Reactor Operating Procedures for Startup of Continuously-Operated Chemical Plants

J. W. Verwijs, P. H. Kösters, and H. van den Berg
Process Development & Control Dept., Dow Benelux N.V., 4530 AA Terneuzen, The Netherlands

K. R. Westerterp
Chemical Reaction Engineering Laboratories, Dept. of Chemical Engineering,
Twente University, 7500 AE Enschede, The Netherlands

Rules are presented for the startup of an adiabatic tubular reactor, based on a qualitative analysis of the dynamic behavior of continuously-operated vapor- and liquid-phase processes. The relationships between the process dynamics, operating criteria, and operating constraints are investigated, since a reactor startup cannot be isolated from an entire plant startup. Composition control of the process material is critical to speed up plant startup operations and to minimize the amount of offgrade materials. The initial reactor conditions are normally critical for a successful startup. For process conditioning, a plant should have an operating mode at which the reactor can be included in a recycle loop together with its feed system and downstream process section. Experimental data of an adiabatic tubular reactor startup and thermal runaway demonstrate some operational problems when such an intermediate operating stage is missing. The derived rules are applied to an industrial, highly heat-integrated reactor section, and the resulting startup strategy is summarized in an elementary-step diagram.

Introduction

The chemical industry has put much effort on process optimization, resulting in increased process yields, reduced energy consumption, decreased environmental pollution, and improved product quality. To support these activities, extensive research has been carried out in the area of heat exchanger network design for energy integration. In the classic concept, energy integration is the final step in developing the process structure, but the process conditions as such remain unchanged. New approaches manipulate also the operating conditions to obtain a more efficient energy utilization (Westerberg, 1992).

Another trend in chemical engineering is to integrate more than one process function in a single piece of equipment, like reaction, mass, heat or momentum transport operations. This multifunctional equipment can have a significant impact on the entire process structure, as was demonstrated for a methanol plant design by Westerterp (1992). The process structure was drastically simplified by selective methanol absorption in the reactor section, which increased the raw material conversion to almost 100% and eliminated the need for material recycles.

The tight coupling of process functions may make the entire plant more difficult to control (Amundson, 1988). Therefore, integrated processes ask for a combined process and control design approach. An actual industrial case according this strategy is reported by Bouwens and Kösters (1992). They concluded from the design of a highly integrated heat exchange section that controllability analysis should cover complete process networks, because the best control structure design for a heater unit investigated as a stand-alone system appeared to be unstable when operated in combination with other process units.

The integration of process functions may complicate the plant startup or shutdown operations too. Unfortunately, the required dynamic process models describing a plant startup or shutdown are necessarily much more complex, and costly, than a model which covers the range of conditions encountered during normal operations only (Wolff et al., 1992). Nevertheless, fundamental research in nonsteady-state process de-

---

Correspondence concerning this article should be addressed to K. R. Westerterp.

sign, process control, and operating procedure synthesis is strongly needed, because most process related incidents occur when a chemical plant is not operating at a steady state (Amundson, 1988). Two types of process knowledge are necessary to study nonsteady-state plant operations (Stephanopoulos, 1988):

- *Procedural knowledge*, representing the operating strategy employed by plant personnel and process control systems to run the process
- *Declarative knowledge*, based on first principles, characterizing the dynamic behavior of process units.

A dynamic process model should answer questions about process behavior and operating limits, while a representation of the operating procedures should answer questions about "how" and "when" to take some operational action. Note that modern process control systems may perform several tasks, like analog control to maintain the process state variables at their target values, on/off control to establish material routing through the process, interlocking to ensure process safeguarding, and sequence control to guide the process through a series of operating phases (Slijk, 1985). Well-defined operating targets, operating constraints, and operating procedures are necessary to perform these tasks automatically. The relationship between the above mentioned elements and the dynamic operation of a process is shown in Figure 1.

Some studies have been published on formal methods for operating procedure synthesis. Fusillo and Powers (1987, 1988) developed a modified means/ends planning technique to determine intermediate operating states in between shutdown and the normal production state. These intermediate operating goals are based on the existence of stationary states at which the system can remain until the next operational action can be taken. A constraint guided strategy searches for a feasible sequence of actions to drive the process from shutdown to the production state. Lakshmanan and Stephanopoulos (1988a,b, 1990) developed a similar approach, based on a hierarchical object-oriented modeling technique in combination with a nonlinear planning method. By applying this methodology, it is possible to include mixing constraints in the synthesis problem to avoid the formation of undesirable or potentially dangerous mixtures. Aelion and Powers (1991a,b) developed a strategy for the retrofit synthesis of flowsheet structures and operating procedures. If no effective operating procedure can be generated, flowsheet structure modifications are proposed by the operating procedure planner.

The above mentioned research is focused mainly on the development of computerized operating procedure synthesis techniques, and showed some promising results. However, the operating constraints as such are assumed to be known *a priori*, while to our best knowledge the problem of determining convenient startup criteria is not addressed yet.

Also, almost no studies are published about process dynamics and operating procedures of industrial reactor systems during a plant startup. In a preceding study, the behavior of an industrial adiabatic tubular reactor during the startup is described, together with the impact of a failure of the feed-pump

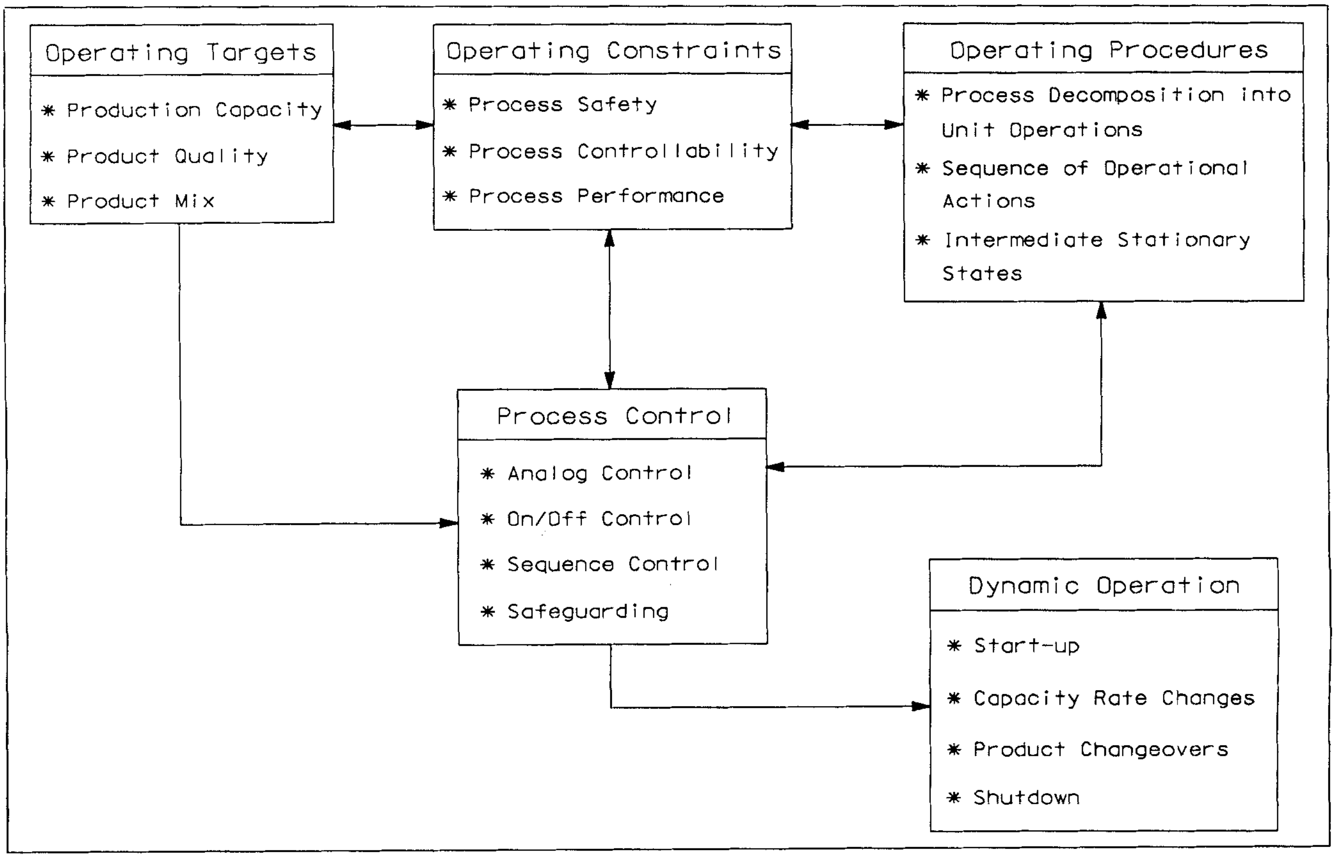

Figure 1. Relationship between process control elements and nonsteady-state process operation.

of one of the reactants (Verwijs et al., 1992). It is shown that for an exothermal adiabatic tubular reactor a much higher initial temperature is required, compared to the reactor inlet temperature at normal steady-state conditions, to ensure high reactant conversion levels during the startup. Another important conclusion is that a reactor startup cannot be studied effectively without taking into account the operational aspects of a plant startup.

This article defines some rules for the startup of tubular reactor systems in continuously-operated chemical plants:

- First, some axioms are defined to determine convenient startup criteria.
- Secondly, an entire plant has to be unraveled into smaller units, which can be operated stand-alone during the startup. Some rules for process decomposition are described, together with some guidelines for sequencing the startup of individual process units. The rules are based on an analysis of operational problems in vapor and liquid phase processes, but can be extended potentially to polymer and solid processing units.
- Thirdly, the problem is addressed of how and when to put an exothermal adiabatic tubular reactor system into a production state. Industrial examples are used (a) to demonstrate some points regarding the response of operating personnel to dynamic reactor operations, and (b) to show some shortcomings about reactor conditioning operations which are incorporated in many industrial designs.

The derived rules are applied to an industrial, highly heat-integrated reactor section, and the resulting startup strategy is described in a step-by-step procedure.

Deviations from Operating Targets

In general, the steady-state conditions of a continuously-operated chemical plant have been proven to be safe, and the observation of a few key state variables is often sufficient for experienced operating personnel to control the process status. Unfortunately, process data generated during the startup can confuse even the best operators, due to control loop interactions, inverse process responses, or time delays in process and measurement responses. Ultimately, this may lead to operating errors, due to an improper understanding of the process dynamics (Stephanopoluos, 1988).

Hazardous situations may result from running a chemical plant outside the range of the normal operating conditions. Therefore, process hazard and operability studies are widely used in the chemical industry to improve process design, control and safeguarding. In these, so called, HAZOP studies a systematic, qualitative analysis is carried out on impossible deviations from the desired operating conditions, the causes are identified, and their consequences are evaluated (Lees, 1991).

Maintaining process performance, like product quality, product consistency and process efficiency, is also critical for a successful plant operation. An important trend in today's industrial practice is to define product quality no longer as "high purity" or "within certain specification limits," but rather as "low variability around a specification target" (Villermaux, 1991). This is because there are always some losses associated with deviations from given target values (Roy, 1990). Consequently, the process state variables should be kept at the desired nominal targets, and their variability should be decreased by making the appropriate changes in the operating conditions and/or strategies to improve process performance and product quality (Saraiva and Stephanopoulos, 1992).

It can be concluded from the above mentioned arguments that process safety and performance are determined by how well a continuously-operated chemical plant can be operated at the target values of the state variables. Process performance requirements ask for process control within tight operating constraints, while hazardous situations may result from (large) deviations from the required process conditions. Fortunately, *steady-state process operation adhering to performance constraints will generally also comply with process safety constraints simultaneously*. This rule is used as a leading principle in HAZOP studies. It was proved quantitatively for cooled, fixed-bed, tubular reactors by Westerterp et al. (1984), Westerterp and Ptasinsky (1984), Westerterp and Overtoom (1985), and Westerink and Westerterp (1988). They demonstrated for this reactor type that a thermal runaway will not occur if the selectivity and conversion criteria are adhered to.

Operating constraints

From an operational point of view, three categories of process constraints can be defined:

- *Process safety constraints* are set by the design pressure and temperature of equipment, the relief-pressure of safety devices, the maximum allowable temperature differences in heat exchanger equipment, the chemical and/or physical nature of process materials, and environmental safety. Normally, a process is safeguarded for exceeding these constraints by interlock systems based on temperature, pressure or flow measurements, and by safety devices. Exceeding of safety constraints may lead to immediate process shutdowns.
- *Process controllability constraints* are determined by operating capacity turndown ratio's of process equipment with respect to the design capacity, control valve ranges, control loop interactions, and process control stability. For a *well-designed* process, the controllability constrained range of operating conditions is more confined than the range of possible operating conditions set by safety constraints. Violation of controllability constraints may lead to process upsets and ultimately to hazardous situations.
- *Process performance constraints* are determined by product quality, product consistency and process efficiency requirements. Usually, these are tight operating constraints. Economic losses result from violating performance constraints.

The startup of a continuously-operated chemical plant is a complex operational task, and known to be critical with respect to process safety. Consequently, operating personnel and process engineers are focused, intuitively, on running a chemical plant within its safety constraints. Nevertheless, uncontrolled process upsets are quite easily obtained during the startup, since equipment and control loops are designed and tuned usually for steady-state operations only (Amundson et al., 1988). To avoid these upsets, and to ensure a safe operation during startup, the process should be limited to the controllability constraint range of operating conditions:

- By a proper plant design. For example, if the composition of a mixture of two chemicals should be restricted to certain limits, it may be necessary to install parallel control valves in the feed line, upstream of the mixer, to avoid an overdosing of one chemical at low production rates, even in case of a loss of control.

- By appropriate operating procedures. As discussed above, process operation adhering to controllability constraints will generally also comply with safety constraints simultaneously. Hence, operating procedures should be designed with respect to criteria founded on process controllability considerations instead of on safety constraints only.

Convenient criteria for startup operations

Generally, the most important controlled process variables are the temperature, pressure, inventory (level), material composition and flow. Fortunately, the flow and process inventory variables can be controlled usually at their intermediate targets during all phases of the plant startup operations (inventory control). The impact of controlling the material composition too (material balance control), as of the moment when equipment is filled with material from storage, can be explained qualitatively by focusing on the dynamic behavior of a process system.

First, the response time to a feed flow rate and/or composition change, is determined by the average residence time and the residence time distribution of the material in a process unit. The average residence time is controlled by the total feed rate into the system and the total volume of the process inventory. The residence time distribution depends on the mixing characteristics of the installed process equipment, like the plug-flow behavior of a tubular reactor or the well-mixed tank behavior in a distillation column sump. The response time to a step change in the process inlet conditions will vary between one to more than several orders of magnitude of the average residence time to reach the new operating conditions. For example, liquid-phase tubular reactors may have a response time close to the average residence time of the system. On the other hand, the response time of systems with a large thermal capacitance compared to that of the total feed into the system, similar to exothermic vapor-phase reactions in fixed-bed reactors, can be several orders of magnitude greater than the residence time of the gaseous feed itself. In practice, *manipulated state variables are ramped up (slowly) to their new target values*, and a change in process conditions will take even longer than the time span mentioned before. Secondly, several recycle streams may be present in a chemical plant, because per pass only a certain proportion of the raw materials is converted into products; the rest has to be recovered and recycled. Processes with recycle streams are quite common, but their dynamics are poorly understood at present (Luyben, 1992). Nevertheless, some key conclusions from studies on the relationship between the process structure and its dynamics are that (a) *recycles increase the process sensitivity to disturbances*, and (b) *the response time of recycle processes is substantially longer than the response time of the forward path alone* (Denn and Lavie, 1982; Kapoor et al., 1986).

As a consequence of this dynamic process behavior, upset conditions for the material composition may be sustained for a long period in the process. Therefore, the overall plant startup time will increase significantly in case the material composition has to be corrected, either by a mismatch of the charged material or by a process upset. On the other hand, a plant startup can be accelerated by restricting the material composition, as close as possible, to its (steady-state) target value when the process units are charged with material from storage. Minimizing the total volume of the process inventory will have a similar effect. Additionally, the amount of offgrade materials produced during the startup may be decreased too.

These aspects can be illustrated by focusing on a distillation column which is running out of specification on its distillate product. Depending on the reflux drum holdup time, the reflux ratio, and the distillate to feed ratio, the distillate specifications may be obtained much faster by dumping the offgrade contents of the reflux drum into the distillation column or into a storage tank, followed by filling up the reflux drum again with on-specification product, either by distillation or from storage, than bringing the offgrade material on specification by a continued operation.

Process Decomposition into Unit Operations

Decomposition of an entire plant into smaller subsystems is necessary to decrease the complexity of the plant startup operations. Additionally, it is a means to focus the attention of operating personnel to a particular plant segment where the next operational action is taken (Aelion and Powers, 1991a). Some generic criteria to determine the boundaries of a subsystem within an entire process system are reported by Fusillo and Powers (1987) and Aelion et al. (1991c). The following sections describe some process decomposition rules in relationship with the startup of continuously-operated reactors. The rules are based on an analysis of operational problems in vapor- and liquid-phase processes, but can be extended potentially to polymer and solid processing units.

The nonheat-integrated process in Figure 2 will be used to illustrate the various steps of the analysis. In this process, the products are formed by an exothermal, liquid-phase reaction between reactant A and B. Reactant A is fed from storage into a buffer tank, which receives recycle material also from a recovery unit. Reactant A is fed from the buffer tank into the reactor, together with reactant B which is fed from storage. The reactor system consists of a feed mixer, a preheater and an adiabatic reactor vessel. Reactant A is fed in excess, because reactant B should be totally converted at the reactor exit. A breakthrough of reactant B in the reactor effluent is not allowed for process safety and operability reasons. The excess amount of reactant A is recovered and recirculated. The crude product is discharged from the recovery unit into the product refining unit. The finished products are routed to storage.

Reversible and irreversible unit operations

The usual way to bring a process unit into operation is to charge the required amount of materials into the system, as soon as purging and leak testing are finished. Subsequently, the process unit is driven in steps to predefined operating conditions at which it can be integrated operationally with neighboring process units.

Fusillo and Powers (1987) developed a so-called *stationary state* concept to determine stable intermediate operating states in between shutdown and the normal production state at which a process system can remain until the next operational action can be taken. The presence of *simultaneous inverse operations* within the system boundaries, like heating vs. cooling or separation vs. mixing, indicate the possibility of a stationary state.

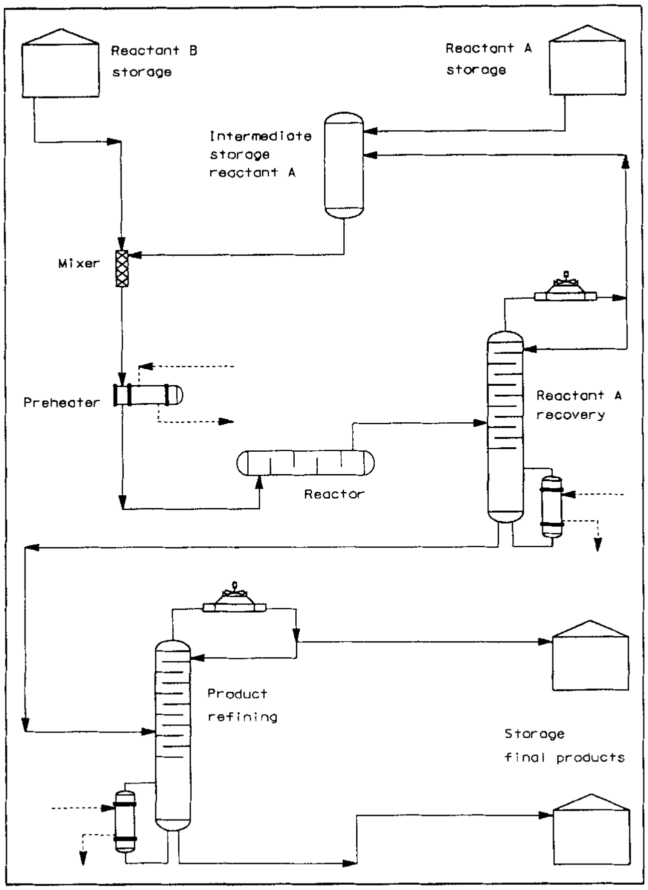

Figure 2. Process scheme.

Systems with a large capacitance for a physical quantity, like thermal energy or mass, may also have stationary states. A distillation column running at total reflux conditions is an example of a system exhibiting a stationary state due to the presence of simultaneous inverse operations, being evaporation in the reboiler vs. condensation in the overhead condenser (Fusillo and Powers, 1987).

The concept of *simultaneous inverse operations* provides also a key to distinguish between reversible and irreversible unit operations:

A *reversible unit operation* is defined as a process system that can be operated stand-alone, without any process streams fed into or exiting the subsystem, due to the presence of inverse operations. This yields the possibility of conditioning a process system during startup operations. A prerequisite for the simultaneous operation of the inverse process functions is that material can be recycled between them, like between the reboiler and condenser of a distillation column.

Irreversible unit operations are started up by supplying the appropriate feed into the system, and *production is started.* An example is the reactor system in Figure 2. Other examples are drying, filter, and centrifuge operations. Theoretically, it is possible for the latter type of operations to suspend the solids again in the solvent, but in practice the equipment to do so is not installed. Generally, whether a process unit is reversible or irreversible depends often on the type of operations present in the process, an example being a mixer; however, a separator is not installed. It can be determined by thermodynamics also due to irreversible state transitions or chemical reactions.

Distinguishing between reversible and irreversible unit operations serves as a guiding principle in planning the startup order of different process units. Reversible process units are put into operation first. The sequence is controlled by their heating and cooling sources. Units with process independent heating or cooling sources, like aircoolers or steam reboilers, are usually started up first. Finally, the irreversible units are put into operation, and production is started. Generally, this rule implies that product finishing sections are started up first for vapor- and liquid-phase processes, followed by the reactor feed preparation section, the reactant recovery section, and the reactor section, respectively.

Startup of reversible unit operations

Severa (1973) presented a simplified operating procedure for the startup of a crude and vacuum distillation unit of a refinery. Some principal steps are:

- Fill the distillation unit through the normal flow route with raw material from the crude charge tank, as soon as purging and leak testing are finished.
- Establish a cold product circulation from the distillation unit to the crude charge tank, with all streams being returned into the crude charge tank.
- Bring the entire unit to the required operating conditions by putting the reboiler and condenser systems into service, while recirculating all products to the crude charge tank via coolers in the rundown lines, *until all products are running reasonably well on specification.*
- Start production by routing all products into storage instead of into the crude charge tank within a short period of time to avoid excessive changes in the composition of the crude charge tank.

In the first step, the initial process conditions are established with respect to the process inventory. In the second step, pumps, level and flow controllers are put into service (inventory control). In the third step, the unit is driven to the normal operating conditions, without being in a production state (simultaneous material and heat balance control). Once reaching these, the unit is put into a production state.

This policy can be used for many different types of reversible unit operations. Of course, the strategy should be adjusted for the particular unit characteristics, if necessary, however the basics *being inventory control followed by simultaneous material and heat balance control* will remain the same.

Two additional notes should be made on the startup of reversible unit operations. First, during a plant startup, operating personnel is often focused on getting the entire process into a production state. Nevertheless, it is profitable to put (some) additional time in running the particular process units strictly on the required operating targets before continuing with the operational integration with neighboring units. The time "spent" at this stage will be gained many times in the tail end of the startup operations. The impact of a process upset is limited for stand-alone operated units, and corrections can be made relatively easily, because there are no interactions with neighboring units. On the other hand, operational difficulties may arise when process upsets propagate through a number of process units, especially during startup operations when many process state variables are still far from their target values.

Secondly, there may be a restriction on holding a material for a prolonged period in the process, due to reactive chemicals hazards or (thermal) product degradation. Also, the introduction of polymer or solid materials is postponed in many cases, until the process is running reasonably well at the target conditions. Polymer and/or solids handling is often difficult, and the process conditions should be well under control before solids and polymers can be treated properly. This kind of consideration should be incorporated into a startup procedure, if necessary, by selecting the correct material composition targets for the intermediate operating states.

Startup of irreversible unit operations

Irreversible process units are started up by supplying the appropriate feed into the system, and by discharging almost simultaneously the effluent streams into the downstream process units. Process upsets will result when the downstream units cannot properly treat the effluent streams from the irreversible unit during this operating stage. These operational links complicate the startup of an irreversible process unit, which can be demonstrated by some studies available on the startup of tubular reactor systems.

The startup of a sulfuric acid plant should ideally be fast and clean. However, SO_2 emission levels to atmosphere during plant startup operations exceed often considerably the steady-state values, due to insufficient SO_2 conversion levels in the reactor system. Mann et al. (1979, 1980) developed a dynamic model of a SO_2 fixed-bed oxidation reactor to study the influence of some variables on SO_2 conversion rates during the startup, because almost all SO_2 present in the reactor effluent is ultimately vented to atmosphere. The generated startup policies were experimentally verified in a laboratory reactor (Mann et al., 1986). To mimic plant startup problems, the reactor system was maintained at ambient temperature. In a sequential step, the hot reactor feed was instantaneously switched from bypassing to flowing directly into the cold fixed-bed reactor. Significant differences are found on SO_2 emission levels as a function of the initial reactor temperature, the SO_2 concentration at the reactor inlet, and the total feed rate into the reactor.

Aelion and Powers (1991a,b) developed a computerized planning program for operating procedure synthesis, and demonstrated its purpose by analyzing a startup problem of a continuously-operated reactor. At normal operating conditions, two reactants are fed via a mixer into the reactor, and the reactor effluent is discharged into a separator. In the case study, the reactants are to be mixed within tight composition constraints. It is not possible to meet the composition goal by simply opening the respective control valves during the startup. The proposed startup policy is to feed both reactants into the mixer, while all material is recycled over the mixer and the separator until the material composition in the mixer reaches its target value. In a sequential step, the mixer effluent is switched from bypassing to flowing directly into the reactor.

There is a strong similarity between the startup strategies just described: *no stationary state is included in the startup strategy to control the initial reactor conditions.* Mann et al. (1979, 1980, 1986) switched the hot reactor feed instantaneously from bypassing to flowing directly into the cold fixed-bed reactor, without controlling the initial reactor temperature. The effect of thermal shocks in process equipment was neglected too. Also, Aelion and Powers (1991a,b) did not include a separate step in their sequence of consecutive actions to bring the values of the reactor state variables at certain predefined conditions before both reactants are fed into the reactor.

The importance of including an additional intermediate operating state, in order to control the initial reactor conditions, will be demonstrated by the startup of an industrial adiabatic tubular reactor. The presented experimental data were collected prior to the reactor startup described by Verwijs et al. (1992). The configuration of the process is in a simplified form shown in Figure 2. A detailed description of the reactor system, including a dynamic model, is presented in the above mentioned study.

In this reactor, product C is formed by an exothermal, liquid-phase reaction between reactants A and B. Reactant B should be converted totally in the reactor for process safety reasons. Experimental data of reactants A and B flows, and the reactor pressure, are shown in Figure 3 as a function of the dimensionless time σ. The data are expressed as a percentage of the range of the particular pressure and flow measurement devices. The time σ is scaled by taking the time origin ($\sigma = 0$) just before reactant B is added into the system. The time origin taken at this point conforms to the preceding study on reactor startup behavior (Verwijs et al., 1992). As a result of this choice, time σ appears to be negative in these figures. The dimensionless temperature θ over the entire reactor is shown in Figure 4. In this figure, the lines parallel to the σ axis represent the response of the individual thermoelements at the dimensionless location z, and the lines parallel to the z axis connect the data at the same moment. The z axis is scaled from $z = 0$ at the reactor inlet to $z = 1$ at the exit. Note that the σ axis is drawn from the right side to the left. The reactor is prepared for startup by filling the system via the normal flow route with a mixture of reactant A and product C. The material is heated up in the reactor preheater simultaneously. These operations are completed before the actual reactor startup. The temperature profile θ over the entire reactor length z at time $\sigma = -2.0$ results from these operations, as shown in Figure 4.

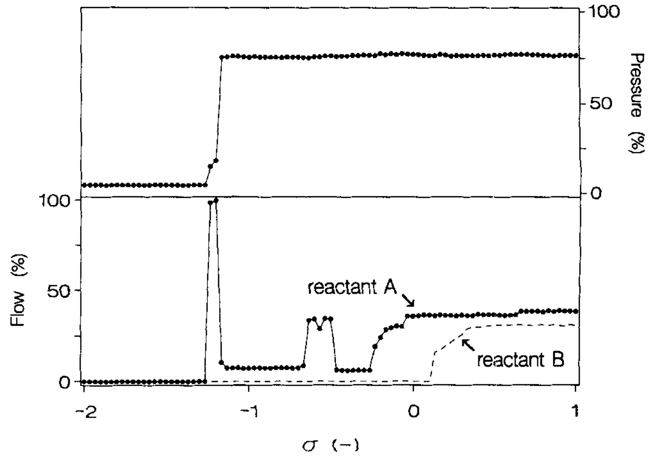

Figure 3. Observed reactor pressure and flow of reactants A and B as a function of time.

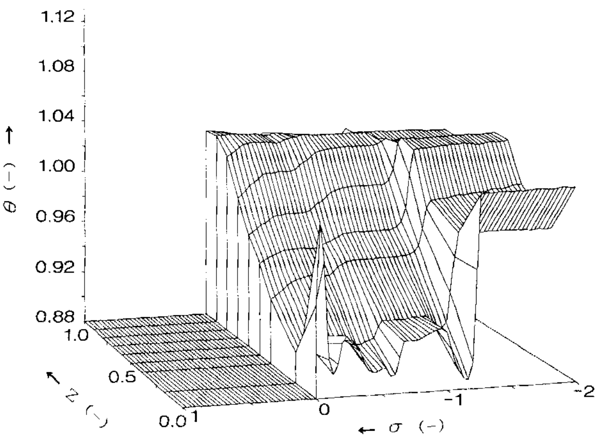

Figure 4. Observed reactor temperature vs. reactor location and time.

During the period $\sigma = -2.0$ until $\sigma = -1.27$, the reactor is waiting for the next operational action. At $\sigma = -1.27$, virginal reactant A is fed into the reactor. The system was not completely filled up with liquid at that time, and the reactant A flow was raised initially to maximum capacity until the reactor pressure reached the normal operating value. During the period $\sigma = -1.27$ until $\sigma = -0.14$, relatively cold material entered the reactor. At $\sigma = -0.14$, steam is fed into the feed preheater to control the reactor inlet temperature; $\sigma = 0.10$, the feed of reactant B is established into the reactor. All these process manipulations resulted in the initial temperature profile θ at $\sigma = 0$ shown in Figure 4. The reactor behavior from $\sigma = 0$ and onwards has been described by Verwijs et al. (1992). In reality, the reactant A recovery system is much more complex than shown in Figure 2, and highly heat integrated. When the reported reactor startup took place, no auxiliary systems were available to operate the recovery system before the reactor was started up. Hence, the reactor and recovery system were started up simultaneously.

The procedure followed was to feed reactant B into the reactor as soon as the reactant A flow rate and the reactor *inlet temperature* reached the required target values, as shown in Figures 3 and 4. However, Verwijs et al. (1992) showed that for an adiabatic tubular reactor a much higher *initial temperature along the reactor* is required during startup, compared to the reactor inlet temperature at normal steady-state conditions, to ensure a complete reactant B conversion at the reactor exit. By starting up according to the policy just described, the required *initial temperature profile* over the entire reactor is difficult to establish, because the total amount of reactant A fed into the system should be minimized since the recovery system is not able to process the reactor effluent properly at this operating stage! Consequently, the reactor startup criteria were defined on reactor inlet conditions, instead of on conditions for the entire reactor. As a result, the reactor operating constraints were exceeded in the reported startup (Verwijs et al., 1992).

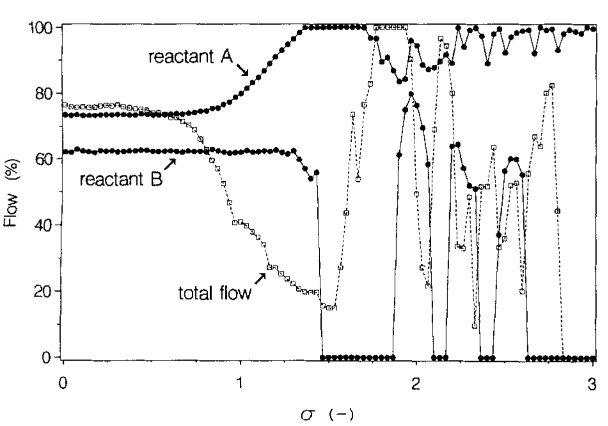

Figure 5. Observed reactants A and B, and total flow as a function of time during the temperature runaway.

Therefore, including an additional intermediate operating state is strongly needed to generate the required initial reactor conditions. Process material has to be recycled over the reactor to drive the system to the required initial temperature conditions. For the process in Figure 2, this can be done by recycling reactant A over the buffer tank, the mixer, the feed preheater, the reactor, and the recovery unit. Therefore, the recovery system has to be designed and operated in such a manner that it can process the reactor effluent during all phases of the startup operations. For a highly heat integrated process section, a possible startup strategy according this method will be described in a following section.

Based on the above mentioned arguments the following axiom can be formulated: *a continuously-operated reactor system should be included in a recycle loop, together with its feed system and downstream process section, for process conditioning purposes.* At reaching the required operating conditions, the reactor system can be put into the production state safely.

Shutdown of irreversible unit operations

As discussed above, intermediate stationary states are an important aspect of process safeguarding strategies, since process units can be put into these intermediate operating states in emergency or process wait situations. At these intermediate operating states production as such is stopped, but most of the process units remain (almost) at their normal operating conditions until production can be restarted. These intermediate operating states will help plant personnel to make decisions about operational interventions in case of significant deviations from the normal operating conditions. Data are presented of a temperature runaway in the same industrial adiabatic tubular reactor as described above, to emphasize the importance of a correct choice of these intermediate operating states. Experimental data of the reactant A, reactant B, and the total flow into the reactor are presented in Figure 5 as a function of the dimensionless time σ. The data are expressed as a percentage of the range of the individual flow measurement devices. The reactant B flow rate is controlled at a set point defined by a production capacity target. The reactant A flow is controlled in ratio with the actual flow of reactant B.

During freezing weather conditions, the heating of the reactant A flow device failed, resulting in an erroneous flow measurement. At about $\sigma = 0.45$, the reactant A flow indicator starts rising to the maximum range of the flow device, as shown in Figure 5. The ratio controller responded to this "increasing" flow signal by closing the reactant A flow control valve, which can be seen from the total flow data. As a result, the reactants were fed in a wrong ratio into the reactor. At time $\sigma = 1.45$, the process control computer stopped the reactant B feed to the reactor, due to a reactor inlet temperature problem.

At time $\sigma = 1.90$, 2.20, and 2.47, the operator tried to restart the reactant B feed pump to obtain again the normal production conditions, because he noted that the temperature in an aircooler of the recovery section dropped to the solidification temperature of the product. To avoid more serious process upsets in the recovery system, the decision was made to restart the reactant B feed pump. However, the feed pump was stopped every time by the process control system, due to pressure upsets in the reactor.

As a result of all flow manipulations just described, the reactor contained too much unconverted reactant B, which resulted in a temperature runaway. Fortunately, no damage resulted from this temperature excursion.

The dimensionless reactor temperature profile θ over the entire reactor length z as a function of time σ is shown in Figure 6. Note the temperature change in the center of the reactor, starting at about $\sigma = 0.75$. These kind of temperature excursions occur also during plant capacity and/or reactant-ratio changes, which complicates the design of a simple safeguarding system based on temperature measurements along the reactor. Note also that it takes about one time interval ($\Delta\sigma = 1$) after the flow device failure before the reactor temperature exceeds the normal maximum operating temperature. As a result, *process interlock systems based only on high reactor temperature values will not prevent against such a temperature excursion.*

Correct flow control of the reactants fed into the reactor is, of course, strongly needed to prevent such a runaway. However, the question of how to control the progression of the reaction taking place based on the temperature profile along the entire reactor length, also during flow rate and/or ratio changes, is not solved yet.

What went wrong beside the flow device failure? Basically, no correct "recovery state" was designed for this process. When the reactant B feed to the reactor was stopped, the downstream process section went also into shutdown. This would result in many other problems when the system was kept at shutdown conditions for a prolonged period, due to the outside weather conditions. From this point of view, the decision made by the operator to restart the reactant B feed pump was correct. Principally, the failure was in the process structure and operating strategy, because in the design phase no intermediate operating state was included to run the recovery section when the reactor is fed with reactant A only.

Therefore, the same conclusion holds for the reactor shutdown as for the startup procedure: a continuously-operated reactor system should be included in a recycle loop, together with its feed system and downstream process section, to bring/maintain the entire process system at predefined, intermediate operating conditions during startup, process wait, or emergency shutdown operations.

Industrial Example

The high heat integrated process section in Figure 7 will be used to demonstrate the derived heuristics for the startup of a continuously-operated, industrial reactor system. The process and control strategy design of this system has been reported by Bouwens and Kösters (1992).

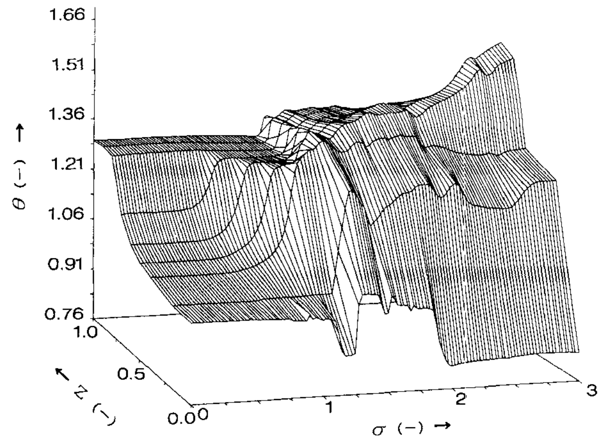

Figure 6. Observed reactor temperature vs. reactor location and time during the temperature runaway.

In this process, the products, indicated by C, yield from an exothermal catalytic reaction between reactant A and B:

$$A + B \rightarrow C$$

Reactant A is fed in excess, because reactant B should be almost totally converted at the reactor exit.

The process consists of a multifunctional heater H-1, a re-

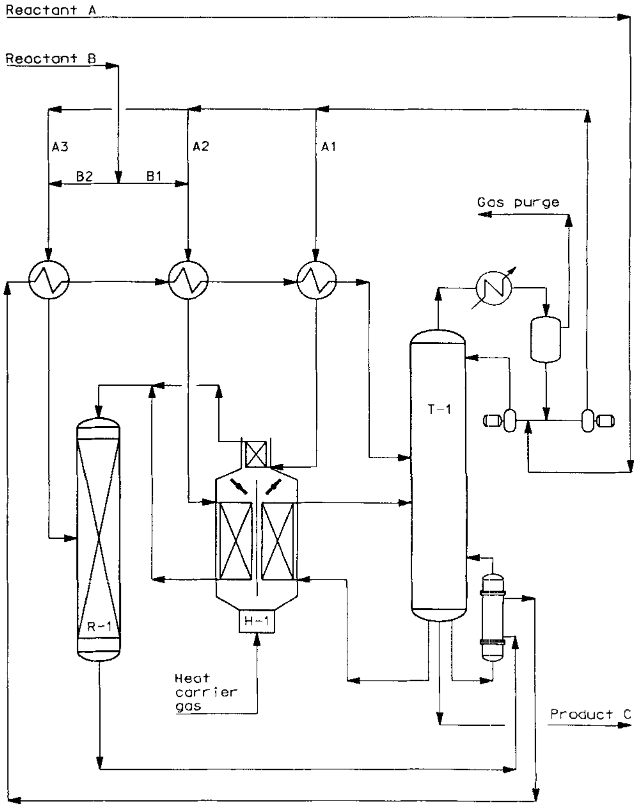

Figure 7. High-heat-integrated process section.

actor R-1, a reactor feed/effluent heat exchanger network, and a distillation column T-1. The heat exchanger network in Figure 7 is denoted in a simplified form. The reactant B feed is divided into the streams B1 and B2. The distillate flow from column T-1, being the reactant A feed into reactor R-1, is divided into the streams A1, A2 and A3. Stream A1 is evaporated in the heat exchanger network and superheated in heater H-1. Stream A2 is mixed with stream B1, evaporated in the heat exchanger network, superheated in heater H-1, mixed with stream A1, and fed into reactor R-1. Stream A3 is mixed with stream B2, evaporated and superheated in the heat exchanger network, and fed into reactor R-1 as a second feed. The reactor effluent exchanges heat in the reboiler of column T-1 and subsequently in the heat exchanger network. Finally, this stream is fed into column T-1 and separated into bottom product C and distillate product A.

Reactant A is supplied into the process via the suction line of the reflux pump of column T-1. Heater H-1 operates also as a second reboiler of column T-1. Inert gases can be removed from the process via a purge system on the reflux drum of column T-1.

Process decomposition

The catalyst in reactor R-1 deactivates during run time, and can be regenerated, off-line, via the system shown in Figure 8. To regenerate the catalyst, a gas is recycled over the reactor by a compressor. The system is heated up to the required catalyst regeneration temperature by heater H-1. This additional heat exchange section for regeneration purposes is eliminated from the process diagram in Figure 7. The reactor effluent is cooled, and liquid is knocked out in a flash drum. The liquid and noncondensable gases are purged from the system.

Due to this catalyst regeneration facility, the entire process section can be divided into two subsystems for startup purposes: (a) the reactor R-1 lined up to the regeneration system, and (b) the subsystem which consists of column T-1, heater H-1 and the heat exchanger network.

Reactor R-1 is an irreversible operation at normal operating conditions, which is not the case when the reactor is lined up to the regeneration system for startup purposes. The entire reactor can be driven to a target temperature by recycling an inert gas over the recovery system. The required heat can be supplied via heater H-1. A stationary state can be maintained by simultaneous inverse operations with respect to thermal energy, those operations being the heater H-1 and the cooler in the regeneration system, until the reactor can be operationally integrated with the column T-1 subsystem.

The column T-1 subsystem consists of reversible unit operations. An intermediate stationary state can be maintained by simultaneous inverse operations with respect to thermal energy, those being the heater H-1 and the overhead condenser of column T-1, until the reactor R-1 is operationally integrated and production is started by supplying reactant B into the process.

Choice of convenient startup criteria

Now we have to focus on the choice of convenient operating criteria to demonstrate some aspects of startup operations with respect to material composition control. Since the system in Figure 7 is part of a commercial process, the safety and controllability aspects are beyond the scope of this article to avoid revealing confidential information.

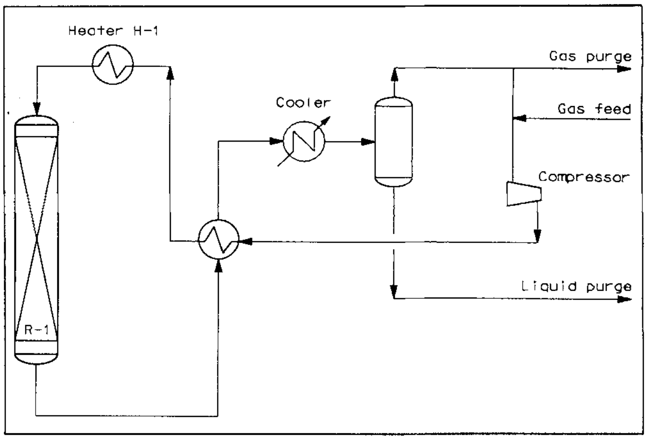

Figure 8. Catalyst regeneration system.

At normal operating conditions column T-1 contains reactant A and product C, the reflux drum contains reactant A, the heat exchanger network contains reactant A and B at the reactor feed side, and reactant A and product C at the reactor effluent side.

It is not allowed to feed any liquid into reactor R-1 for process safety reasons. Hence, reactor R-1 is bypassed until the feed flows to reactor R-1 are completely vaporized, and the entire reactor is above a minimum temperature limit to avoid condensation of the feed in the catalyst bed. The heat exchangers are filled initially with liquid only, resulting in an excess amount of material in the system at reaching the required operating conditions, due to the liquid to vapor phase transition. This excess amount of material has to be removed from the system. Additionally, the reactant A feed composition to the reactor is critical for a proper reactor operation.

To avoid reactor feed composition upsets during the startup operations, and to bypass a purification step for the material discharged from the process, virginal reactant A is used to drive the reactor to its startup conditions. At reaching these, product C is fed into column T-1 to bring this column at production state conditions. Reactant B will be fed into the plant as the final operational action of the startup, since production is started at that moment.

Startup strategy

The various aspects of the derived heuristics can be identified easily in the following steps of the startup strategy:

- Inert gases, originating from purging and leak testing operations, have to be removed from the system. Therefore, the vent-gas treating system, not shown in Figure 7, is started up before any material is charged into the system. Also, the coolant flow to the overhead condenser of column T-1 is established to avoid excessive venting of process material during filling operations.
- Reactant A is charged into the reflux drum of column T-1 via the normal flow route. The reflux pump is started up, and also the column T-1 sump is filled up with reactant A. When a sufficient amount of material is charged into the sys-

tem, the supply is stopped, and reactant A is recycled over column T-1 by the reflux pump. A startup line is installed for this purpose in between the product C discharge line of column T-1 and the suction line of the reflux pump. This startup line is not shown in Figure 7. In a later stage, when material is recycled over the cold heat exchanger network, an insufficient amount of material is initially boiled up to keep the reflux pump running. By installing this startup line, a cold material recycle can be generated over the system, and thermal shocks are avoided in a subsequent step when the heat carrier gas is supplied to heater H-1.

- The distillate pump of column T-1 is started up, and reactant A is recycled over the heat exchanger network, while reactor R-1 is bypassed. The inert gases present in the heat exchangers can be purged via the vent system on the reflux drum.
- At this stage, the column T-1 subsystem is running at total recycle conditions without any heat supplied into the system. Before the heat carrier gas is supplied to heater H-1, the compressor and coolers in the reactor R-1 subsystem in Figure 8 should be first put into service. This subsystem should be operated at total recycle conditions also, without any heat supplied into the system. An inert gas will be used for this operation.
- The heat carrier gas is supplied to heater H-1 to drive the temperature in both subsystems to the required target values.
- The startup line from the column T-1 bottom to the suction line of the reflux pump is closed when a sufficient amount of reactant A is evaporated in the reboilers, and the excess amount of reactant A is discharged from the system.
- Upon reaching the required operating conditions, both subsystems can be integrated operationally. The reactor R-1 is isolated from the regeneration system, and lined up as under normal operating conditions. The reactor bypass lines are closed, and the inert gas present in the reactor is removed from the system. *The reactor is driven to the required initial temperature conditions by recycling reactant A over the system. At this initial temperature level, a complete conversion of reactant B is warranted during the reactor startup.*
- Product C is supplied into column T-1, via a startup line (not shown in Figure 7), to bring the column to production state conditions. At reaching these, reactant B can be fed into the system. Production is started, and the process can be ramped up to the required production capacity.

It should be noted that, despite the high heat integration, the system can be started up without the use of startup heaters. Subsequently, it should be stressed that the whole process, excluding the reactor, is running at production state conditions before reactant B is fed into the process. The heat of reaction is not available at these intermediate operating conditions; therefore, the process heater H-1 is designed for these startup conditions!

If production should be interrupted, the system can be put into a process wait step by stopping the reactant A and B feed. The system can be kept at production state conditions by recycling reactant A over the system. In case reactant A recycle cannot be maintained, the content of the entire system is discharged into storage. The system is recharged with virginal reactant A, as soon as possible, and the system is started up again according to the procedure described above.

Conclusions

Some rules are presented for the startup of industrial adiabatic tubular reactor systems, based on a qualitative analysis of the dynamic behavior of continuously-operated vapor and liquid-phase processes. The rules can be extended potentially to polymer and solids processing units.

First, the relationships between the process dynamics, operating criteria, and the operating constraints are investigated, because reactor startup cannot be studied effectively without taking into account the operational aspects of the entire plant section which includes the reactor. Dynamic process operations should adhere to the process controllability constraints, and preferably also to the process performance constraints, to ensure fast and safe startup operations. It is shown that composition control of the process material is critical in order to speed up plant startup operations, and to minimize the amount of offgrade materials.

Secondly, the initial reactor conditions at which the system can be put into a production state are normally critical for a successful startup. Therefore, a plant should have an operating mode at which the reactor can be included in a recycle loop, together with its feed system and downstream process section, for process conditioning purposes. At this intermediate operating stage, the entire process system can be driven to the required operating conditions to start production safely. Also, the process can be put into this intermediate operating state in emergency or process wait situations. The correct choice of intermediate operating states or process wait steps is becoming more and more important in the startup strategy of modern chemical plants, due to the increasing degree of process integration and automation. It will help plant personnel to make decisions about operational interventions in case of significant deviations from the normal operating conditions. In practice, when operator interventions have a massive impact on the entire plant operation, the decision to stop some unit operations is delayed naturally. Ultimately, this may lead to more critical circumstances. Experimental data of an adiabatic tubular reactor startup, and of a thermal runaway in the same system, are used to demonstrate some operational problems which arise when such intermediate operating stages are missing.

Finally, the derived rules are applied to an industrial, highly heat-integrated reactor section, and the resulting startup strategy is summarized in an elementary step diagram to picture the subsequent intermediate operating stages.

Notation

L = reactor length, m
t = time, s
T = fluid temperature, K
T_r = reference temperature, K
v_r = reference fluid velocity, m/s
x = length coordinate in direction of flow, m
z = $\{x/L\}$; dimensionless reactor length

Greek letters

θ = $\{T/T_r\}$; dimensionless fluid temperature
σ = $\{v_r t/L\}$; dimensionless time

Literature Cited

Amundson, N. R., et al., *Frontiers in Chemical Engineering: Research Needs and Opportunities*, National Academy Press, Washington, DC (1988).

Aelion, V., and G. J. Powers, "A Unified Strategy for the Retrofit Synthesis of Flowsheet Structures for Attaining or Improving Operating Procedures," *Comput. Chem. Eng.*, **15**, 349 (1991a).

Aelion, V., and G. J. Powers, "Synthesis and Evaluation of Operating Procedures and Flowsheet Structures," Paper 143h, AIChE Meeting, St. Louis, MO (Nov. 17-22, 1991b)

Aelion, V. J., Kalagnanam, and G. J. Powers, "Evaluation of Stationary State Stability for the Synthesis of Operating Procedures," Technical Report EDRC-06-112-91, Engineering Design Research Center, Carnegie Mellon Univ., Pittsburgh, PA (1991c).

Bouwens, S. M. A. M., and P. H. Kösters, "Simultaneous Process and System Control Design: An Actual Industrial Case," *Interactions between Process Design and Process Control*, J. D. Perkins, ed., IFAC Workshop, London, p. 75 (1992).

Denn, M. M., and R. Lavie, "Dynamics of Plants with Recycle," *Chem. Eng. J.*, **24**, 55 (1982).

Fusillo, R. H., and G. J. Powers, "A Synthesis Method for Chemical Plant Operating Procedures," *Comput. Chem. Eng.*, **11**, 369 (1987).

Fusillo, R. H., and G. J. Powers, "Operating Procedures Synthesis using Local Models and Distributed Goals," *Comput. Chem. Eng.*, **12**, 1023 (1988).

Kapoor, N., T. J. McAvoy, and T. E. Marlin, "Effect of Recycle Structure on Distillation Tower Time Constants," *AIChE J.*, **32**, 411 (1986).

Lakshmanan, R., and G. Stephanopoulos, "Synthesis of Operating Procedures for Complete Chemical Plants: 1. Hierarchical Structures Modelling for Nonlinear Planning," *Comput. Chem. Eng.*, **12**, 985 (1988a).

Lakshmanan, R., and G. Stephanopoulos, "Synthesis of Operating Procedures for Complete Chemical Plants: 2. A Nonlinear Planning Methodology," *Comput. Chem. Eng.*, **12**, 1003 (1988b).

Lakshmanan, R., and G. Stephanopoulos, "Synthesis of Operating Procedures for Complete Chemical Plants: 3. Planning in the Presence of Qualitative Mixing Constraints," *Comput. Chem. Eng.*, **14**, 301 (1990).

Lees, F. P., *Loss Prevention in the Process Industries*, Vol. 1, Butterworth-Heinemann, Oxford (1991).

Luyben, W. L., "Design and Control of Recycle Processes in Ternary Systems with Consecutive Reactions," *Interactions between Process Design and Process Control*, J. D. Perkins, ed., IFAC Workshop, London, p. 65 (1992).

Mann, R., I. J. Gardner, and C. Morris, "Sulphur Dioxide Emissions during Start-up of a Contact Sulfuric Acid Plant," *I. Chem. E., Symp. Ser.*, **57**, L1 (1979).

Mann, R., I. J. Gardner, and C. Morris, "Reactor Dynamics and Strategies for Minimizing SO_2 Emissions during Start-up of a Contact Sulfuric Acid Plant," *Chem. Eng. Sci.*, **35**, 185 (1980).

Mann, R., E. Stavridis, and K. Djamarani, "Experimental Fixed-Bed Reactor Dynamics for SO_2 Oxidation," *Chem. Eng. Res. Dev.*, **64**, 248 (1986).

Roy, R. K., *A Primer on the Taguchi Method*, Van Nostrand Reinhold, New York (1990).

Saraiva, P. M., and G. Stephanopoulos, "Continuous Process Improvement through Inductive and Analogical Learning," *AIChE J.*, **38**, 161 (1992).

Severa, J. E., "Plant Start-up Problems: Start-up of a Crude/Vacuum Distillation Unit," *Chem. Eng. Prog.*, **69**(8), 85 (1973).

Slijk, A. N., "Application of DDC Control in a Polyol Plant," *J. A*, **26**, 133 (1985).

Stephanopoulos, G., "The Scope of Artificial Intelligence in Plantwide Operations," *Foundations of Computer-Aided Process Operations*, G. V. Reklaitis and D. Spriggs, eds., CACHE-Elsevier, Austin, TX (1988).

Verwijs, J. W., H. van den Berg, and K. R. Westerterp, "Startup of an Industrial Adiabatic Tubular Reactor," *AIChE J.*, **38**, 1871 (1992).

Villermaux, J., "Future Challenges for Basic Research in Chemical Engineering," *Proc. Fourth World Congress of Chem. Eng.*, Karlsruhe, Germany, p. 77 (1991).

Westerberg, A. W., "An Overview of Process Integration Methodologies," Technical Report EDRC, Engineering Design Research Center, Carnegie Mellon Univ. (1992).

Westerterp, K. R., K. J. Ptasinsky, and R. R. M. Overtoom, "Safe Design of Cooled Tubular Reactors for Exothermic, Multiple First Order Reactions," *ACS. Symp. Ser.*, **237**, pp. 323-335 (1984).

Westerterp, K. R., and K. J. Ptasinsky, "Safe Design of Cooled Tubular Reactors for Exothermic, Multiple Reactions; Parallel Reactions: 1. Development of Criteria," *Chem. Eng. Sci.*, **39**, 235 (1984).

Westerterp, K. R., and R. R. M. Overtoom, "Safe Design of Cooled Tubular Reactors for Exothermic, Multiple Reactions; Consecutive Reactions," *Chem. Eng. Sci.*, **40**, 155 (1985).

Westerink, E. J., and K. R. Westerterp, "Safe Design of Cooled Tubular Reactors for Exothermic, Multiple Reactions; Multiple Reaction Networks," *Chem. Eng. Sci.*, **43**, 1051 (1988).

Westerterp, K. R., "Multi-functional Reactors," *Chem. Eng. Sci.*, **47**, 2195 (1992).

Wolff, E. A., S. Skogestad, and M. Hovd, "Controllability of Integrated Plants," Paper 67a, AIChE Meeting, New Orleans (1992).

Manuscript received July 3, 1993, and revision received Jan. 3, 1994.