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Note

Development of a micro methanol to gasoline convertor on-line to a gas–liquid chromatograph equipped for mass and radioactivity measurements

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The "Mobil" methanol to gasoline (MTG) process, using the zeolite catalyst H-ZSM-5, has recently gone on stream at the world's first industrial scale plant in Motonui, New Zealand. Our laboratory is using radiotracer techniques and ^{3}H NMR to investigate various aspects of the mechanism of the conversion reaction, particularly the formation of the first carbon–carbon bond. This study requires:

(i) The construction of a micro MTG convertor.

(ii) Modification of existing gas–liquid chromatographic (GLC) equipment for the accurate sampling, separation and analysis of the complex mixture of hydrocarbons produced.

(iii) Facilities for simultaneous mass and activity determinations for radiotracer studies.

There is considerable literature available[1,2] based on studies using "stand-alone" laboratory scale convertors from which liquid and gas samples are collected in traps prior to analysis. This method can suffer from loss of gaseous products, condensation and/or fractionation of high-boiling-point products. Changes in observed product distribution may occur due to changes in collection methods. The process is also slow and tedious and does not allow quick routine analyses.

Attempts have been made[3–5] to overcome these problems by constructing on-line systems where the stand-alone convertors are connected directly to a GLC system by heated tubing. Our early MTG system was of this type with the effluent being sampled for analysis using a 10-port valve situated in the GLC column oven. This method still suffered from condensation and surface sorption of some of the higher boiling point materials (especially pseudocumene and durene). These problems led to non-reproducible results particularly when no vector gas was used or when low initial column temperatures were employed. Our solution to these problems was to:

(1) Mount the sampling valves into a separate heated valve oven.

(2) Mount the convertor directly onto the GLC valve oven input section.

EQUIPMENT

Convertor

The convertor consisted of a side-opening aluminium tube furnace and was heated by 2 × 150 W cartridge heaters fitted into aluminium blocks (Fig. 1). These

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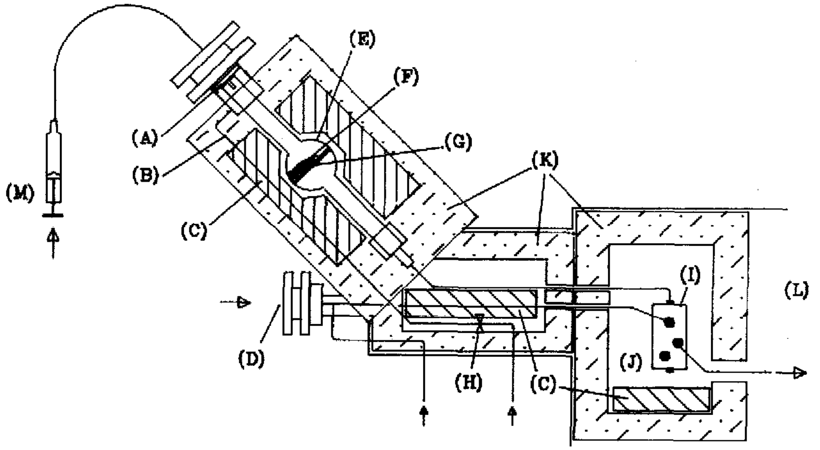

Fig. 1. Micro MTG convertor and heated valve oven on-line to a GLC system. A = high-temperature septum; B = pre-heated vector gas line; C = aluminium block heater; D = injector for standards; E = pyrex glass reactor tube; F = catalyst (H-ZSM-5); G = glass frit; H = 10-turn valve for vector gas; I = 10-port/6-port valves; J = valve oven; K = Rocboard insulation; L = GLC column oven; M = syringe drive.

were thermostatically controlled to ± 2°C from room temperature to 500°C. The pelletised H-ZSM-5 catalyst was supported on a glass frit and contained in a Pyrex glass reactor tube allowing rapid visual inspection of its condition (extent of coking) with time. Feedstocks were delivered directly onto the catalyst, via a 1-m long syringe needle passing through a high-temperature septum, from a multispeed syringe drive. Hydrocarbon products were fed directly to the heated sampling valve system.

Sampling valve system

The sampling system for capillary analyses consisted of a 6-port valve, with a 1-ml sample loop. For packed column analysis, however, a 10-port valve, also with 1-ml sample loop, was used. In this case a change in valve position reversed carrier gas flow, thus enabling the column to be backflushed. The dual valve sampling system allowed either capillary or packed column analysis to be carried out at any one time or, if necessary, simultaneously.

All tubing and fittings used were 1.5-mm stainless-steel to reduce unswept dead volumes between the convertor and capillary column system. The valves and tubing were enclosed in an insulated valve oven heated to 200°C with 4 × 150 W cartridge heaters.

Valves in load position (Fig. 2, top). Effluent from the convertor is directed through 1-ml sample loops on both valves and then vented to atmosphere. With the valves in this position direct injection of standards for analysis is possible through either the packed column injector [(D) in Fig. 2, top] or capillary split/splitless injector [(K) in Fig. 2, top].

Valves in run position (Fig. 2, bottom). Effluent from the convertor now goes directly to vent. The contents of the appropriate loop are directed to the column required for separation.

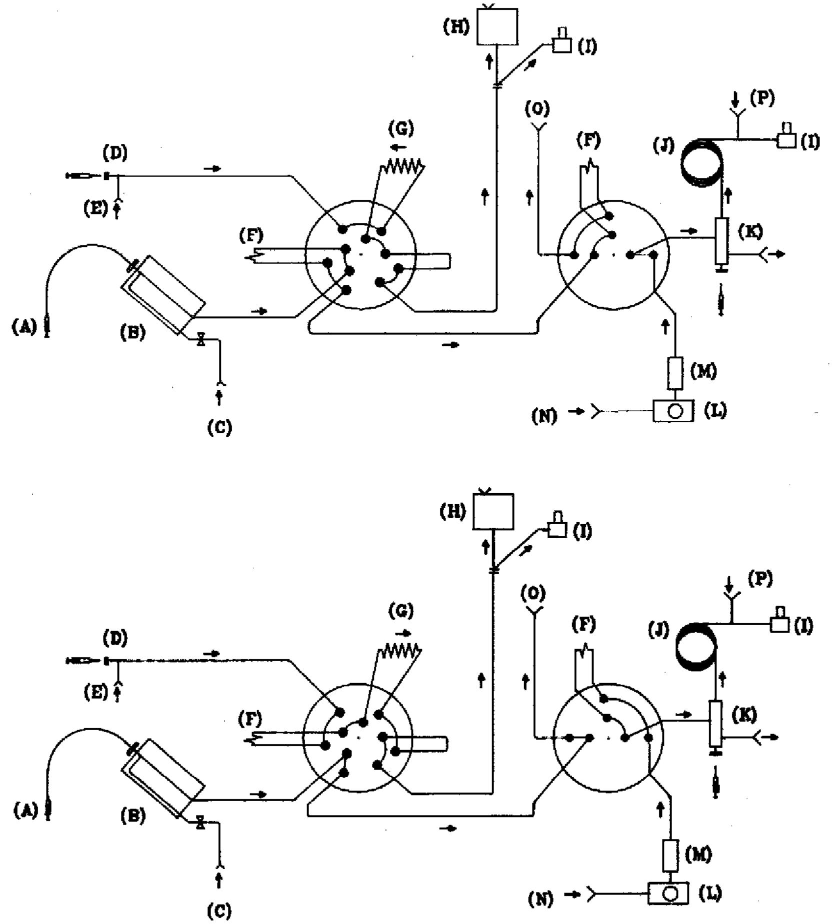

Fig. 2. 10-port valve (for packed column) and 6-port valve (for capillary column) for sampling of convertor products and direct injection of standards. Top: load position; bottom: run position. A = syringe drive; B = MTG convertor; C = nitrogen vector gas; D = packed column injector; E = nitrogen carrier gas; F = sample loops; G = packed column; H = ion chamber; I = flame ionization detector; J = capillary column; K = capillary split/splitless injector; L = capillary carrier gas regulator; M = oxygen trap; N = hydrogen carrier gas; O = vent to atmosphere; P = make-up gas.

Mass and activity detectors

Effluent from the packed column was divided using a variable splitter (usually 1:10 mass to activity ratio) for mass analysis on a flame ionisation detector and radiochemical analysis using a low volume (5 ml) ion chamber. From the capillary column the products were directed, with make-up gas, to an flame ionisation detector for mass analysis. Radiochemical analysis was not feasible due to the very high specific activity requirements and the large dead volumes introduced with the use of an ion chamber.

Columns and optimum conditions

(i) Capillary Column (50 QCZ/BP1-0.25): 50 m × 0.22 mm I.D. vitreous silica with bonded phase (dimethyl siloxane). Carrier gas: hydrogen at 2 ml min^{-1}. Column temperature programmed from 0°C (liquid nitrogen, subambient control) for 2 min then ramp 2°C min^{-1} to 100°C. Injector and detector block temperature: 200°C. Split-ratio of split injector, 100:1 (column supplied by SGE).

(ii) Packed column for C_1-C_4 hydrocarbon analysis: 1.5 m × 3 mm stainless-steel packed with *n*-octane – Porasil C (Durapak™) 80 – 100 mesh. Carrier gas: nitrogen at 25 ml min^{-1}. Column temperature program: 10°C hold 2 min (liquid nitrogen, subambient control), ramp 15°C min^{-1}, hold 50°C.

(iii) Packed column for C_6-C_{10} aromatic hydrocarbon analysis: 1.8 m × 3 mm stainless-steel packed with 5% AT 1200 + 1.75% Bentone 34 on Chromosorb W AW, 100 – 120 mesh. Carrier gas: nitrogen at 30 ml min^{-1}. Column temperature program: 50°C hold 3 min, ramp 6°C min^{-1}, hold 120°C.

RESULTS

This system has provided reproducible and consistent results over a two-year period. Any variation in product distribution has been shown to be due to changes in catalyst activity (because of coking) and other running conditions (*e.g.* convertor temperature, liquid hourly space velocity or type of feedstock). Coked and inactive catalyst was regenerated by injecting dry air over the catalyst (5 ml min^{-1}, 450°C, 16 h).

Capillary column analysis

The primary use of the capillary column was to enable fast analysis, with good resolution, of the complete range of hydrocarbons produced (from methane to tetra methyl benzenes). The SGE column gave good separation of approximately 200 hydrocarbon components within 25 min (Fig. 3). This type of analysis was used routinely to "fingerprint" changes in the product distribution resulting from:

(a) Changes in activity of H-ZSM-5 catalyst (because of coking and/or regeneration).

(b) Chemical and physical modification of H-ZSM-5 catalyst.

(c) Temperature and space velocity changes.

(d) Additives to methanol or hydrocarbon feedstocks.

Packed column analysis

Packed columns, when used with backflushing, can give very fast and excellent separations of small groups (5 – 10 components) of close boiling point components. For example, the time take for a conversion – separation – analysis – backflush cycle is limited only by the (slowest) separation step. Using a single packed column, we have been able to study of effects of time on-stream of hydrocarbon feedstocks over H-ZSM-5 on yields of C_6, C_7 and C_8 aromatic hydrocarbons (benzene, toluene, ethyl benzene, *o*-, *m*- and *p*-xylenes) with samples analysed every 5 min[6].

The higher sample loadings possible on such columns allow the use of lower specific activity radio-labelled materials when conducting radiotracer experiments. This is an advantage in the synthesis and/or cost of such materials. Fig. 4, which

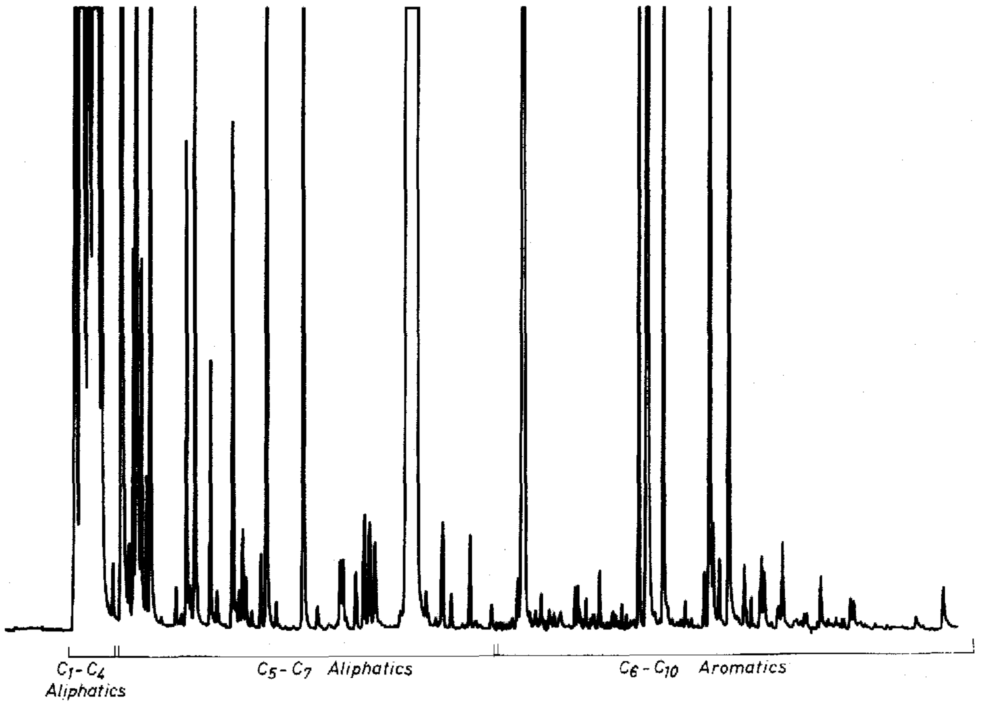

Fig. 3. A capillary column analysis of synthetic gasoline produced by the micro MTG convertor.

gives mass and activity traces of three radio-labelled xylene isomers, shows that it is possible to achieve difficult separations with our system. The peak resolution is seen to be somewhat reduced as a consequence of the need to split the carrier gas flow (10:1 ion chamber, flame ionisation detector). The resulting low flow-rate (3 ml min^{-1})

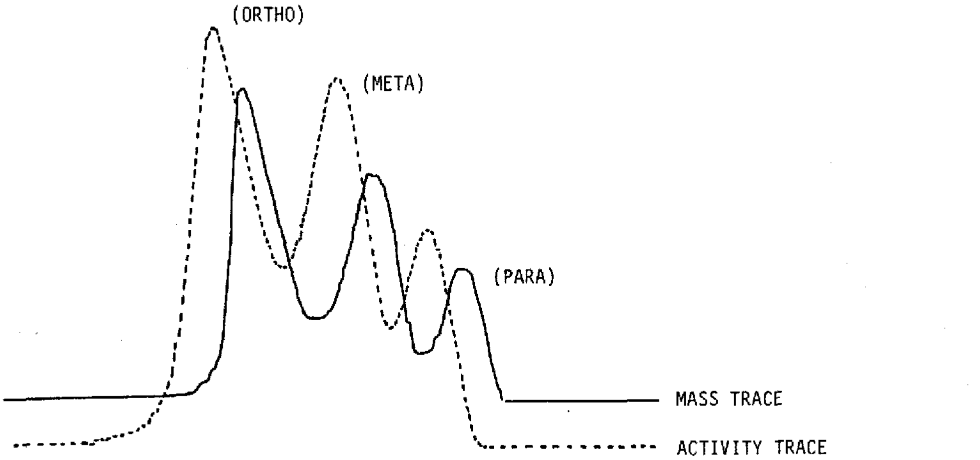

Fig. 4. Radio/mass GLC trace showing products from isomerization of *o*-xylene over H-ZSM-5 catalyst.

broadens peaks in the mass trace and the dead volume of the ion chamber produces a similar effect on the activity peaks.

CONCLUSION

The apparatus described in thes paper provides a highly flexible system for the study of the catalytic conversion of methanol, and other feedstocks, to gasoline using radiotracer methods. Our reactor design allows rapid alterartions to the experimental variables: temperature, space velocity, vector gas, catalyst and type of feedstock. Mounting the convertor and heated valve oven directly onto the GLC system has eliminated condensation problems and given consistently reproducible results. A variable splitter at the packed column outlet allows simultaneous mass and radioactivity analysis.

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