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EXPERIMENTAL STUDY OF A LABORATORY-SCALE SIMULATED COUNTERCURRENT MOVING BED CHROMATOGRAPHIC REACTOR

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Abstract—An experimental investigation of the catalytic hydrogenation of 1,3,5-trimethylbenzene to 1,3,5-trimethylcyclohexane in a simulated countercurrent moving-bed chromatographic reactor is reported. A multiple column configuration of the simulated countercurrent moving-bed chromatographic reactor has been designed and assembled. A microcomputer has been interfaced with the reactor and an analytical gas chromatograph for computer control, data acquisition and analysis. This separative reactor gives a reaction product that contains relatively small amounts of unconverted reactant, and conversions that are considerably in excess of the thermodynamic equilibrium that would be the maximum achieved in non-separative reactors. With appropriate operating conditions, a product purity of 96% and reactant conversion of 0.83 was obtained. Under the conditions of the experiment the equilibrium conversion is 0.4.

INTRODUCTION

Processes employing solid adsorbents in chromatographic beds for treatment of fluids have not gained wide acceptance except in cases in which the quantity of material to be treated is small. In the usual batch, fixed-bed process, the feed stream is discontinuous and the product streams vary in composition. Continuous chromatographic processing for larger-scale processes can be accomplished in countercurrent moving beds (Barker and Ganetsos, 1993). However, in the design and operation of a countercurrent moving bed there are a number of problems associated with the movement of solids that have to be overcome, including attrition, entrainment, fines removal, and other problems associated with two-phase flow. These can be avoided by employing simulated countercurrency, in which the continuous countercurrent flow of the adsorbent and the mobile phase is simulated without actual movement of the solid adsorbent.

Simulation of countercurrency is accomplished by switching the feedstream and product take-off points sequentially along a fixed bed, or through a series of columns, in the direction of mobile-phase flow. The switching is done at intervals such that relatively weakly adsorbed species are swept ahead of the feed point, while more strongly adsorbed species lag behind it. This principle has been successfully applied to separations. It was developed and commercialized by UOP in its Sorbex processes for separation of liquid mixtures (Broughton, 1978; Broughton *et al.*, 1984). More recent laboratory studies have demonstrated the utility of simulated countercurrent moving-bed separators for separation of glucose–fructose mixtures (Barker and Abusabah, 1985; Ching and Ruthven, 1985) and for enzyme separation and purification (Huang *et al.*, 1986). Other work on simulated countercurrent moving beds has been recently reviewed (Ganetsos and Barker, 1993).

In spite of the potential of combined reaction-separation in the simulated countercurrent moving bed, the application of this principle has been virtually neglected until recently. A hybrid apparatus consisting of fixed-bed enzyme reactors and simulated countercurrent separators was reported (Hashimoto *et al.*, 1983), while more recently a model study of a gas/solid system using mixed catalyst and adsorbent (Ray *et al.*, 1994), and a preliminary report of methane oxidative coupling (Tonkovich *et al.*, 1993). The experimental work reported in this paper on the simulated countercurrent moving bed is a gas–solid system which builds on the design for simulated moving-bed separators (Fish *et al.*, 1993). This extension to a reaction with separation explores the potential for application to solid catalyzed gas-phase reactions, of which there are many examples in commercial use. An advantage of gas phase over liquid-phase operation is that the effective selectivity of the adsorbent is higher in gases due to lesser non-selective hold-up in macropores (Morbidelli *et al.*, 1986).

An experimental investigation of the SCMCR would prove valuable for testing the model predictions. Theoretical analysis of a dispersionless model of the SCMCR has shown that if a first-order equilibrium limited reaction occurs on the solid surface, then under certain operating conditions the chemical reaction process and the adsorption process interact to break the local thermodynamic equilibrium limitation and it is possible to obtain improved conversions and product purity than would be obtained in a traditional fixed-bed reactor (Ray *et al.*, 1994). However, the assumptions made in the mathematical model cannot be met experimentally as dispersion will always be present.

The aim of the experimental investigation is to achieve three goals. The first is to determine whether the simulated countercurrent moving-bed reactor can produce a pure product at a higher conversion than the fixed-bed reactor for a given reactor length and carrier gas flow rate, as predicted by models. The second is to characterize the effect of changing variables on overall performance, and the third is to compare experimental results with that of a true countercurrent moving-bed reactor.

In this work we report an experimental investigation of the hydrogenation of 1,3,5-trimethylbenzene, trivial name mesitylene (MES), in a five column laboratory SCMCR. The SCMCR is interfaced with a computer to control the switching of reactant, product and carrier gas flows via a network of two- and three-way solenoid valves, and to enable rapid acquisition and analysis of data.

REACTOR CONFIGURATION

For laboratory-scale experimental studies, the most convenient way to configure the SCMCR is to design a reactor configuration consisting of a series of packed columns with provision for feed entry and product withdrawal from the ends of each column and with an appropriate sequence of column switching designed to simulate a countercurrent flow system. In the true moving-bed system, solid flows continuously past fixed positions for introduction of reactant and withdrawal of products. The mobile-phase flows countercurrent to the solid. In the simulated countercurrent system the same process results are obtained with a stationary bed by periodically moving the positions at which the various streams enter and leave. A shift in the positions of feed and withdrawal, in the direction of mobile-phase flow through the bed, simulates the movement of the solids in the opposite direction.

An important design decision is the number of columns or number of subdivisions in the case of a single fixed bed. It is evident that with infinitesimally short columns or subdivisions and infinitely fast switching times the feed movement becomes continuous, and the SCMCR becomes a countercurrent chromatographic reactor in which the feedport moves along the bed, rather than the bed moving past the feed. On the other hand, with only a few columns or subdivisions one might expect a poor approximation to countercurrent flow. However, it has been reported for liquid–solid separation of binary mixtures that most of the benefit of countercurrent flow can be achieved by a rather modest number of columns or degree of subdivision of the bed. It has been shown that with as few as 12 columns, concentration profiles are similar to those obtained for the steady-state countercurrent moving bed (Barker and Deeble, 1973), whereas in a gas/solid separation with only four columns the output is periodic (Fish *et al.*, 1993). Simulated countercurrent moving-bed separators with 12 columns have been successfully modeled as a true countercurrent moving-bed separator at steady state (Hidajat *et al.*, 1986; Ching *et al.*, 1985).

The configuration used for experimentation in this work is shown in Fig. 1, and differs from the one previously developed in this laboratory (Fish *et al.*, 1993) for separations. In the present configuration (see Fig. 1), the outlet from the feed column is completely collected at port B and contains the reaction product, which in this case is less strongly adsorbed than the reactant. Make-up carrier gas is introduced at the top of column 3 and serves to elute the more strongly adsorbed reactant from the bottom of column 5 at port A. The additional column (column 5) and the make-up carrier help to remove unconsumed reactant from the next column and to obtain better product purity than would be obtained with the four column configuration. The reactor is divided into two distinct sections. In the first two column section, feed and carrier gas are introduced, and the product is completely collected, while in the other, a make-up carrier is introduced to purge unconsumed reactant. The major design feature that differentiates the separator and the reactor is the use of one carrier stream and split flow in the former, and two carrier streams and complete removal of exit streams in the latter. The advantage for the separator is the reduction in dead time before the least adsorbed component breaks through the feed column. The major disadvantage of this configuration results from the split flow. Since the product moves faster than the reactant and the movement of feed points, it would contaminate the reactant rich exit stream at port A. The configuration given in Fig. 1 is selected, as obtaining a high product purity was given priority over productivity.

Since TMC breaks through before MES, it is possible to recover a product stream containing TMC (plus carrier) from the exit of the feed column, but the feed must be switched to the next column in line

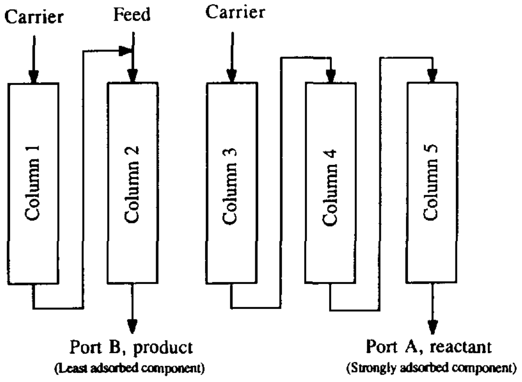

Fig. 1. Five column reactor configuration designed for simultaneous reaction and separation.

before the MES front breaks through to avoid contaminating the product. The effluent from the new feed column then becomes the new TMC product stream. Since one must wait for TMC to break through each time the feed is switched, its concentration is expected to be periodic. When a switch is made, the former feed column contains both MES and TMC. However, TMC will elute more rapidly than MES, and the column will contain only MES after a time equal to the TMC breakthrough time. A product stream containing MES can then be taken from this column. With a series of columns available, the feed and product streams can be switched at appropriate time intervals. When the last column is reached the first should no longer contain either component, and the next switch returns the feed to the first column. Thus a continuous process with periodic output is obtained.

EXPERIMENTAL

The experimental apparatus consists of three interconnecting parts. (1) The multiple column reactor with valving for flow switching between sections, (2) the computer, which is interfaced with the reactor for control of the entire switching operation and for data acquisition, and (3) a gas chromatograph for analyzing the effluent streams from the reactor.

The five section reactor has 25 solenoid valves, as shown in Fig. 2, along with the necessary piping and swagelock connections to simulate countercurrent flow. The IBM PC-XT computer controls the valves for the switching program, and the gas chromatograph for automated sampling of the reactor at preset time intervals. The computer also receives raw data on composition of the reactor effluent from the gas chromatograph, carries out rapid quantitation of the GC signals, converts the analog data into digital data and stores it.

Reactor. Five stainless-steel tubes 0.305 m long × 0.013 m OD were each packed with an equal weight of catalyst/adsorbent mixture and connected by 3.2×10^{-3} m OD stainless-steel tubing by swagelok unions filled with Pyrex wool. They were arranged in a bank, as shown in Figs 1 and 2, with the last column connected to the first so that switching of feed and product streams can cycle continuously. This arrangement is very flexible since columns can be added or removed as desired without any major difficulty.

The valves that connect the gas inflow, MES, hydrogen, carrier gas and make-up carrier, are all two-way valves. The other valves are three-way valves used for directing exiting flows. When a particular two-way valve is open the gas will flow into the system at that location only. When a three-way valve is powered, the fluid will flow in one direction, and it will be directed to a different line if the power is off.

The five reactor columns are wound with heating tape and insulated with glass wool cloth. Each heating tape is separately powered by a variac. This permits fine tuning to maintain each column at the same temperature, compensating for changes that may occur due to the heat of reaction or other causes. The

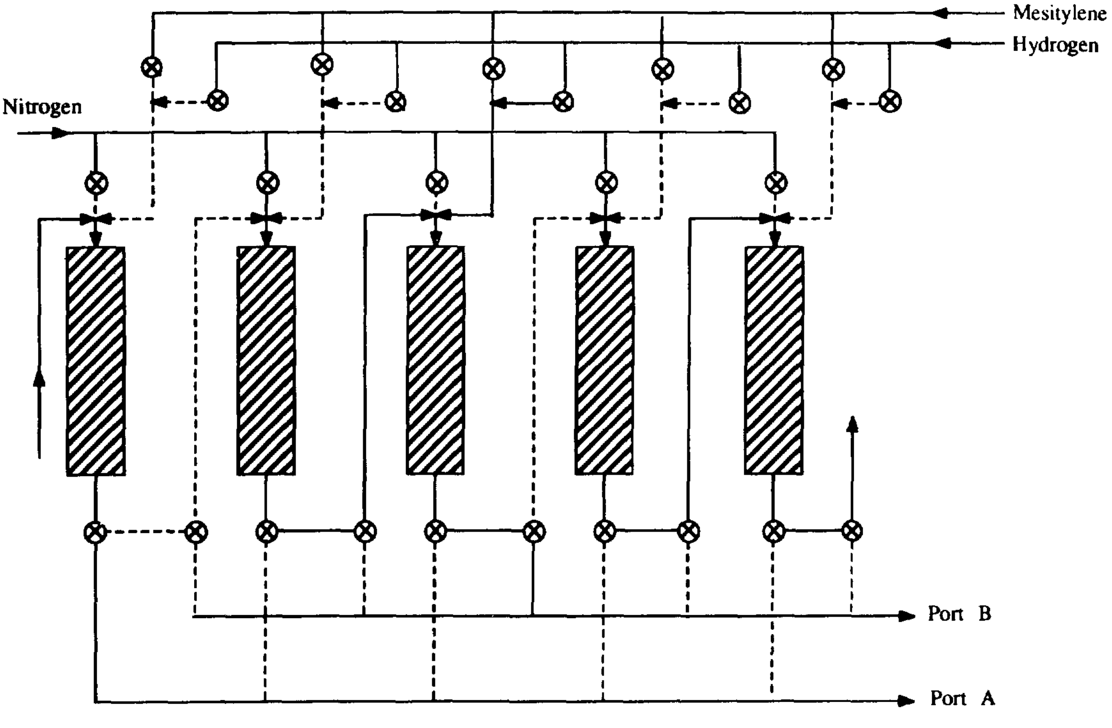

Fig. 2. Valving diagram of the five column experimental configuration.

temperature along the column is measured with copper–constantan thermocouples, and monitored by a digital thermocouple indicator.

Mesitylene is fed to the reactor via a syringe pump. The liquid flow rate can be adjusted to one of 20 different flow rates from 8.33×10^{-11} m^3/s to 2.5×10^{-9} m^3/s. The liquid feed enters a hot injection area, vaporizes into a carrier gas stream, and is routed to the proper column.

Computer control. In the operation of a laboratory SCMCR decisions must be made on the time between successive switches of the feed. The decisions can be based upon numerical simulations using models, but these are not expected to be highly accurate due to uncertainties in model parameters and any inadequacies of the model. The simultaneous switching of feed and product streams at precisely the correct time, and the rapid acquisition and analysis of data for making the next decision can be best accomplished by use of a computer. Also, for testing model predictions, it would be very desirable to determine the time-dependent outlet concentrations. Since switching intervals may be very short in some cases, many rapid analyses must be done in a short time. Computer data acquisition and control is clearly necessary.

A laboratory microcomputer is used for data acquisition and for process control. Two Data Translation A/D boards (2801 and 707) provide the interface with the hardware. A schematic of the data acquisition and control system is given in Fig. 3. Lab Tech Notebook is the software used to manage all operations. Notebook provides the interface between the experimental system and its control by computer.

GC analysis. A Varian 3700 gas chromatograph equipped with a flame ionization detector (FID) is used for qualitative and quantitative analysis of all samples. A Carle gas sampling valve is used for sampling the effluent streams. The Notebook software program contains preset information regarding when to draw samples from the effluent streams. In this work samples were taken every 40 s. A small fraction of the exit stream at port A or port B is diverted to the gas sampling valve and subsequently analyzed at 473 K on a 0.305 m long by 3.18×10^{-3} m diameter column packed with Chromosorb 106. At a carrier gas (He) flow rate of 5×10^{-5} m^3/s the retention times of the two components are less than 30 s, permitting characterization of the periodic concentration profiles that develop. The signal from the FID is sent to the computer, where the signal is plotted on the display screen and stored on disk.

Chemical reaction. The hydrogenation of 1,3,5-trimethylbenzene (MES) to trimethylcyclohexane (TMC) was selected as a test reaction. The catalyst is 0.74% w/w platinum supported on alumina. The reaction is reversible, and over the range of temperatures for which equilibrium favors the dehydrogenation step the reaction is very selective, giving no other detectable products. An unidentified side product was previously reported (Petroulas, 1984), but it never comprised more than 1% of the reaction. For MES hydrogenation in the vicinity of 463–473 K reaction rates are suitable and the equilibrium conversion of MES to TMC in excess H_2 (25% v/v in the N_2 carrier) is about 40% at 473 K and 62% at 463 K (Egan and Buss, 1959). The reaction is exothermic with

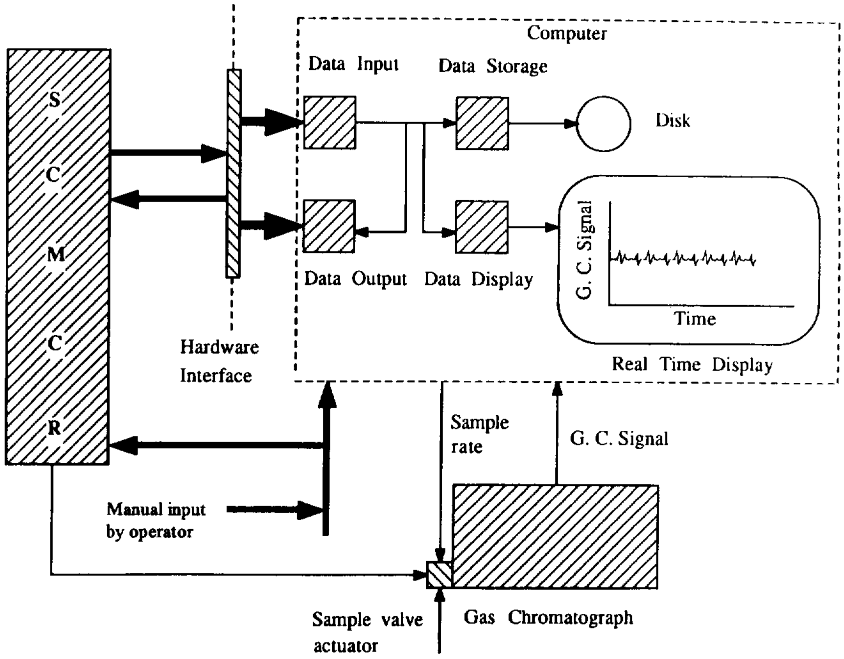

Fig. 3. Schematic diagram of data acquisition and control of the SCMCR.

$\Delta H = -196.6$ kJ/mol. Both the hydrogenation and dehydrogenation steps take place over the catalyst at temperatures between 453 K and 493 K. This is the appropriate temperature region for our experimental study since at much higher or lower temperatures the reaction is practically irreversible with equilibrium favoring MES or TMC, respectively. Hydrogen is fed in excess so that the reaction appears to have the stoichiometry $A \rightleftarrows B$. The MES (MW = 120.2; density = 0.864) and TMC used in the experiments are 99+% purity, and are supplied by Aldrich Chemical Company.

Adsorbent. As the catalyst for the hydrogenation reaction is supported on alumina, and alumina exhibits selective adsorption of alicyclics and aromatics, it was first tried as the adsorbent. However, some problems are realized with alumina for this particular chemical reaction. The MES adsorbs very strongly on alumina, shows a large degree of peak tailing, and very broad conventional chromatograms. This would cause difficulties in the SCMCR where better behaved desorption curves are desirable.

After trying several adsorbents, Chromosorb 106, a porous polymer material, was selected as having the best properties. A granular mixture (60/80 mesh) of 90% of this cross-linked polystyrene adsorbent was used with 10% Pt/Al_2O_3 catalyst in all subsequent experiments. In a pulsed injection experiment at 463 K with this mixture, the retention time of MES was 391.8 s, and TMC was 103.8 s. The MES peak is only slightly tailed and the chromatogram is not very broad.

MES is adsorbed more strongly than TMC, and will travel slower than TMC in the SCMCR columns. The hydrogen does not interact appreciably with the solid, and will move through faster than TMC. The detector responds equally to TMC and MES, whereas hydrogen is not detected by the FID.

RESULTS

Figures 4–6 show experimental results from the five column configuration of Figs 1 and 2. Effluent compositions vs time after about 1 h of continuous cycling are given. They are seen to have regular periodicity characteristic of a periodic steady state. These waveforms are attributed to breakthrough curves and desorption curves for the two adsorbable species, TMC and MES.

Figure 4(a) shows the mole fractions of TMC (open circles) and MES (filled circles) eluting form the feed column (port B) at 40 s intervals for a 5 min switching time, and 463 K reactor temperature. At the beginning of each 5 min period there is little TMC present, but thereafter it breaks through strongly with a fairly steep front. The concentration of TMC reaches a maximum within the switching interval, then decreases. Each 5 min interval shows a fairly reproducible waveform. Mesitylene is present in this stream, with a concentration profile that is characteristic of a rather shallow breakthrough curve. The average composition at port A is 86% TMC and 14% MES, discounting contamination by carrier gas. The average TMC conversion is 79%. Conversion was calculated from the ratio of moles of TMC collected from the feed column to the total moles of mesitylene fed to the column for the 5 min feed period. Conversion was also determined by another method, suggested by a reviewer. In the second method the sum of the TMC and MES removed from both ports during any given cycle was divided into the total TMC taken from both ports during the same cycle. The two methods are in excellent agreement. For example, the method 2 conversion for the data of Fig. 4 is 78%, with similar agreement for other experiments. Furthermore, the agreement of these two methods indicates that the mass balance is complete.

Figure 4(b) shows the composition of the effluent from the purge column (port A), which was located

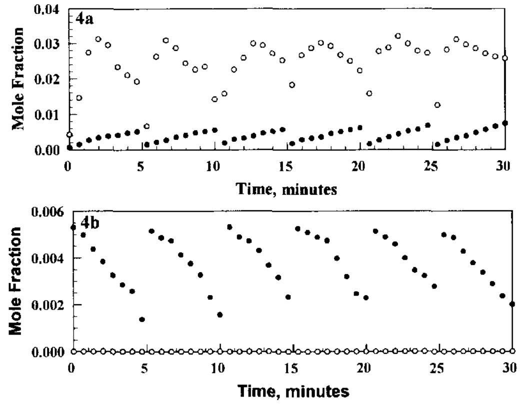

Fig. 4. Mole fraction of reactant (MES) and product (TMC): (a) port B (feed column); (b) port A (purge column); (○○○○○) TMC; (●●●●●) MES; *Experimental condition*: feed rate = 4.95×10^{-6} mol/s; carrier flow rate = 1.32×10^{-4} mol/s; switching time = 300 s; column temperature = 463 K.

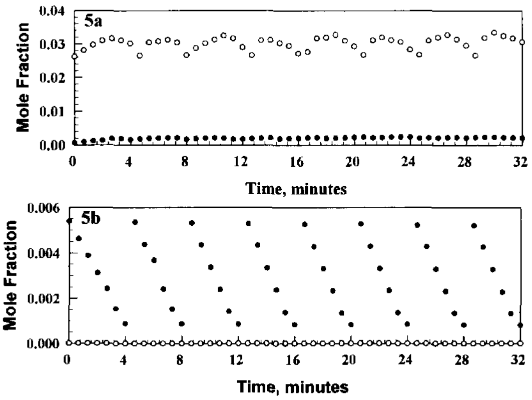

Fig. 5. Mole fraction of reactant (MES) and product (TMC): (a) port B (feed column); (b) port A (purge column); (○○○○○) TMC; (●●●●●) MES; *Experimental condition*: feed rate = 4.95×10^{-6} mol/s; carrier flow rate = 1.32×10^{-4} mol/s; switching time = 240 s; column temperature = 473 K.

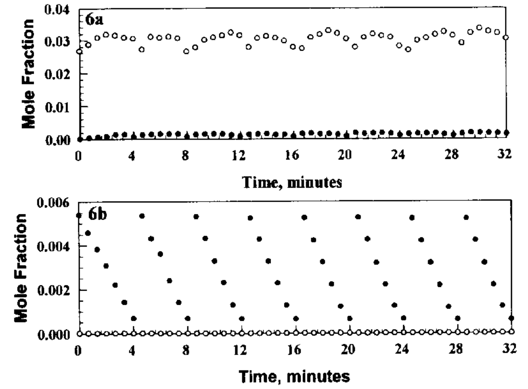

Fig. 6. Mole fraction of reactant (MES) and product (TMC): (a) port B (feed column); (b) port A (purge column); (○○○○○) TMC; (●●●●●) MES; *Experimental condition*: feed rate = 4.95×10^{-6} mol/s; carrier flow rate = 1.32×10^{-4} mol/s; switching time = 240 s; additional make-up carrier flow in purge column = 2.77×10^{-5} mol/s; column temperature = 473 K.

two columns behind the feed column. The open circles represent TMC and the filled circles represent MES. The column is purged with nitrogen carrier gas. MES is present in greatest amount at the beginning of each 5 min switching period, and decreases to a somewhat lower value at the end of the switching interval. This is the MES desorption curve. However, at the end of the 5 min period it can be seen that MES is not completely removed from the purge column. There are only traces of TMC present at the exit of the purge column.

The next set of experiments was done for a switching time of 240 s instead of 300 s, and for columns operating at 10 K higher temperature, 473 K. Figure 5(a) shows the periodic steady-state mole fractions for TMC and mesitylene at the feed column (port B). The open circles represent TMC and the filled circles represent MES. TMC concentration waves grow in and decay with reproducible regularity over the 4 min switching interval, but the breakthrough fronts are not as pronounced as those in Fig. 4(a). A significant difference between Figs 4(a) and 5(a) is the greater uniformity of TMC concentration in the latter. It can also be seen that the MES mole fraction is lower than in the previous experiment. The average conversion of MES for this experiment is 82.5%, and the average product purity is 94.6%.

Figure 5(b) shows mole fractions of MES and TMC at port A (purge column), which is again located two columns behind the feed. MES is present at the beginning of each switching period, and tails steeply. There are only traces of TMC present and the purity of MES is essentially 100%. Comparison of Fig. 5(b) with Fig. 4(b) shows that MES concentration at the end of each period is lower when the reactor is operated at higher temperature and with faster switching of the feed position.

In the results presented in Figs 4(b) and 5(b), it can be seen that MES is not completely removed from the purge column (port A), and ends up leaving the system through port B. This deteriorates the purity of the TMC, and is the principle reason why conversions approaching unity are not achieved. The switching speed might be increased further to keep ahead of the MES front moving through the feed column, but with faster switching speed there will be a problem in the purge column. The MES desorption curve is "tailed" and takes some time to exit the purge column. If the switching speed is increased to stay ahead of the MES front in the feed column there may not be enough time to get the MES tail out of the purge column. The options for combatting this tailing problem are limited with the present catalyst/adsorbent combination. With the configuration of Fig. 1, an increased carrier gas flow rate could be put through the purge column so that mesitylene could be more readily desorbed at a lower partial pressure. Another option, to operate the purge section at higher temperature would require rapid thermal cycling of the solids, which is probably not practical.

The next set of experiments exercised the increased purge gas option. Experiments were done for the same switching time of 240 s, and column temperature of 473 K, except using two different carrier flow rates in the two sections. The make-up carrier flow rate in the purge section was increased to 1.66×10^{-6} m^3/s from 1×10^{-6} m^3/s. Figure 6(a) shows the periodic steady-state mole fractions for TMC and MES at the feed column exit. Figure 6(b) shows the results for port A. There is no significant difference between Fig. 5(a) and Fig. 6(a) except that the concentration of MES is slightly lower in this experiment, the expected result from increasing the carrier flow rate. However, Fig. 6(b) shows that in spite of the higher carrier flow rate, MES cannot be removed completely from the purge column. Under these operating conditions, the average product purity and average conversion for TMC are 95.8 and 82.9%, respectively.

DISCUSSION

At 473 K, and with excess H_2 at the same concentration as in this work, the equilibrium conversion of mesitylene to TMC in a non-separative system is about 40% and the equilibrium composition of the hydrocarbons is calculated to be 58.8% TMC and 41.2% MES. The experiments reported here demonstrate that the SCMCR gives considerably higher product purity, and greater conversion, than is possible in conventional chemical reactors.

Table 1 compares the performance of the countercurrent moving-bed chromatographic reactor (CMCR) with the SCMCR for the MES hydrogenation reaction. The conversions, X_{MES}, and purities, $p_{\mathrm{TMC}}/(p_{\mathrm{TMC}} + p_{\mathrm{MES}})$, depend upon operating conditions. The values quoted are the best obtained for each of the cited studies. The performances predicted for the CMCR and the SCMCR are both for an isothermal, dispersionless, one-dimensional model with a competitive Langmuir adsorption isotherm and first-order, reversible surface reaction. The

Table 1. Comparison of reactor performance

Reactor	X_{MES}	Y_{TMC}
CMCR[†]	0.88	0.95
CMCR[‡]	0.97	1
SCMCR[§]	0.83	0.96
SCMCR[¶]	0.97	0.98

[†] Experiment, Fish and Carr (1989).
[‡] Model prediction, Fish and Carr (1989).
[§] Experiment, this work.
[¶] Model prediction, Ray *et al.* (1994).
X_{MES}: mesitylene conversion. Y_{TMC}: TMC as a fraction of total hydrocarbon.

CMCR model (Fish and Carr, 1989) is a stationary state formulation that predicts shock formation, while the SCMCR model (Ray *et al.*, 1994) is a stage model that must retain the transient terms to follow the concentration transients that accompany each switch of the feed position. Despite these differences, the model predictions are remarkably similar. The experimental studies reveal conversions and purities that are less than predicted, but still considerably better than the maximum that could be obtained in a non-separative reactor. It should be noted that the SCMCR experimental and model studies are not strictly comparable because of different reactor configurations. The model is of a 20-stage packed tower with an inlet and outlet at each stage, in contrast to the five column reactor of this study.

The concentration waveforms presented in Figs 4–6 give some insight into reactor performance. Upon changing feed position, MES should enter the new feed column with a steep front, and upon the next switch be turned off with a steep back. Thus the entering MES waveform can be considered to be a rectangular pulse. Since the adsorption isotherm (Langmuir) is favorable, the only mechanisms broadening this front will be dispersion and possibly finite rates of adsorption. Pore diffusion and external mass transfer should not be important for the granular (60/80 mesh) packing. The TMC fronts that are discernible in Fig. 4(a) are fairly steep, but include the additional factor that they evolve from the MES front via chemical reaction and thus are somewhat more complex than the simple rectangular pulse picture. The MES elution curves seen in Figs 4(b), 5(b) and 6(b) are quite broad. While the elution curves are expected to be broadened not only by dispersion, but by the favorable isotherm, there is most probably another factor also at play here. The Al_2O_3, which comprises 10% of the solids, has a distribution of adsorption energies of MES, as revealed by pulse chromatography studies alluded to above. Some, if not most of the MES tail may be due to desorption from high energy Al_2O_3 surface sites. The Chromosorb 106 may contribute something to this as well.

The broad elution curve causes unreacted MES to not be completely removed from the purge column before it becomes the feed column. The newly formed TMC then acts as a desorbent, and MES elutes from the feed column in a broad front, most apparent in Fig. 4(a), that contaminates the product. The "stickiness" of MES can account for the lower than predicted TMC purity that is experimentally observed. It can also account for the smaller than predicted MES conversion, which can be attributed to loss of unreacted MES from the purge column.

The TMC fronts elute more quickly than the 104 s predicted by the single-pulse retention time measurement. This may be due to the presence of both MES and TMC in the columns, which will increase the TMC velocity, and to the MES remaining in the feed column from its previous use. The MES will hydrogenate, causing prompt elution of TMC.

Reactor performance could be improved if a catalyst support and an adsorbent with more uniform adsorption energetics could be found. It also seems likely that better performance would be obtained if one or more additional columns were added between the carrier entrance and port A of Fig. 1. Column 3 should then be cleaner when it becomes the feed column and higher product purities would result. Furthermore, if H_2 were added at column 3, the MES in this section could be converted to TMC and recovered at port A, thus increasing conversion.

It has been demonstrated that in a simulated countercurrent moving-bed chromatographic reactor higher conversions and better product purities can be achieved over conventional fixed-bed processes for selected chemical reactions. Application of this novel reactor may lead to substantial cost savings compared to conventional processes. The technology of simulated countercurrency and its application for large-scale processes is evident from widespread commercial use of Sorbex processes for liquid-phase adsorptive separation. This provides a strong basis for developing and scaling up of these novel reactors. The use of the SCMCR may be most beneficial when the production rates required are not so high. However, the viability of the SCMCR rests on choosing the right stationary phase since it must exhibit good retention properties and be an effective catalyst.

CONCLUSIONS

An experimental investigation of a simulated countercurrent moving-bed chromatographic reactor has been presented. A laboratory-scale reactor in a multiple column configuration has been designed and built. The reactor consists of a series of columns, each packed with a granular mixture of catalyst and chromatographic stationary phase, and with provision for feed entry and product withdrawal from the ends of each column. The continuous feedstream (and product take-off stream) was switched periodically from one column to the next in order to achieve relative movement between the feed and the bed, thus simulating countercurrent movement of the stationary and mobile phases. A microcomputer has been interfaced with the experimental apparatus for computer control, data acquisition and analysis. The reaction selected for investigation was the catalytic hydrogenation of 1,3,5-trimethylbenzene to 1,3,5-trimethylcyclohexane. Chromatographic separation of the reactant and product was possible by using Chromosorb 106, a porous polymer adsorbent. The retention time ratio for the two components was about 4 at 463 K.

A series of experiments was performed to investigate reactor performance. With proper operating conditions, a product purity for TMC of 96% and MES conversion of 83% was obtained. The conversion is considerably in excess of the 40% equilibrium conversion that would be obtained in a non-separative reactor. The observed operating characteristics are in good qualitative agreement with expectations based on physical arguments. Direct comparison with the predictions of a mathematical model (Ray *et al.*, 1994) is not possible at this stage as there is a significant difference in reactor configuration considered in the model and experiments.

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REFERENCES

Barker, P. E. and Abusabah, E. K. E., 1985, The separation of synthetic mixtures of glucose and fructose and also inverted sucrose feedstocks using countercurrent chromatographic techniques. *Chromatographia* **20**, 9–12.

Barker, P. E. and Deeble, R. E., 1973, Production scale organic mixture separation using a new sequential chromatographic machine. *Anal. Chem.* **45**, 1121–1125.

Barker, P. E. and Ganetsos, G., 1993, Continuous moving-column chromatographic systems, in *Preparative and Production Scale Chromatography*, Vol. 61, Chromatographic Science Series (Edited by G. Ganetsos and P. E. Barker), pp. 173–186. Marcel Dekker, New York.

Broughton, D. B., 1978, Adsorptive Separations—Liquids, in *Kirk–Othmer Encyclopedia of Chemical Technology*, Vol. 1, 3rd Edition. Wiley, New York.

Broughton, D. B. and Gembicki, S. A., 1984, Adsorptive separations by simulated moving bed technology: the Sorbex process, in *Fundamentals of Adsorption* (Edited by A. L. Myers and G. Belfort), p. 115. Engineering Foundation, New York.

Ching, C. B. and Ruthven, D. M., 1985, An experimental study of a simulated countercurrent adsorption system—I. Isothermal steady state operation. *Chem. Engng Sci.* **40**, 877–885.

Ching, C. B., Ruthven, D. M. and Hidajat, K., 1985, Experimental study of a simulated countercurrent adsorption system—II. Sorbex operation. *Chem. Engng Sci.* **40**, 1411–1417.

Egan, C. J. and Buss, W. C., 1959, Determination of the equilibrium constants for the hydrogenation of mesitylene. The thermodynamic properties of the 1,3,5-trimethylcyclohexanes. *J. phys. Chem.* **63**, 1887–1890.

Fish, B. B. and Carr, R. W., 1989, An experimental study of the countercurrent moving-bed chromatographic reactor. *Chem. Engng Sci.* **44**, 1773–1783.

Fish, B. B., Carr, R. W. and Aris, R., 1993, Design and performance of a simulated countercurrent moving-bed separator. *A.I.Ch.E. J.* **39**, 1783–1789.

Ganetsos, G. and Barker, P. E., 1993, Semicontinuous countercurrent chromatographic refiners, in *Preparative and Production Scale Chromatography*, Vol. 61, Chromatographic Science Series (Edited by G. Ganetsos and P. E. Barker), pp. 233–255. Marcel Dekker, New York.

Hashimoto, K., Adachi, S., Noujima, H. and Udea, Y., 1983, A new process combining adsorption and enzyme reaction for producing higher fructose syrup. *Biotechnol. Bioengng* **25**, 2371–2393.

Hidajat, K., Ching, C. B. and Ruthven, D. M., 1986, Simulated countercurrent adsorption processes: a theoretical analysis of the effect of subdividing the adsorbent bed. *Chem. Engng Sci.* **41**, 2953–2956.

Huang, S. Y., Lin, C. K., Chang, W. H. and Lee, W. S. 1986, Enzyme purfication and concentration by simulated moving bed chromatography: an experimental study. *Chem. Engng Commun.* **45**, 291–309.

Morbidelli, M., Sorti, G. and Carra, S., 1986, Comparison of adsorption separation processes in liquid and vapor phase. Application to the xylene isomer mixture. *Ind. Engng Chem. Fundam.* **25**, 89–95.

Petroulas, T., 1984, A countercurrent moving bed chromatographic reactor. Ph.D thesis, University of Minnesota.

Ray, A. K., Carr, R. W. and Aris, R., 1994, The simulated countercurrent moving bed chromatographic reactor: a novel reactor-separator. *Chem. Engng Sci.* **49**, 469–480.

Tonkovich, A. L., Carr, R. W. and Aris, R., 1993, Enhanced C_2 yields from methane oxidative coupling by means of a separative chemical reactor. *Science* **262**, 221–223.