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Note

Gas chromatographic separation of the products of the conversion of methanol to alkenes*

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The conversion of methanol to hydrocarbons and especially alkenes over ZSM zeolite catalysts is of great industrial importance and has been the subject of several investigations^{1–6}. Rapid screening of catalysts for the conversion of methanol to alkenes requires a suitable gas chromatographic (GC) analytical column capable of separating alkenes. Some workers used columns packed with Porapak Q, 17% sebaconitrile on Chromosorb and squalane. Others used multiple columns^{7,8}. Stockinger⁹ described an on-line analytical system consisting of two columns: a 200 ft. × 0.01 in. I.D. squalane-coated SCOT column and a Porapak Q column for the separation and determination of all products in the methanol reaction. Porapak Q, which is widely used in the analysis of hydrocarbon gases and offers the advantage of the separation and determination of dimethyl ether and unconverted methanol, is incapable of separating alkenes from alkanes beyond C₃. It is our experience that even the separation of a mixture of propylene and propane becomes difficult on a 6 ft. × $\frac{1}{8}$ in. I.D. Porapak Q column if the relative concentration of either of the two is very small.

A survey of the literature on the analysis of hydrocarbon gases^{10–14} indicated that Durapak® (*n*-octane–Porasil C), a chemically bonded stationary phase, is the most useful packing material for routine analysis. This paper reports the results of the chromatographic analysis of a gaseous mixture from the methanol reaction carried out on columns of Porapak Q (6 ft. × $\frac{1}{8}$ in. I.D.) and *n*-octane–Porasil C (5 ft. × $\frac{1}{8}$ in. I.D.). A Hewlett-Packard 5840A gas chromatograph provided with dual flame-ionization detectors (FID) and an assembly of valves for stream selection, gas sampling and column selection was used. A refinery gas test sample (Part No. 5080-8755, supplied by Hewlett-Packard, Avondale, PA, U.S.A.) was chosen for component identification. Isobutene, dimethyl ether and methanol were identified by injecting standard compounds and comparing the retention times.

Fig. 1 shows the chromatogram obtained when the gaseous mixture from the methanol reaction obtained by passing the total products through a trap cooled with an ice–salt mixture was analysed using the two columns. Table I shows the retention times (t_r) for the components of the gas mixture and also the corresponding peak areas. Quantitative analysis was not attempted.

The only drawback of the *n*-octane–Porasil C column is that it co-elutes ethane

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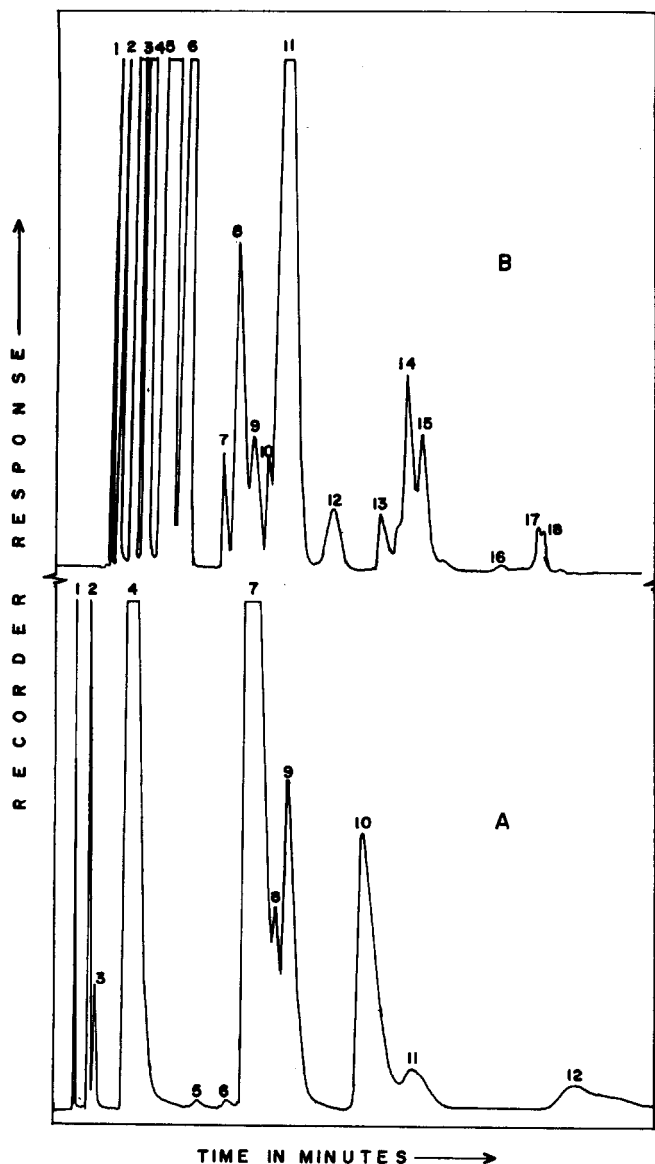


Fig. 1. Chromatograms of gaseous products on Porapak (A) and *n*-octane-Porasil C (B). For peak identification, see Table I.

and ethylene in the presence of water vapour in the gas stream. This can be overcome either by passing the gas mixture through an anhydrous potassium carbonate trap prior to analysis¹¹ or preferably by a preliminary analysis on a 2 ft. \times $\frac{1}{8}$ in. I.D. Porapak Q column at 40°C with a carrier gas flow-rate of 15 ml/min. The latter method separates C₂ hydrocarbons in 2 min and subsequent GC analysis on *n*-octane-Porasil-C under the conditions listed in Table I, is complete in less than 20 min. Repeated injection of gaseous mixtures containing moisture do not shorten the column life as more than 300 routine analyses have been carried out with no deterioration of the separation efficiency. The chief advantage of this column is that it provides faster analysis of the complete range of gaseous reaction products and

TABLE I

ANALYSIS OF GASEOUS PRODUCTS OF THE METHANOL REACTION

GC conditions. Porapak Q column: column, 6 ft. \times 1/8 in. I.D.; isothermal, 100°C for 10 min, programmed at 10°C/min to 150°C, held for 25 min; injector, 100°C; FID, 250°C; N₂ flow-rate, 16 ml/min. *n*-Octane-Porasil C column: column, 5 ft. \times 1/8 in. I.D.; isothermal, 40°C for 10 min, programmed at 10°C/min to 150°C, held for 5 min; injector, 150°C; FID, 250°C; N₂ flow-rate, 15 ml/min.

Column				Column			
Porapak Q				<i>n</i> -Octane-Porasil C			
Peak No.	Compound	<i>t_r</i> (min)	Area (%)	Peak No.	Compound	<i>t_r</i> (min)	Area (%)
1	C ₁	1.08	1.5	1	C ₁	0.90	1.4
2	C ₂ =	1.92	3.6	2	C ₂ - + C ₂ =	1.07	4.7
3	C ₂ -	2.31	0.8	3	C ₃ -	1.42	16.8
4	C ₃ + C ₃ =	5.45	26.4	4	C ₃ =	1.78	8.3
5	Dimethyl ether + methanol	9.45	0.50	5	Isobutane	2.24	33.6
6		11.19		6	<i>n</i> -Butane	2.94	7.3
7	Isobutane	12.20	33.5	7	Butene-1	4.15	0.7
8	Butene-1 and isobutene	13.97	3.8	8	Isobutene	4.47	3.6
9	<i>n</i> -Butane, <i>cis</i> -butene-2, <i>trans</i> -butene-2	14.64	10.5	9	<i>trans</i> -Butene-2	5.00	1.7
10		5.44	0.6	10	<i>cis</i> -Butene-2	5.64	15.8
11		5.64	15.8	11	Isopentane	7.34	1.2
10	Isopentane	21.14	12.8	12	<i>n</i> -Pentane		
11	<i>n</i> -Pentane	24.13	2.9	13	to		
12	Others (C ₆ +)	39.02	3.7	16	C ₆ aliphatics	12.48	4.0
17				Dimethyl ether	16.92	0.4	
18				Methanol	17.15		

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REFERENCES

- 1 J. Scott (Editor), *Zeolite Technology and Application's. Recent advances 1980*, Noyes Data Corp., NJ, pp. 174-178.
- 2 R. A. Stowe and C. B. Murchison, *Hydrocarbon Process.*, 61 (1982) 147.
- 3 N. Y. Chen and W. J. Reagan, *J. Catal.*, 59 (1979) 123.
- 4 J. R. Anderson, K. Foger, T. Mole, R. A. Rajadhyaksha and J. V. Sanders, *J. Catal.*, 58 (1979) 114.
- 5 B. E. Langer, *Appl. Catal.*, 2 (1982) 289.
- 6 H. Itoh, T. Hattori and Y. Murakami, *Appl. Catal.*, 2 (1982) 19.
- 7 P. Dejaifve, J. C. Vadrine, V. Bolis and E. G. Derouane, *J. Catal.*, 63 (1980) 331.
- 8 J. P. Vander Berg, J. P. Wolthuizen and J. H. C. van Hoof, *Proc. V Int. Conf. Zeolite Catal.*, (1980) 649.
- 9 J. H. Stockinger, *J. Chromatogr. Sci.*, 15 (1977) 198.
- 10 S. M. Csicsery and H. Pines, *J. Chromatogr.*, 9 (1962) 34.
- 11 H. H. Westburg, R. A. Rasmussen and M. Holdren, *Anal. Chem.*, 46 (1974) 1852.
- 12 M. K. Sarkar and G. G. Haselden, *J. Chromatogr.*, 104 (1975) 425.
- 13 A. Kumar, R. D. Dua and M. K. Sarkar, *J. Chromatogr.*, 107 (1975) 190.
- 14 R. Mindrup, *J. Chromatogr. Sci.*, 16 (1978) 380.