This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Separation of Trimethylbenzene Isomers on Molecular Sieves 13X in High Pressure Carbon Dioxide

Chung-Sung Tan[a]; Chin-Hsin Huang[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, NATIONAL TSING HUA UNIVERSITY, HSINCHU, TAIWAN, REPUBLIC OF CHINA

To cite this Article Tan, Chung-Sung and Huang, Chin-Hsin(1996) 'Separation of Trimethylbenzene Isomers on Molecular Sieves 13X in High Pressure Carbon Dioxide', Separation Science and Technology, 31: 15, 2011 — 2019
To link to this Article: DOI: 10.1080/01496399608001028
URL: http://dx.doi.org/10.1080/01496399608001028

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION SCIENCE AND TECHNOLOGY, **31**(15), pp. 2011–2019, 1996

Separation of Trimethylbenzene Isomers on Molecular Sieves 13X in High Pressure Carbon Dioxide

CHUNG-SUNG TAN* and CHIN-HSIN HUANG
DEPARTMENT OF CHEMICAL ENGINEERING
NATIONAL TSING HUA UNIVERSITY
HSINCHU, TAIWAN 30043, REPUBLIC OF CHINA

ABSTRACT

An experimental study of the separation of 1,2,4- and 1,3,5-trimethylbenzenes from a mixture containing the weight composition 56% 1,2,4-trimethylbenzene and 44% 1,3,5-trimethylbenzene on molecular sieves 13X in high pressure carbon dioxide was performed. For a pulse of 1.18 cm^3 of trimethylbenzene isomers and 40 g of molecular sieves 13X, the effects of pressure, temperature, and flow rate on separation effectiveness were examined. The results indicated that the most appropriate operating conditions for obtaining a higher recovery of each isomer with a purity of at least 98% and a shorter mean retention time for 1,3,5-trimethylbenzene were a temperature of around 363 K, a pressure of 74.8 atm, and a flow rate of 15.0 cm^3/min.

INTRODUCTION

1,2,4-Trimethylbenzene is a valuable compound which can be used as the starting material for producing plasticizer, water-soluble coating agent, and polyimide. One of its sources is the C_9+ aromatic hydrocarbon mixtures which are the by-products in production of BTX in naphtha crackers and reformers. Because of the virtually closing boiling points possessed by isomeric tri-alkylsubstituted benzenes (for example, 1,2,4- and 1,3,5-trimethylbenzenes are 442.4 and 437.7 K, respectively), it is difficult to separate them effectively by distillation. A possible means for obtaining high purity 1,2,4-trimethylbenzene is to adopt a selective adsorption pro-

---

* To whom correspondence should be addressed.

cess employing a proper adsorbent. While several adsorption processes have been developed for the separation of alkylaromatic isomers (1–6), little information is available on the separation of trimethylbenzene isomers. Fleck et al. (7) used Linde 10X molecular sieves to separate a mixture containing 56% 1,2,4-trimethylbenzene and 44% 1,3,5-trimethylbenzene at approximately 477 K. A purity of 82% 1,2,4-trimethylbenzene could be obtained. In their study, toluene was used as the desorbent.

Most selective adsorption separation processes are carried out under liquid-phase operation (8–10). Recent publications, however, showed that more effective separation can be achieved under gas-phase conditions (11–13). The improvement might be attributed to higher mass transfer rates in the vapor phase. However, both operations require a desorbent; some C_7 to C_{10} aromatics are commonly employed. Because high pressure CO_2 possesses several unique properties, such as gas-like viscosity, liquid-like density, solubilities of organic compounds that are dependent on density, high mass transfer rates, and nonflammability, it appears to be an alternative carrier and desorbent. In a study of the separation of xylene isomers on silicalite in high pressure carbon dioxide, Tan and coworkers (14, 15) observed that the separation was promising in gaseous carbon dioxide which acted not only as a desorbent but also as a carrier. The objective of this report is to study the separation of 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene using the technique proposed by Tan and Tsai (14).

EXPERIMENTAL

The experimental apparatus used for the pulse injection experiments is illustrated in Fig. 1. Several adsorbents, such as silicalites, ZSM-5, and molecular sieve 13X, were tested in this study. However, only molecular sieve 13X (Fluka Co.) was found to provide satisfactory separation in the preliminary study, and for this reason only the results using molecular sieve 13X are reported in this paper. Before they were used, molecular sieve 13X pellets of 0.078 cm diameter were dried for 12 hours at 423 K. Approximately 40 g of the pellets were then packed into a stainless-steel 316 column of 2.12 cm i.d. and 25 cm length. To make full use of the adsorbent, glass beads of 0.07 cm diameter were packed both above and below the molecular sieve 13X packing to a height of about 5 cm in each section.

The trimethylbenzene mixture containing 56 wt% 1,2,4-trimethylbenzene and 44 wt% 1,3,5-trimethylbenzene was prepared by mixing research grade samples of the two isomers. The composition of the mixture was also confirmed by GC analysis. This mixture was pumped to a six-port

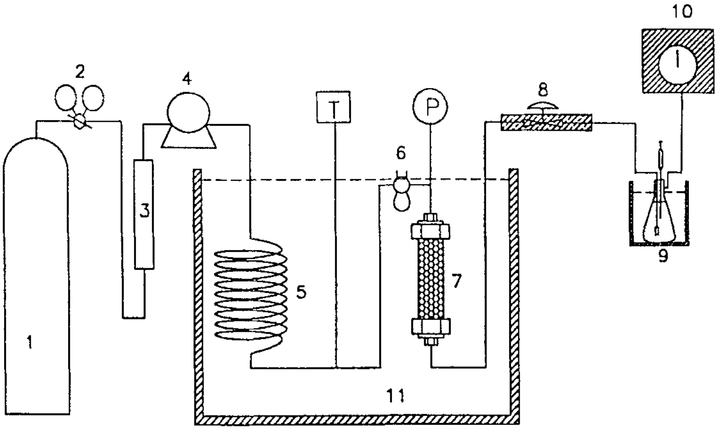

FIG. 1 Schematic diagram of the experimental apparatus.

sampling valve (Rheodyne), and the sampling loop of 1.18 cm^3 was allowed to fill with the mixture. High purity CO_2 (99.9%) was first passed through a bed of zeolite 3A to remove any possible water from the gas, and the gas was then compressed to the desired pressure with a minipump (LDC Analytical). The pressure could be maintained to within 3% of the desired value in all experiments. The temperature was controlled by means of an oil bath whose accuracy was about 0.5 K. A preheating coil was immersed in the oil bath to allow the fluid to reach the desired temperature.

Before injecting the trimethylbenzene mixture into the carrier, the fluid bypassed the sampling loop. When the flow rate of the fluid became stable, the six-port sampling valve was switched to allow the fluid to carry the trimethylbenzene mixture and flow into the packed column. The effluent fluid from the column was expanded across a metering valve. The trimethylbenzene isomers were collected in a cold trap containing 200 cm^3 of alcohol and 0.2 g of decane as an internal standard. The temperature of the cold trap was maintained at 263 K. Samples of 5 μL volume were frequently sent to a GC for compositional analysis. The flow rate in the adsorption column was determined by measuring the volume of the expanded gas with a wet test meter.

RESULTS AND DISCUSSION

The overall masses of 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene collected in the cold trap were determined by measuring the final concentrations in the cold trap. These amounts were compared with those injected. The agreement was satisfactory. The deviation was less than 4.0% in general. This indicated that the components injected were not retained on the adsorbent after the experiment. The reproducibility tests were also performed at several operating conditions. Some results listed in Table 1 show that the data were reproducible to within 8% with respect to the mean retention time for 1,3,5-trimethylbenzene and the recoveries for both isomers. The mean retention time is defined as

TABLE 1

Experimental Results of Retention Time and Recovery[a] at Various Operating Conditions

T (K)	P (atm)	Q (cm^3/min)	$\bar{t}_{135}$ (min)	R_{135} (%)	R_{124} (%)
		Reproducibility Test			
333	74.8	15	153	54.3	56.2
333	74.8	15	151	55.2	56.0
363	74.8	15	256	82.2	81.3
363	74.8	15	236	82.5	79.1
		Effect of Pressure			
363	61.2	15	552	86.2	89.3
363	74.8	15	256	82.2	81.3
363	81.6	15	182	71.5	66.1
363	88.4	15	117	65.5	58.9
		Effect of Temperature			
333	74.8	15	153	54.3	56.2
353	74.8	15	225	74.3	72.8
363	74.8	15	256	82.2	81.3
373	74.8	15	304	83.9	81.7
393	74.8	15	389	85.6	87.7
		Effect of Flow Rate			
363	74.8	10	362	72.4	72.3
363	74.8	15	256	82.2	81.3
363	74.8	20	207	73.9	72.9
363	74.8	25	173	65.2	65.7

[a] Recovery represents the amount of each trimethylbenzene isomer with a purity of at least 98% collected divided by the amount injected.

$$\bar{t} = \frac{\int_0^{t_0} ctdt}{\int_0^{t_0} cdt} \tag{1}$$

where t_0 is equal to the time required to complete the experiment. The recovery is defined as the amount collected with a purity higher than 98% over the total experimental period divided by the amount injected. An optimum separation process should exhibit low retention times and high recoveries.

Effect of Pressure

When the temperature and flow rate were maintained at 363 K and 15.0 cm^3/min, respectively, the results shown in Fig. 2 and Table 1 indicate that the higher recoveries for both trimethylbenzene isomers with a purity of at least 98% were obtained at relatively lower pressures; for example, at 61.2 and 74.8 atm. However, the operation at 61.2 atm is not recommended because a relatively long operation time was required (a longer retention

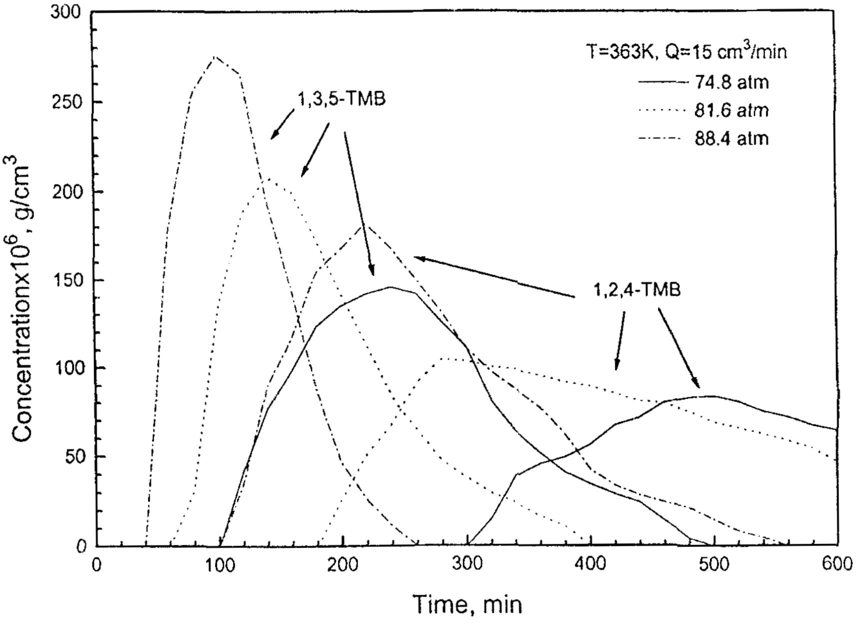

FIG. 2 Trimethylbenzene response curves at various pressures.

time for 1,3,5-trimethylbenzene represents a longer operation time required). The retention time of 1,2,4-trimethylbenzene was not our main concern and is therefore not reported in Table 1. This is because that it could be reduced drastically by a sudden increase in pressure to a value higher than the CO_2 critical pressure when 1,3,5-trimethylbenzene is completely removed from the adsorption column. The solubility of organic solutes in supercritical fluids generally increases with pressure at constant temperature (16, 17). As a result, the interaction forces between the solute and the supercritical fluid are greater than those between the solute and the adsorbent. Because of this fact, the supercritical fluids have proved to be effective desorbents to regenerate the solid matrices loaded with organic compounds (18–20). Figure 3 illustrates that more 1,2,4-trimethylbenzene could be obtained in a shorter period when the pressure was suddenly raised from 74.8 to 108.8 atm at 500 minutes. It can also be envisioned that a greater increase in pressure would reduce the operation time further.

When the pressure was raised further to 81.6 and 88.4 atm, while the retention time for 1,3,5-trimethylbenzene was reduced, the recoveries became less and the desired separation effectiveness could not be obtained. The reduction in retention and recovery with increasing pressure might

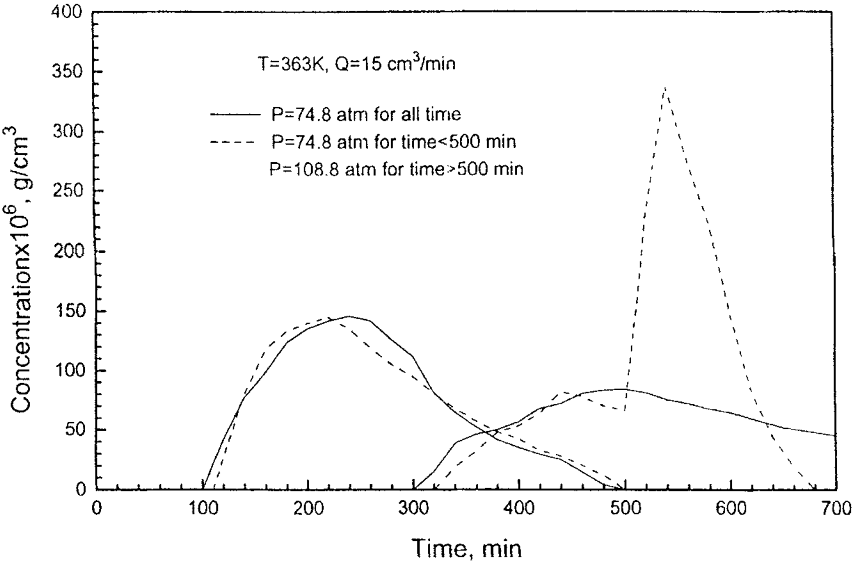

FIG. 3 Trimethylbenzene response curves at 363 K and 15 cm^3/min.

be attributed to the desorption power of supercritical CO_2 as mentioned above. Under this situation, the screening effect of the adsorbent is reduced, and consequently a desired separation becomes impossible. From the above discussion it seems that an appropriate pressure exists around 74.8 atm which compromised both the operation time and the recoveries.

Effect of Temperature

The effect of temperature on separation when the pressure was fixed at 74.8 atm and the flow rate at 15 cm^3/min is shown in Fig. 4 and Table 1. It can be seen that a higher recovery could be obtained at higher temperatures, but a longer operation time was required to complete the separation. Under this situation, an appropriate temperature compromising the recovery and the operation time exists. From Table 1 it is found that this appropriate temperature was at about 363 K where the recoveries of both isomers are more than 80% and the retention time for 1,3,5-trimethylbenzene is reduced about 20% compared with that for the temperatures higher than 363 K. No economic analysis was made in this study to select an optimum temperature.

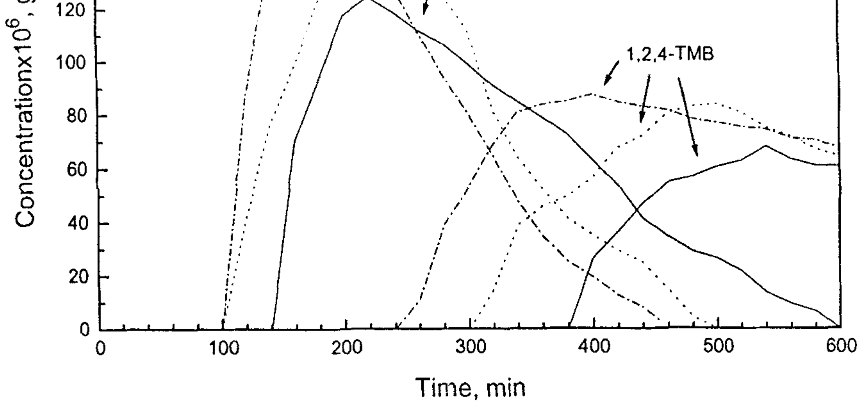

FIG. 4 Trimethylbenzene response curves at various temperatures.

Effect of Flow Rate

When the temperature and pressure were fixed at 363 K and 74.8 atm, respectively, the effect of the flow rate on separation was also studied, and the results are shown in Fig. 5 and Table 1. It can be seen that the mean retention time for 1,3,5-trimethylbenzene was influenced to a greater extent by the flow rate than were recoveries. Since the flow rate had an effect, interphase mass transfer resistances might play a role during separation. From consideration of the recoveries and operation time, the flow rate suggested for the present operation was 15 cm^3/min.

CONCLUSION

The separation of 1,2,4-trimethylbenzene from a mixture containing the weight composition 56% 1,2,4-trimethylbenzene and 44% 1,3,5-trimethylbenzene on molecular sieve 13X in high pressure CO_2 was studied. The experimental results indicated that a satisfactory separation allowing a recovery of each trimethylbenzene with a purity of at least 98% and an acceptable mean retention time for 1,3,5-trimethylbenzene could be obtained by a proper combination of operating temperature, pressure, and flow rate where CO_2 functioned as both a carrier and desorbent. The mean

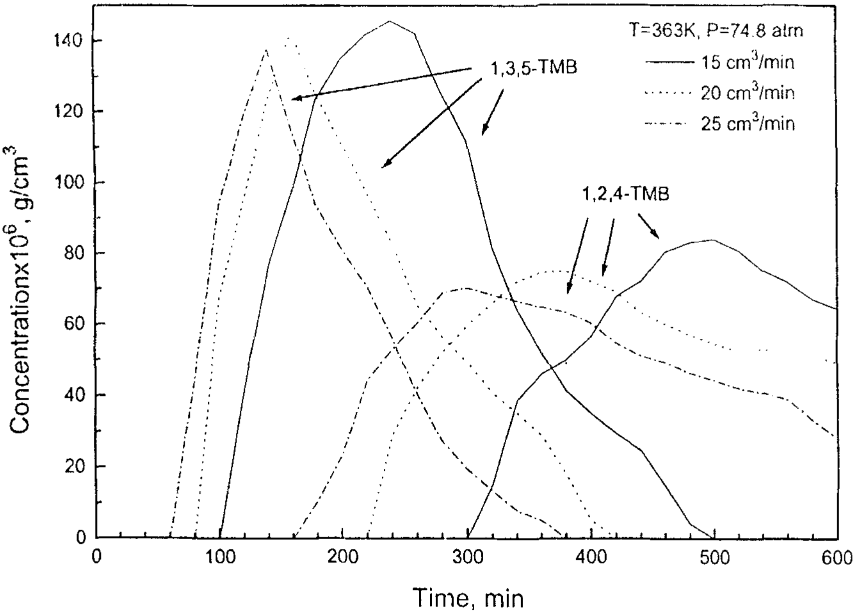

FIG. 5 Trimethylbenzene response curves at various flow rates.

retention time for 1,2,4-trimethylbenzene was not considered because it could be reduced significantly by suddenly raising the pressure to a value far above the CO_2 critical pressure when 1,3,5-trimethylbenzene had been completely removed from the adsorption column. For a pulse of 1.18 cm^3 of the prepared trimethylbenzene mixture, the most appropriate operating combination was a temperature of about 363 K, a pressure of 74.8 atm, and a flow rate of 15 cm^3/min.

The experimental results obtained by the proposed method were also compared with those provided by Fleck et al. (7). The method used in this study showed several advantages over the conventional adsorption method since a larger amount of each trimethylbenzene isomer with a higher purity could be obtained and a much lower operating temperature was employed. The most important aspect of the proposed method is that no organic desorbent is required. The trimethylbenzene isomers can be collected simply by releasing the pressure of the fluid leaving the adsorption column.

REFERENCES

1. D. H. Rosbach, US Patent 3,943,183 (1976).
2. R. W. Neuzil and D. J. Korous, US Patent 4,051,192 (1977).
3. F. J. Healy and P. R. Geissler, US Patent 4,029,717 (1977).
4. M. Seko, T. Miyake, and K. Inada, *Ind. Eng. Chem., Prod. Res. Dev., 18*, 263 (1979).
5. D. B. Broughton, US Patent 4,306,107 (1981).
6. R. J. Maas and R. M. Visser, US Patent 4,326,091 (1982).
7. R. N. Fleck et al., US Patent 3,114,782 (1963).
8. R. W. Neuzil and D. Groves, US Patent 3,558,732 (1971).
9. S. Carra, E. Santacesaria, M. Morbidelli, G. Storti, and D. Gelosa, *Ind. Eng. Chem., Process Des. Dev., 21*, 451 (1982).
10. W. S. Fishkill and J. H. Ester, US Patent 4,439,535 (1984).
11. E. Santacesaria, D. Gelosa, P. Danise, and S. Carra, *Ind. Eng. Chem., Process Des. Dev., 24*, 78 (1985).
12. M. Morbidelli, G. Storti, and S. Carra, *Ind. Eng. Chem., Fundam., 25*, 89 (1986).
13. T. S. Lu and T. Y. Lee, *Ind. Eng. Chem. Res., 26*, 2024 (1987).
14. C. S. Tan and J. L. Tsai, *Ibid., 29*, 502 (1990).
15. W. F. Lin and C. S. Tan, *Sep. Sci. Technol., 26*, 1549 (1991).
16. H. J. Ng and D. B. Robinson, *J. Chem. Eng. Data, 23*, 325 (1978).
17. M. A. McHugh and V. J. Krukonis, *Supercritical Fluid Extraction Principles and Practice*, Butterworth, Stoneham, MA, 1986.
18. R. P. DeFilippi, V. J. Krukonis, R. J. Dobey, and M. Modell, *Supercritical Fluid Regeneration of Activated Carbon for Adsorption of Pesticides, EPA Report*, EPA, Washington, D.C., 1980.
19. B. O. Brady, C. P. C. Kao, K. M. Dooley, F. C. Knopf, and R. P. Gambrell, *Ind. Eng. Chem. Res., 26*, 261 (1987).
20. C. S. Tan and D. C. Liou, *Ibid., 27*, 988 (1988).

Received by editor November 9, 1994
First revision received September 11, 1995
Second revision received November 20, 1995