대해서는 반응 차수가 변한다. 그때의 겉보기 활성화에너지는 13Kcal/mol 이었다.

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