Sorption-Enhanced Reaction Process

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A process for carrying out simultaneous reaction and separation of desired products in a single unit operation is described. It uses a fixed packed column of an admixture of a catalyst and a sorbent that selectively removes a reaction by-product from the reaction zone. The sorbent is periodically regenerated by using the principles of pressure-swing adsorption. The process steps allow direct production of the desired product at high purity and at the reaction pressure. High conversion of the reactants to products in an endothermic, equilibrium-controlled reaction can be achieved while operating the reaction at a substantially lower temperature than would be necessary by a plug-flow reactor packed with the catalyst alone. The equilibrium-controlled reverse water-gas shift reaction for the production of carbon monoxide is experimentally evaluated as a proof of the concept.

Introduction

The concepts based on Le Chatelier's principle that (1) the conversion of reactants to products, and (2) the rate of forward reaction in an equilibrium-limited reaction can be increased by selectively removing some of the reaction products from the reaction zone are very well known (Gluud et al., 1931). Numerous applications of this concept using fixed-bed, continuous-countercurrent moving-bed, and simulated-countercurrent moving-bed chromatographic reactors have been published (Roginskii et al., 1962; Magee, 1963; Chu and Tsang, 1971; Takeuchi and Uraguchi, 1977; Cho et al., 1980, 1982; Petroulas et al., 1985; Fish et al., 1986; Tonkovich and Carr, 1994a,b; Kruglov, 1994). Numerous articles have also been published under the general category of membrane reactors, where the reaction products are removed from the reaction zone by selective permeation through the reactor wall acting as a membrane (Sun and Khang, 1988; Wu et al., 1990; Uemiya et al., 1991; Tsotsis et al., 1992; Itoh et al., 1993; Adris et al., 1994; Hsieh, 1988; Armor, 1995). The third category of application of this concept is the use of a mixture of a sorbent and a catalyst in a chemical reactor. The sorbent selectivity removes some of the reaction products from the reaction zone (physi- or chemisorption). The sorbent is then (1) periodically regenerated *in situ* by using the principles of pressure-swing adsorption (Vaporciyan and Kadlec, 1987, 1989; Lee and Kadlec, 1989; Kadlec and Vaporciyan, 1993; Goto et al., 1993; Alpay et al., 1993, 1994; Han and Harrison, 1994; Chatsiriwech et al., 1994; Kirkby and Morgan, 1994; Lu and Rodrigues, 1994), or (2) continuously regenerated by removing it from the reactor and using the principles of thermal-swing adsorption (Brun-Tsekhovoi et al., 1986), so that it can be reused.

The process concepts combining chemical reaction and adsorptive separation of reaction products in a single unit operation in conjunction with sorbent regeneration using the principles of pressure-swing adsorption are generally called Periodic Separating Reactors (Vaporciyan and Kadlec, 1987, 1989) or Pressure-Swing Reactors (Lee and Kadlec, 1989; Kirkby and Morgan, 1994). Table 1 lists some of the key experimental studies reported in the literature and Table 2 summarizes the published theoretical models describing the processes under the general acronym of PSR.

A two-, three-, or four-step simplistic process is considered by most of the published works. Kadlec and coworkers experimentally (Vaporciyan and Kadlec, 1989) and theoretically (Vaporciyan and Kadlec, 1987; Lee and Kadlec, 1989) evaluated a three-step process consisting of (1) introduction of the reactant-feed-gas mixture into a packed bed of catalyst and adsorbent at an elevated pressure for a short period of time, followed by (2) a short delay period when the feed-gas introduction was stopped, and finally (3) countercurrent depressurization of the packed bed to the lowest pressure level of operation. A product stream consisting of reactants and reaction products was continuously withdrawn from the reactor during steps 1–3. Oxidation of carbon monoxide to carbon dioxide using a mixture of supported platinum catalyst and

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Table 1. Experimental Evaluation of PSR Systems

Authors	Process Steps	Reaction	Sorbent	Products
Vaporciyan and Kadlec, 1989	Feed, delay, exhaust	$2CO + O_2 \rightleftharpoons 2CO_2$ feed diluted with N_2	5A for CO_2	CO_2 distributed in both reaction effluent and desorption gas. Dilute CO_2 in both products.
Goto et al., 1993	Feed, helium purge (or evacuate)	$C_6H_{12} \rightleftharpoons C_6H_6 + 3H_2$ feed diluted with helium	$CaNi_5$ for H_2	H_2 product obtained in mixture with helium as desorbed product. C_6H_6 product obtained as reactor effluent partly mixed with helium.
Han and Harrison, 1994	No process, feed only.	$CO + H_2O \rightleftharpoons CO_2 + H_2$ feed (CO_2, CO, H_2, and H_2O mixture) diluted with N_2.	Dolomite for CO_2	Dilute H_2 in N_2 obtained during feed step.

5A zeolite as the CO_2 selective adsorbent was investigated experimentally (Vaporciyan and Kadlec, 1989). An enhanced conversion of carbon monoxide to carbon dioxide (in the combined product and depressurization gas), greater than that possible with only the catalyst, was demonstrated. A dilute stream of CO and O_2 in inert N_2 was used as the feed gas in order to maintain reactor isothermality. CO_2 was present in both product and depressurizing effluents. However, a very interesting composition reversal of CO_2 in the product and depressurization gases was observed. The CO_2 composition increased in the product gas when the O_2 concentration in the feed was low, and it increased in the depressurization gas when the O_2 concentration in the feed was high. The model qualitatively traced this behavior.

Alpay and coworkers (Alpay et al., 1993, 1994; Chatsiriwech et al., 1994; Kirkby and Morgan, 1994) evaluated model solutions of PSR systems using a similar process as above except where step (2) was eliminated (Alpay et al., 1993). They also theoretically evaluated a four-step process (Alpay et al., 1994; Chatsiriwech et al., 1994; Kirkby and Morgan, 1994) consisting of (1) pressurizing the packed bed of catalyst and adsorbent with the reactant-feed mixture to a superambient pressure level, (2) feeding the reactant mixture at the elevated pressure and withdrawing a product gas, (3) countercurrently depressurizing the reactor to the lowest pressure level of operation, and (4) countercurrently purging the reactor with the effluent from step 2. A variation of this cycle included partial countercurrent pressurization of the reactor with the effluent from step 2 before step 1 started (Kirkby and Morgan, 1994). These theoretical studies combined many different forms of reversible and irreversible reactions using isothermal and nonisothermal reactors as well as different adsorption selectivities of reactants and products by the adsorbent. Enhanced conversion of reactants to products (compared to the conversion for the catalyst-alone case) were theoretically calculated by the models. The reaction products in the effluents from step 2 and step 3 were produced at different compositions, depending on the selective adsorptive

Table 2. Theoretical Modeling of PSR Systems

Authors	Process Steps	Reactions	Key Assumptions
Vaporciyan and Kadlec, 1987	Feed, delay, exhaust	General reversible reaction with multicomponent reactants and products	Local equilibrium of sorption and reaction, linear sorption isotherms, isothermal, Darcy's law for flow through packed bed
Vaporciyan and Kadlec, 1989	Same as above	Same as above	Same as above except finite reaction rate
Lee and Kadlec, 1989	Same as above	$A \Leftrightarrow B$; $2A \Leftrightarrow B + C$; $B \Leftrightarrow A \Leftrightarrow C$	Same as above but distributed catalyst and adsorbent in reactor
Alpay et al., 1993	Feed, exhaust	$A \Leftrightarrow B + 3C$	Linear and nonlinear adsorption isotherms, nonisothermal reactor, local equilibrium of sorption, finite reaction rate, Darcy's law for flow through packed bed
Chatsiriwech et al., 1994	Feed pressurization, product (inert) withdrawal, exhaust, product purge	$2A \Leftrightarrow B + C$ Dilute reactant in inert as feed	Same as above except isothermal and linear adsorption isotherms
Alpay et al., 1994	Same as above	$aA \Leftrightarrow bB + cC$ Dilute reactant in inert as feed	Same as above
Kirkby and Morgan, 1994	Same as above with product (inert) backfill	Irreversible reaction $A \rightarrow B$ Dilute reactant in inert as feed	Same as above
Lu and Rodrigues, 1994	Feed, delay, back purge	$A \Leftrightarrow B + C$	Nonlinear adsorption equilibrium local equilibrium of sorption, isothermal, Ergun relation for pressure drop

properties of the sorbent. The reactant feed was diluted with an inert gas and the reactor effluent from step 2 contained a mixture of the inert, the reactants, and the products. Lu and Rodrigues (1994) theoretically investigated a three-step process consisting of steps 1–3 of the Kadlec and coworkers process while simultaneously purging the reactor countercurrently with a part of the product gas during step 3.

Goto et al. (1993) experimentally studied the dehydrogenation of cyclohexane to benzene and hydrogen using a mixture of platinum on alumina catalyst and a hydrogen adsorbing alloy ($CaNi_5$) in the reactor. The feed gas to the reactor consisted of a dilute stream of cyclohexane in inert helium. It was passed through the reactor at ambient pressure and 150–190°C. The effluent consisted of a pure helium stream followed by a stream containing benzene and helium. The adsorbent was then regenerated by evacuation or by countercurrently flowing a pure helium stream (purging) for the same period of time as the reaction step. The purge volume per cycle was ~20 times larger than the feed-gas volume per cycle and the effluent was a very dilute stream of H_2 in helium. The overall conversion of cyclohexane to benzene exceeded that for the catalyst-only case.

Han and Harrison (1994) experimentally demonstrated that high conversion of carbon monoxide to hydrogen (larger than that dictated by thermodynamic equilibrium) could be achieved in the absence of a catalyst by the water gas-shift reaction [$CO + H_2O \gtrless CO_2 + H_2$] when one of the reaction products (CO_2) was removed from the reaction zone by reacting with calcium oxide [$CaO + CO_2 \rightarrow CaCO_3$]. They used dolomite ($\sim 55\%$ CaO + 45% MgO) as the sorbent at a reaction temperature of 550°C and at a total gas pressure of 15 atm. No process scheme for regeneration of dolomite was disclosed.

Brun-Tsekhovoi et al. (1986) used a specially treated form of dolomite containing active CaO and chemically inert MgO as sorbent in a continuous fluidized-bed reactor containing microspheres of nickel on alumina catalyst. Freshly regenerated particles of the sorbent were fed to the fluidized-bed reactor in a direction countercurrent to reactant-gas flow. Large sorbent particles were used so that they could travel under gravity through the fluidized catalyst particles toward the feed gas end of the bed. The size and density differences of the catalyst and the sorbent materials allowed complete separation between them at the gas inlet end. The sorbent particles were pneumatically carried to a thermal regenerator for desorption of CO_2. A very significant enhancement of CH_4 conversion to H_2 (compared to that achieved by catalyst alone) at pressure levels of 10–100 atm and at a reaction temperature of 627°C was reported. The product gas leaving the fluidized-bed reactor contained 92–96% H_2. However, a dust separator was required to clean the H_2 product gas. The proposed process scheme also included a gas turbine to recover power from the hot effluent gas exiting the sorbent regenerator. The turbine generated power to drive the pneumatic compressor for transporting the exhausted sorbent to the regenerator at the reaction pressure and temperature.

The purpose of the present work is to describe a novel fixed-bed-process scheme that (1) combines chemical reaction and partial product separation in a single unit containing an admixture of catalyst and sorbent, (2) directly produces the desired product gas at high purity and at reaction pressure, and (3) regenerates the sorbent *in situ* by using the principles of pressure-swing adsorption. We call this process the Sorption Enhanced Reaction Process (SERP). A patent application for the process has been filed to the U.S. Patent Office by Air Products and Chemicals, Inc. (Anand et al., 1995).

Sorption-Enhanced Reaction Process

We consider a general equilibrium-controlled reaction involving one or more reactants (A,B) producing a desired reaction product (D) and a by-product (C):

$$aA + bB \gtrless cC + dD, \tag{1}$$

where a, b, c, and d are stoichiometric coefficients for the reaction. The fixed-bed reactor contains an admixture of a catalyst and a sorbent that selectively removes the by-product C from components A, B, and D at the reaction temperature (T_R) and pressure (P_R). The cyclic steps of the SERP scheme are as follows.

Step 1. Sorption-Reaction. Flow a stoichiometric mixture of the reactants at T_R and P_R through the regenerated reactor that has been previously saturated with the component D at T_R and P_R. An effluent stream containing essentially pure component D is produced from the reactor at pressure P_R. The step is continued until the other components (A, B, C) of the system break through the reactor or somewhat short of it. A part of the effluent gas is removed as product D and the balance is used in steps 4 and 5.

Step 2. Depressurization. Depressurize the reactor to a lower pressure level of P_D ($<P_R$) in a direction countercurrent to that of the reactant-feed gas flow. A gas stream containing all components (A, B, C, D) of the system exits the reactor. It consists of interparticle void gas in the column as well as some adsorbed gases present in the reactor at the end of step 1.

Step 3. Purge I. Introduce an extraneous purge gas (component E) to the reactor at P_D and T_R in a direction countercurrent to that of the reactant feed gas flow. Component E is very weakly adsorbed on the sorbent or the catalyst. This step desorbs the remaining adsorbed components (primarily C), and the reactor effluent gas contains a mixture of A, B, C, D, and E. The reactor is essentially saturated with component E at P_D and T_R at the end of this step.

Step 4. Purge II. Purge the reactor countercurrently at P_D and T_R with a part of the product gas (component D) produced during step 1 in order to remove component E from the reactor void space.

Step 5. Pressurization. Pressurize the reactor from P_D to P_R by countercurrently introducing a part of the effluent gas (component D) from step 1. The reactor is now ready to start a new cycle from step 1.

At least two parallel reactors are needed to run the SERP cycle in a continuous mode. The cycle times for the steps are so designed that one reactor undergoes step 1 for a period of time while the companion reactor undergoes steps 2–5 during the same period of time. A continuous flow of reactants and products can be achieved in this manner. The reactors are maintained at near isothermal condition at T_R by indi-

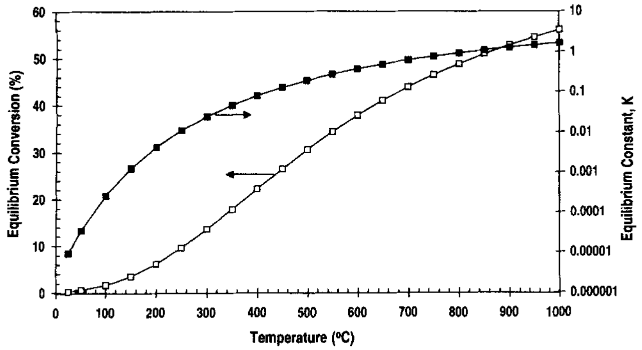

Figure 1. Equilibrium constants as functions of temperature for the reverse water-gas shift reaction.

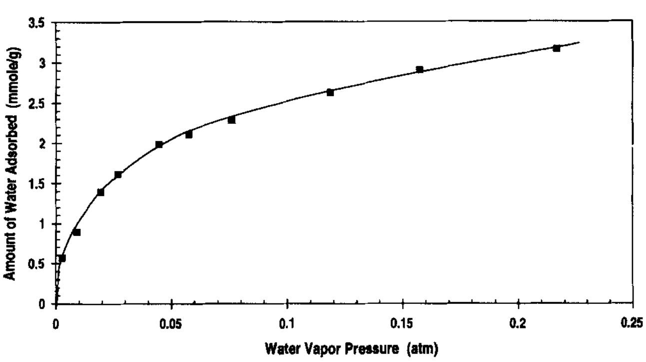

Figure 2. Equilibrium adsorption isotherm of pure water vapor on NaX zeolite at 275°C.

rectly supplying or removing heats of reaction and sorption through the reactor walls.

The key advantages of the SERP scheme are listed below.

(a) Direct production of the desired high-purity reaction product (component *D*) during step 1 of the process at the reaction pressure P_R.

(b) Enhanced conversion of reactants to products and faster forward reaction for an equilibrium-controlled reaction over that which could be achieved by using the catalyst alone.

(c) Efficient *in-situ* regeneration of the sorbent.

Advantage (b) permits the operation of the reactor at a much lower temperature than needed for the catalyst alone case at the same conversion of reactants to products. This, in conjunction with advantage (a), provides opportunity for capital cost savings by using less expensive materials of construction for the reactor and by eliminating or significantly reducing product purification equipment. Lower temperature operation can also reduce sensible heat losses and heat-exchange equipment sizes associated with the conventional high-temperature operation. Advantage (c) eliminates problems associated with moving solid systems (fluidized reactor), such as attrition, dust removal, and high-pressure pneumatic transport. It also offers complete control over the degree of sorbent regeneration for optimum operation of the process.

Reverse Water-Gas Shift Reaction by SERP

We evaluated the reverse water-gas shift reaction for the production of carbon monoxide by SERP in a bench scale reactor. The reaction is controlled by thermodynamic equilibrium:

$$\begin{array}{ccccccc} CO_2 & + & H_2 & \gtrless & H_2O & + & CO \\ (A) & & (B) & & (C) & & (D) \end{array} \qquad (2)$$

$$K(T)=\frac{[H_2O][CO]}{[CO_2][H_2]}; \qquad [CO]=\frac{K(T)[CO_2][H_2]}{[H_2O]} \qquad (3)$$

$CO_2(A)$ and $H_2(B)$ are reacted to form $H_2O(C)$ and $CO(D)$. CO is the desired product. It is an endothermic, equimolar reaction that is not thermodynamically favored at temperatures below 800°C. Figure 1 shows the equilibrium constant $[K(T)]$ as a function of temperature for the reaction (Twigg, 1989). The figure also shows the equilibrium conversion of CO_2 to CO as a function of temperature for a stoichiometric feed mixture of CO_2 and H_2 as calculated by Eq. 3. It may be seen that a temperature of 565°C is needed to get 36% conversion of CO_2 to CO. The equilibrium gas-phase composition of reaction products at 565°C is 22% CO, 39% CO_2, and 39% H_2 on a dry basis. The heats of reaction are, respectively, 9.4 and 8.6 kcal/mole of CO at temperatures of 250 and 565°C. A practically acceptable rate of reaction can be achieved by using a commercial low- or medium- (copper-zinc oxides on alumina) or high-temperature (iron oxide on alumina) shift catalyst in the temperature range of 250–500°C (Lloyd et al., 1989).

Clearly, the reverse water-gas shift reaction is not an attractive method to produce CO using a conventional reactor, even though the feed stock may be cheap. This is due to the high reaction temperature needed for reasonable conversion of CO_2 to CO and the subsequent separation requirements. The SERP scheme can change that. Equation 3 shows that the conversion of CO_2 to CO can be significantly increased at a lower operating temperature if a very selective adsorbent to remove water (by-product *C*) from the reaction zone is available. The process can also directly produce a high-purity CO product.

Commercial NaX zeolite can be used as a water-selective adsorbent from gas mixtures containing CO, CO_2, and H_2 at a moderately high temperature. Figure 2 shows the equilibrium adsorption isotherm of pure water vapor at 275°C on the NaX zeolite. The isosteric heat of adsorption of water is 18 kcal/mole. The data were measured in our laboratory using a conventional gravimetric apparatus. They show that the water adsorption capacity of the zeolite at 275°C is sufficiently large to be practical for this process.

Bench Scale Unit for Testing SERP

We constructed a bench-scale apparatus for testing the SERP concept for the reverse water-gas shift reaction. Figure 3 is a diagram of the unit. It consists of a single reactor vessel (3.8-cm internal diameter and 53 cm long) enclosed in a tube furnace. The reactor was packed with 0.5 kg of a mixture (1:1 weight ratio) of commercial low-temperature shift catalyst (8 × 12 mesh) produced by BASF of Germany and commercial NaX zeolite (0.3-cm particle diameter) produced by UOP of the United States. The reactor was fitted with inlet and outlet lines for introducing feed gas (stoichiometric CO_2 and H_2

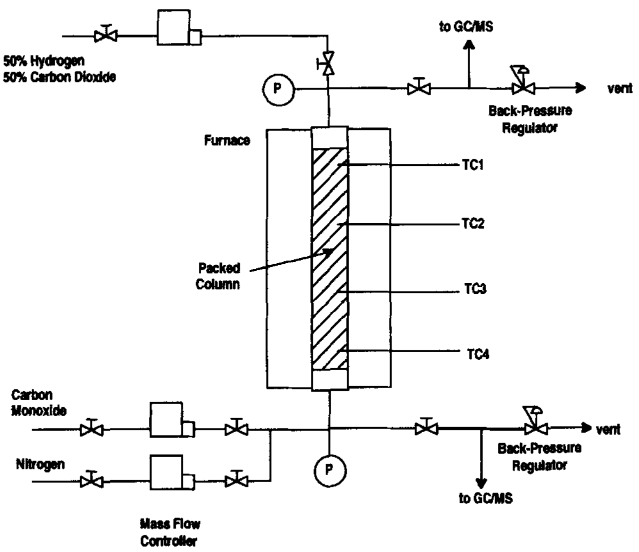

Figure 3. Diagram of the apparatus for testing the SERP concept.

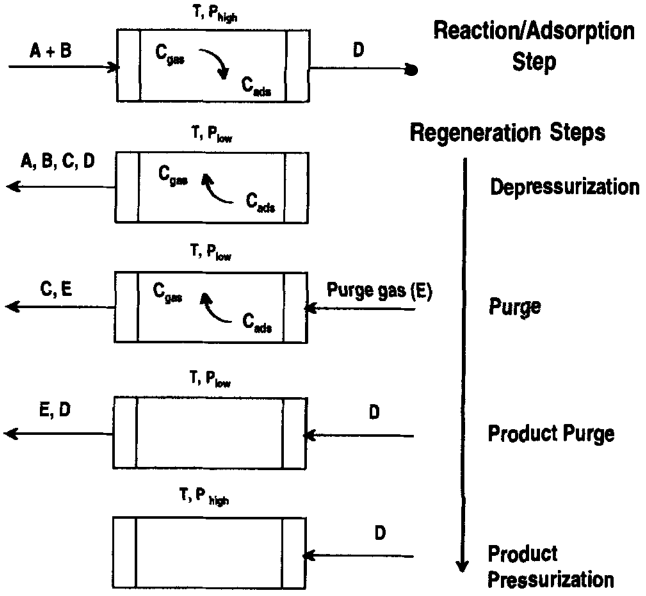

Figure 4. Diagram of the sequential SERP steps for the production of carbon monoxide by the reverse water-gas shift reaction.

mixture), purge gas (CO and N_2) and pressurization gas (CO) as well as removing depressurization gas (CO, CO_2, H_2, H_2O) and purge effluent gases (CO, CO_2, N_2, H_2, and H_2O). The inlet flow rates (fixed composition) were controlled by mass flow controllers. Back-pressure regulators were used to maintain constant reactor pressures (P_R, P_D) during steps 1, 3, and 4 of the process. Four thermocouples (TC) measured the temperature profiles within the reactor during all steps of the process. All inlet gases were preheated to the reaction temperature (T_R). Effluent gas quantities were measured as functions of time using dry test meters and soap bubble flowmeters. Gas compositions were monitored continuously using a gas chromatograph–mass spectrometer (GC–MS).

Figure 4 shows a diagram of the sequential process steps used for testing the SERP concept. N_2 was used as the extraneous gas for step 3. However, other inert gases like CH_4 could be used.

Experimental Results and Analysis

An experiment was carried out according to the SERP concept described earlier. The feed gas consisted of an equimolar mixture of CO_2 and H_2. The reaction-adsorption pressure was 55 psig (480 kPa) (P_R) and the reaction temperature was 250°C (T_R). The reactor was maintained nearly isothermal (250±6°C) during all steps of the process. The final depressurization pressure and the purge-step pressures were 2–4 psig (115–129 kPa) (P_D). The reactor was initially saturated with pure CO at 55 psig (480 kPa) and 250°C.

Figure 5 shows the composition of CO (mol %) in the reactor effluent as a function of time during step 1 of the process. A stream of essentially pure CO is produced by the reactor for a certain period of time (t^a), and then the CO composition gradually approaches the value of the thermodynamic equilibrium gas-phase composition of CO (5 mol %) for the reaction in the absence of the sorbent. The total quantity of CO leaving the reactor up to the time t^s (represented by the hatched area in Figure 5) is the amount of CO initially present in the column at the start of step 1 of the process. Thus, Figure 5 shows that a certain amount of essentially pure CO is produced (between times t^s and t^a) as product gas during step 1 of the SERP process. This quantity represents the net amount of CO produced by the SERP process provided that step 1 is terminated at time t^a.

Figure 6 schematically illustrates the gas-phase composition profiles of the reactants and products within the reactor (as functions of dimensionless distance z) at time t^a. There are two reaction mass-transfer zones (RMTZ) separated by an equilibrium section where the gas-phase mole fraction of component i is y_i^*. CO_2 and H_2 react to form CO and H_2O in both RMTZs. Consequently, the mole fractions of CO_2 and H_2 decrease and the mole fractions of CO increase in both of these zones. Water, on the other hand, is desorbed by the incoming dry reactant mixture in the rear RMTZ at the feed inlet end and it is adsorbed from the gas mixture in the front RMTZ at the product outlet end. Thus, the mole fraction of water increases from zero to $y_{H_2O}^*$ in the rear RMTZ

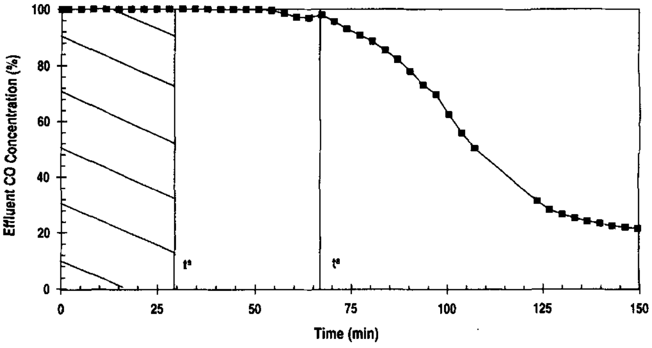

Figure 5. Carbon monoxide composition in the SERP reactor effluent as function of time during step 1 of the process (pressurized with CO).

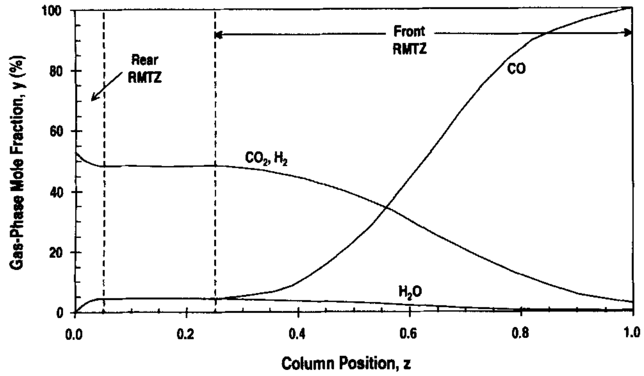

Figure 6. Gas-phase mole fractions of CO_2, H_2, CO and H_2O within the SERP reactor as a function of the dimensionless column distance at the time of incipient breakthrough of impurities.

and decreases from $y^*_{H_2O}$ to zero in the front RMTZ. The reactant compositions change from the feed-gas composition to $y^*_{CO_2}$ $(=y^*_{H_2})$ in the rear RMTZ, and from $y^*_{CO_2}$ $(=y^*_{H_2})$ to zero in the front RMTZ. The CO mole fraction changes from zero to y^*_{CO} in the rear RMTZ and from y^*_{CO} to unity in the front RMTZ. These transfer zones are formed within the reactor after a certain amount of reactants have been fed. The front RMTZ moves toward the product end as more reactants are introduced. The separation between the two transfer zones also increases with time (the length of the equilibrium section increases with time).

The leading edge of the front RMTZ reaches the product end of the reactor at time t^a. H_2O, CO_2, and H_2 start breaking through the reactor effluent end at this time. Consequently, the CO mole fraction starts decreasing from unity, and those for CO_2, H_2, and H_2O start increasing from zero in the reactor effluent gas at times larger than t^a. The composition of the components in the front RMTZ can thus be measured, provided that the transfer zone is constant pattern (shape and size not changing with time), by monitoring the effluent gas composition from step 1 past the time interval of t^a. For example, Figure 5 shows the CO mole fraction in the reactor effluent gas after time t^a. It begins decreasing from unity and approaches a value of y^*_{CO}.

The size and shape of the front RMTZ is critical in determining the conversion and production capacity of CO from CO_2 by the SERP. They are determined by many factors like the rate of the reverse water-gas shift reaction and the rate and capacity (isotherm shape) of adsorption of water by the sorbent. The front RMTZ is a shock profile (zero length) when the reaction and sorption rates are infinitely fast. Loss of CO during steps 2 and 3 of the SERP is lowered as the length of the front RMTZ is decreased.

SERP Performance for Carbon Monoxide Production

We analyzed the SERP test data given by Figure 5. The total amount of reactants introduced into the reactor until incipient breakthrough of CO_2, CO and H_2O (time t^a) was 540 mmol. The amount of CO present in the reactor at the start of step 1 was 194 mmol. The net amount of essentially pure CO product was 97 mmol.The total amount of CO, CO_2, and H_2 removed from the reactor during the regeneration steps 2 and 3 were, respectively, 73, 100, and 100 mmol. The length of the front RMTZ was estimated to be 39.7 cm using the conventional methods of column breakthrough data analysis (Sircar and Kumar, 1983).

Table 3. Performance of the SERP Concept for Production of Carbon Monoxide by Reverse Water-Gas Shift Reaction

	SERP	PFR with Catalyst Only
Operating temperature	250°C	565°C
Operating pressure	55 psig	55 psig
CO_2 to CO conversion	36%	36%
Product composition	99+% CO	22% CO+39% CO_2 +39% H_2 (dry basis)
CO product pressure	~ 55 psig	5–10 psig

Table 3 compares the performance of SERP for CO production by the reverse water-gas shift reaction at 250°C and 55 psig (480 kPa) with that of a straight plug flow reactor (PFR) operated without the adsorbent. The net CO conversion from CO_2 by the SERP under the conditions of the experiment was 36%. The CO product was produced at a pressure of 55 psig (480 kPa) and its purity was 99+ (mol %). According to Figure 1, the reaction has to be carried out at 565°C in order to get the same CO_2 to CO conversion in a straight catalytic PFR. Furthermore, Figure 1 shows that the CO_2 to CO conversion in a PFR operated at a temperature of 250°C would be only 9.8%. Thus, the SERP can significantly reduce the temperature of operation of an equilibrium-controlled reaction and yet deliver a high conversion of reactants to products. The product is directly produced at high purity.

It should be noted here that the relatively large length of the front RMTZ compared to the length of the experimental reactor of the present case was responsible for the moderate conversion (36%) of CO_2 to CO. A longer reactor would decrease the relative size of the front RMTZ and significantly increase the CO_2 to CO conversion.

Table 3 also shows that the effluent from the straight PFR for this reaction would consist of a gas mixture containing 22% CO. This mixture needs to be separated in order to produce a 99+% CO product. The conventional method of separation of this gas mixture involves an elaborate separation scheme consisting of (1) condensation of water, (2) removal of CO_2 by a solvent-absorption system, (3) removal of trace CO_2 and H_2O by a thermal swing adsorption system, and (4) cryogenic separation of CO and H_2 (Haddleland, 1979). Alternatively, the PFR effluent can be purified by (1) condensation of water, and (2) pressure-vacuum swing adsorption (Guro et al., 1995). In either case, the CO product is produced at a relatively low pressure (5–10 psig) and must be compressed to meet the product specifications. The separation and compression costs are formidable for both cases. Thus, the SERP concept saves capital and energy costs by partially or completely eliminating the product purification and compression requirements.

Pressurization of Reactor with Pure Desired Product Gas

The step 5 of the SERP concept where the reactor is pres-

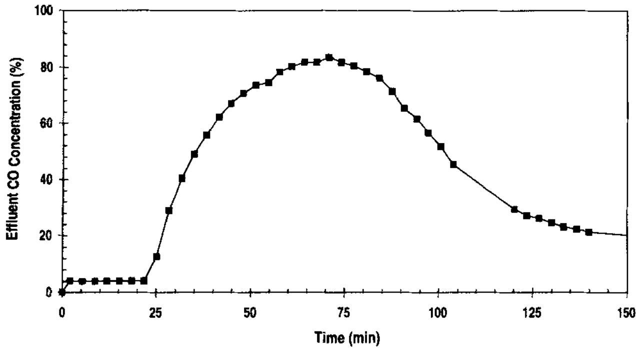

Figure 7. Carbon monoxide composition in the SERP reactor effluent as a function of time during step 1 of the process (pressurized with CO_2).

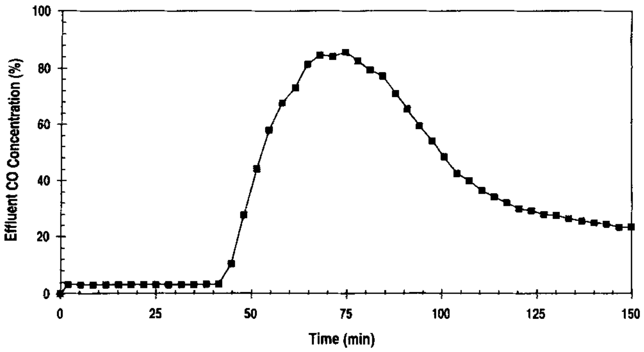

Figure 8. Carbon monoxide composition in the SERP reactor effluent as a function of time during step 1 of the process (pressurized with H_2).

surized to the reaction pressure with essentially pure (desired) product is a critical step of the process. We ran step 1 of the process by pressurizing the reactor with the pure reactants CO_2 and H_2 (water is not a choice because it is adsorbed). The reactant feed flow rates were the same as that of the previously described case. Figures 7 (CO_2 pressurization) and 8 (H_2 pressurization) show the reactor effluent profiles for these cases at a reaction temperature of 250°C and a pressure of 55 psig. The mole fractions of the CO in the reactor effluent gases for both cases were initially very low when the pressurization gases from the reactor voids were being displaced by the front RMTZ. Then the CO composition of the effluent rose to a level of about 80 mole % before approaching y^*_{CO} values. Thus, both cases exhibited higher conversions of CO_2 to CO than would be achieved by the straight PFR with catalyst only, but the effluent CO concentration varied continuously during step 1, and no high-purity CO product could be directly produced as by the proposed SERP concept.

Conclusions

A sorption-enhanced reaction process (SERP) concept is described that can be used to directly produce the desired reaction product at high purity and at reaction pressure from an equilibrium-controlled reaction described by Eq. 1. The process uses an admixture of a catalyst and a sorbent in the reactor. The sorbent selectively removes the undesired by-product of the reaction from the reaction zone at the reaction conditions and thus enhances the conversion of reactants to products according to Le Chatelier's principle. The sorbent is periodically regenerated *in situ* by using the principles of pressure-swing adsorption. The steps of the cycle are so designed that only a single unit operation is needed to carry out the reaction with enhanced conversion of reactants to products as well as the desired product purification. High conversion of reactants to products can be achieved at a much lower reaction temperature by the SERP concept than would be required to a straight catalytic reactor. Lower temperature operation of the reactor and the subsequent reduction or elimination of the product purification operations (required by a straight catalytic reactor) by the SERP concept provide opportunity for cost savings and process simplification.

The reverse water-gas shift reaction for the production of CO by SERP is described in this work as an example only. All equilibrium-controlled reactions producing a desired product and a by-product are amenable to this concept. The catalytic steam–methane reformation reaction to produce H_2 (desired product) and CO_2 (by-products) is another viable candidate for the SERP concept (Sircar et al., 1995).

Literature Cited

Adris, A. M., C. J. Lim, and J. R. Grace, "The Fluidized Bed Membrane Reactor System: A Pilot Scale Experimental Study," *Chem. Eng. Sci.*, **49**, 5833 (1994).

Alpay, E., C. N. Kenney, and D. M. Scott, "Simulation of Rapid Pressure Swing Adsorption and Reaction Processes," *Chem. Eng. Sci.*, **48**, 3173 (1993).

Alpay, E., D. Chatsiriwech, L. S. Kershenbaum, C. P. Hull, and N. F. Kirkby, "Combined Reaction and Separation in Pressure Swing Processes," *Chem. Eng. Sci.*, **49**, 5845 (1994).

Anand, M., S. Sircar, and B. T. Carvill, "Processes for Operating Equilibrium Controlled Reactions," U.S. Patent, Pending (1995).

Armor, J. N., "Membrane Catalysis: Where Is It Now, What Needs to Be Done?" *Cat. Today*, **25**, 199 (1995).

Brun-Tsekhovoi, A. R., A. N. Zadorin, Ya. R. Katsobashvili, and S. S. Kourdyumov, "The Process of Catalytic Steam-Reforming of Hydrocarbons in the Presence of Carbon Dioxide Acceptor," *Hydrogen Energy Process VII, Proc. World Hydrogen Energy Conf.*, Vol. 2, Pergamon Press, New York, p. 885 (1986).

Chatsiriwech, D., E. Alpay, L. S. Kershenbaum, C. P. Hull, and N. F. Kirkby, "Enhancement of Catalytic Reaction by Pressure Swing Adsorption," *Catal. Today*, **20**, 351 (1994).

Cho, B. K., R. Aris, and R. W. Carr, "A Continuous Chromatographic Reactor," *Chem. Eng. Sci.*, **35**, 74 (1980).

Cho, B. K., R. Aris, and R. W. Carr, "The Mathematical Theory of a Countercurrent Chromatographic Reactor," *Proc. R. Soc. (London)*, **A38**(3), 147 (1982).

Chu, C., and L. C. Tsang, "Behavior of Chromatographic Reactor," *Ind. Eng. Chem., Proc. Des. Dev.*, **10**, 47 (1971).

Fish, B., R. W. Carr, and R. Aris, "The Continuous Countercurrent Moving Bed Chromatographic Reactor," *Chem. Eng. Sci.*, **41**, 661 (1986).

Gluud, W., K. Keller, R. Schonfelder, and W. Klempt, "Production of Hydrogen," U.S. Patent 1,816,523 (1931).

Goto, S., T. Tagawa, and T. Omiya, "Dehydrogenation of Cyclohexane in a PSA Reactor Using Hydrogen Occlusion Alloy," *Chem. Eng. Essays (Japan)*, **19**(6), 978 (1993).

Guro, D., T. Cook, T. C. Golden, W. Kratz, and T. Sabram, "Commercialization of the HYCO VSA Process for Production of High Purity Carbon Monoxide," AIChE Meeting, Miami Beach, FL (1995).

Haddleland, G. E., "Carbon Monoxide," *SRI Int. Rep.*, **123** (1979).

Han, C., and D. P. Harrison, "Simultaneous Shift Reaction and Carbon Dioxide Separation for the Direct Production of Hydrogen," *Chem. Eng. Sci.*, **49**, 5875 (1994).

Hsieh, H. P., "Inorganic Membranes," *AIChE Symp. Ser.*, **84**, 1 (1988).

Itoh, N., W. C. Xu, and A. M. Sathe, "Capability of Permeate Hydrogen through Palladium-based Membranes for Acetylene Hydrogeneration," *Ind. Elec. Chem., Research*, **32**, 2614 (1993).

Kadlec, R. H., and G. G. Vaporciyan, "Periodic Chemical Processing System," U.S. Patent 5,254,368 (1993).

Kirkby, N. F., and J. E. P. Morgan, "A Theoretical Investigation of Pressure Swing Reaction," *Trans. Inst. Chem. Eng.*, **72**, 541 (1994).

Kruglov, A. V., "Methanol Synthesis in a Simulated Countercurrent Moving Bed Adsorptive Catalytic Reactor," *Chem. Eng. Sci.*, **49**, 4699 (1994).

Lee, I. D., and R. H. Kadlec, "Effects of Adsorbent and Catalyst Distributions in Pressure Swing Reactors," *AIChE Symp. Ser.*, **84**, 167 (1989).

Lloyd, L., D. E. Ridler, and M. V. Twigg, "The Water Gas Shift Reactor," *Catalyst Handbook*, M. V. Twigg, ed., Wolfe, London, p. 288 (1989).

Lu, Z. P., and A. E. Rodrigues, "Pressure Swing Adsorption Reactors: Simulation of Three-Step One-Bed Process," *AIChE J.*, **40**, 1118 (1994).

Magee, E. M., "The Course of a Reaction in a Chromatographic Column," *Ind. Elec. Chem. Fundamentals*, **2**, 32 (1963).

Petroulas, T., R. Aris, and R. W. Carr, "Analysis and Performance of a Countercurrent Moving Bed Chromatographic Reactor," *Chem. Eng. Sci.*, **40**, 2233 (1985).

Roginskii, S. Z., M. J. Yanovskii, and G. A. Graziev, "Catalytic Reactions and Catalysis Under Chromatographic Conditions," *Kinet. Katal.*, **3**, 529 (1962).

Sircar, S., and R. Kumar, "Adiabatic Adsorption of Bulk Binary Gas Mixtures: Analysis by Constant Pattern Model," *Ind. Elec. Chem., Proc. Des. Dev.*, **22**, 271 (1983).

Sircar, S., M. Anand, B. T. Carvill, J. R. Hufton, S. G. Mayorga, and R. N. Miller, "Sorption Enhanced Reaction Process for Production of Hydrogen," *Proc. 1995 U.S. DOE Hydrogen Program Review*, **1**, 815 (1995).

Sun, Y. M., and S. J. Khang, "Catalytic Membrane for Simultaneous Chemical Reaction and Separation Applied to a Dehydrogenation Reaction," *Ind. Elec. Chem., Research*, **27**, 1136 (1988).

Takeuchi, K., and Y. Uraguchi, "Experimental Studies of a Chromatographic Moving Bed Reactor," *J. Chem. Eng. Japan*, **10**, 455 (1977).

Tonkovich, A. L. Y., and R. W. Carr, "A Simulated Countercurrent Moving Bed Chromatographic Reactor for the Oxidative Coupling of Methane: Experimental Results," *Chem. Eng. Sci.*, **49**, 4647 (1994a).

Tonkovich, A. L. Y., and R. W. Carr, "Modelling of the Simulated Countercurrent Moving Bed Reactor used for Oxidative Coupling of Methane," *Chem. Eng. Sci.*, **49**, 4657 (1994b).

Tsotsis, T. T., A. M. Champagnie, S. P. Vasileiadis, Z. D. Zraka, and R. G. Minet, "Packed Bed Catalytic Membrane Reactor," *Chem. Eng. Sci.*, **47**, 2903 (1992).

Twigg, M. V., ed., *Catalyst Handbook*, Append. VII, Wolfe, London (1989).

Uemiya, S., N. Sato, H. Ando, and E. Kikuchi, "The Water Gas Shift Reaction Assisted by a Palladium Membrane Reactor," *Ind. Elec. Chem., Research*, **30**, 585 (1991).

Vaporciyan, G. G., and R. H. Kadlec, "Equilibrium Limited Periodic Separating Reactors," *AIChE J.*, **33**, 1334 (1987).

Vaporciyan, G. G., and R. H. Kadlec, "Periodic Separating Reactors: Experiments and Theory," *AIChE J.*, **35**, 831 (1989).

Wu, J. C. S., T. E. Gerdes, J. L. Pszczolowski, R. Bhave, and P. K. T. Liu, "Dehydrogenation of Ethylbenzene to Styrene Using Commercial Ceramic Membranes as Reactors," *Sep. Sci. Tech.*, **25**, 1489 (1990).

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