

Periodic operation of catalytic reactors —introduction and overview

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Abstract

A review is presented on the subject of periodic operation of catalytic reactors by composition forcing. Possible objectives of this mode of reactor operation are increased conversion, improved selectivity, reduced catalyst deactivation and insight into mechanisms of reactor models. Several forcing strategies may be used: manipulating one or more reactant concentrations, or interspersing pulses of inerts between pulses of reactants. These strategies are distinct from the variables in periodic operation, i.e., frequency, wave shape, amplitude, and phase lag. Laboratory-scale equipment for periodic forcing makes use of single reactors along with the control of reactant and/or diluent flows. On an industrial scale, two catalyst beds are used, each operating with different feeds under different conditions. Catalyst transfers between the beds. A large literature has developed over the 25 years since periodic operation was first proposed.

1. Background

Periodic operation is primarily an engineering tool for control of conversion or selectivity in a chemical reactor. It is a contacting technique. The choice of contacting pattern and, where applicable, the level of mixing are well-known techniques for influencing reactor performance. We will demonstrate in this contribution and those which follow that, as far as reactor performance is concerned, the effects of this time-based contacting technique can be of the same order of magnitude as those that involve spatial contacting (back-mixing, spatial distribution of feed). The peculiarity of this contacting technique is that it forces a reaction system to proceed under transient rather than steady-state conditions. Production

becomes a time-average quantity under this type of operation.

Periodic operation of chemical reactors is hardly new. Any heterogeneous catalytic reactor in which the catalyst is regenerated in situ operates periodically. Even those reactors in which catalyst is removed for regeneration or replaced periodically share many similarities with periodic operation. Normally, the periods encountered for systems involving catalyst regeneration are measured at least in days, but often in months or even years. In such cases, the reactor operates at steady state on the time scale set by the residence time of reactants in the system, an important difference between past practice and the systems we consider in this paper. When we discuss periodic operation, the reaction system is transient at all times. Of course, not all catalyst regeneration operates over long periods. One of the largest regenerative sys-

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tems, catalytic cracking of gas oils, employs periods of the order of minutes. Nevertheless, catalytic cracking is still treated as if a pseudo-steady state exists. Periodic operation as dealt with in this special issue differs significantly from catalyst regeneration in that regeneration restores performance whereas periodic operation provides performance that is either difficult or impossible to attain under steady-state operation.

Why consider periodic operation? Let us consider for the moment evidence that will not be discussed in the contributions that follow. For ammonia synthesis using a ruthenium catalyst, a thousand-fold increase in the synthesis rate has been demonstrated in an operation that switches the reactor feed every several seconds between H_2 and N_2 [1]. For the oxidation of SO_2 in the presence of air and water over an activated carbon catalyst, the rate of conversion of SO_2 to sulfuric acid can be increased by about 50% if the water flow is periodically turned on for a short time rather than flowing continuously through the bed [2]. The yield of acrolein in the partial oxidation of propene over Sb–SnO catalyst can be doubled by switching between air and propene mixtures of different composition [3]. Moreover, since peri-

odic operation is sensitive to amplitude and the shape of the forcing function, the true kinetics of a catalytic process can be investigated and it becomes possible to separate model parameters that would be lumped if determined under steady-state conditions [4].

2. What is periodic operation?

The terms periodic operation, cycling or cyclic operation, modulation and forcing or periodic forcing will be used interchangeably, reflecting the wide range of terminology used in the current literature. All of these terms refer to an operation in which one or more inputs into a chemical reactor vary with time, but in such a way that each input 'state' is revisited after a time corresponding to the period. This mode of reactor operation is shown schematically in Fig. 1. Here, two inputs, the volumetric flow rates of reactants 'A' and 'B', are switched periodically between two values so as to generate a chain of step-changes representing a square-wave variation of reactant concentrations in the reactor feed. In most of the systems studied in the laboratory, the flow rate variations are

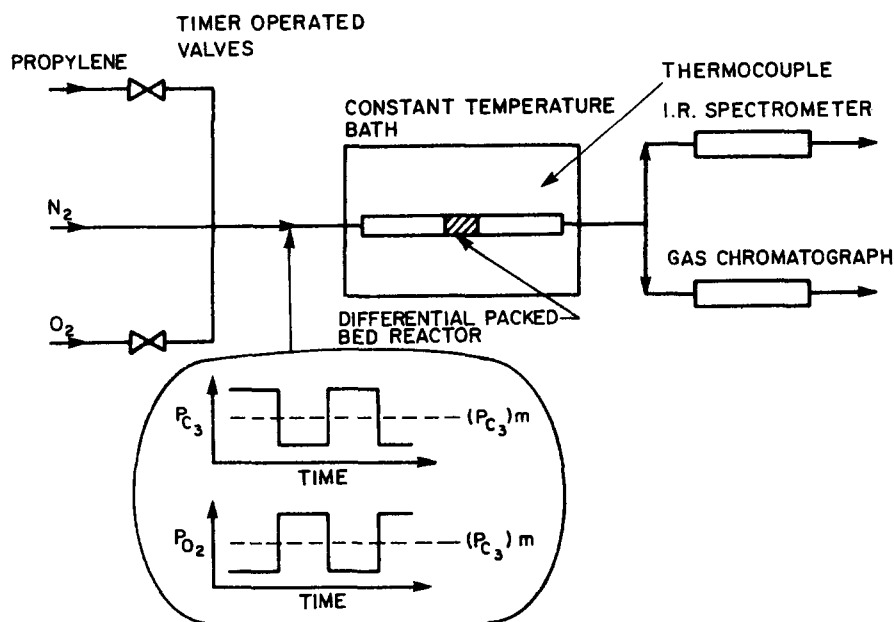


Fig. 1. Schematic of a periodically operating reactor with two feed streams.

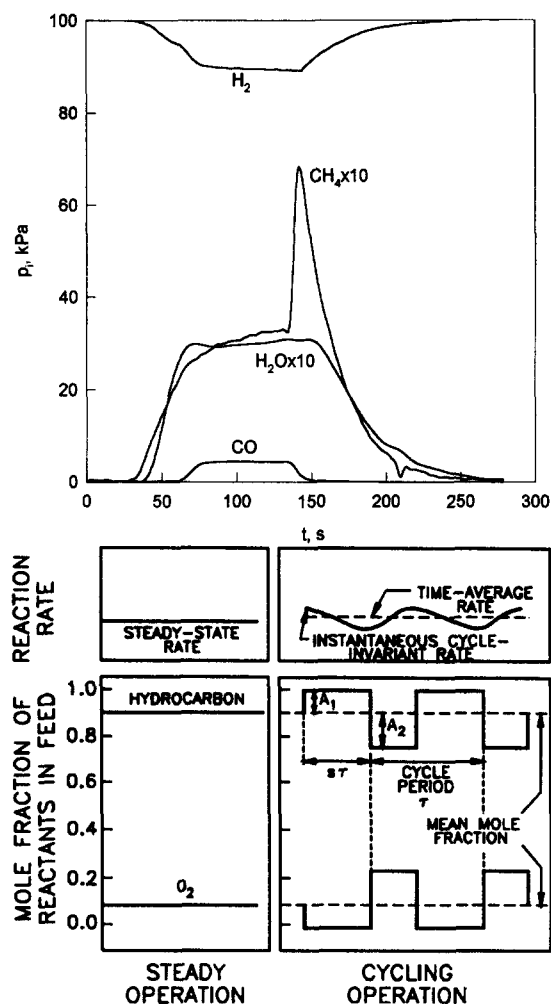


Fig. 2. Comparison of steady state (left side) and periodic (right side) operation showing definition of the cycling variables: cycle period (frequency), τ , cycle split (duty fraction), s ; amplitudes, A_1 , A_2 .

matched so that the space velocity in the reactor remains constant, but this is not a necessary condition. The figure typifies the system most frequently studied; however, other inputs may be varied, such as reactor temperature, flow rate, and flow direction.

Fig. 2 not only compares periodic operation to steady-state, it also defines the terms used to describe modulation. Periodic operation appears on the right of the figure, while steady-state is shown on the left. Input variations result in a time-varying output shown in the upper right of the figure. These are referred to as instantaneous concentrations, yields, or rates. More important are

the mean or time-average production rate, and yield or product concentration. Many studies have shown that these time-averages are greater than steady-state values under identical mean feed conditions. This is illustrated in Fig. 2.

In comparing periodic with steady-state operation, a ratio of performance will be used and referred to as the enhancement under periodic operation:

$$\psi = r / r_{ss} \quad (1)$$

where r is the time-average rate of a periodically operated reaction and r_{ss} is the rate at steady state for a reactant composition corresponding to the time-average composition under cycling. Another, often more meaningful, characterization is the global enhancement:

$$\psi^* = r / (r_{ss})_{\max} \quad (2)$$

where the denominator is the maximum rate achievable at steady state at any composition with temperature and pressure of the system held constant.

Fig. 2 illustrates most of the variables that arise in periodic operation: period (τ) —the time between repetitions of a change in an input condition; split (s) —the duration of one part of cycle relative to the period; amplitude (A) —the change in the value of an input condition from its mean, and mean composition. The split, sometimes referred to as the duty fraction, measures the symmetry of a cycle. A value $s = 0.5$ indicates a symmetrical cycle with both parts of equal duration. Split must be defined relative to one of the reactants. The convention is that split measures the relative duration of the portion of the cycle in which that reactant is at its highest concentration. Amplitude takes on just a single value for symmetrical forcing, but, if $s \neq 0.5$, two amplitudes must be given, one for each portion of the cycle. Mean composition is also a variable for periodic operation, just as in steady state.

A further variable, not illustrated in Fig. 2, is the phase lag. The composition changes shown in the figure are 180° or π radians out-of-phase.

Other phase lags could be used. In a pulsing operation, the phase lag is zero.

Other choices are possible in periodic operation, such as the reactant(s) to be modulated or, indeed, the input itself. In principle, temperature, pressure, or even flow velocity could be varied. A distinction should be made between strategy and variables. The choice of inputs, mode of variation, and cycle structure are a matter of strategy.

3. Modes of periodic operation

It is useful to distinguish among different types of cycles. The simplest differentiation is in the cycle structure. On one hand, there is a more or less even division of a cycle as illustrated in Fig. 2, the cycle structure most frequently investigated. The other extreme occurs when one part of the cycle is very short. This will be referred to as a pulse mode.

Distinction between modes can also be made with respect to the characteristic response or relaxation time of the catalytic reaction or reactor that is being periodically forced. At one extreme are cycles with long periods relative to the relaxation time (t_c), that is, $\tau \gg t_c$. At this extreme, the reactor remains overwhelmingly at steady state. The transient portion of a cycle, roughly $2t_c$, is a negligible portion of the cycle period. Referring to Fig. 2, we see that r becomes the time-average of the steady-state rates for the two feed concentrations shown in the figure. Even though the operation is periodic, the time-average reaction rate, r , is uniquely determined by the steady-state behaviour of the reaction or reactor. The term 'quasi-steady state' (qss) is commonly used for this mode.

At the other extreme of short cycle periods, two situations can arise. If mixing occurs, as it does in all real situations, and the characteristic mixing length is large, time variations in an input (reactant concentration) will be smoothed out. In this extreme, the reaction or reactor system behaves as though it is at steady state at a condition represented by the time-average of the forced inputs.

The situation arises with recycle reactors or reactors in which large-scale back-mixing takes place.

If mixing is negligible or the mixing length is small so that the system approaches the plug-flow limit, the 'relaxed steady-state' mode arises if $t_c \gg \tau$. Transport to the catalyst surface and adsorbate concentrations are no longer able to follow the variations in feed composition. The state of the catalyst surface and product concentrations then become time-invariant, but the state and concentrations are often different from those occurring with a continuous, steady feed. The relaxed steady state is widely used in analytical treatments of periodic operation, e.g., Bailey [5,6], but is reported only rarely in experimental studies. Reaction rate at the relaxed steady-state limit will be represented by $(r)_{\text{rss}}$. Both $(r)_{\text{qss}}$ and $(r)_{\text{rss}}$ are asymptotic conditions for periodic forcing.

Between the fast- and slow-cycling extremes lies the region in which $\tau \approx t_c$. Past and current research focus in this region. Even for this cycling mode, several different types of operations can be distinguished. Consider the common situation in catalytic reactors where there are two vastly different characteristic response times, one associated with response of the surface to changes in reactant concentration or reactor temperature and the other associated with catalyst deactivation. Response times of the first sort are typically measured in seconds or minutes, whereas those associated with deactivation are measured in hours, days, or months. An operation at $\tau \approx t_c$ is one displaying significant decay of catalyst activity. Once fouling or surface poisoning has reduced catalyst activity to a low fraction of its initial level, the catalyst is regenerated or replaced and the cycle begins again. Clearly, period, i.e., the time between regeneration or replacement, is about equal to the characteristic response time for deactivation. Bailey [5] calls such cases 'process life cycles'. With respect to the first characteristic response time, the process life cycle is much longer than this response time, so at any instant the reaction system can be treated as operating at steady state if temperature or feed composition are undisturbed. The steady state is a conventional

assumption for models of catalytic reactors. Process life cycles will not be discussed further here or in papers that follow.

Two modes of periodic operation that arise in the $\tau \approx t_c$ region have been introduced already, but in a somewhat different manner. The first of these is shown in Fig. 2. In this mode, the changes in reactant concentration (or volumetric flow, if Fig. 1 is considered) are 180° out of phase. While reactant 'A' increases in concentration, reactant 'B' decreases. This is the 'standard' cyclic mode. Phase lags other than 180° are also possible. Several investigators have used a mode in which the concentration or flow changes have a phase angle of zero. Usually, in this case, the duration of reactant flow to the reactor is very short compared to the period. This is referred to as pulsed operation or as periodic pulsing. If the parts of the cycle are about equal, it is called a stop-flow operation.

Pulsed operation has attracted considerable research attention because it offers mechanistic insights into phenomena that occur before the responses become cycle-invariant, e.g., [7]. In reaction engineering, the pulsed mode is interesting because chromatographic effects can arise, leading to reactant and product separation and significant yield and/or selectivity improvement when equilibrium limitations occur.

Unforced, spontaneous oscillations are also possible in reacting systems. Such oscillations have attracted a substantial research effort, even though they appear to be unusual in industrial processes. Several comprehensive reviews of spontaneous oscillations have been published [8–11]. Spontaneous oscillations appear to have periods of the order of the characteristic relaxation time.

4. Objectives for periodic operation

Increased catalyst activity, expressed as conversion or rate of reaction, is often given as the reason to explore periodic operation. Is this reasonable? Periodic operation is more complicated and probably more expensive than steady opera-

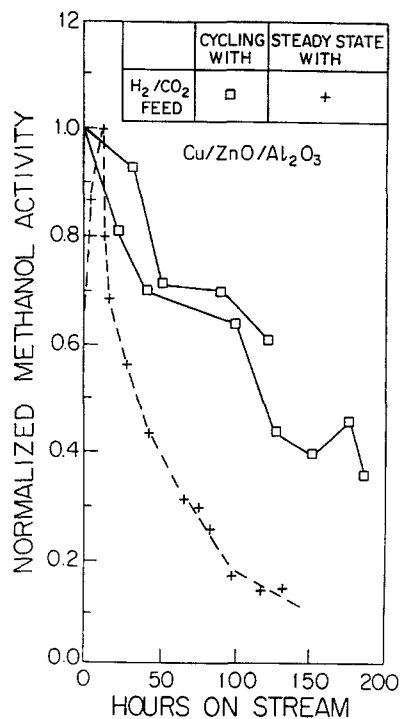


Fig. 3. Loss of catalyst activity for methanol synthesis with time on stream under steady state and composition modulation (after Chanchlani et al. [43] with permission of publisher).

tion; consequently, if increased conversion is the goal, it could be achieved more cheaply by increasing reactor size or the amount of catalyst employed. Under these circumstances, changing from steady to periodic operation could only be justified by a large increase in catalyst activity, perhaps 100% or more.

There are some situations in which increased conversion is a reasonable goal. One of these is a reaction carried out at extreme temperature and/or pressure, or one with an expensive catalyst. Savings in vessel size or catalyst charge from higher catalyst activity could offset the higher cost of periodic operation. Another attractive situation occurs when it is desirable to increase capacity of an existing reactor. Finally, periodic operation may be attractive for reactions in which conversion per pass is limited, often by equilibrium, so that reactants must be separated downstream and recycled. Briggs et al. [12] claim SO_2 conversion in excess of equilibrium in their study of periodically flushing the final stage of an SO_2 converter with air.

The above considerations about conversion have modified the objectives, so that current studies of periodic composition forcing are targeted at improved selectivity or yield. Unlike the advantages associated with improvements in conversion, enhancing selectivity or yield seems to be attainable and may be the best among available techniques apart from changing catalysts. Another situation in which periodic operation might be beneficial occurs when hysteresis is possible. For such reaction systems, unstable operating states can exist at steady state. If it is advantageous for the reactor to function at an unstable state, it has been demonstrated by both simulation and experiment [13,14] that this is possible by periodic operation. Indeed, there is evidence that periodic forcing may be a means of permitting reactors to operate safely in regions of high parametric sensitivity. Working with ammonia synthesis, Jain et al. [15] demonstrated composition forcing smooths the reactor temperature distribution and reduces peak temperatures, while maintaining the conversion achieved under steady state.

There is evidence that periodic operation can decrease the rate of catalyst deactivation. Thus, control of catalyst deactivation could be a goal attainable by forced modulation. Fig. 3 compares deactivation data for a Cu/ZnO/Al₂O₃ catalyst under periodic and steady-state operation. The loss of activity is clearly less for composition forcing. The reaction is methanol synthesis and its H₂/CO₂ feed composition is being modulated. The catalyst employed is similar in composition and performance to the widely used ICI low-pressure methanol catalyst.

Certain scientific objectives can also be achieved by means of modulation. This mode of operation can be used to identify the rate-controlling step in a reaction or the mechanism by which products are formed or, occasionally, how the catalyst deactivates [16,17]. A mechanistic goal for periodic operation should not be surprising. Pulse experiments, in which a catalyst sample is exposed to a series of reactant pulses, is now a standard research tool in catalysis.

5. Strategy in periodic operations

There are many ways of operating a reactor periodically. It is this richness of opportunity that makes it possible to find at least one mode that will achieve the various objectives just mentioned. On the other hand, this very richness presents a challenge, namely, which mode to use and how to find it efficiently.

5.1. Choice of manipulated variable

A reactor input is a manipulated variable and almost all inputs can be forced periodically. Choice of input is thus part of the selection of a forcing strategy. In principle, more than one input can be modulated, but this strategy has not been reported.

Table 1 shows those variables that have been discussed in the literature. Only concentration forcing will be discussed in this contribution. Table 2 gives a list of reactions that have been discussed in the open literature.

5.2. Choice of manipulation

At least two components are required for composition modulation. These could be two reactants or a reactant and a non-reactant (either a promoter or an inert). This limiting case, shown as two-reactant cycles in Fig. 4, presents two strategy options. The figure, taken from a study of methanol synthesis [43] shows the manipulations to be: (1) simultaneously varying both reactants (in this case H₂ and CO mole fractions), and (2) holding the concentration of one reactant constant, such as H₂, while varying the other periodically, (i.e., the CO mole fraction).

If the reaction system has three components (e.g., three reactants), many different periodic operations are possible, reflecting three manipulation strategies. In the three-reactant cycles in Fig. 4, operation (a) represents the manipulation of all three reactants with cycles exhibiting changes both in-phase and 180° out-of-phase. Two of the reactants are forced and one is held

Table 1
Reactor inputs subjected to periodic operation

Input	Comment
Flow rate	Has been studied mainly by simulation. Though not a promising variable for single-phase flow, it is attractive for two-phase flows
Flow direction	This is the input forced in periodic flow reversal. It has had a number of industrial applications and continues to be a popular study topic world-wide
Feed composition	By far the most widely studied input, it is the subject of this contribution and others in this special issue
Pressure	Little studied, probably because effects are minor
Feed temperature	This input has had only limited study by either simulation and experiment. Any large thermal inertia tends to defeat the effect of sudden changes in this variable
Wall temperature	The manipulated variable is actually the coolant temperature or the temperature of a heating fluid or furnace. High thermal inertia makes wall temperature difficult to modulate for cycle periods that affect performance. This input variable, therefore, has had only limited study

Table 2
Reactions studied under periodic operation (Stankiewicz and Kuczynski [18])

Authors	Year	Process	Forced parameter	Investigated effects
Lehr et al. [19]	1968	EtOH dehydration to diethyl ether	Flow	Study of process nature
Denis and Kabel [20]	1970	As above	Flow	Selectivity
Wandrey and Renken [21]	1973	Hydrocarbons oxidation (propene, cyclohexene)	Concentration	Product distribution
Renken et al. [22]	1974	EtOH dehydration to diethyl ether	Concentration	Selectivity
Helmrich et al. [23]	1974	Ethylene hydrogenation	Concentration	Rate
Baiker and Richarz [24]	1976	As above	Concentration	Rate
Renken et al. [25]	1976	Ethylene oxidation	Concentration	Selectivity
Dautzenberg et al. [26]	1977	Fischer–Tropsch synthesis	Concentration	Product distribution
Briggs et al. [27]	1977–80	SO ₂ oxidation	Concentration	Rate
Leupold and Renken [28]	1977	Ethyl acetate from ethylene and acetic acid	Concentration	Rate
Al-Taie and Kershenbaum [29]	1978	Butadiene hydrogenation	Concentration	Selectivity
Bilimoria and Bailey [30]	1978	Acetylene hydrogenation	Concentration	Selectivity
Crone and Renken [31]	1979	Styrene polymerization	Concentration	Rate, product distribution
Cutlip [32]	1979	CO oxidation	Concentration	Rate
Abdul-Kareem et al. [33]	1980	As above	Concentration	Rate
Lee et al. [34]	1980	Saponification of diethyl adipate	Concentration	Selectivity
Silveston and Hudgins [35]	1981	SO ₂ oxidation	Concentration	Rate
Jain et al. [15,36]	1982–83	NH ₃ synthesis	Concentration	Rate
Wilson and Rinker [37]	1982	NH ₃ synthesis	Concentration	Rate
Adesina et al. [38]	1984	Fischer–Tropsch synthesis	Concentration	Rate
El-Masry [39]	1985	Claus reaction	Concentration	Rate
Nappi et al. [40]	1985	Low-pressure methanol	Concentration rate	
Müller-Erlwein and Guba [41]	1988	Methacrolein from IBA	Concentration	Selectivity
Haure et al. [2]	1989	SO ₂ oxidation in trickle bed	Flow	Rate
Saleh-Alhamed et al. [42]	1992	Propylene oxidation to acrolein	Concentration	Selectivity

constant in the operations shown by (b), (c) and (d); the mole fraction of a different reactant is held constant and the variation of the other two mole fractions are 180° out-of-phase. These variations could also be in-phase. The third manipulation strategy is to force the concentration of one reactant and hold the remaining two reactant concentrations constant, as seen in (e), (f) and (g) of Fig. 4.

In several of these operations in Fig. 4, for example, (b) in the two-reactant and three-reactant cycles, when the variations are in-phase, both the flow rate through the reactor and the feed composition must vary together. If flow rate variation is to be avoided in the latter case, a fourth component, an inert, must be introduced and must vary periodically with time. This requires four components and a further growth in the strategies is

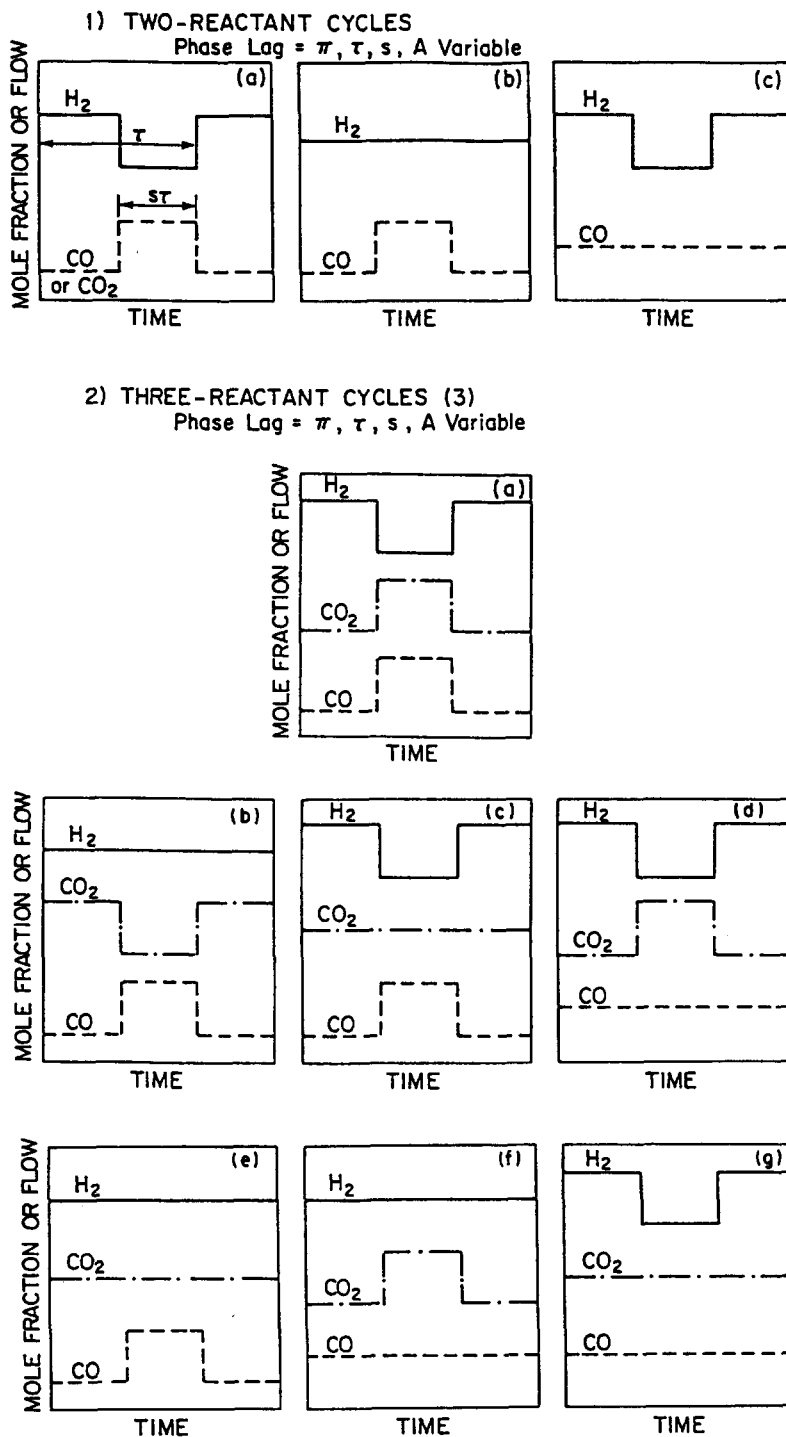


Fig. 4. Different possible composition forcing operations with two and three components (reactants, promoters, or diluents) for methanol synthesis (after Chanchlani et al. [43] with permission of publisher).

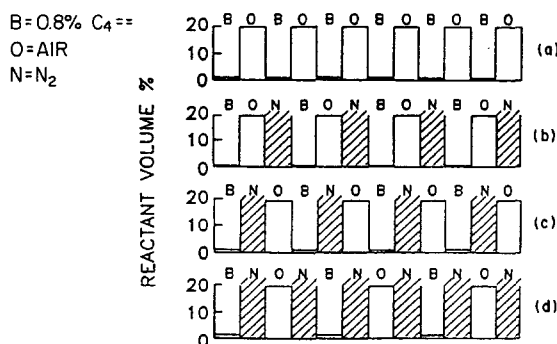


Fig. 5. Modulation strategies with two-, three-, and four-part cycles for partial oxidation of butadiene to maleic anhydride with and without diluent flushing (after Lang et al. [46] with permission of publisher).

possible, although maintaining a constant flow rate through the reactor limits these possibilities considerably.

Further manipulation strategies can arise when more than two components are modulated. Although only two-part cycles are shown in Fig. 4, multi-part cycles are possible. Multi-part cycles could be useful in some circumstances, such as flushing the catalyst surface to desorb reactant or product before exposing the surface to a second reactant. Park et al. [44] and Lang et al. [45,46] have employed multi-part cycles in their investigations of the partial oxidation of C₄ hydrocarbons. Fig. 5 [46] illustrates three-part cycles in operations (b) and (c), while the bottom operation in the figure shows a four-part cycle. Note that the location of the N₂ flush differs in (b) and (c). The figure illustrates strategies explored for modulation of the partial oxidation of butadiene to maleic anhydride [46].

5.3. Choice of mode

Periodic and pulse modes, relaxed and quasi-steady state were introduced earlier as modes of operation. Switching between feed mixtures and pure reactants, between just pure reactants, or between an inert and a reactant mixture are also modes of operation. They can all have a large influence on reactor performance. They are also illustrated in Fig. 4 and Fig. 5. All of the operations shown in Fig. 4 could represent switching

between reactant mixtures, while alternating between two reactants is shown in Fig. 5.

Description of the above operations as modes has become established in the literature of periodic operation. Modes imply strategies, so operating a reactor in the relaxed steady state could be called a strategy. But is it one? The difference in periodic and pulse strategies is only in cycle split, s . Fig. 2 introduced cycle split as a variable. Similarly, the difference in switching between mixtures and pure reactants is the amplitude, which is a variable. Quasi-steady state and the relaxed steady state differ only in the cycle period, also a variable. Consequently, cycling strategies in periodic operation and the variables that arise can overlap.

Designating the modes or policies just mentioned as strategies rather than the consequences of the choice of variables can be justified by noting, in each of the three cases cited, that they represent the extreme ranges of the variables. Performance at these extremes can be dramatically different.

6. Variables in periodic operation

The variables in periodic operation have already been introduced and defined. Cycle period or its inverse, frequency, is a variable for all cycling strategies, but other variables such as cycle split, amplitude, time-average feed composition and phase lag are variables only in certain strategies. For example, split is not the appropriate variable in pulse strategies; instead, pulse length is preferred. Similarly, amplitude, as defined in the section on Background, tends to infinity for these strategies and should be replaced by pulse magnitude, for example, a flow rate or the reactant concentration in the pulse. Phase lag becomes a variable only when more than one input is changing with time.

When there are two components, as in feed composition modulation, and the phase lag is not held at 0 or 180°, a periodic operation can have two cycle periods and two cycle splits, one for each component. Even when the phase lag is 180°

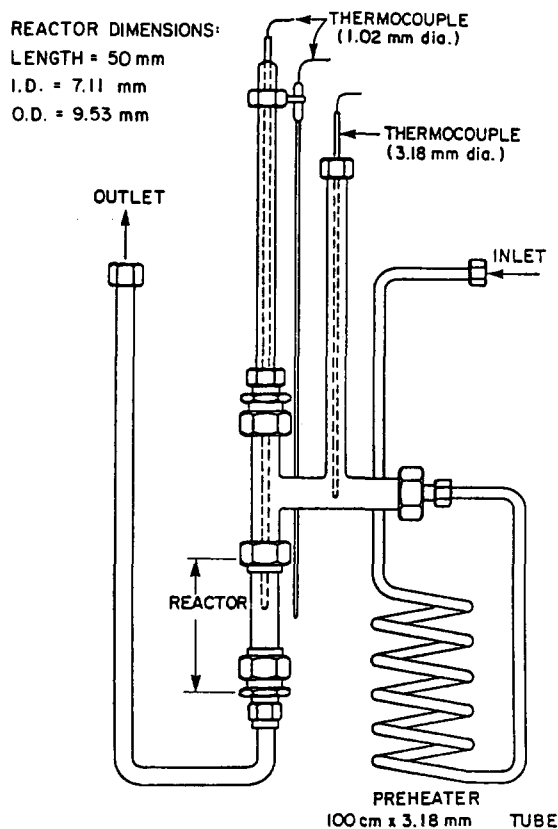


Fig. 6. Schematic of a microreactor for use in composition forcing studies (after Chanchlani et al. [43] with permission of publisher).

out-of-phase, cycling must be described by two amplitudes if $s \neq 0.50$. When the number of components becomes greater than two, multi-part cycles become the general rule and the number of variables needed to define a cycling operation increases rapidly. Finally, neither simulated nor experimental investigations have been attempted for systems having more than three inputs under periodic operation.

7. Equipment for periodic operation

Periodically altering the catalyst environment within the reactor can be undertaken by changing the feed concentration or by using two reactors, each having a constant feed in both flow and composition and transporting the catalyst from one reactor to the other. Composition switching within a single reactor is simple and is the system widely

used in experimental investigations. A two-reactor design with a circulating catalyst is the design favored for industrial-scale operations.

7.1. Laboratory-scale equipment

In almost all published studies of composition modulation, a single reactor vessel has been used with a valving system to change periodically the composition of the feed flowing to the reactor.

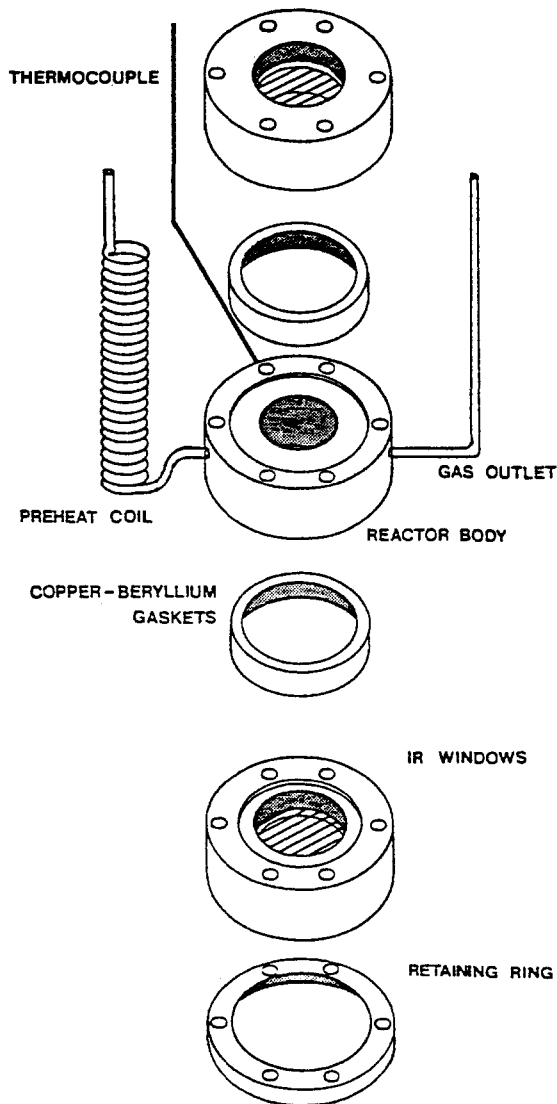


Fig. 7. Schematic of high temperature, pressurized cell for transmission IR, Raman or UV spectroscopy used to study CO oxidation over a copper oxide catalyst under composition forcing (after Prokopowicz et al. [48] with permission of publisher).

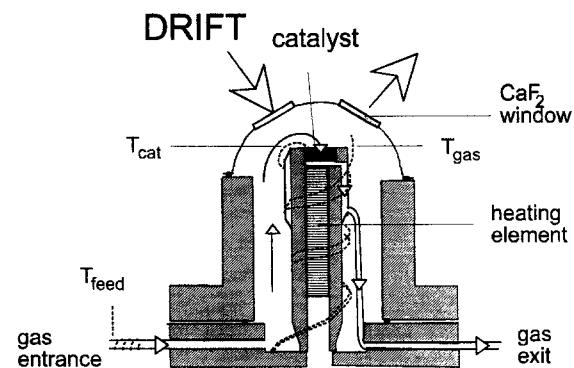


Fig. 8. Schematic of an infra-red cell using DRIFTS technique (after Harrick HVC-DRP with permission).

Modulation equipment of this type is easily fabricated and is inexpensive. Microreactors can be used that require just milligram samples of catalyst and provide differential performance. Fig. 6 shows a microreactor frequently used in the Waterloo studies of periodic operation [47]. This reactor is made from 1-cm o.d. steel tubing. The catalyst is supported on a steel screen held in place by the fitting. A screen is often press-fitted on top of the bed to prevent disturbance when the reactor is moved. Prior to pressing the top screen in place, the tube is vibrated to settle the catalyst to its maximum random-packed density. The figure shows a separate coil for preheating the reactants. Two thermocouples are also shown in Fig. 6. The upper one is fixed above the bed and measures the temperature reached in preheating. The second thermocouple penetrates the bed from the top and

passes through the supporting screen. It measures the bed temperature. Catalyst-bed depths in these microreactors range from 1 to 6 cm. The depth depends on catalyst activity at the reaction temperature.

Using a microreactor permits observation of reaction dynamics by means of a continuous analyzer, such as an IR or UV spectrophotometer, attached to the reactor outlet. Indeed, if the packed, tubular reactor in Fig. 6 is replaced by an optical cell containing the catalyst in an IR transparent wafer, it is possible to observe the dynamics of the catalyst surface. Fig. 7 shows a cell built [48] to investigate the modulation dynamics of CO oxidation on a copper oxide catalyst. Copper oxide is opaque to IR light, so the wafer was formed from KCl with some copper oxide admixed.

The main disadvantages of a catalyst wafer are that the catalyst is modified during pressing of the disk and that additional diffusional interference can occur. Furthermore, flow patterns in the cell are not well-defined. These problems can be solved by using DRIFTS (diffuse reflectance infra-red Fourier transform spectroscopy) [49]. The DRIFTS technique uses a small amount of catalyst powder through which the reaction mixture flows, as shown in Fig. 8. Usually this small amount of catalyst can be considered to be a differential reactor. Simultaneous measurements of

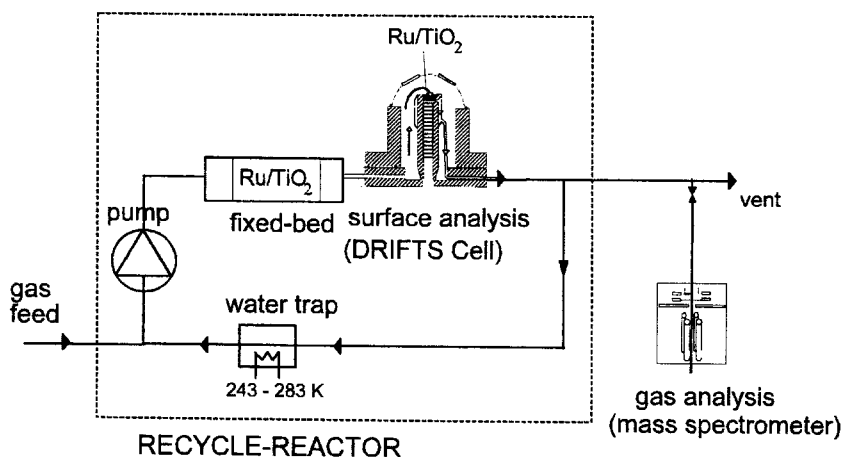


Fig. 9. Experimental setup for the simultaneous measure of gas-phase and the surface species during the CO₂ methanation (after Harrick HVC-DRP with permission).

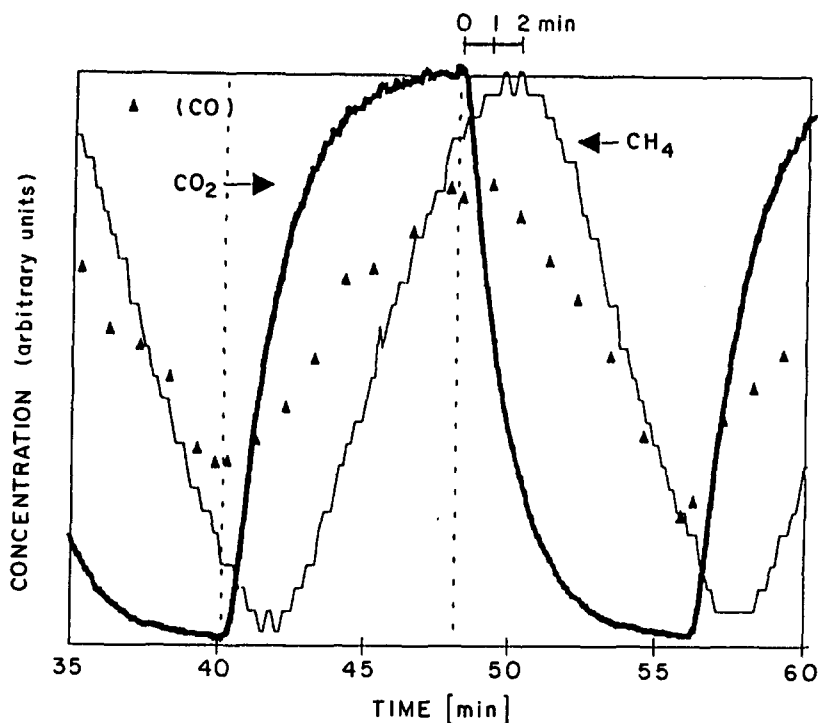


Fig. 10. Response curves to periodic CO_2 feed variations during CO_2 methanation. 1.2-min time shift between adsorbed CO (CO_a) and methane and 0.8-min time shift between CO_2 and (CO_a) (after Marwood et al. [50] with permission of publisher).

gas phase concentrations and surface adsorbates can be undertaken by placing the IR cell in the loop of the external recycle reactor. Fig. 9 [50] shows a schematic design for CO methanation on a Ru/TiO_2 catalyst. Four grams of catalyst are placed in a fixed bed while 0.6 to 0.8 g are placed in the DRIFTS cell. Both catalyst charges are heated to the same temperature. Hydrodynamic characteristics of the external recycle reactor (operated at high recycle ratios) are such that the concentrations in the fixed bed and IR cell are almost identical. Since conversion in the cell can

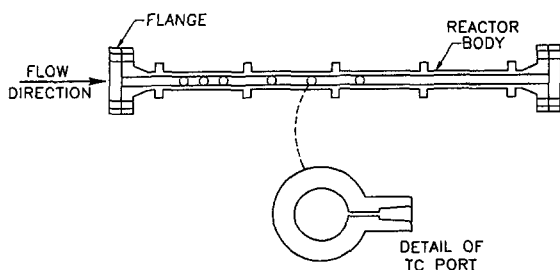


Fig. 11. Schematic of an integral reactor used for composition modulation of ethanolamine formation from ethylene oxide and ammonia (after Vamling [51] with permission of author).

be neglected, the cell becomes a 'window' into the reactor showing the catalyst surface under reaction conditions. For example, during CO_2 methanation, the CO concentration on the Ru/TiO_2 catalyst correlates with methane formation in the gas phase. Fig. 10 shows a typical result.

For integral reactors, isothermality is often important. A 1-cm o.d. tube is usually adequate to make the bed isothermal provided $L/d > 10$ and the reactor is immersed in a constant-temperature bath or furnace. Larger diameter tubing with heavy insulation and counter-heating can be used to obtain near-adiabatic behaviour. Fig. 11 shows an integral reactor design used by Vamling [51] in his study of the production of ethanolamines from ethylene oxide and ammonia over an ion exchange resin catalyst. Reactor i.d. was 24 mm and its length was 1000 mm.

Integral reactors often have non-uniform temperature distributions that make data difficult to interpret. Several investigators [33,36,40] have overcome the non-uniformity problem by using an internal circulation reactor in place of a fixed

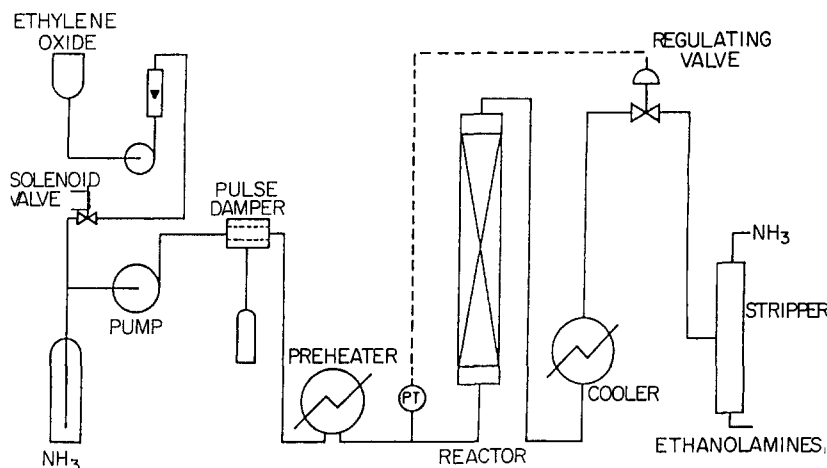


Fig. 12. Two reservoir system with a flow switching valve for composition forcing (after Vamling [51] with permission of author).

bed. All internal recirculation reactors have a mixing problem, however, caused by void space inside and outside of the reactor bed. Mixing distorts the square-wave concentration input and thereby limits cycle periods to about 60 s. Capillary tubing with short connections, welded or brazed, and carefully chosen valves can be used to shorten periods. Luu [52] describes a design that allows the use of half-second periods with just a small distortion of the square-wave input. A similar performance has been obtained by Barshad and Gulari [53] using catalyst cast as a monolith of uniform, parallel channels.

Time-average product concentrations and rates of formation can be obtained by placing a mixer of sufficient volume, about 3 to 4 times the volume passing through the reactor in a single period, after the reactor. With gases, mechanical stirring of the mixer is not necessary; the design must only prevent short-circuiting.

The simplest feed arrangement for composition forcing with two reactants uses separate reservoirs for the two feed compositions and a flow-switching valve, such as a three-port solenoid. In laboratory-scale work, a reservoir would be a compressed gas or liquid cylinder. Fig. 12 shows just such a two-reservoir system with an on-off solenoid valve. This system periodically adds ethylene oxide to a continuous flow of ammonia. It was used in a study of the modulation of ethanolamine formation [51]. Hugo et al. [54] used a

similar arrangement but with a three-port solenoid valve and with reservoirs that were gas cylinders, each containing a different feed composition. Fig. 13 shows a three-component system consisting of O_2 , N_2 cylinders, a benzene-air reservoir and timer-operated, three-port solenoid valve used by Cordova and Gau [55] to produce three- and four-part cycles, so that the catalyst is flushed by an inert prior to receiving a reactant.

For laboratory-scale studies at low gas flows, a four-way valve system can be used for switching between different mixtures of reactants. Fig. 14 shows a layout for an investigation of acetoxylation of ethylene under periodic operation [56]. Two different feed compositions are premixed in two different lines. One of these, a gaseous C_2H_4 , O_2 and N_2 mixture, is prepared by mass flow controllers. The other is formed by evaporating CH_3COOH . These feeds are switched between the reactor, in this case a Berty-type reactor, and the exhaust. It is important to keep the pressure in both systems constant in order to avoid pressure surges during switching.

Flexibility of the equipment increases if feed compositions are prepared by mixing the pure reactants. Needle valves in two separate lines leading from each gas cylinder set different flow rates for each reactant. Solenoid valves switch the flows between the lines. Thus, opening a specific combination of lines creates a feed mixture and sends it to the reactor. Closing the first combination and

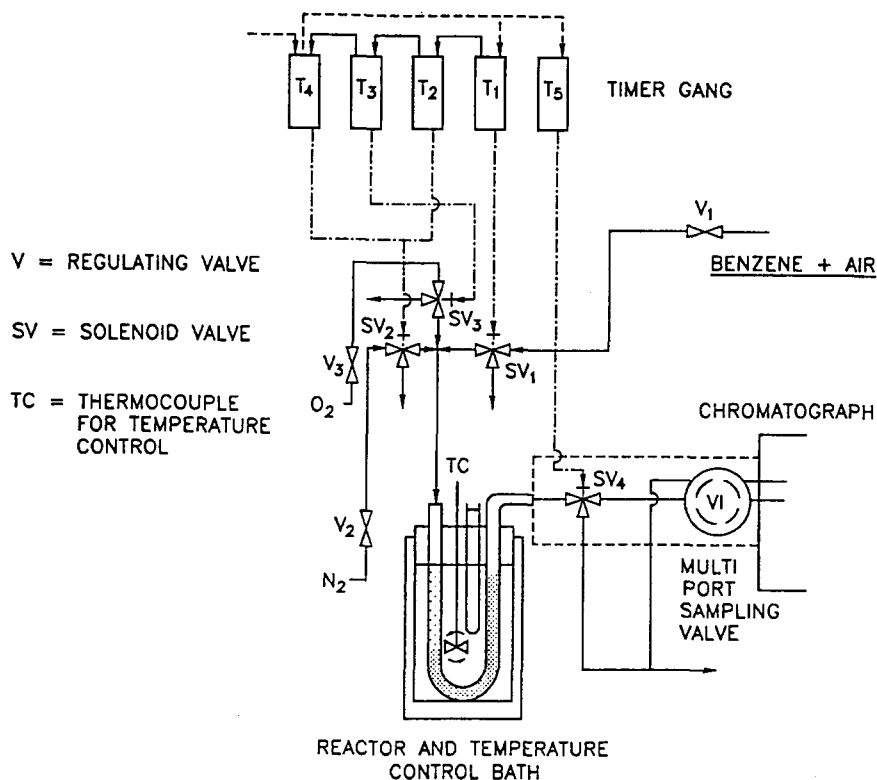


Fig. 13. Flow switching system for composition forcing with three- and four-part cycles (after Cordova and Gau [55] with permission of publisher).

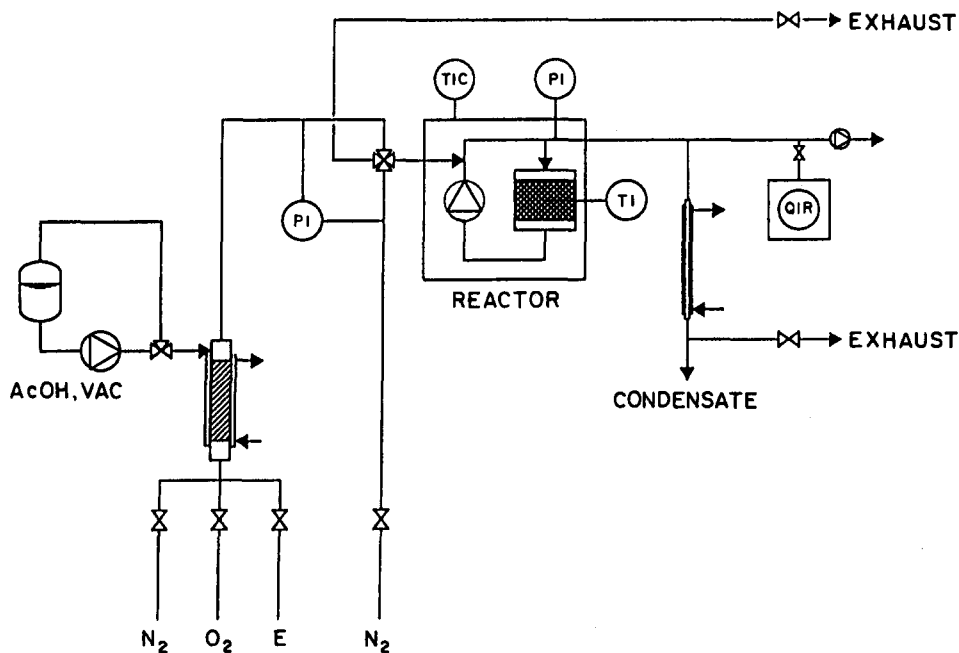


Fig. 14. Experimental setup for non steady-state investigations on the ethylene acetoxidation (after Doepper and Renken [56] with permission of publisher).

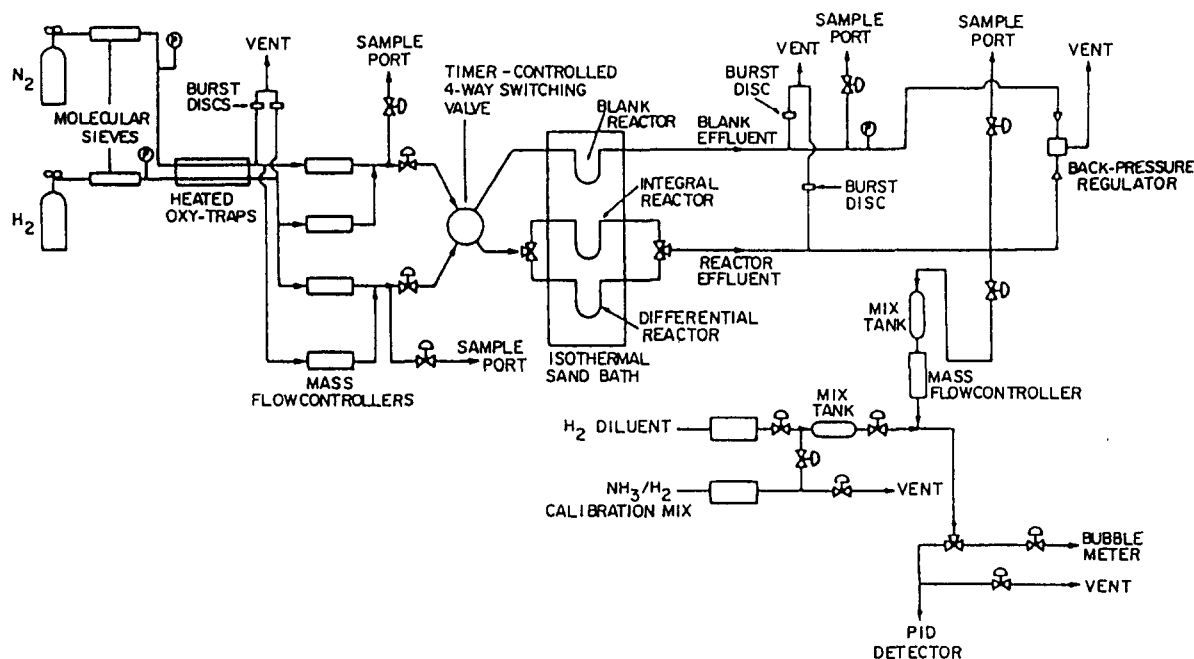


Fig. 15. Computer-driven apparatus for composition modulation by flow rate control used for ammonia synthesis over an iron catalyst (after Chiao et al. [57] with permission of publisher).

opening another formulates the feed composition for the second part of the cycle. A timer controls the switching. Compositions of the feeds can be changed from one experiment to another by adjusting the needle valves. With this arrangement, composition forcing is accomplished by flow control. Switching and blending can be automated by replacing the needle valves by mass flow controllers and by driving flow controllers and solenoid valves from a computer. This arrangement is shown in Fig. 15, a schematic of the apparatus used by Chiao et al. [57] in their high-pressure study of ammonia synthesis under feed composition modulation. These investigators were able to switch between reactors, measure feed composition and calibrate their flow and detection instruments with the arrangement shown.

Multiple reactors with catalyst transported back and forth between reactors can be used in laboratory studies, but this has been not done heretofore, probably because of the difficulty of controlling catalyst transport at very low rates. Multiple reactors can be used with feed switching closely to

simulate catalyst transport systems. In principle, a separate reactor is required for each part of a cycle. If composition forcing employs a two-part cycle so that two different feed streams are required, then at least two reactors must be used. Similarly, if a cycle has three parts, three reactors are needed, and so forth. Only one two-bed periodically operating reactor employing feed stream switching is described in the literature [27]. This was used to study composition forcing of the final stage of a SO₂ converter. Fig. 16 presents a schematic of the experimental system developed by Briggs et al. [27]. A preconverter operating at steady state converts about 90% of the SO₂ to SO₃, simulating the first three or four beds in a conventional converter. As the figure shows, the stream leaving the preconverter is periodically switched between beds 'A' and 'B'. Air is the other stream switched. Outputs from the two beds are mixed and flow to analysis. Flow through the two-bed system is continuous, although small flow and composition fluctuations occur at the moment of switching.

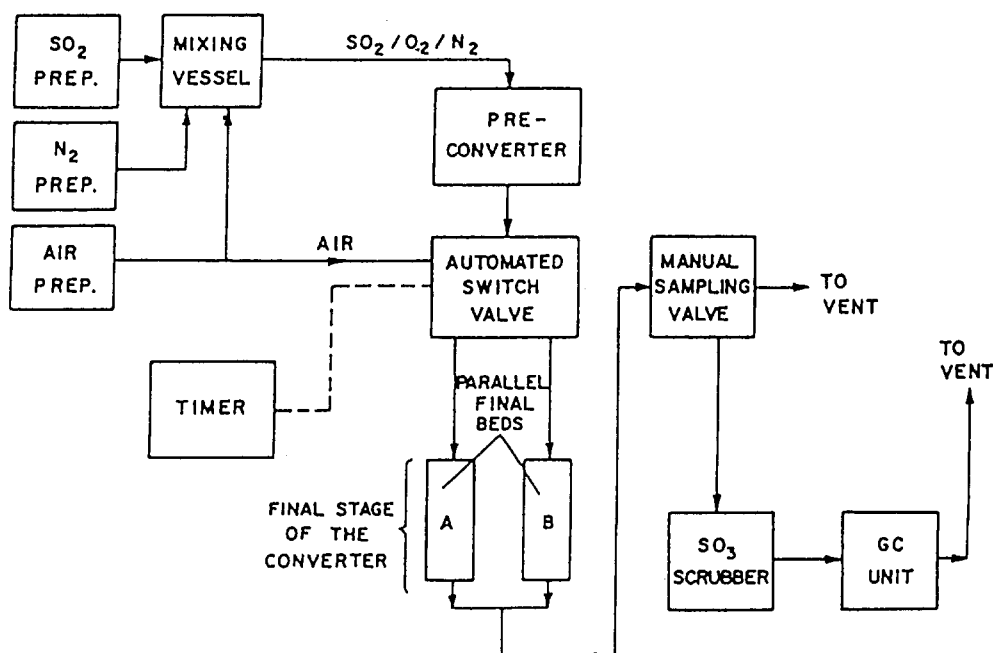


Fig. 16. Schematic of a two catalyst bed system with flow switching used for composition modulation of final stage of an SO_2 converter (after Briggs et al. [27] with permission of publisher).

7.2. Industrial-scale equipment

The single reactor system for periodic operation seems poorly suited to large-scale operation because of the problem of rapidly opening and then tightly shutting large valves. Switching between reactor feed and a recycle line would be easier, but it would require hold-up vessels and recycle blowers for gaseous feeds, making the system complicated and costly. On the downstream side of the reactor, a hold-up vessel would be needed in most situations to smooth out composition variations forced on the reactor. Using two reactors simplifies the design by permitting feed streams to be periodically switched between the reactors, so that the problem of tight shut-off and quick-opening is avoided. In addition, blending the streams that leave the reactors substantially reduces the time-variation of the product gas, so that a vessel with smaller hold-up becomes feasible.

Circulating the catalyst between two reactors operating with different feed compositions (and, if desirable, different flow rates) achieves periodic operation, and in addition, segregates the dis-

charge streams. This could be advantageous for product separation. Let us consider partial oxidation using this system. One reactor is fed a hydrocarbon stream with little or no air, while the second reactor is fed just air for catalyst regeneration. Only the hydrocarbon stream contains product and so it alone flows to the product-recovery train. The product is at higher concentration than in the comparable discharge stream from a continuous, steady-state operation and should be separable from the discharge at lower cost. Such separation advantages were recognized many years before the periodic operation concept appeared in the literature. Fig. 17 shows a system of two fluidized beds and catalyst transfer via a pneumatic lift proposed in 1949 by Lewis et al. [58]. A strong resemblance to early versions of catalytic cracking can be seen. One of the beds is fluidized by a hydrocarbon that is selectively oxidized, while the catalyst is reduced. The second bed is fluidized with air that reoxidizes the catalyst. The catalyst thus functions in this system as the O_2 carrier.

The advantages of this system are obvious. Molecular oxygen is absent during oxidation of

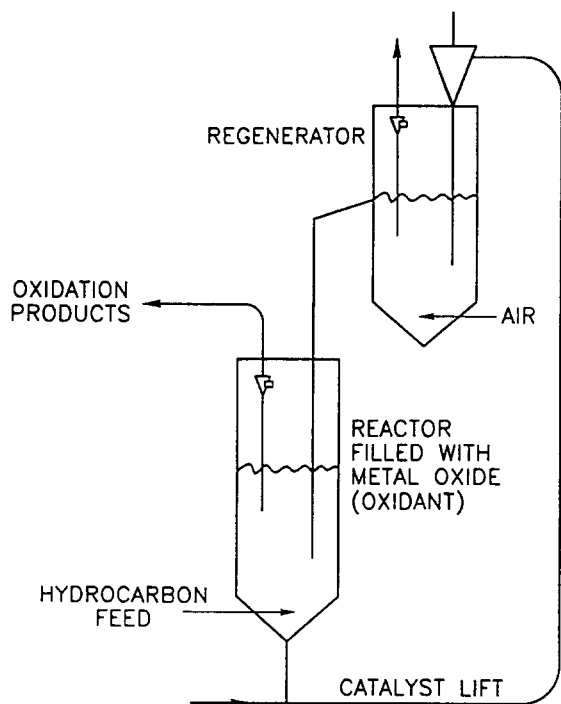


Fig. 17. Conceptual system for composition forcing of partial oxidation reactions using fluidized beds with catalyst transfer between beds (after Lewis et al. [58] with permission of publisher).

the hydrocarbon, reducing, it is hoped, the extent of total oxidation. Increased hydrocarbon concentrations are possible in the reactor because there is no longer a detonation hazard. This reduces the cost of downstream separation. Air can be used as the oxidant in place of oxygen, because the oxidant is separated from the hydrocarbon so that N_2 does not become a load on the downstream separation. Furthermore, the catalyst oxidation and reduction steps can be carried out at different temperatures to minimize contact time because each step occurs in a different reactor. A less obvious advantage is that the heat release for the highly exothermic partial oxidation reaction is split between two vessels, reducing the cost of cooling.

The two-fluidized-reactor, circulating-catalyst system was first studied experimentally in the late 1960's [59]. It was not adopted for commercial use because the advantages just mentioned are offset by the cost of circulating large amounts of catalyst [59]. Because redox catalysts are seldom reducible reversibly to the metal, a large mass of catalyst must be circulated per mass of product

created. Furthermore, subjecting a catalyst to transport, often at high speed and alternating environments, leads to its attrition and loss.

The balance between advantages and disadvantages can be shifted if periodic operation provides higher selectivities. This is the case for the partial oxidation of butane to maleic anhydride as long as a short butane contact time is used. To attain short contact times, a riser reactor or a fast fluidized bed replaces one of the conventional fluidized beds shown in Fig. 17. The du Pont Company has announced the construction of a maleic anhydride facility using the two-bed, circulating-catalyst scheme. Fig. 18 shows a recirculating reactor system employing a riser and a fluidized bed proposed for the partial oxidation of butane to maleic anhydride [60,61]. Re-oxidation of the catalyst is not a critical step to reach high maleic anhydride yields, so this step is performed in a fluidized bed. Higher selectivity to maleic anhydride is attained by stripping the catalyst with steam or N_2 between contact with the reactants. This results in a multi-part cycle of catalyst exposure. With recirculating solids in fast fluidized beds, the catalyst separation and transport steps provide the opportunity for stripping, so a further vessel is not needed. Stripping of the hydrocarbons and oxygenates from the catalyst is accom-

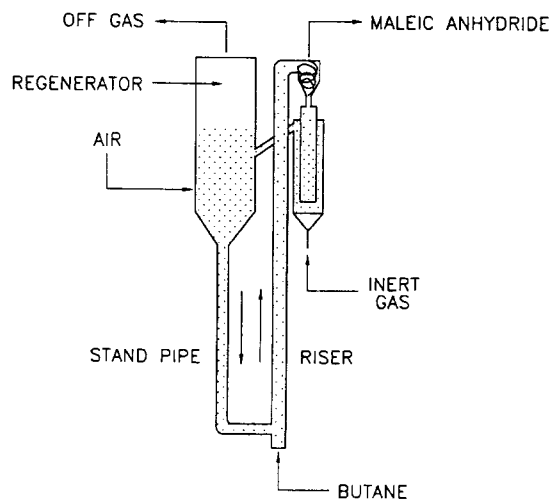


Fig. 18. Schematic of a riser reactor-fluid bed reactor recirculating solids proposal for partial oxidation under periodic operation (after Contractor et al. [60] with permission of publisher).

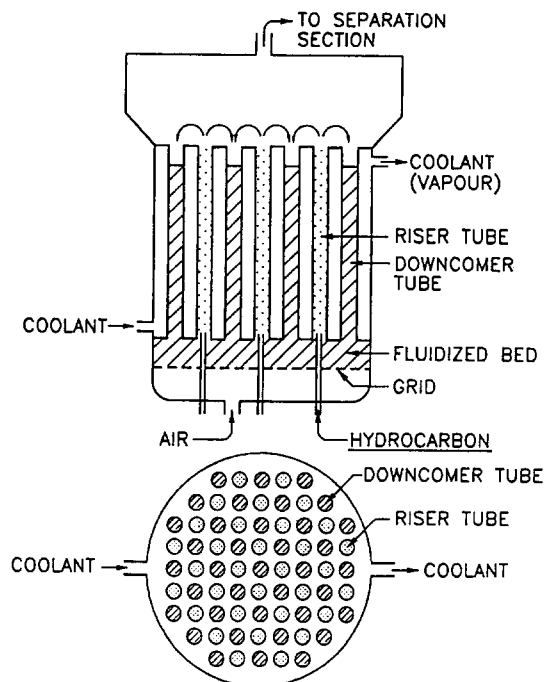


Fig. 19. Multi-tubular reactor proposed for partial oxidation under periodic operation (after Park and Gau [62] with permission of publisher).

plished in the accumulator following the riser cyclone and in the line conveying the catalyst to the fluidized bed regenerator.

Park and Gau [62] propose carrying out the hydrocarbon and air contacting steps in a single vessel with different zones. They refer to their arrangement as a multi-tubular circulating solids fluid bed. Fig. 19 shows their concept. The hydrocarbon feed carries the catalyst upward in one group of tubes and it descends in an air flow in the second group into a bed fluidized by air where the catalyst is reoxidized. As the figure illustrates, the multi-tubular circulating fluidized bed can be set in a boiler to remove the heat of reaction. Park and Gau have experimented on a two-tube version of the multi-tubular system. The multi-tubular design offers the advantage of a single vessel, but at the expense of the downstream separation steps, because the hydrocarbon and oxidant streams mix in the reactor effluent. There may also be a detonation hazard or else a limit on the concentration of the hydrocarbons and oxygenates within the reactor. Other single-vessel versions are possible, such as a spouted bed.

8. Literature on periodic operations

Although periodic operation in the guise of catalyst regeneration or the in-situ gasification of coke in cracking tubes has been practised for some sixty years, while the use of flow pulsing to improve separation performance was introduced over fifty years ago, application to chemical reactors was first considered only in the mid 1960's. Curiously, the reactor application seems to have been inspired by research in process control, specifically the application of time-varying controls, such as 'chattering' controls to reactors [63]. Since then, the literature on periodic operations has expanded rapidly. Indeed, several reviews have appeared [5,64–68] although they have been restricted in scope (e.g., Bailey [5] deals just with theory, Meira [64] with polymerization applications, and the others with experimental studies).

Chronologically, the important contributions have been the applications of relaxed steady-state methods to simple, multiple reaction systems [69]. Experimental work on periodic operation got underway soon after the first theoretical publications. Denis and Kabel [20] described flow-cycling studies. A later dynamic study of ethanol dehydration led these authors to suggest catalyst activity could be improved through reactor-temperature cycling. Experiments in which catalytic reactors were operated with periodic composition forcing were published almost simultaneously in Germany and Canada [21,23,70]. This early experimental work is discussed by Renken [65,66]. Renken's reviews address the question of the proper comparison of periodic and steady-state operations. Two bases may be used: (1) steady-state performance corresponding to the time-average of the manipulated input variables, or (2) maximum steady-state performance for any values of the manipulated variables. Renken also notes that models predicting improved performance under cycling are not supported by experimental data, whereas experimental systems for which improvement has been found do not have adequate models. This regrettable situation persists.

Experimental studies of periodic composition forcing of important industrial reactions continued into the 1980's. Papers appeared on ammonia synthesis [15,37,57] and sulfuric acid production [12,37]. Large rate enhancements through cycling were demonstrated for CO oxidation over noble metal catalysts [53] and for the ammonia synthesis over ruthenium and osmium [1,71]. The presence of unintentional periodic operation in the noble metal catalytic mufflers used for automotive exhausts was identified and studied with conflicting results on the benefits of this mode [72,73]. During the 1980's, the emphasis in experimental studies began to shift towards complex reactions and questions of selectivity. Several papers were published on the partial oxidation of hydrocarbons [3,45,74] and on the Fischer-Tropsch synthesis [47,75].

The theoretical or analytical literature of the 1980's concentrated on three questions: (1) can periodic operation improve the performance of a chemical reaction system; (2) can performance under periodic operation exceed the best possible performance under steady state as a function of the manipulated input; and (3) what properties of the reaction system result in improved performance under periodic operation? The first question was extensively discussed in the 1970's where the issue was the criteria that could be used for determining optimal periodic operation. The discussion continued into the next decade [76–78]. Several contributions have dealt with the second question [79,80], while Schaedlich et al. [81] and Grabmueller et al. [82], among others, consider both of the final questions.

Modelling and experimental work on the application of periodic operations to polymerization reactions were summarized by Meira [64] who concluded that periodic variation of initiator, monomer, or transfer agent concentration increased operating flexibility with respect to molecular weight distribution. Improvements, however, were modest. Research on this application appears to have languished since the 1980's.

A physical explanation and a conceptual foundation for periodic operations was developed in

the early 1980's by Boreskov and Matros [67]. In addition to effects caused by shifts in adsorbate concentrations on catalyst surfaces, Boreskov and Matros pointed out that improvements in reactor performance under periodic operation result from favourable changes in catalyst activity through a variety of mechanisms, often a change in the composition of the catalyst surface. When the catalyst state is altered in response to adsorbate composition and/or temperature, both the activation energy and the frequency factor change. Consequently, as input variables are cycled between two or more conditions, reaction rates vary because of adsorbate changes as well as changes in the activation energy and the frequency factor. If surface or bulk phase transitions are slow relative to the forcing period, the catalyst will operate in a transient (i.e., periodic) state, that can lead to improved rates, selectivity, or yields. Bailey [5] commented on the difficulty of analyzing reaction systems in which the switching period is of the same order as the relaxation time. To consider systems in which catalyst properties depend on the gas phase and on temperature makes the analysis even more challenging. Not only the states of the catalyst corresponding to different composition and temperature environments must be known, but also the dynamics of the transition from state to state must be determined.

Late 1980's discoveries that periodic operation is applicable to gas–solid reactions [83] and to three-phase reactors [2,84] seems likely to furnish new research themes in the 1990's. A further theme will be the coupling of reaction and separation. A 1989 paper by Vaporciyan and Kadlec [85] discusses catalytic CO oxidation in a specially modified pressure-swing adsorber.

Before leaving this brief overview of the cycling literature, we should consider another development stream. In the Background section, fluid bed catalytic cracking was mentioned as an example of a periodic operation already in wide use. In this operation, catalyst circulates between a reactor in which cracking occurs and a regenerator in which carbon deposits are burnt off. An endothermic reaction takes place in the reactor

while an exothermic reaction is carried out in the regenerator. Thus, the catalyst transports heat needed for the cracking reaction. Apparently this aspect of fluidized-bed catalytic cracking suggested to Lewis et al. [58] as early as 1949 that such a two-bed system could be used for selective oxidation of hydrocarbons, in which the catalyst transports the oxygen needed for the oxidation reaction. Sohio Company (now BP) in the US pursued this two-bed concept and tested the reactor part as the catalyst reoxidation was thought not to be a critical step [59], but rejected it, as mentioned in Section 7.2, because of the cost of circulating catalyst. Research on the two-bed system using the catalyst to transport one of the reactants, usually oxygen, continued into the 1970's and 1980's and a small literature has developed describing experimental work [55,62,86]. The Lummus Company has developed technology for the two-bed system and an application of this technology to the ammoxidation of *m*-xylene into isophthalonitrile has been implemented [87]. Laboratory research and pilot-scale application of a circulating fluidized bed arrangement to the selective oxidation of butane to maleic anhydride was mentioned in Section 7.2. A full-scale plant is under construction. It has been only recently realized that the two-bed operation with circulating catalyst is just one of several possible versions of periodic feed composition forcing.

Another application of periodic operation should also be mentioned. Since performance improvements (or at least performance changes) are to be expected, such information may be used for more fundamental investigations of reaction mechanisms and the formulation of more useful models. Indeed, non-steady-state experiments have become a common tool for investigating mechanisms of heterogeneous catalyzed reactions. This seems to be a necessity, since kinetics measured under steady-state conditions yield models unable to predict dynamic behaviour.

Yet, not all transient techniques are suitable tools of investigation. For example, the use of a single-step or pulse input suffers from the dependence of model discrimination and parameter

determination on precise and accurate measurement of low concentration tails in tracer responses. Even so, concentration step and pulse techniques are still commonly used for qualitative and quantitative purposes because of their simplicity. Multi-step or periodic techniques may provide better models. Lynch and Waters [88] demonstrated the accuracy of frequency response techniques (a periodic stimulation of the system) using methane, CO₂ and CO adsorption on α -alumina in an external recycle reactor. Recent experiments using periodic composition forcing have shown this procedure to be more robust for model development than single-pulse methods. Examples are the work of Cider and Schön [89] and Marwood et al. [50].

9. Notation

A	Reactant species amplitude (various units)
B	Reactant species
R	Product species
r	Rate of reaction, product formation, reactant disappearance (mol/s g cat)
\bar{r}	Time-average rate
r_i	Rate of disappearance or formation of species i (mol/s g cat)
s	Cycle split, duty fraction (–)
T	Temperature (K)
t	Time (s, min)
t_c	Characteristic or relaxation time (s, min)
y	Mol fraction (–)

Greek

τ	Cycle or forcing period (s, min)
ψ	Enhancement or improvement factor (–)
ψ^*	Global enhancement or improvement factor (–)

Subscript

m-	Maximum steady state
ax	
rss	Relaxed steady state
qss	Quasi-steady state
ss	Steady state

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