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Research Note

An Experimentally Determined Configuration for Simulated Moving Beds as a Separative-Reactor in Gas Phase

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One of the most attractive features of Simulated Moving Beds (SMBs) is their ability to perform reaction and separation simultaneously in order to increase reaction yields. In this paper, an appropriate configuration for the operation of such systems in gas phase has been presented and to improve the separation efficiency, Pressure Swing Adsorption (PSA) is also employed. Fischer-Tropsch Synthesis (FTS) has been chosen to verify this idea. After preparing the catalyst, choosing appropriate adsorbent and constructing the necessary experimental set up, experiments have been performed to achieve maximum yield of desired products (i.e., ethylene and ethane). Effective variables, such as flow rates of the feed and carrier gas, ratio of reactants in the feed, switching time and the number of reaction and separation columns have been optimized empirically. The results of these experiments show that the combination of PSA and catalytic reaction causes an increase of product yields. Ultimately, experiments performed under optimized conditions demonstrated not only a reduction in consumption of CO by 10 percent but also indicated a rise in production of desired materials by the same amount. In addition, products are split into two extract and raffinate streams where the purity of desired C_2 products in the former stream is about 47 percent, which indeed is an improvement over most other previous techniques.

INTRODUCTION

Simulated Moving Bed (SMB) is an engineering innovation avoiding solid circulation difficulties in Moving Beds (MBs), such as channeling of the fluid stream, abrasion and attrition of the moving solid particles and fines removal from the system, while incorporating MB privileges. It is known that continuity and countercurrency increases the driving force and efficiency of mass transfer processes. Thus, MB has been introduced into the adsorption processes, where a solid phase (i.e., the adsorbent) moves countercurrent to the fluid phase in a continuous manner.

The countercurrent motion can be simulated by employing a fixed bed with several axially aligned inlets and outlets, moving the feed and product positions sequentially along them in the direction of the fluid flow. From the feed point of view, the fluid phase is moving forward while the solid phase is traveling backward. Alternatively, a configuration in which the fixed bed is replaced by a series of packed beds may be foreseen. In a multiple-column SMB, a port which can serve as inlet or outlet, is located between each column. Feed, desorbent and product ports advancement in direction of the fluid flow simulates countercurrent motion in discrete steps at particular intervals. This is depicted in Figure 1. It is found that a multiple-column configuration of SMB is more convenient for laboratory investigation [1].

In binary separations, one component must be more strongly sorbed than the other. In true countercurrent flow, the strongly sorbed component convectively travels with the solid phase, while the weakly sorbed component is swept out of the system with the fluid phase. The column switching time (i.e., the time interval that a feed enters a column before it moves to the next column) is set between the breakthrough time of the two components. The weakly sorbed component elutes from the feed column before the feed is moved to the next column. The strongly sorbed

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product is retained in the feed column and is desorbed later. Countercurrent flow is simulated because the strongly sorbed component travels behind the moving feed point, while the weakly sorbed component moves ahead of it.

SMB can also be modified into different configurations to further improve productivity in accordance with specific applications. The number of beds or segments of a column is one of the effective parameters in optimal operation of these systems. On the other hand, it is possible to use more than one desorbent stream that adds yet another variable to evaluate the optimal configuration.

There is an SMB system that uses a single desorbent stream known as Sorbex family processes. These were developed by the UOP for petrochemical and sugar industries to facilitate liquid phase separations. The other class of separators uses multiple-desorbent streams. It is possible to use two or more desorbent streams for specific applications. In some difficult separations, use of multiple-desorbent streams helps to obtain products with higher purity. In these systems, each desorbent stream either elutes a product stream, or purges a column, thus, regenerating the adsorbent [2].

In reviewing of the recent investigation of these systems, one can find some invaluable results. Ruthven et al. [3], Hashimoto et al. [4] and Barker and coworkers [5] pioneered the multiple-deqsorbent configuration, successfully separating mixtures which differ in equipment design. Some different section flow schemes have been evaluated by Tonkovich and Carr [2]. They compared advantages and disadvantages of them and concluded that each configuration may be proper for a particular separation.

On the other hand, SMB can also be used as a separative-reactor. A separative-reactor, initially known as a chromatographic reactor, is a device for carrying out chemical reaction and separation simultaneously in a fixed bed, filled by catalyst and adsorbent. It might not be a continuous process as a conventional fixed bed, since adsorbent should be regenerated. Therefore, an innovative application of SMB process involving a reactive mixture is termed a Simulated Moving Bed Reactor (SMBR). This is a novel reactor type in which separation occurs at the site of chemical reaction to improve product purity and conversion beyond those prescribed by thermodynamic equilibrium. When reaction and separation can be achieved simultaneously, the yield of the reversible reaction may be improved noticeably.

Through a simultaneous reaction and separation process, the purity of a multi-product reaction can be increased by separating out the products into two streams of extract and raffinate. Also, in this

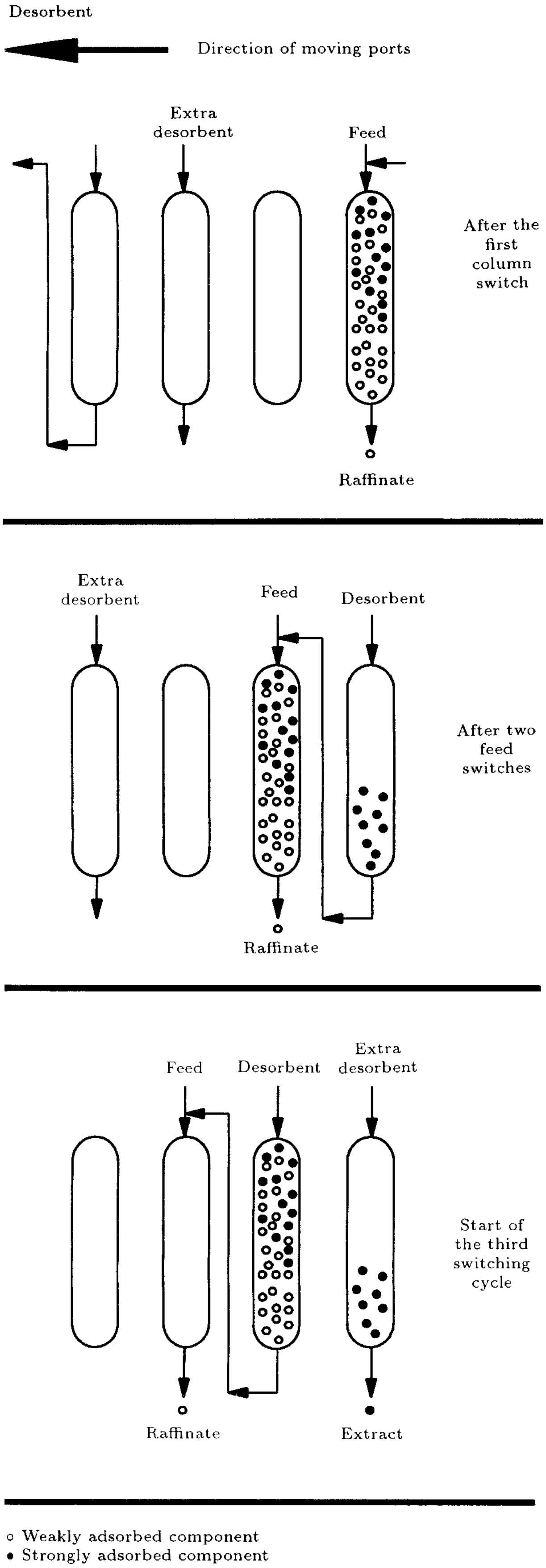


Figure 1. A multiple-columns configuration of SMB.

phenomena, wastage of unreacted species is prevented while the reacting stream progresses to the next column in line.

Several investigations of SMBR have appeared in the open literature. A modified configuration of SMBR utilized for the Oxidative Coupling of Methane (OCM) reactions, has been recently employed by Tonkovich [6]. The other reaction investigated by Ray is the catalytic hydrogenation of mesitylene [7]. A conceptual evolution of SMBR is reviewed by Bjorkland and Carr [8]. Recently, Mazzotti [9] and Kawase et al. [10] have obtained good results in estrification reactions between organic acids and alcohols. In this work, ester and water were easily separated into high purity products. In Table 1 a list of major experimental work on SMBR available in the literature is sited in a compact manner.

In the present research, a new configuration of SMBR for a gas phase coupled with Pressure Swing Adsorption (PSA) to improve separation is introduced. For this purpose, Fisher-Tropsch synthesis is chosen for kinetic description of the system.

NEW CONFIGURATION FOR SEPARATIVE- REACTOR WITH PRESSURE SWING IN GAS PHASE

Adsorbent regeneration is a vital step in every continuous adsorption process. Amongst different regeneration methods such as, temperature rising up, pressure decreasing and desorbent flow based upon the displacement technique, the latter one is very commonly utilized in SMB processes. However, pressure decreasing may also be combined together with desorbent flow in gas phase to improve regeneration process. Pressure increasing usually has a good effect on selective adsorption while pressure decreasing is a proper method for desorption step. However, one may use pressure swing adsorption as an alternative,

Table 1. A list of some experimental work on SMBR system.

Research Subject	**Researcher(s)**	**Ref.**
CO oxidation and simultaneous separation in a MB	Takeuchi, Uraguchi (1977)	[11]
Esterification reaction and separation in a SMBR	Sardin, Villermax (1979)	[12]
Utilizing of a rotary feed entrance port in a chromatographic reactor	Cho, et al. (1980)	[13]
Glucose to fructose isomerization reaction in a SMBR	Hashimoto, et al. (1983)	[4]
Theoretical and experimental evaluation of a MB	Petroulas, et al. (1985)	[14]
Simultaneous reaction and separation for an equilibrium reaction in a MB	Fish, et al. (1986)	[15]
SMBR development as an enzyme reactor	Barker, et al. (1987)	[16]
Comparison between MB and SMB as chromatographic reactors	Fish, et al. (1988)	[17]
Experimental evaluation of reversible reactions in a MB	Fish , Carr (1989)	[18]
Different configurations evaluation of SMB as a chromatographic reactor	Ray, et al. (1990)	[19]
A few configurations for SMBR evaluation as a chromatographic reactor and separator	Tonkovich (1992)	[6]
Using SMBR as a chromatographic reactor and separator	Ray (1992)	[7]
Utilizing a modified configuration of SMBR for the OCM reaction	Tonkovich, et al. (1993) Tonkovich, Carr (1994)	[20,21]
A review of different chromatographic reactors	Sardin, et al. (1993)	[22]
A review of countercurrent and continuous chromatographic reactors	Carr, et al. (1993)	[23]
Reversible reaction of mesitylene hydrogenation in an SMB chromatographic reactor	Ray, et al. (1994) Ray, Carr (1995)	[24,25]
A review of MB and SMB separative-reactors	Bjorkland, Carr (1995)	[8]
Acetic acid and β-phenyl alcohol esterification in an SMBR	Kawase, et al. (1996)	[10]
Modification of SMBR for OCM reactions	Kruglov, et al. (1996)	[26]
Experimental evaluation of esterification reaction in an SMBR	Mazzotti, et al. (1996)	[9]

in order to enhance separation efficiency of SMB operation.

On the other hand, for a catalytic reaction in gas phase at high pressure, it is possible to make use of pressure swing together with a SMBR process. At high pressure, while the reaction is progressing, and after some separation has occurred, the desorbent must be regenerated. For this reason, first the pressure must be decreased and then desorption will start.

In Figure 2, a new configuration for Simulated Moving Bed Reactor together with Pressure Swing Adsorption (i.e., SMBR-PSA) is demonstrated. Two kinds of carrier gas, one in high (equal to operating) and the other in low (atmospheric) pressure, are employed in this pattern. According to the presented configuration, a complete cycle of the process contains six steps including: 1) Extract removal, 2) Elution by carrier gas, 3) Raffinate removal and simultaneous reaction and separation (or conventionally termed feed step), 4) Pressurization, 5) Purge and 6) Blowdown. All of these steps are included in one column, except the feed step. The number of columns in this step depends upon operational circumstances and must be optimized.

In the feed step, a mixture of reactants with a proper feed ratio at a high pressure enters into the column. The catalytic reaction goes forward and a mixture of products and reactants is subsequently formed. Since each component has different adsorption affinity (particularly at high pressures), the more strongly adsorbed species move slower, while the more weakly sorbed component breakthrough sooner, thus, eluting from the column as a raffinate stream. The elution by carrier gas step (i.e., feed column in previous step) contains a major part of more strongly adsorbed components and part of more weakly sorbed species. At this time, the weakly adsorbed components (e.g., unreacted species) are eluted by a high pressure carrier gas and added to feed which is entering into the feed column. It is very important that after this combination, a proper ratio of reactants is introduced into the feed column. According to the principles of SMB operation, after discharging less strongly adsorbed species into the feed column, just before the strongly sorbed component would leave the elution column, all inlet and outlet port advancements in direction of the fluid flow should take place. Therefore, switching time must be evaluated between breakthrough times of two key components from the elution column. The separating boundary is located between these components, in other words the most strongly adsorbed component in the raffinate and the most weakly adsorbed one in the extract stream.

After proper displacement of streams, a high pressure carrier gas causes exiting of the more strongly sorbed species from the extract removal column (i.e., elution column in the previous step). Next, the blowdown column (i.e., the end column of the raffinate removal section in the previous step) is discharged to

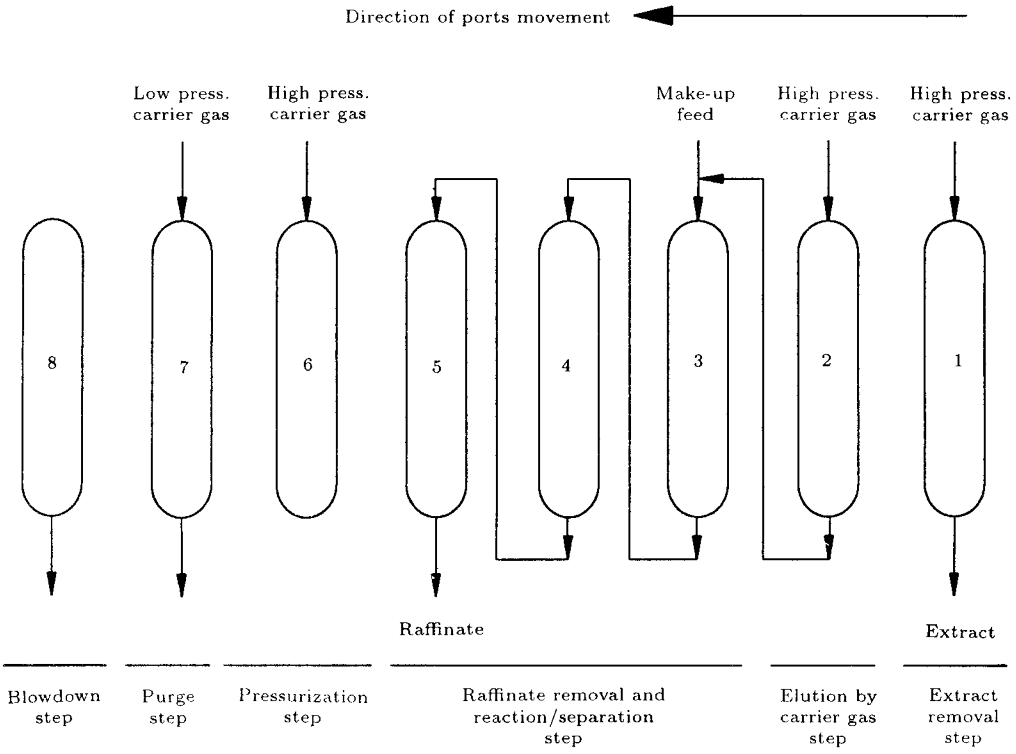


Figure 2. SMBR-PSA configuration.

the atmosphere in order to be prepared for regeneration at low pressure through the next step. The low pressure carrier gas enters into the purge column to remove the residue of the more strongly adsorbed components and prevent their build up on the adsorbent. Thus, the column is cleaned up and prepared for the next reaction and separation step. After this stage, a high pressure carrier gas is utilized to pressurize the column up to the operating amount needed in the pressurization step.

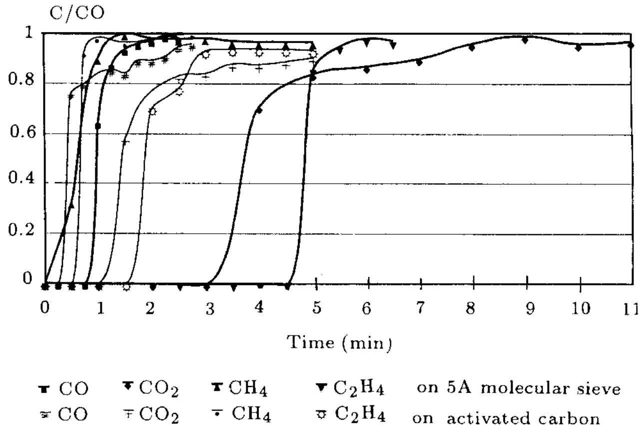
The presented SMBR-PSA configuration has some key parameters which affect the desired operation. These include switching time, selectivity of adsorbent, differences between breakthrough time of key components, number of columns in the reaction-separation step, flow rates of the streams, particularly feed and carrier gas of elution step and proper ratio in the feed make up through the feed column. Therefore, it is best to evaluate such systems experimentally.

EXPERIMENTAL SECTION

Preliminary Experiments

In order to evaluate the developed configuration of SMBR-PSA, one needs to first, select a proper catalyst and adsorbent. The catalytic hydrogenation of CO, that is termed Fischer-Tropsch Synthesis (FTS), is a gas phase reaction which goes forward at high pressure and is also compatible with SMBR-PSA idea. It is possible to produce a variety of hydrocarbon products, such as paraffins, olefins, aromatics and oxygenated components. The catalyst and operating conditions define the specific product. In this research, C_2 hydrocarbons (i.e., ethylene and ethane) have been chosen as desired products of the FTS. For this purpose, some catalysts with Fe, Cu and Mn as an active metal, and ZSM5, 5A molecular sieve and Y-zeolite as a support were made and tested in different operating conditions in a fixed bed reactor experimentally. According to the experiments, Fe-Cu-K/ZSM5 catalyst shows the best results amongst all prepared catalysts. The optimum operating conditions evaluated experimentally include, $P = 18$ bar, $T = 280°C$, $CO/H_2 = 0.773$ and He (i.e., carrier gas) flow rate = 0.580 nml/s [27,28]. Reaction products over the selected catalyst at optimized conditions are CH_4, C_2 (i.e., C_2H_6 and C_2H_4) and CO_2.

Nevertheless, it is necessary to use a proper adsorbent for a good separation. Thus, some experiments were performed to select the best amongst available adsorbents. In Figure 3, breakthrough curves for four major components (i.e., CO, CO_2, CH_4 and C_2H_4) over two adsorbents, 5A molecular sieve and activated carbon (L'Air liquid), are illustrated. Based on the performed experiments for determining the isotherm and breakthrough curves, the 5A molecular sieve demonstrated a better capability to separate these components [28].



$T = 30°C$, P=atm.

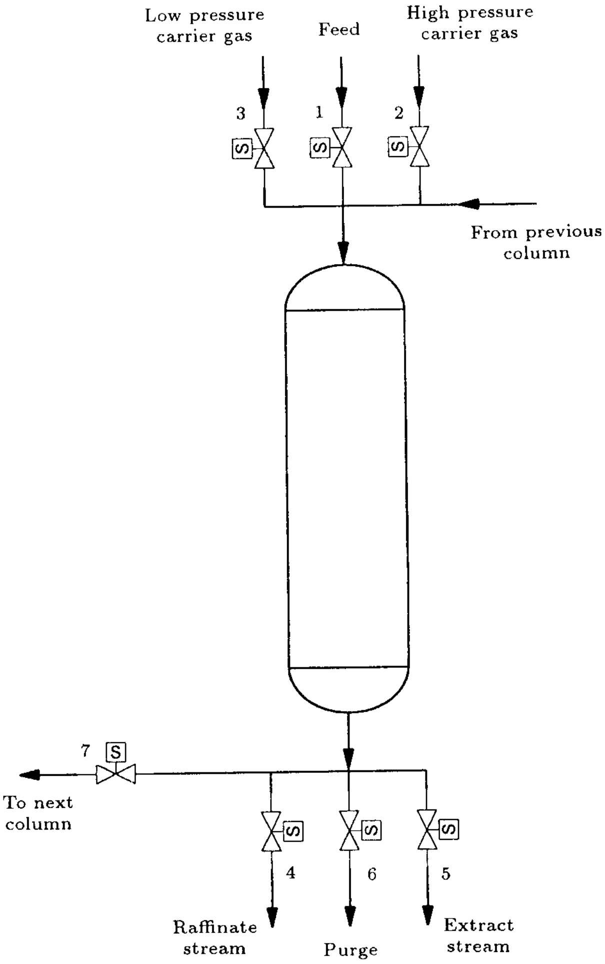
Figure 3. Breakthrough curves of major components of FTS over 5A molecular sieve and activated carbon.

Experimental Set up

The configuration of SMBR-PSA pilot unit designed and constructed in the laboratory is shown schematically in Figure 4. The experimental apparatus is employed to monitor the progress of the FTS reaction and separate reactants and products simultaneously to enhance C_2 productivity and purity. The apparatus consists of eight columns co-packed with the adsorbent (i.e., 24.1 gr of 16/30 mesh 5A molecular sieve) and selected catalyst (i.e., 6.6 gr of 16/30 mesh). The length of each stainless steel column was 38 cm with a 12 mm inside diameter. The ends of the columns were fitted with a proper connection to 1/8 in swagelok unions and were packed with glass wool to hold solid particles in place. All connections between columns were made with 1/8 in. OD stainless steel tubing. All columns were located in an electrical heater that should be heated up to 450°C. The temperature is measured by a thermocouple in the thermowell that is embedded in each column and controlled by a TLC.

Several solenoid valves are used to accomplish switching of entering streams, including make-up feed, high and low pressure carrier gas and exiting streams. These include extract and raffinate products, vent and stream to the next column. Seven solenoid valves (Rapa Germany, size 1/8 in.) were used for each column to direct the gases to enter and exit the appropriate column. The valve diagram, which is identical for all columns, is presented in Figure 5. The position of all the 56 solenoid valves is controlled by a personal computer IBM/80-486 for data acquisition and process sequencing control, equipped with a data translation and a series of solid state relays.

The precise flow rate of input gases are indicated and controlled by mass flow meter / controller (Brooks



		Step No.							
		T1	T2	T3	T4	T5	T6	T7	T8
Valve NO.	1	-	-	-	-	-	-	+	-
	2	+	-	-	+	-	-	-	+
	3	-	-	+	-	-	-	-	-
	4	-	-	-	-	+	-	-	-
	5	+	-	-	-	-	-	-	-
	6	-	+	+	-	-	-	-	-
	7	-	-	-	-	-	+	+	+

Figure 4. Schematic diagram of a SMBR-PSA set up.

- model 5879). Regulating and reducing pressure (Grove) valve and back pressure relief (Grove) valves are used to set the pressure of the system. After the two product streams (i.e., raffinate and extract) leave the respected columns, they enter into appropriate condensers in order to remove any condensate existing in them.

A computer-controlled sampling system is designed, constructed and connected directly to effluent streams to collect and reserve 11 gas samples from product streams and inject them (one by one) to the GC at a pre-determined time. A microprocessor linked to this system is employed to command sampling and injecting to the GC automatically.

A Shimadzo GC-6PT gas chromatograph with a Thermal Conductivity Detector (TCD) is used to measure effluent gas concentrations. This GC is connected to the computer for data processing.

Experimental Procedure and Results

In order to verify the aforementioned SMBR-PSA idea, it was necessary to run appropriate tests. Also, it was very important to design experiments in order to find the optimum parameters for successful operation. Certainly, breakthrough times for different components are the most important variables in these systems. They should be used to determine the switching time, which is a key parameter in this process.

The dynamic response of the reactor for the catalyst and then the mixture of catalyst and adsorbent being co-packed in a bed should be evaluated. Finally, after estimating optimum parameters, a complete cycle of SMBR-PSA will be run to investigate the system capability for simultaneous reaction and separation. Since SMBR-PSA operation is affected by transient behavior, due to switching of streams alternatively, dynamic response of catalyst should be evaluated.

Test of the dynamic response of the catalyst is performed in an individual reactor. The selected catalyst is loaded, then optimum operating conditions which were determined at prior steady state concentration tests, are set. For each experiment, the catalyst and adsorbent have been regenerated by a mixture of 90% He and 10% H_2, with 11.7 nl/hr total flow, for 17 hours at 450°C. The stream of reactants (i.e., $CO = 0.194$ and $H_2 = 0.251$ nml/s) is allowed to enter into the reactor (i.e., $t = 0$) and then 11 samples are taken and reserved from the outlet of this reactor at pre-determined intervals. Ultimately, the transient response of the reactor is obtained by GC analysis of these samples.

Figure 6 shows the composition variation of components from the transition up to steady state period. These results indicate that CO content in the effluent stream has an increasing trend. At initial operation period, when the reactor is still clean, the catalyst has a higher activity. Therefore, CO conversion shows a decreasing trend and ultimately reaches down the steady state plateau as time goes by. Hydrocarbons produced here are mainly based upon the four reactions on the iron catalyst as follows:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{A}$$

$$CO + 5/2H_2 \rightarrow 1/2C_2H_6 + H_2O \tag{B}$$

$$CO + 2H_2 \rightarrow 1/2C_2H_4 + H_2O \tag{C}$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \tag{D}$$

It is observed that CO_2 is produced from reaction D

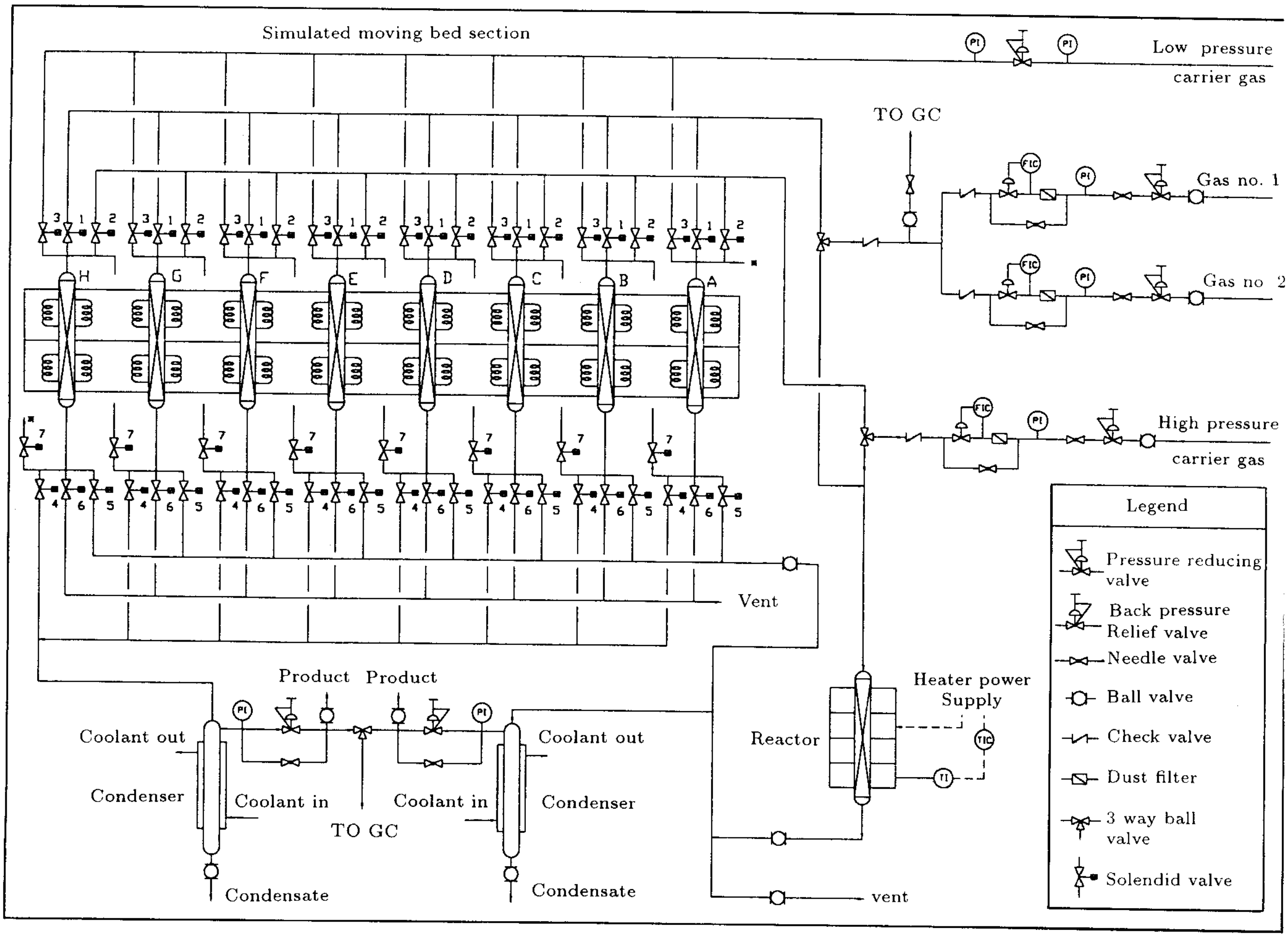
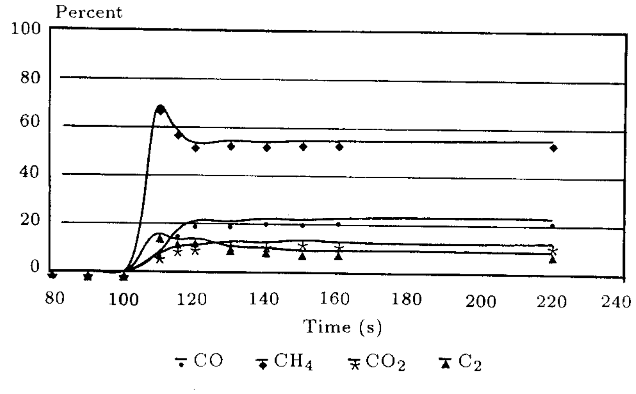


Figure 5. Valve diagram for one column.



CO/H_2 =0.773, GHSV=528 (1/hr), $T = 280°C$, $P = 18$ bar

Figure 6. Dynamic analysis for catalyst in the reactor.

(also known as the Water Gas Shift or WGS reaction) and effected by H_2O production in other reactions. Thus, increasing of CO_2 and decreasing of CH_4, C_2H_6 and C_2H_4 through time may be reasoned out.

In order to determine the share of each reaction in the overall production scheme presented by the above mechanism, one may use the results of the dynamic testing in addition to the overall material balance. The results of these calculations, summarized in Table 2, indicate that increasing the CO_2 production (i.e., D reaction) causes a decrease in hydrocarbons production. The backward reaction in the WGS helps to produce CO which inturn causes an increase in CH_4 production up to the steady state concentration. It is seen from Figure 6 that the dead time of this system is about 100 seconds and after 140 seconds concentration of all species will approach their steady state amounts.

In the next set of experiments, the transient response for a column of SMBR-PSA system, which is loaded with a mixture of catalyst and adsorbent, is determined. All operating conditions and experimental procedures are applied just as before. Figure 7 shows the obtained results of GC analysis for 11 samples taken from the effluent stream of the aforementioned column at pre-determined times. Although these results display similar trends as previous ones, dead and breakthrough times for species in the latter case are shorter. This is due to the fact that this column possesses a smaller volume than the reactor. The dead time of 30 seconds and necessary time to arrive

Table 2. The share of each main FTS reactions in the overall production scheme.

Loop No.	Time (s)	CO%	CH_4%	CO_2%	C_2%	X%	A%	$B+C$%	D%
1	80	—	—	—	—	—	—	—	—
20	90	—	—	—	—	—	—	—	—
3	100	—	Trace	—	—	—	—	—	—
4	110	8.19	68.64	7.42	15.72	92.92	63.80	29.24	6.90
5	115	17.08	58.92	10.47	13.53	84.95	61.09	28.06	10.86
6	120	21.12	53.78	11.19	13.91	81.46	57.96	29.99	12.06
7	130	21.32	54.76	12.81	11.09	80.81	61.00	24.71	14.27
8	140	22.52	54.41	12.70	10.36	79.59	61.94	23.59	14.46
9	150	22.14	54.89	13.63	9.31	79.75	62.97	21.36	15.64
10	160	22.75	54.90	12.91	9.43	79.21	63.34	21.76	14.89
11	220	22.99	55.45	12.64	8.90	78.89	64.54	20.72	14.71

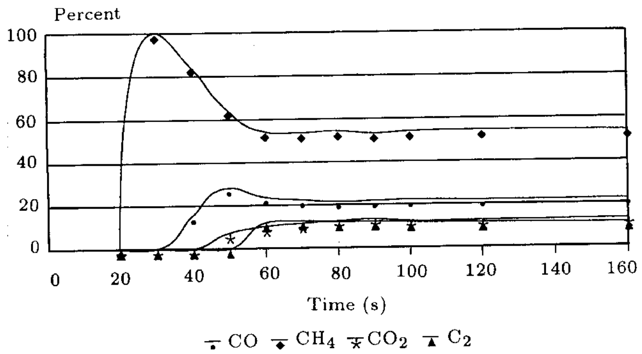


Figure 7. Dynamic response for a mixture of catalyst and adsorbent in a column.

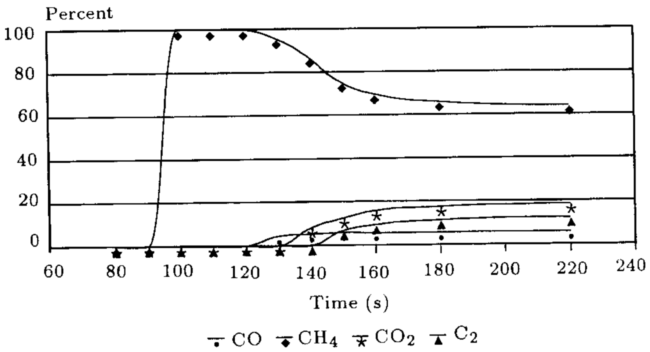


Figure 8. Dynamic analysis of which three consecutive columns co-packed catalyst and adsorbent.

at the steady state concentration of 80 seconds after introducing the feed into the column is seen in the outlet. CO, CO_2 and C_2 appear in the effluent stream after 40, 50 and 60 seconds, respectively. This is related to the reaction kinetics and the adsorbent-chemical species interactions.

Because of these results and based on the main purpose of this research, an appropriate separating boundary should be considered. According to the obtained results in this work, the best position for the separating boundary, in order to distinguish unreacted feed and products, is to locate it between the column for CH_4 and CO species are close to each other, yet different from CO_2 and C_2 products. It should be reiterated that the aim of this study is to produce and separate C_2 components. Thus, the extract stream will be concentrated with C_2 and CO_2 , while the raffinate stream is purified with CH_4 and CO. The location of the separating boundary is, ultimately, specified by the switching time. The proper switching time allows only for the passage and entrance of raffinate components into the next column. From these results, it is predicted that switching time should be in the range of 30 to 50 seconds in this system.

The difference in breakthrough time for components in one column is not sufficient to have a good separation and the desired purification. In order to omit this problem, one may increase the number of reaction and separation columns in this system.

Through the next run of experiments, three columns co-packed with catalyst and adsorbent are employed. All of the process circumstances are as before. The dynamic analysis for three consecutive columns is illustrated in Figure 8. From these results, dead time is about 100 seconds. Methane, as a main product, with the shortest residence time is eluted first followed by CO, CO_2 and C_2 at 130, 140 and 150 seconds, respectively. These results indicate that by increasing the number of columns, one may achieve a better separation.

On the other hand, increasing the number of columns causes a decrease in the unreacted CO and an increase in the undesired CO_2 product of the effluent stream. This is related to the WGS reaction progress when the H_2O is produced and reacted with CO in the column. Also, the hydrocarbon reactions are prevented from occurring due to lack of hydrogen content in these columns. Therefore, further increase in the

Table 3. Selectivity and yield of products in different situations.

	S_{CH_4}	Y_{CH_4}	S_{C_2}	Y_{C_2}	S_{CO_2}	Y_{CO_2}
Reactor	0.714	0.550	0.116	0.089	0.164	0.126
One Mixed Column	0.695	0.54	0.141	0.110	0.164	0.128
Three Mixed Column in Series	0.678	0.64	0.128	0.120	0.194	0.183

Operating conditions:

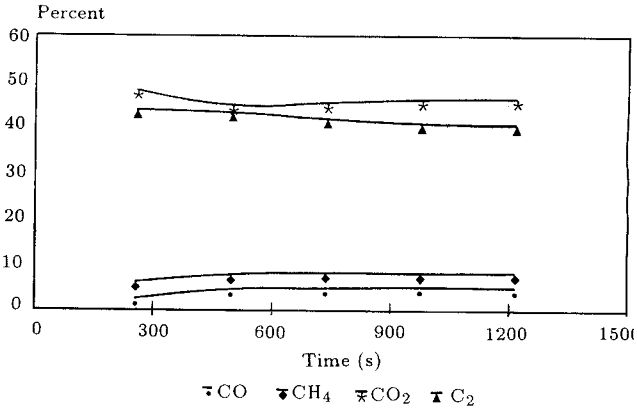
$T = 280°C$, $P = 18$ bar, H_2 flow rate = 0.251 nml/s, CO flow rate = 0.194 nml/s, He flow rate = 0.580 nml/s

number of columns decreases the selectivity of the desired products. Thus, it is a foregone conclusion that there would be a trade off between a good selectivity and separation when employing optimum number of columns. In order to compare results of these cases, selectivity and yield of products at the steady state situation are shown in Table 3. Therefore, based on these findings, asystem of three mixed columns in series is proposed in order to obtain a better yield for C_2 products.

In order to evaluate SMBR-PSA scheme, a complete cycle of the process based on obtained results and optimum parameters is tested. The reaction and separation steps include three columns; therefore, accounting for the five steps previously described, the total number of columns needed is eight. All eight columns are loaded with 6.6 gr of catalyst and 24.1 gr of adsorbent, similar to previous tests. The same operating conditions including $T = 280°C$, $P = 18$ bar and elution carrier gas flow rate equal to 0.580 nml/s are utilized.

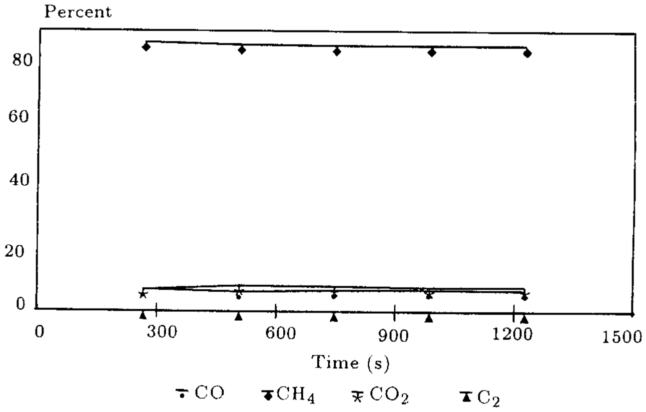
After regeneration of the catalyst and adsorbent and initial preparation, the feed stream containing CO and H_2 with flow rates of 0.194 and 0.251 nml/s, respectively, is introduced into the feed column. The stream switching and sequencing system is set by entering the position of solenoid valves and switching times into an interfaced PC with the system for this purpose. Since a part of unreacted CO will exit from the elution step and add to the feed, the amount of CO should be decreased in the make-up feed. After many experiments, 0.175 nml/s is determined to be a suitable flow rate of CO. Thus, the process starts up with 0.194 nml/s for CO flow rate and decreases rapidly to 0.175 nml/s after the first switching.

In order to analyze product streams, five samples are taken from each of the extract and raffinate streams, at pre-determined times for second through sixth cycles. Experiments are fulfilled for 30, 40 and 50 seconds switching times. Figures 9 and 10 show the analysis of the extract and raffinate streams for the switching time of 30 seconds. It is seen that a part of the raffinate stream (containing CH_4 and CO) cannot come out of the elution column, hence contaminating the extract stream.



Extract flow rate = 0.123 nml/s

Figure 9. Extract stream analysis for switching time of 30 seconds.



Raffinate flow rate = 0.321 nml/s

Figure 10. Raffinate stream analysis for switching time of 30 seconds.

Figures 11 and 12 indicate the same results for switching time of 40 seconds. It is observed that the desired product (i.e., C_2 hydrocarbons) has a better purification in the extract stream. However, the amount of heavy components (CO_2 and C_2) in the raffinate stream shows a little increase relative to the previous runs.

For switching time of 50 seconds, some of the desired product enters into the raffinate stream and is lost (Figures 13 and 14).

In Table 4, the amount of different components in the extract stream versus the switching time is

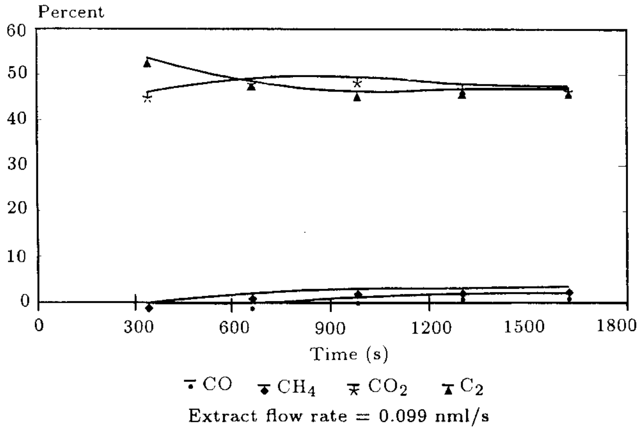


Figure 11. Extract stream analysis for switching time of 40 seconds.

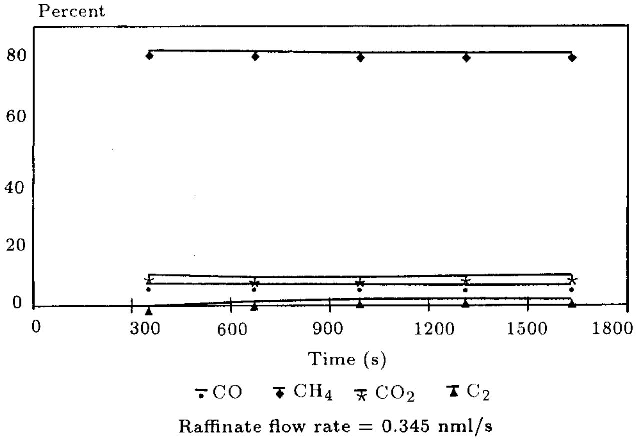


Figure 12. Raffinate stream analysis for switching time of 40 seconds.

Table 4. Variation of mole percent of different components versus t_s in the extract stream.

t_s	CO	CH_4	CO_2	C_2
30	5.08	8.35	46.20	40.37
40	2.07	3.52	47.51	46.90
50	0	2.77	54.26	42.97

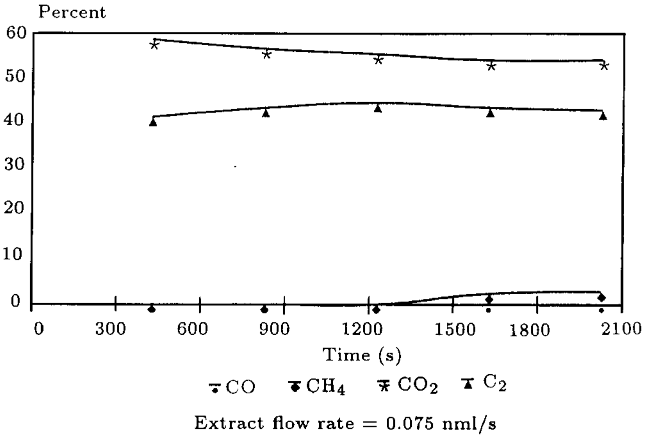


Figure 13. Extract stream analysis for switching time of 50 seconds.

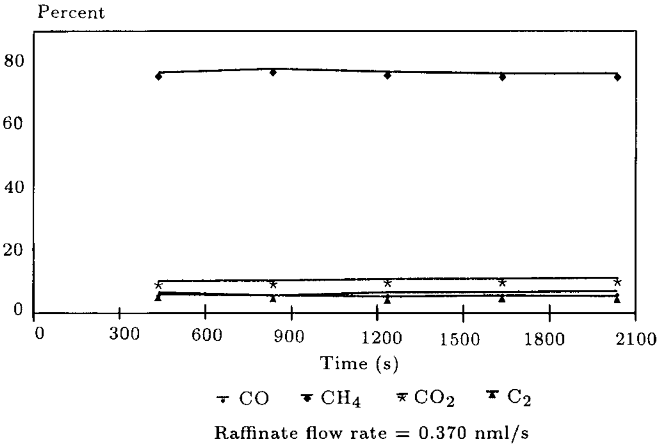


Figure 14. Raffinate stream analysis for switching time of 50 seconds.

displayed. As is observed, the best purity of C_2 components is obtained at $t_s = 40$ s. Also, in Table 5, the recovery of C_2 components in the extract stream versus the switching time is illustrated. According to these results, it is a foregone conclusion that with an increase in switching time, even though the recovery of desired products is decreased, the best separation results is obtained at $t_s = 40$ s.

It is a good idea to compare SMBR-PSA results with those of a Fixed Bed reactor (FB). In Table 6 the ratio of the outlet components of the SMBR-PSA (i.e., extract and raffinate streams) to those of an FB at similar conditions are presented. It is observed that despite the reduction of CO introduced into the feed column from 0.194 to 0.175 nml/s, the amount of unreacted CO in the outlet is lower in SMBR-PSA compared with that of an FB. It may also be seen that due to an increased CO conversion, all products have an increase in yield. Furthermore, the selectivity of CO_2 has a more pronounced increase than other species. Ultimately, according to this table, the best results to produce desired products is expected to appear at $t_s = 40$ s, where an increase of 10 percent in the amount of these species is reached.

CONCLUSIONS

In this study, the feasibility of SMB application to the simultaneous gas phase reaction and separation has been determined experimentally. For this purpose, a new configuration including a combination of SMBR and PSA has been employed and verified through experiments. Moreover, some guidelines for optimization of the process have been discussed.

Although this technique needs more complicated controllers (for stream switching) and uses a lot of gas (as a carrier or purge), it has many advantages over

Table 5. The recovery of components in the extract stream versus the switching time.

t_s (s)	$(CO)_{Ext}/(CO)_{SMB}$	$(CH_4)_{Ext}/(CH_4)_{SMB}$	$(CO_2)_{Ext}/(CO_2)_{SMB}$	$(C_2)_{Ext}/(C_2)_{SMB}$
30	0.223	0.036	0.691	1.000
40	0.082	0.012	0.580	0.872
50	0	0.007	0.494	0.618

Table 6. Product ratio of SMBR-PSA to fixed bed reactor.

t_s (s)	$(CO)_{SMB}/(CO)_{FB}$	$(CH_4)_{SMB}/(CH_4)_{FB}$	$(CO_2)_{SMB}/(CO_2)_{FB}$	$(C_2)_{SMB}/(C_2)_{FB}$
30	0.285	1.18	1.45	1.02
40	0.256	1.18	1.43	1.10
50	0.264	1.18	1.44	1.07

fixed beds. Ultimately, from the work described above, the following conclusions may be drawn:

1. The use of unreacted materials without utilizing of the recycle stream causes an increase in reaction conversion in a smaller column of SMBR-PSA compared with that of a fixed bed. It has been realized through SMBR-PSA technology that in spite of decreasing COin the make-up feed, the conversion rises up, due to the use of reactants in columns ahead;
2. All product yields increase with increasing the reaction conversion in the SMBR-PSA process. However, due to reaction kinetics and dynamics of the system, different products show different elevation in their yields. It is obvious that all products have higher yields in SMBR-PSA setting, however, the CO_2 has the most noticeable extent. This should be related to the reversibility of the WGS reaction, which produces CO_2. Therefore, it is demonstrated that due to simultaneous reaction and separation, reversible reactions progress further than their irreversible counterparts;
3. The split of products into two streams (i.e., raffinate and extract) is yet another important advantage of SMBR-PSA process. The combination of separation and reaction sections has an effective role in process cost reduction. Thus, it is realized that with correct selection of effective parameters, one may achieve a highly successful process.

REFERENCES

1. Ray, A. et al. "The simulated countercurrent moving bed chromatographic reactor", *Chem. Eng. Sci.*, **45**(8), pp 2431-2437 (1990).
2. Tonkovich, A.L. and Carr, R.W. "Experimental evaluation of designs for the simulated countercurrent moving bed separator", *AIChE J.*, **42**(3), pp 683-690 (1996).
3. Ruthven, D.M. and Ching, C.B. "Countercurrent and simulated counter-current adsorption separation processes", *Chem. Eng. Sci.*, **44**(5), pp 1011-1038 (1989).
4. Hashimoto, K. et al. "A new process combining adsorption and enzyme reaction for producing higher-fructose syrup", *Biotech. & Bioeng.*, **XXV**, pp 2371-2393 (1983).
5. Barker, P.E. et al. "A new process for the continuous fractionation of Dextran", *Ind. Eng. & Chem. Proc. De. & Dev.*, **17**(3) (1978).
6. Tonkovich, A.L "The simulated countercurrent chromatographic reactor and separator", Ph.D Thesis, University of Minnesota (July 1992).
7. Ray, A.K. "The simulated counter-current moving bed chromatographic reactor: A novel reactor separator", Ph.D. Thesis, University of Minnesota (April 1992).
8. Bjorkland, M.C. and Carr, R.W. "The simulated countercurrent moving bed chromatographic reactor: A catalytic and separative reactor", *Catalysis Today*, **25**, pp 159-168 (1995).
9. Mazzotti, M. et al. "A continuous chromatographic reactor: SMBR", *Chem. Eng. Sci.*, **51**(10), pp 1827-1836 (1996).
10. Kawase, M. et al. "Increased esterification conversion by application of the simulated moving bed", *Chem. Eng. Sci.*, **51**(11), pp 2971-2976 (1996).
11. Takuchi, K. and Uraguchi, Y. "Experimental studies of a chromatographic moving bed reactor", *J. Chem. Eng.*, Japan, **10**, pp 455-460 (1977).
12. Sardin, M. and Villermax, J. "Esterification catalysee par une resine echangeuse de cation dans un reacteur chromatographique", *Nouv. J. Chim.*, **3**, pp 255-261 (1979).
13. Cho, B.K. et al. "A continuous chromatographic reactor", *Chem. Eng. Sci.*, **35**, pp 74-81 (1980).
14. Petroulas, T. et al. "Analysis and performance of a countercurrent moving bed chromatographic reactor", *Chem. Eng. Sci.*, **40**(12), pp 2233-2240 (1985).
15. Fish, B. et al. "The continuous countercurrent chromatographic reactor", *Chem. Eng. Sci.*, **41**, pp 661-668 (1986).

16. Barker, P.E. et al. *Bioreactors and Biotransformation*, Moody, G.W. and Barker, P.E., Eds., Elsevier, Amsterdam, pp 141-145 (1978).

17. Fish, B. et al. "Computer-aided experimentation in countercurrent reaction chromatography and simulated counter-current chromatography", *Chem. Eng. Sci.*, **43**, pp 1867-1873 (1988).

18. Fish, B. and Carr, R.W. "An experimental study of the countercurrent moving bed chromatographic reactor", *Chem. Eng. Sci.*, **44**(9), pp 1773-1783 (1989).

19. Ray, A. et al. "The simulated countercurrent moving bed chromatographic reactor", *Chem. Eng. Sci.*, **45**(8), pp 2431-2437 (1990).

20. Tonkovich, A.L et al. "Enhanced C_2 yields from methane oxidative coupling by means of a separative chemical reactor", *Science*, **262**, pp 221-223 (1993).

21. Tonkovich, A.L. and Carr, R.W. "A simulated countercurrent moving bed chromatographic reactor for the oxidative coupling of methane: Experimental results", *Chem. Eng. Sci.*, **49**, pp 4647-4656 (1994).

22. Sardin, M. et al. "Preparative fixed-bed chromatographic reactor", in *Preparative and Production Scale Chromatography.*, **61**, Chromatographic Science Series, Ganetsos, G. and Barker, P.E., Eds., Marcel Dekker, New York, pp 477-521 (1993).

23. Carr, R.W. "Continuous reaction chromatography", in *Preparative and Production Scale Chromatography*, **61**, Chromatographic Science Series, Ganetsos, G. and Barker, P.E:, Eds., Marcel Dekker, New York, pp 477-521 (1993).

24. Ray, A.K. et al. "The simulated countercurrent moving bed chromatographic reactor: A novel reactor separator", *Chem. Eng. Sci.*, **49**(4), pp 469-480 (1994).

25. Ray, A.K. and Carr, R.W. "Experimental study of a laboratory-scale simulated countercurrent moving bed chromatographic reactor", *Chem. Eng. Sci.*, **50**, pp 2195-2202 (1995).

26. Kruglov, A.V. et al. "Optimization of the simulated countercurrent moving bed chromatographic reactor for the oxidative coupling of methane", *Chem. Eng. Sci.*, **51**(11), pp 2945-2950 (1996).

27. Pakseresht, S. et al. "Experimental optimization of parameters affecting ethylene-ethane selectivity in Fischer-Tropsch synthesis", *13th International Congress of Chemical and Process Engineering*, **CHISA'98**, Praha, Czech Republic, pp 23-28 (Aug. 1998).

28. Pakseresht, S."Evaluation of simulated moving beds performance as a separative-reactor", Ph.D. Thesis, Sharif University of Technology (Nov. 1999).