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The simulated countercurrent moving bed chromatographic reactor: a catalytic and separative reactor

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Abstract

A novel reactor design which simulates countercurrent reaction chromatography is described. Rapid separation of products from reactants allows high conversions in both equilibrium limited and low per pass conversion reactions. Two studies of solid catalyzed reactions are reviewed. Application of this technology to a mesitylene hydrogenation reaction shows an increase in conversion from 40% (at equilibrium, 473 K) to over 80%. A modified reactor configuration applied to the oxidative coupling of methane to ethane and ethylene shows a 12 fold increase in conversion for this low per pass conversion reaction, with yields twice that reported in conventional reactors.

1. Introduction

1.1. Overview

The simulated countercurrent moving bed chromatographic reactor (SCMCR) is a novel catalytic reactor design which allows equilibrium limited and low conversion reactions to proceed to near completion in theory. Experimental implementation of this reactor scheme has resulted in great improvements in product purity and yield when compared to the same reactions carried out in conventional reactors. This reactor configuration takes advantage of: (1) *reaction chromatography* for increased conversion and product purity due to separation of products from reactants; (2) *countercurrency* for continuous operation and throughput; and (3) *simulation of countercurrency* to avoid solid handling problems. The following brief conceptual evolution of the SCMCR shows how this catalytic and separative reactor has come to have its current configuration. The current apparatus will be described in some detail. Experimental results from two SCMCR configurations will be presented. One study reports conversions greater than equilibrium conversion. The other shows dramatic improvement in conversion and yield for a low conversion reaction.

1.2. Conceptual evolution of the SCMCR

Traditional chromatographic reactors (Fig. 1) are fixed beds with mixed catalyst and adsorbent

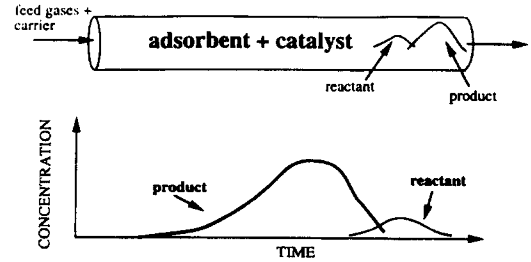

Fig. 1. Fixed bed chromatographic reactor with eluent profile.

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as the solid phase. The reactant is introduced at one end of the reactor in the fluid phase along with a carrier. As the reactant moves along the reactor, some of it reacts to form products. The success of this reactor depends on selective adsorption. The difference in affinity for the solid phase between the reactants and products must be sufficient to give good separation. In the following discussion, until otherwise stated, the reactant will be taken as the more strongly adsorbed species. This assumption is not necessary for successful operation of these reactors, but is taken for simplicity of explanation. The more strongly adsorbed reactants will be held up by the adsorbent in the solid phase while the products are swept away with the fluid phase and separation is achieved. Separation of the products from the reactants allows equilibrium limited reactions to proceed toward completion. Another advantage of this separation is product purity.

The major problem with these chromatographic reactors is that they are batch processes. In order to get continuous operation and product elution, the countercurrent moving bed chromatographic reactor (CMCR) (Fig. 2) is used [1]. In this reactor the solid phase is again mixed catalyst and adsorbent, but now is introduced at the top of the column and moves down. The fluid phase is introduced at the bottom of the column and moves up. The reactant is fed either in the bottom or the middle of the column. For appropriate parameter values (see operating principles section) the more strongly adsorbed reactants can be made to move down the column while the less strongly adsorbed products are eluted from the top of the column with the fluid phase. The product stream should be essentially free from reactants (diluted only with carrier) and preferably almost all of the reactants will react before leaving the bottom of the column with the solid phase.

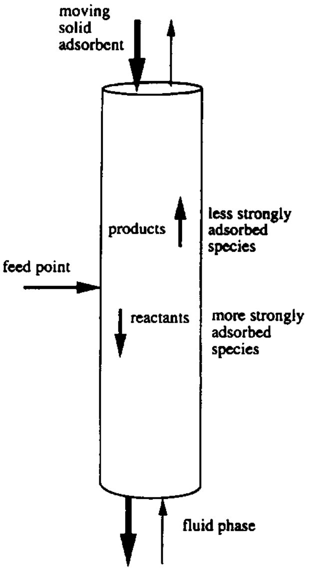

Fig. 2. True countercurrent moving bed chromatographic reactor (CMCR).

The majority of research to date on the CMCR has been concerned with the development of mathematical models. Viswanathan and Aris [2,3] were first to develop such a model. An irreversible, first order, solid catalyzed reaction with instantaneous adsorption and bottom fed reactants was studied. The model predicted complete conversion and pure product in a finite length of reactor. Similar conversions and purities were predicted using other model modifications [1,4–9] which use various combinations of; linear or Langmuir adsorption isotherms, reversible reactions (equilibrium conversion exceeded), side fed reactors and dispersionless or dispersion included models. More specific CMCR modeling issues have been studied and reported [10–13].

Only a few experimental studies have been reported on the CMCR. The first [14], a study on the oxidation of CO over Al_2O_3, verified model predictions of simultaneous reaction and separation and agreed with species concentration profiles for low gas to solid flow ratios (a linear isotherm model).

The other reaction investigated is the catalytic hydrogenation of mesitylene to trimethylclycloh-exane. Preliminary results have been reported [9]. Fish et al. describe design and construction of [15], as well as computer aided experimentation with, the CMCR [16]. This group reports conversions much greater than equilibrium with high product purity [17] in the CMCR (see Table 1).

One major drawback to the CMCR is that of solids handling. Problems such as channeling,

Table 1
Comparison of performance between the CMCR, SCMCR and the modeled SCMCR

	Conversion (%)	Purity (%)	Temp. (K)
CMCR	88	95	463
SCMCR	83	96	473
Modeled SCMCR	97	98	463

abrasion, attrition and fines removal can be avoided by simulating countercurrency. This leads to the single column [18] or multi-column SCMCR [19]. In the single column configuration (Fig. 3), rather than moving the solid phase countercurrent to the fluid phase, the reactant feed point is moved along a fixed bed in the same direction as fluid flow, but at a slower speed. This configuration is similar to early Sorbex simulated countercurrent separation processes [20–24]. Now, in the frame of reference of the feed point, the fluid phase is moving forward and the solid phase backwards. For properly chosen parameters, the products and reactants move forward and backward relative to the feed point rather than up and down the column.

If the feed point were to move continuously along the bed, this would exactly simulate the CMCR. In practice there are feed point inlets and product removal outlets spaced evenly along the column. Because of these discrete feed points, the product profile for the SCMCR will be approximately a step function, with dead times and periods of high product concentration, rather than the constant product concentration of the CMCR.

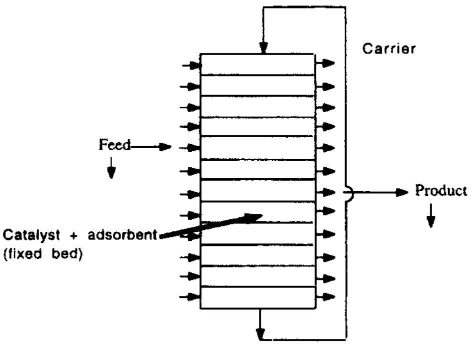

Fig. 3. Single column SCMCR (Sorbex configuration). Feed and product ports move in the same direction as carrier. The catalyst and adsorbent are co-packed in a fixed bed.

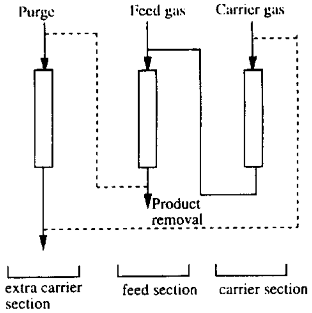

Fig. 4. Multi-column SCMCR design-generalized apparatus. More columns may be used, but are not necessary. There is no flow through the dashed lines. Ports move to the left after switching time.

More sections in a SCMCR will give output profiles which more closely approximate the CMCR, although this does not mean that more sections will necessarily yield better performance. The feed point speed (analogous to the solid phase velocity) is determined by the switching time, the time interval between switching the feed from inlet to inlet. Thus, the SCMCR is a periodic reactor.

It was found that a multiple column configuration of the SCMCR is more convenient for laboratory investigations [19]. If the single column SCMCR is divided at the feed points into several smaller columns with inlet and outlet ports between columns, one arrives at the multi-column SCMCR (Fig. 4). A multi-column SCMCR was modeled and experimentally tested using an equilibrium limited mesitylene hydrogenation reaction [19]. This reaction was shown to proceed to near completion in both theory and experiment, when carried out in this SCMCR design. A more recent investigation undertaken was the oxidative coupling of methane to ethane and ethylene. Modifications of the multi-column SCMCR lead to the reactor currently in use. Besides avoidance of solid handling problems, other advantages gained by the SCMCR over the CMCR are reduction of adsorbent inventory by elimination of the recycle stream and top and bottom holding vessels, and minimizing catalyst cost for solid catalyzed reactions. Also the absence of bed expansion, which occurs in the CMCR, would allow a smaller reactor volume for the SCMCR.

2. Experimental

2.1. General apparatus

The experimental apparatus currently being used in the oxidative coupling reaction of methane to ethane and ethylene is a modified version of the SCMCR [25,26]. In the non-modified SCMCR the adsorbent and catalyst are co-packed in several columns. The feed is switched from column to column to simulate countercurrent flow. Carrier gas enters one column behind the feed and an extra carrier gas is used to remove products two columns behind the feed. This design allows the products which are less strongly adsorbed to be swept away from the reactants and allows higher conversions of equilibrium or otherwise limited reactions.

Two problems posed by the reaction of interest necessitated modifications of the original design. One problem is that because of the high temperatures needed the catalyst and adsorbent cannot be packed together. Reaction temperatures are in the range of 873 K to 1073 K. Most solid chromatographic quality adsorbents have an upper temperature limit less than or equal to 673 K. The other problem is that the reactants, rather than the products, are the less strongly adsorbed species. In an addition reaction such as the oxidative coupling of methane to ethane and ethylene the products have a higher molecular weight than the reactants and are therefore more strongly adsorbed on almost any adsorbent.

Since the catalyst and adsorbent cannot be housed together the originally simultaneous process of reaction and separation must be done separately with different columns for reaction and separation. Each column which was originally filled with mixed catalyst and adsorbent is replaced with a high temperature reaction column followed by a low temperature separation column. Fig. 5 shows the new configuration.

This configuration also solves the problem of reversed elution order. The unused reactant is, in effect, temporarily stored in the separation column. It is held up, and shortly before the methane breaks through the separation column the feed is advanced to the next reactor/separator section. The carrier gas which enters in the column behind the feed sweeps the unused reactants from the separation column into the next reaction column.

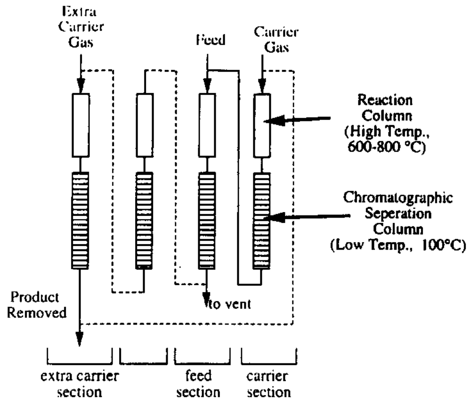

Fig. 5. Multi-column SCMCR with reaction and separation columns separate. There is flow through the solid lines, none through the dashed lines. All ports move to the left at switching time.

Because the products are so strongly adsorbed they would take more than four switching times to elute from the separation column. This cannot be allowed. Since there are only four sets of columns in the current configuration, the reactants would catch up with and mix with the products if the products are not removed in four switching times. This problem is solved by splitting the separation column into two sections. A three-way valve is placed between the two sections. This valve switches the effluent from the first separation section to the GC for analysis when products are being removed, and otherwise allows effluent from the first section to continue to the second section. The products are removed from the first section with an extra carrier gas after two feed switches (two columns behind the feed). The second section acts as a storage tank for the unused reactant. Fig. 6 shows how the separation columns have been modified.

All three SCMCR configurations (single and multi-column and modified multi-column) employ the use of a make-up feed. Its use will be described in conjunction with the oxidative coupling reaction in the modified configuration. This reaction requires a high ratio of methane to oxygen

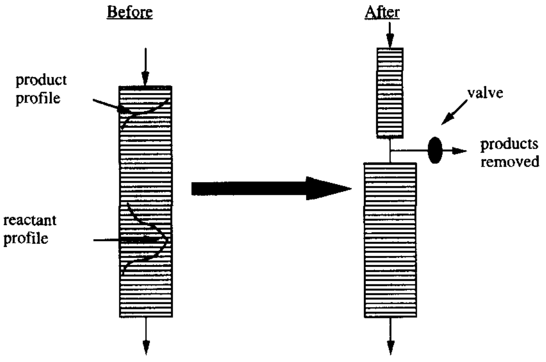

Fig. 6. Schematic for separation column modification.

for selectivity purposes. During the first switching time a high methane to oxygen ratio (around 50:1) is fed. Only a small amount of the reactants react as they pass through the first reaction column. The unreacted methane from the first column is added to the feed of the second column after one switching time. If the feed to the second column is the same as the feed to the first column, the methane would begin to concentrate. The methane adsorption isotherm would become nonlinear and the methane would start to break through the separation column before the next switching time.

To solve this problem a make-up feed is used for every switching time after the first. The feed flow rates for the first switching time are high (with a high methane to oxygen ratio for selectivity). All subsequent feeds are make-up feeds with much lower flow rates (and lower methane to oxygen ratios, since in theory four methane molecules are consumed per oxygen molecule). Fig. 7 shows a schematic of the modified SCMCR currently in use.

It should be noted that this reactor configuration has considerable flexibility. It is easily modified to accommodate different reactions and different optimal reaction conditions. To change the number of columns all that is needed is to add in the extra columns and connections and input the number of columns to the computer software (see below). If a change in separation is needed the separation columns may easily be replaced with columns having a different adsorbent or size. Reaction columns are also easily replaced with columns containing a new catalyst.

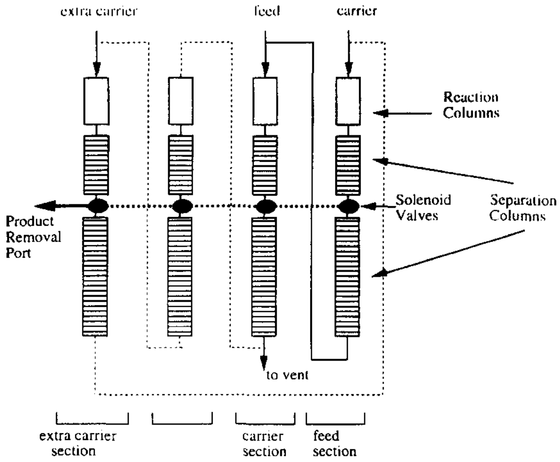

Fig. 7. Schematic of current apparatus. There is not flow through dashed lines. Ports move to the left.

2.2. Valving and micro-computer control

Two-and three-way Skinner solenoid electric valves are used to switch the gas streams. They are inexpensive, reliable and controlled via microcomputer. Maximum recommended pressure is 345 kPa (50 psia) for these valves. Two other solenoid valves are manually operated to select which effluent stream (purge or product) will be sampled.

The computer which controls these valves and the sampling valve for the gas chromatograph is an IBM XT used in conjunction with a Data Translation DT2801 high performance analog and digital I/O board, a DT707 screw terminal panel, and a series of Opto-22 solid state relays. The DT2801 functions as a analog to digital converter. The DT707 is an accessory product which permits all user connections to the DT2801 board to be made on the screw terminals. The relays translate the signals they receive into 5 V step signals which turn on (or off) the solenoid valves and the sampling valve.

Notebook is the software package which in conjunction with a BASIC program controls the system. Input parameters to Notebook include switching time, sampling time and number of columns. This combination of software allows storage of chromatographic data and display in the form of an on screen chromatograph and printed peak heights along with control of switching and sampling times.

2.3. Reaction columns

In order to minimize side reactions and withstand high temperatures, quartz reaction columns are used. The columns have a 6.4 mm (1/4 inch) outside diameter and are 50.8 cm (20 inches) long. Teflon ferrules and Swagelock fittings are used to connect the reaction columns to the 3.2 mm (1/8 inch) stainless steel tubing used to transport gasses around the system. A Thermolyne 21100 tube furnace houses the reaction columns. Four reaction columns are used. This is the optimal number of columns for the simulated countercurrent moving bed chromatographic separator (SCMCS) [27], but it has not been shown what the optimum number for the SCMCR will be.

The reaction columns are prepared as follows. Approximately 14 cm of quartz wool is packed with a glass tamping rod in one end of the column. This is followed by 70 mg (around 3 mm in length) of catalyst packed in a similar manner.

The catalyst used is a pure Samarium oxide powder from Aldrich Chemicals Inc. A short plug (approximately 2.5 cm) of quartz wool is packed on the other side of the catalyst to maintain uniform catalyst packing. Packing the columns in this manner places the catalyst plug well inside the furnace which ensures temperature uniformity.

The packed powder catalyst causes large pressure drops which may be different from column to column. In order to insure identical feed rates entering each reaction column a constant pressure drop is needed. This is accomplished by the installation of a needle valve after each of the reaction columns. The reactor is operated at typical conditions with the needle valves initially wide open. The needle valve of the column with the largest pressure drop is left open while the other needle valves are iteratively (each pressure drop is not independent) closed and opened until all of the pressure drops are the same.

2.4. Separation columns

The separation columns are packed with an activated charcoal adsorbent from Alltech Inc. As stated previously the methane is the least strongly adsorbed species with the breakthrough times of ethane and ethylene being 8 and 6.5 times longer, respectively.

Stainless steel tubing with an outside diameter of 6.4 mm (1/4 inch) is used for each separation column. Four 7.6 cm (3 inch) long tubes and two 11.4 cm (4 1/2 inch) long tubes are used in the present apparatus (only two of the larger columns are needed at one time). A plug of glass wool is used in the end of each column to prevent adsorbent loss in packing. Connections are made with Swagelock fittings and transport between columns is achieved with 3.2 mm (1/8 inch) stainless steel tubing. The columns are housed in the analytical G.C. oven at 373 K.

2.5. Gas chromatograph

A Varian 3700 Gas Chromatograph with a flame ionization detector and a 1.83 m (6 foot), 3.2 mm (1/8 inch) outside diameter Poropak QS analytical column is used to measure the concentrations of methane, ethane and ethylene in effluent streams. Either the purge or the product stream may be sampled via a computer controlled sampling valve. The oven temperature is kept at 373 K. A nitrogen carrier gas rate of 50 ml/min gives breakthrough times of 25, 45 and 50 seconds for methane, ethane and ethylene, respectively. The detector signal is sent to the computer for analysis.

2.6. Flowmeters

The reactants are metered by low flow rate rotameters from Cole–Parmer. Nitrogen carrier and extra carrier flow rates are set via needle valves and are measured with a bubble meter at the effluent of the modified SCMCR. The rotameters show large fluctuations due to pressure discontinuites as switching occurs and are considered a major source of error.

3. Operating principles

To understand the functioning of the SCMCR, first consider the fixed bed chromatographic column. Eq. (1) gives the velocity of the concentration front of a single adsorbate, V_s, in a fixed bed with Langmuir adsorption and neglected fluid phase dispersion [15]

$$V_s = \frac{U_g}{1 + \frac{1-\epsilon}{\epsilon}\frac{NK}{1+CK}} \tag{1}$$

where U_g is the mobile phase velocity, ϵ is the bed void fraction, N is the total concentration of surface sites, K is the adsorption equilibrium constant and C is the mobile phase concentration of adsorbate. Eq. (1) is modified for the CMCR to account for the relative motion of the two phases (with V_s still in the laboratory coordinate frame)

$$V_s = \frac{U_g(1-\sigma)}{1 + \frac{1-\epsilon}{\epsilon}\frac{NK}{1+CK}} \tag{2}$$

where

$$\sigma = \frac{U_s}{U_g}\frac{1-\epsilon}{\epsilon}\frac{NK}{1+CK} \tag{3}$$

where U_s is the solid phase velocity. Given two or more components in a fixed bed, separation is achieved by choosing and/or adjusting the parameters such that the velocities of the concentration fronts are different. Eq. (2) gives the dependence of V_s on σ. Note that if $\sigma > 1$, $V_s < 0$, and that front moves down the column. If $\sigma < 1$, $V_s > 0$, and that species moves up the column. Generally, one starts with products and reactants that have sufficiently different NK's and adjusts U_s and U_g such that $\sigma < 1$ for one component and $\sigma > 1$ for the other, thus causing movement in opposite directions. High concentration gradients near the top and bottom of the reactor permit a high purity product stream (except for carrier dilution) to be taken off the top of the column and very little reactant to leave the bottom [9].

Note also the dependence of σ on concentration. At a particular C, σ may be greater than 1. If the concentration of this species changes sufficiently, σ may become less than one and the motion of this species would change direction in the column, spoiling the separation.

The equation which describes the velocity of concentration fronts in the single column SCMCR is nearly identical to Eq. (2) with σ' replacing σ as the critical parameter in the CMCR equation, with V_s now in a coordinate frame moving with the feed point

$$\sigma' = \frac{\zeta}{U_g}\frac{1-\epsilon}{\epsilon}\frac{NK}{1+CK} \tag{4}$$

where $\zeta = \Delta x / t_S$, t_S is the switching time (between switching from one feed point to the next) and Δx is the distance between ports. ζ is obviously a pseudo solid phase velocity that replaces U_s in Eq. (3). Again we can adjust parameters such that $\sigma' < 1$ for one component, and $\sigma' > 1$ for the other. This would correspond to one component moving faster than the feed point and one more slowly.

For the multi-column SCMCR ζ in Eq. (4) is replaced with $\zeta' = L/t_S$, with L being the length of the reaction columns. For the modified multi-column configuration L would be the length of the reaction column plus the length of the separation column.

4. Results

4.1. Multi-column SCMCR (nonmodified)

A schematic of the multi-column SCMCR configuration used is shown in Fig. 4. The computer control of the switching, and chromatographic analysis for this system is virtually identical to that described for the modified multi-column apparatus. The switching is less complicated for this set-up because the catalyst and adsorbent are co-packed in a single column, rather than having separate reaction and separation columns and subdivided separation columns as in the modified SCMCR. The reaction columns used are 30.5 cm (1 foot) long with a 6.4 mm (1/2 inch) outside diameter [19].

The reaction investigated in this system was the hydrogenation of mesitylene (1,3,5 trimethyl benzene) to trimethylcyclohexane (TMC) over an activated platinum on alumina catalyst. The reaction is reversible, and gives no side products. This is an exothermic reaction with $\Delta H^0_{298} = -47$ kcal/mole. The temperature range over which the reaction gives appreciable amounts of both species is 453 K to 493 K. This equilibrium limited reaction has equilibrium conversions of 40% and 60% in excess H_2 at 473 K and 463 K, respectively [28].

Chromosorb 106, a porous polymer adsorbent, was selected as the adsorbent for this study. The solid phase in the reaction columns consisted of 10% Pt/Al_2O_3 containing 0.74% w/w platinum and 90% Chromosorb 106.

Several sets of experiments were conducted. The effects of temperature, switching time and reactant and carrier flow rates was studied. The optimal conditions reported are as follows:

Temperature: 473 K
Switching time: 4 min
Mesitylene flow rate: 4.1 ml/min
Hydrogen flow rate: 50 ml/min
Nitrogen flow rate: 60 ml/min
Purge N_2 flow rate: 100 ml/min
Pressure drop: 18.6 kPa

The hydrogen fed is in excess to make the reaction pseudo first order. At these conditions, the average conversion of mesitylene to TMC is 83% with 96% product purity. Note the conversion is much higher than the 40% equilibrium conversion at 473 K. The high product purity reported (excludes carrier) is another advantage of the use of this technology.

This mesitylene hydrogenation reaction was chosen as a test reaction because it is equilibrium limited, very clean (gives virtually no side products), and has suitable reaction rates at reasonable temperatures. This reaction was also investigated in the CMCR [17], so comparisons in reactor performance between the SCMCR and the CMCR may be made. The SCMCR was modeled [18,19] for this reaction using simplifying assumptions such as neglecting dispersion and the use of linear adsorption isotherms. Table 1 compares the performance of the CMCR, the SCMCR and the model predictions for the SCMCR. Values given in Table 1 are for similar temperatures (463–473 K) and $\sigma_{\text{reactant}}/\sigma_{\text{product}}$ ratios (approximately 4). The lower conversions and purities reported experimentally, as compared to model predictions, are blamed mostly on the heterogeneous nature of the adsorbent, which is not taken into account in the model, and to some extent on the other simplifying assumptions of the model.

4.2. *Modified multi-column SCMCR*

More recently, simulated countercurrent reactor technology was applied to the oxidative coupling of methane to ethane and ethylene [25,26]. Interest in converting large reservoirs of natural gas to more valuable feedstocks has driven a large number of investigations into this metal oxide-catalyzed reaction [29–31]. In traditional reactors, the high ratio of CH_4 to O_2 necessary for high selectivity limits CH_4 conversion and has limited C_2 yields to 20–25%. Significant improvements in conversion and C_2 yield have been reported in a modified SCMCR (as described above) as compared to conventional fixed bed and fluidized reactors.

Microcatalytic reactor experiments were conducted with the Sm_2O_3 catalyst. At 998 K selectivity to C_2's was over 95% at CH_4/O_2 ratios of more than 20. Conversion however was only a few percent. The modified SCMCR configuration allows the same reaction conditions (same selectivity) while increasing the conversion to near unity in theory, and far beyond previously reported results experimentally.

The apparatus and its operation have been described in detail above. The effect of temperature, switching time, and CH_4/O_2 ratio has been studied. It was found that conversion and selectivity were highly sensitive to changes in temperature and switching time. Conversions of over 65% were obtained with yields of > 50% using the following conditions:

Temperature: 973–1048 K
Switching time: 27–28 s
Nitrogen carrier: 100 ml/min
Nitrogen extra carrier: 250 ml/min
Pressure: atmospheric[1]

1st switching time
CH_4 feed: 18 ml/min
CH_4/O_2 ratio: 50:1

2nd switching time and following
CH_4 make-up feed: 1.4–1.7 ml/min
CH_4/O_2 ratio: 2:3

These yields are more than 2 times larger than previously reported yields for this reaction in conventional reactors.

Note that if this system is treated as a black box, the only things going in are methane, oxygen and carrier (with a relatively low CH_4/O_2 ratio), and the only things coming out are C_2's, CO_x, H_2O carrier and a small amount of CH_4. The CO_2 is an unwanted side product and is kept low by the high selectivity conditions. The CH_4 which exits the reactor is a result of poor adsorption dynamics. The activated charcoal has heterogeneous adsorption sites, so some of the methane is held up long enough to be purged with the products. Present research in optimizing yield in this reactor will center on finding a better adsorbent.

5. Conclusion

The success of simulated countercurrent moving bed chromatographic reactor technology has been demonstrated on both an equilibrium limited and a low per pass conversion reaction. A multicolumn SCMCR improved conversion from 40% (at equilibrium) to over 80% with pure (although dilute in carrier) products. This configuration was modified and applied to the oxidative coupling of methane to C_2's, improving conversion more than 12 fold over microcatalytic results while maintaining high selectivity. Yields obtained were more than twice that reported in the literature to date in conventional reactors. These results suggest that this technology could be successfully applied to many equilibrium and low per pass conversion reactions.

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