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Selectivity Versus Conversion and Optimal Operating Policies for Plants with Recycle

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A simple and fast procedure is developed for determining optimal steady state operating policies for chemical plants with recycle. This article improves upon the previous findings by Griffin et al. (Ind Eng Chem Res. 2006;45:8056-8062) and now provides a more general classification procedure for process chemistries that have reversible reactions or reactions of unequal overall order or both. Selectivity vs. conversion relationships are indirectly determined herein, requiring only the reaction orders of reaction species. The effect of these relationships allows process chemistries to be classified into two equivalence classes: bounded and nonbounded. This classification has important implications for the optimal operation and plantwide control structure of a flexible plant with spare equipment capacity. For instance, using the classification procedure and decision tree developed in this article, it can be determined quickly whether or not it is economically optimal to operate the reactor at the holdup constraint under all operating conditions (bounded) or away from the constraint with a variable holdup operating policy (nonbounded). © 2008 American Institute of Chemical Engineers *AIChE J,* 54: 2597–2609, 2008

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Introduction

A process chemistry is a set of chemical reactions that link reactant species that undergo transformation to product species in a plant reactor. One key way to characterize a process chemistry is by the way in which the selectivity to each product and byproduct changes as a function of reactant conversion. It is well known that the selectivity vs. conversion relationships can provide a basis for selecting a reactor network that is optimal for a particular process chemistry.[1–4] However, it is not well known that, once the reactor has been selected, designed, and built, these relationships can also determine the optimal reactor operating policy. Generally, a reactor is intentionally designed to include additional capacity to provide sufficient process flexibility and operability in handling routine disturbances, production rate changes, and the like.[5–7] This article develops a formal methodology that allows the effect of selectivity vs. conversion relationships on process operation to be evaluated rigorously, yet indirectly, using a profit function that captures the intrinsic tradeoffs. The main result is how this new methodology can then be used to determine the optimal operating policy of a reactor that possesses such additional capacity.

Optimal utilization of additional equipment capacity is an ongoing issue in the area of plantwide operation. The reactor/separator/recycle (RSR) process shown in Figure 1 is a widely studied system that can represent many industrial processes, including the case study that accompanies this article. Several researchers have investigated this process to determine optimal operating policies; even for the case of a single unimolecular reaction, A → B, varying results have been reported for the suggested operation of the reactor and separation system.[8–12] More recently, Ward et al.[13] investigated general process chemistries with a single undesired reaction to determine how the selectivity vs. conversion relationship affects optimal operating policies.

Additional Supporting Information may be found in the online version of this article.

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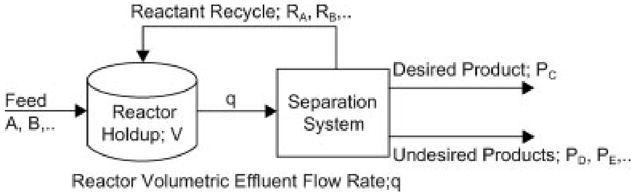

Figure 1. Reactor/separator/recycle structure.

Ward et al. provide a methodology and heuristics that can be used to classify a process chemistry into two equivalence classes based solely on the reaction kinetics. The two classes have been labeled "bounded," where the optimal policy is to operate the reactor completely full at all times, and "nonbounded," which requires a variable reactor holdup operating policy. The heuristics developed by Ward et al.[13] are valid for irreversible process chemistries that have a single undesired reaction, and they are exact when the side reaction has the same overall forward reaction order as the main reaction. This work was recently extended by Griffin et al.[14] to include irreversible process chemistries with multiple undesired reactions, all of equal overall order.

The current work covers much broader and more general cases of process chemistries that include reversible reactions and reactions of unequal overall order. Knowing only the process chemistry, stoichiometry, and the reaction order of all reactant species, process chemistries can be classified as bounded or nonbounded; this classification provides insight into potential plantwide control structures.

Methodology for System Analysis

The current work applies to the generalized RSR process depicted in Figure 1, incorporating various process chemistries. The optimal operating policy for the case of competing reactions depends on the kinetics of the coupled reactions and the selectivity vs. conversion relationships. By inspecting and comparing the overall forward reaction order and the stoichiometric coefficients of every reactant in each reaction, one can quickly and easily obtain insight into the optimal steady-state operation of the entire chemical plant. In this methodology, selectivity-conversion relationships are indirectly determined by evaluating how byproduct formation changes with reactant recycle flow rate which is a surrogate for reactant conversion.

Figure 1 represents a reactor/separation network consisting of a single liquid-phase, isothermal, perfectly mixed reactor. Molar flow rates of products are denoted as P; recycle streams are denoted as R, where any unreacted reactant is separated and recycled back to the reactor. The separation system is not specified, but it is assumed that any desired separation of the reactants and products can be achieved (e.g., by distillation, crystallization, membranes, pressure swing adsorption, etc.). It is assumed that all chemistries involve a single desired product (C) with a fixed desired production rate, P_C.

A degrees of freedom analysis is an important first step in the optimal design of a chemical plant. Conventionally, variables such as the molar ratio of reactants at the reactor inlet or the conversion of limiting reactant are chosen as design variables. The analysis developed by Ward et al. deviates from this conventional procedure, taking recycle flow rates as design degrees of freedom.[13] With the production rate of the desired product fixed, the reactor temperature fixed (isothermal operation), and the reactor holdup allowed to vary, the remaining operating degrees of freedom are simply the recycle stream flow rates. This approach allows for a much easier formalization of the optimization problem when determining an optimal operating policy. Choosing the recycle stream flow rates as design and operating degrees of freedom, not only allows all degrees of freedom to be specified rigorously, but also provides a clear connection between the optimal design and optimal operation of a plant.

Derivation of process unknowns

As discussed by Ward et al.[13] and Griffin et al.,[14] optimal operating policies can be classified based on the kinetics of the process chemistry. All reactions are assumed homogenous and to have elementary kinetic rate expressions (the latter assumption is easy to relax). Elementary reactions occur when the reaction order of a reactant species is equal to its stoichiometric coefficient and the overall reaction order is equal to the molecularity of the reaction. Consider the following illustrative system of irreversible reactions with N reactant species, a single desired product C, and N_R undesired reactions, where the jth side reaction shown produces one or more undesired byproducts, here collectively denoted as D_j. (For convenience and simplicity, no undesired byproducts, D_j, appear as reactant species in subsequent reactions. This is covered in the section *Extensions to the Methodology*.) Note in this formulation, the stoichiometric coefficients in the desired and undesired reactions are always greater than or equal to zero; $\alpha_i, \alpha_{ij} \geq 0$.

$$\alpha_1 A_1 + \alpha_2 A_2 + \cdots + \alpha_N A_N + \alpha_C C \xrightarrow{k_0} C \quad r_0 = k_0 [C]^{\alpha_C} \prod_{i=1}^{N} [A_i]^{\alpha_i}$$
$$\alpha_{1j} A_1 + \alpha_{2j} A_2 + \cdots + \alpha_{Nj} A_N + \alpha_{Cj}\, C \xrightarrow{k_j} D_j \quad r_j = k_j [C]^{\alpha_{Cj}} \prod_{i=1}^{N} [A_i]^{\alpha_{ij}} \tag{1}$$

The product species C appears on the left-hand side of the desired reaction to represent autocatalytic reactions, but it should not be considered as a reactant species that is to be recycled. Undesired products can also be produced in the main reaction at a fixed production rate that is related to P_C by a ratio of stoichiometric coefficients (not shown).

There are N reactant species, and assuming there is one recycle stream per reactant, there will be N available degrees of freedom. For a fixed production rate P_C, the critical unknowns (dependent variables) for this system are the production rate of each jth byproduct, P_{Dj}, and the required reactor volume V. To formulate the optimization problem, the unknowns, P_{Dj} and V, must be expressed in terms of the degrees of freedom. The form of the byproduct production term P_{Dj} determines the conversion vs. selectivity relationship, and the reactor volume term V imposes a physical constraint on operation of the plant; dimensionless forms of these unknowns are derived in the Appendix with the general form of P'_{Dj} shown in Eq. 2 for the chemistry specified in Eq. 1.

$$P'_{\mathrm{D}j} \approx k'_j \frac{\left(1 + \sum_{i=1}^{N} R'_i v'_i\right)^{\left(\alpha^T - \alpha_j^T\right)}}{\prod_{i=1}^{N} R_i'^{\left(\alpha - \alpha_{ij}\right)}} \tag{2}$$

where $\alpha^T = \alpha_{\mathrm{C}} + \sum_{i=1}^{N} \alpha_i$ and $\alpha_j^T = \alpha_{\mathrm{C}j} + \sum_{i=1}^{N} \alpha_{ij}$.

Process economics and optimization

The objective is to minimize the steady-state operating costs of a plant that has been built with additional capacity. The main factors that affect the plant economics in terms of operating costs are selectivity losses from the production of undesired byproduct and the operating costs associated with separating and recycling the unreacted reactants. The following economic cost model for a reaction system with N degrees of freedom is chosen as the objective function to determine optimal values of the recycle flow rates that minimize the operating costs.

$$C = C_{\mathrm{C}} P_{\mathrm{C}} + \sum_{j=1}^{N_{\mathrm{R}}} C_{\mathrm{D}j} P_{\mathrm{D}j} + \sum_{i=1}^{N} C_{Ri} R_i. \tag{3}$$

C is the cost of operating the plant which is to be minimized; C_{C} is the revenue from producing one mole of desired product (negative in this formulation because the costs associated with byproduct production and separation costs are positive); C_{D} is the cost of producing one mole of undesired byproduct including the raw material costs and separation costs; C_{R} is the cost of separating and recycling one mole of reactant species. For ease of presentation, it is assumed that the cost for producing one mole of byproduct is the same for all byproducts produced ($C_{\mathrm{D}j} \rightarrow C_{\mathrm{D}}\ \forall j$), and that the cost of separating and recycling one mole of reactant is the same for all reactants, ($C_{Ri} \rightarrow C_R\ \forall i$). The desired production rate, P_{C}, is fixed as are the cost penalties C_{R} and C_{D}. The cost objective is made dimensionless by dividing by $P_{\mathrm{C}}C_{\mathrm{R}}$. The term $C'_{\mathrm{C}} = C_{\mathrm{C}}/C_{\mathrm{R}}$ is a constant and is subtracted from the cost objective, because it does not change the location of the minimum cost, and only its magnitude. Thus, the dimensionless cost objective function is defined as

$$C' = \frac{C}{P_{\mathrm{C}} C_{\mathrm{R}}} - C'_{\mathrm{C}} = C'_{\mathrm{D}} \sum_{j=1}^{N_{\mathrm{R}}} P'_{\mathrm{D}j} + \sum_{i=1}^{N} R'_i \tag{4}$$

This cost function is minimized (to maximize profit) subject to the reactor volume constraint, $V'_{\max}$, and recycle flow constraints in order to find the economically optimal operating point. The term C'_{D} is the dimensionless cost i.e., ratio of the cost of producing one mole of undesired byproduct to the cost of separating and recycling one mole of reactant species; C'_{D} is normally on the order of 100. The objective function in Eq. 4 and corresponding optimization problem is nonlinear because of the nonlinear relationship between P'_{Dj} and R'_i given in Eq. 2.

Bounded and Nonbounded Chemistries and Species

Irreversible process chemistries can be classified based on their optimal operating policy as bounded or nonbounded by the methodology developed by Ward et al.[13] The optimal operating policy of a bounded chemistry is to operate the reactor at the holdup constraint no matter what the production rate was, whereas with a nonbounded chemistry, the optimal reactor holdup will vary with production rate changes. To classify the overall process chemistry, each reactant species must also be classified as bounded or nonbounded. Definitions of bounded and nonbounded reactant species and chemistries and the corresponding rules on how to classify them have been presented by Griffin et al.[14] and are summarized in this section. The numbering and order of the following rules and definitions have been retained from the original article for consistency of presentation.

The current methodology distinguishes between process chemistries of parallel, series, or series/parallel reactions that can have equal or unequal overall reaction order. The case of all parallel reactions of equal overall order is a special case that is discussed in the *Parallel Reactions of Equal Overall Order* section and is covered by Rule 1 taken from Griffin et al.[14]

Rule 1: If all undesired reactions are in parallel with the main reaction and have the same overall reaction order as the main reaction, then the overall process chemistry is bounded.

If a process chemistry has reactions in series or parallel/series or has reactions of unequal order, then the following definitions and Rules (2–5) can be applied to determine if a species is bounded or nonbounded.

Definition 1: A bounded species is a reactant species for which increasing conversion of that species decreases the total operating costs of the entire process.

Definition 2: Nonbounded reactant species are all other reactant species that do not follow Definition 1.

The operating costs referred to in Definition 1 are selectivity losses and separation costs as discussed in the *Process Economics and Optimization* section. Increasing the conversion of a bounded species will lower byproduct formation and separation costs simultaneously, which is the objective of the economic optimization. Increasing the conversion of a nonbounded species results in a tradeoff between selectivity losses and separation costs, thus leading to an operating policy that generally does not maximize reactant conversion. The following rules are used to classify reactant species following Definitions 1 and 2 and are the basis for the procedure developed herein.

Rule 2: A bounded species is a reactant species for which the selectivity to *all* undesired byproducts either decreases with or is unaffected by increasing conversion of that species.

Rule 3: A nonbounded species is a reactant species for which the selectivity to *any* undesired product increases with increasing conversion of that reactant species.

For a chemistry with a bounded species, reactant conversion and optimal operation are bounded by the reactor holdup leading to an operating policy that maintains the reactor at its maximum holdup at all times. A nonbounded chemistry has a variable reactor holdup policy because of the inherent tradeoff between selectivity and conversion, and so the optimal operating point can change with throughput changes and generally needs to be calculated continuously. Therefore, a reactant species can be classified by determining the selectivity vs. conversion relationship and then the following rules are used to classify the overall process chemistry.

Rule 4: A single-bounded reactant species makes the overall chemistry bounded.

Rule 5: If there are no bounded species (i.e., all reactant species are nonbounded), the overall chemistry is nonbounded.

Reactant Species Classification Procedure

To classify a process chemistry that does not have all parallel reactions of equal overall order, each reactant species must first be classified as bounded or nonbounded by its selectivity vs. conversion relationships to the undesired byproduct(s). Increasing reactant conversion corresponds to decreasing reactant recycle flow rate (and vice versa), and so the two variables are used interchangeably here. The expression for the byproduct formation in Eq. 2 can be shown to be increasing or decreasing with increasing R'_i by a first partial derivative test in which the remaining degrees of freedom, $R'_k,\ldots,R'_N$ $k \neq i$, are held constant.

To determine the classification of a reactant species, the conversion vs. selectivity relationship must be tested for each undesired reaction. Figure 2 shows several possible forms of $P'_{Dj}(R'_i)$, these plots are effectively selectivity-conversion relationships. If it can be shown that, for any reactant species i, $\frac{\partial P'_{\mathrm{D}j}}{\partial R'_i} \geqslant 0$ for *all* values of *all* recycle flow rates in the feasible operating region (Figures 2a, b) for *all* N_R side reactions, then the selectivity to all undesired products either decreases or is unaffected by increasing conversion (or decreasing recycle flow rate) of species i; thus, species i is classified as bounded by Rule 2. On the other hand, if $\frac{\partial P'_{\mathrm{D}j}}{\partial R'_i} < 0$ over *any* range of feasible operating conditions (Figures 2c–e) for *any* recycle flow rate in *any* side reaction, then species i is classified as nonbounded by Rule 3. The form of the byproduct formation rate given in Eq. 2 and its first derivative are dependent on the magnitude of the exponents in the numerator, $n_j = (\alpha^T - \alpha_j^T)$, and in the denominator, $(\alpha_i - \alpha_{ij})$. Let $n_j = (\alpha^T - \alpha_j^T)$ and $m_j = (\alpha_i - \alpha_{ij})$ so that Eq. 2 can be expressed as

$$P'_{\mathrm{D}j} = k'_j \frac{\left(1 + \sum\limits_{i=1}^{N} R'_i v'_i\right)^{n_j}}{\prod\limits_{i=1}^{N} R'^{m_j}_i} \tag{5}$$

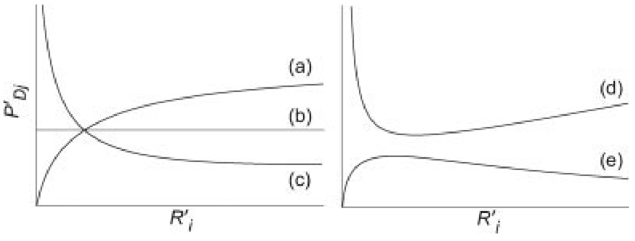

Figure 2. General forms of $P'_{\mathrm{D}j}(R'_i)$, where $P'_{\mathrm{D}j}$ (a) always increases with increasing R'_i (b) is unaffected by increasing R'_i, (c) always decreases with increasing R'_i, (d) first decreases and then increases with increasing R'_i, or (e) first increases and then decreases with increasing R'_i.

Taking the first derivative of Eq. 5 with respect to R'_i yields

$$\frac{\partial P'_{\mathrm{D}j}}{\partial R'_i} = \frac{n_j v'_i k'_j \left(1 + \sum\limits_{i=1}^{N} R'_i v'_i\right)^{n_j - 1}}{\prod\limits_{i=1}^{N} R'^{m_j}_i} - \frac{m_j k'_j \left(1 + \sum\limits_{i=1}^{N} R'_i v'_i\right)^{n_j}}{R'_i \prod\limits_{i=1}^{N} R'^{m_j}_i} \tag{6}$$

Equation 6 can be simplified to the following expression to determine conditions for which $\frac{\partial P'_{\mathrm{D}j}}{\partial R'_i} \geqslant 0$ for all feasible values of all R'_i to determine whether species i is bounded with respect to the jth undesired reaction.

$$(m_j - n_j) R'_i v'_i + m_j \left(1 + \sum_{\substack{k=1 \\ k \neq i}}^{N} R'_k v'_k\right) \leqslant 0 \tag{7}$$

When this condition is satisfied, the selectivity to the undesired product(s) produced in the jth side reaction always decreases or is unaffected by decreasing R'_i, thereby classifying species i as bounded with respect to the jth undesired reaction; if this condition is true for all undesired reactions, then species i is bounded.

The form of the expression given in Eq. 7 depends on the magnitudes of the exponents in Eq. 5, denoted as n_j and m_j. The following sections exhaustively investigate the three possible cases: when the main reaction has higher, equal, or lower overall reaction order than the jth undesired reaction; these cases correspond to $n_j > 0$, $n_j = 0$, and $n_j < 0$, respectively.

Higher overall order ($\mathbf{n_j = \alpha^T - \alpha_j^T > 0}$)

When the main reaction has higher overall order, $n_j > 0$, than the jth undesired reaction in question, the test condition in Eq. 7 now depends only on the sign of m_j, i.e. the difference in reaction orders of species i between the main reaction and the jth undesired reaction. There are three cases: when the reaction order of species i in the main reaction is higher than, equal to, or lower than the reaction order in the jth undesired reaction corresponding to $m_j > 0$, $m_j = 0$, and $m_j < 0$, respectively. The expression in Eq. 7 is now evaluated for these three cases and determined to be true or false for all values of $R'_1,\ldots,R'_N$. A test result of *True* indicates that species i is bounded with respect to the jth undesired reaction; a test result of *False* indicates that species i is nonbounded. The results for the possible cases of m_j for when $n_j > 0$ are determined by inspecting the inequality in Eq. 7 and are shown in Table 1.

Therefore, when $n_j > 0$ and $m_j \leq 0$, species i is bounded with respect to the jth undesired reaction; whereas if $m_j > 0$, then species i is classified as nonbounded.

Equal overall order ($\mathbf{n_j = \alpha^T - \alpha_j^T = 0}$)

The second scenario is encountered when the main reaction has an equal overall reaction order as the jth undesired reaction, $n_j = 0$. The general form of the byproduct formation expression given in Eq. 5 is now represented as

Table 1. Classification of Species *i* in the *j*th Undesired Reaction When $n_j > 0$

When	Eq. 7 Test	Result
$m_j > 0$	False	Nonbounded
$m_j = 0$	True	Bounded
$m_j < 0$	True	Bounded

$$P'_{\mathrm{D}_j} = \frac{k'_j}{\prod_{i=1}^{N} R'^{m_j}_i} \tag{8}$$

The absence of the reactor effluent term, q', in the expression for $P'_{\mathrm{D}j}$ results in a very simple test for boundedness shown in Eq. 9 leading to the results in Table 2.

$$m_j\left(1+\sum_{\substack{k=1\\k\neq i}}^{N} R'_k v'_k\right) \leqslant 0 \tag{9}$$

The results in Table 2 when $n_j = 0$ are identical to those in Table 1 when $n_j > 0$. Thus, summarizing this and the previous section for the cases where the main reaction has higher than or equal overall order than the *j*th undesired reaction:

When $\alpha^T - \alpha_j^T \geq 0$; if

(i) $\alpha_i - \alpha_{ij} \leq 0$ species *i* is bounded w.r.t. the *j*th undesired reaction.

(ii) $\alpha_i - \alpha_{ij} > 0$ species *i* is nonbounded.

Lower overall order ($n_j = \alpha^T - \alpha_j^T < 0$)

The final case covers the situation where the main reaction has lower overall order than the undesired reaction in question, $n_j < 0$. For this case, it is convenient to write Eq. 7 in the following form:

$$(m_j + |n_j|)R'_i v'_i + m_j\left(1+\sum_{\substack{k=1\\k\neq i}}^{N} R'_k v'_k\right) \leqslant 0 \tag{10}$$

The test in Eq. 10 depends on the magnitude of the difference between m_j and $|n_j|$ with three possible scenarios: $m_j > -|n_j|$, $m_j = -|n_j|$, and $m_j < -|n_j|$. By inspection of Eq. 10, recognizing that n_j is strictly negative in this case, the test results are given in Table 3.

These tests are summarized into the following inequalities that are used to classify a reactant species when the main reaction has lower overall order than the *j*th undesired reaction.

Table 2. Classification of Species *i* in the *j*th Undesired Reaction When $n_j = 0$

When	Eq. 9 Test	Result
$m_j > 0$	False	Nonbounded
$m_j = 0$	True	Bounded
$m_j < 0$	True	Bounded

Table 3. Classification of Species *i* in the *j*th Undesired Reaction When $n_j < 0$

When	Eq. 10 Test	Result
$m_j > -\lvert n_j\rvert$	False	Nonbounded
$m_j = -\lvert n_j\rvert$	True	Bounded
$m_j < -\lvert n_j\rvert$	True	Bounded

When $\alpha^T - \alpha_j^T < 0$; if

(i) $\alpha^T - \alpha_j^T \geq \alpha_i - \alpha_{ij}$ species *i* is bounded w.r.t. the *j*th undesired reaction.

(ii) $\alpha^T - \alpha_j^T < \alpha_i - \alpha_{ij}$ species *i* is nonbounded.

Recall that a reactant species must be classified as bounded in *every* side reaction for it to be classified as bounded overall. If a reactant species is classified as nonbounded in *any* side reaction, then it is classified as nonbounded overall. Therefore, by simply determining the stoichiometric coefficients and the overall reaction orders and then using the inequalities presented in the previous sections, one can quickly classify a reactant species as bounded or nonbounded. Table 4 is a summary of the results in this section and is used to classify reactant species *i* in the *j*th undesired reaction.

Parallel Reactions of Equal Overall Order

The definitions, rules, and inequalities presented in the previous section are applicable only to process chemistries that have reactions of unequal overall order or reactions that are in series or series/parallel. Chemistries that have of all parallel reactions of equal overall order constitute a special case that is covered here.

Consider the form of the byproduct formation expression given by Eq. 8 for reactions of equal overall order.

$$P'_{\mathrm{D}j} = \frac{k'_j}{\prod_{i=1}^{N} R'^{(\alpha_i-\alpha_{ij})}_i} = k'_j\frac{\prod_{i=1}^{N} R'^{\alpha_{ij}}_i}{\prod_{i=1}^{N} R'^{\alpha_i}_i} \tag{11}$$

For the case of all parallel reactions where no products or byproducts appear as reactant species, $\alpha_{\mathrm{C}j} = 0\ \forall j$. Now summing up the exponents in the numerator of Eq. 11 gives $\alpha_{1j} + \alpha_{2j} + \cdots + \alpha_{Nj} = \alpha_j^T$ and the sum of the exponents in the denominator is $\alpha_1 + \alpha_2 + \cdots + \alpha_N = \alpha^T$. Every reaction has equal overall order in this formulation, $\alpha^T = \alpha_j^T$, so it can be concluded that the sum of the powers of recycle flow rates must be equal in both the numerator and denominator

Table 4. Reactant Species Classification System for the *j*th Undesired Reaction

Either $\alpha^T - \alpha_j^T \geq 0$	Result
When $\alpha_i - \alpha_{ij} \leq 0$	Species *i* is bounded w.r.t. the *j*th side reaction
When $\alpha_i - \alpha_{ij} > 0$	Species *i* is nonbounded
Or $\alpha^T - \alpha_j^T < 0$	Result
When $\alpha^T - \alpha_j^T \geq \alpha_i - \alpha_{ij}$	Species *i* is bounded w.r.t. the *j*th side reaction
When $\alpha^T - \alpha_j^T < \alpha_i - \alpha_{ij}$	Species *i* is nonbounded

To be used for all process chemistries, except the special case of all parallel reactions of equal overall.

of the byproduct formation expression in Eq. 11. Note that this special condition does not hold for chemistries with series or series/parallel reactions, because α_{cj} will be nonzero for at least one j, making $\alpha_j^T \neq \sum_{i=1}^{N} \alpha_{ij}$. Thus, for series or series/parallel reactions with equal overall order ($\alpha^T = \alpha_j^T$), it does not follow that the sum of powers of recycle flow rates are equal in both the numerator and denominator of Eq. 11.

When $\alpha_i = \alpha_{ij}\ \forall i$, Eq. 13 simplifies to $P'_{Dj} = k'_j$, and the selectivity to the undesired byproduct(s) produced in the jth side reaction is constant and is not affected by changing recycle flow rates. In this case, it is optimal to maximize reactant conversion to minimize separation costs corresponding to a bounded operating policy.

Now consider the case when $\alpha_i \neq \alpha_{ij}$ for any or all reactant species i. Given a reactant species k such that $\alpha_k - \alpha_{kj} > 0$ then R'_k will appear in the denominator of P'_{Dj} to the power of $\alpha_k - \alpha_{kj} > 0$. Based on the fact that the sum of the exponents of recycle flow rates must be equal in the numerator and denominator, there exists at least one reactant species i, such that $\alpha_i - \alpha_{ij} < 0$ causing R'_i to be in the numerator of P'_{Dj}.

$$P'_{\mathrm{D}j} = \frac{{R'}_i^{|\alpha_i - \alpha_{ij}|}}{{R'}_k^{(\alpha_k - \alpha_{kj})}} \frac{{k'}_j}{\prod\limits_{\substack{l=1 \\ l \neq k \neq i}}^{N} {R'}_i^{(\alpha_l - \alpha_{lj})}} \tag{12}$$

Letting R'_i in Eq. 12 approach zero will completely eliminate the formation of P'_{Dj}. For each subsequent jth undesired reaction there will be at least one species i, such that R'_i appears in the numerator of P'_{Dj} and $P'_{Dj} \to 0$ as $R'_i \to 0$. Therefore, by letting each recycle flow rate approach zero, all undesired byproduct formation is suppressed and separation costs are minimized corresponding to a minimum in the cost function given in Eq. 4.

$$\lim_{{R'}_i \to 0\ \forall i} C' \to {C'}_{\min} \tag{13}$$

The optimal operating point of $R'_i = 0\ \forall i$ requires a reactor of infinite holdup, i.e., is outside the feasible operating region, causing optimal operation to be bounded by the reactor volume constraint. This leads to Rule 1 that is identical to the rule from the original article on reactions of equal overall order by Griffin et al.[14]

Rule 1: If all undesired reactions are in parallel with the main reaction and have the same overall reaction order as the main reaction, then the overall process chemistry is bounded.

The case presented in this section is a degenerate one that requires special attention. By inspecting Eq. 12 where $\alpha_k - \alpha_{kj} > 0$, it is seen that $P'_{\mathrm{D}j}$ as well as $\frac{\partial P'_{\mathrm{D}j}}{\partial R'_k}$ become undefined as $R'_k \to 0$. For every jth side reaction there will be at least one reactant species k such that $P'_{\mathrm{D}j}$ becomes undefined as $R'_k \to 0$. But the unconstrained optimal operating point that suppresses all byproduct formation is where all recycle flow rates are zero, thus leading to a point of degeneracy as $R'_i \to 0\ \forall i$ and $P'_{Dj} \to 0/0$. Thus, the functions P'_{Dj} and $\frac{\partial P'_{\mathrm{D}j}}{\partial R'_i}$ are undefined at the optimal operating point of zero recycle flow rates causing the rules and definitions, and the resulting derivative test developed earlier to be invalid for this special case.

Reversible Reactions

In the previous section, rules have been presented to classify process chemistries of strictly irreversible reactions. When reaction reversibility is introduced, this classification can change depending on which reaction(s) is/are reversible. Consider the following system of reactions where only the jth undesired reaction is reversible and the main reaction remains irreversible.

$$\begin{gathered} \alpha_1\mathrm{A}_1 + \alpha_2\mathrm{A}_2 + \cdots + \alpha_N\mathrm{A}_N + \alpha_\mathrm{C}\mathrm{C} \xrightarrow{k_0} \mathrm{C} \\ r_0 = k_0[\mathrm{C}]^{\alpha_\mathrm{C}} \prod_{i=1}^{N} [\mathrm{A}_i]^{\alpha_i} \\ \alpha_{1j}\mathrm{A}_1 + \alpha_{2j}\mathrm{A}_2 + \cdots + \alpha_{Nj}\mathrm{A}_N + \alpha_{\mathrm{C}j}\mathrm{C} \underset{k_{j-}}{\overset{k_j}{\rightleftarrows}} \mathrm{D}_j \\ r_j = k_j[\mathrm{C}]^{\alpha_{\mathrm{C}j}} \prod_{i=1}^{N} [\mathrm{A}_i]^{\alpha_{ij}} - k_{j-}[\mathrm{D}_j] \end{gathered} \tag{14}$$

The general form of P'_{Dj} is shown in Eq. 15 with the term related to the reversible reaction in brackets.

$$P'_{\mathrm{D}j} = k'_j \frac{{q'}^{(\alpha^T - \alpha_j^T)}}{\prod\limits_{i=1}^{N} {R'}_i^{(\alpha_i - \alpha_{ij})}} \left[1 - \frac{P'_{\mathrm{D}j} {q'}^{(\alpha^T - \alpha_{j-}^T)}}{K'_j \prod\limits_{i=1}^{N} {R'}_i^{\alpha_{ij}}} \right] \tag{15}$$

As the jth side reaction reaches the limit of irreversibility, $K'_j \to \infty$; the bracketed term mentioned earlier goes to 1, and the expression in Eq. 15 simplifies to that given in Eq. 2 for a process chemistry consisting of only irreversible reactions.

The reversibility of an undesired reaction helps to improve process economics, because it results in reduced byproduct formation as a result of the back reaction that consumes the undesired byproduct(s). This favorable feature also lowers fresh feed requirements and reduces separation costs while improving selectivity, yet it does not affect the classification of a process chemistry. It can be shown that the bracketed term in Eq. 15 related to equilibrium does not change the sign of $\frac{\partial P'_{\mathrm{D}j}}{\partial R'_i}$ for any species i, regardless of the forward or back reaction orders of any of the reactions. Thus, the existence of reversibility of any or all of the j side reactions only improves the selectivity to those undesired products, causing no change in the process chemistry classification; the optimal operating point will change, however, based on the magnitude of the equilibrium constant.

The other situation to be considered arises when the main reaction is reversible. Consider the following chemistry that has a reversible main reaction with all undesired reactions being irreversible.

$$\begin{gathered} \alpha_1\mathrm{A}_1 + \alpha_2\mathrm{A}_2 + \cdots + \alpha_N\mathrm{A}_N + \alpha_\mathrm{C}\mathrm{C} \underset{k_{0-}}{\overset{k_0}{\rightleftarrows}} \mathrm{C} \\ r_0 = k_0[\mathrm{C}]^{\alpha_\mathrm{C}} \prod_{i=1}^{N} [\mathrm{A}_i]^{\alpha_i} - k_{0-}[\mathrm{C}] \\ \alpha_{1j}\mathrm{A}_1 + \alpha_{2j}\mathrm{A}_2 + \cdots + \alpha_{Nj}\mathrm{A}_N + \alpha_{\mathrm{C}j}\mathrm{C} \xrightarrow{k_j} \mathrm{D}_j \\ r_j = k_j[\mathrm{C}]^{\alpha_{\mathrm{C}j}} \prod_{i=1}^{N} [\mathrm{A}_i]^{\alpha_{ij}} \end{gathered} \tag{16}$$

The expression for byproduct formation is

$$P'_{\mathrm{D}j} = k'_j \frac{q'^{(\alpha^T-\alpha_j^T)}}{\prod\limits_{i=1}^{N} R'^{(\alpha_i-\alpha_{ij})}_i} \left[1 - \frac{q'^{(\alpha^T-\alpha_-^T)}}{K'_0 \prod\limits_{i=1}^{N} R'^{\alpha_i}_i}\right]^{-1} \tag{17}$$

Once again, as the main reaction becomes irreversible, $K'_0 \rightarrow \infty$; the bracketed term in Eq. 17 approaches 1; and Eq. 17 simplifies to the expression for a chemistry consisting only of irreversible reactions, given in Eq. 2.

The reversibility of the main reaction is never beneficial, because the desired product reacts to reform reactant species which can then react further to form undesired byproducts. Also, there may be a limit on reactant conversion in the desired reaction as a result of the chemical equilibrium. This effect can result in a tradeoff between increasing reactor conversion and selectivity, because once the equilibrium conversion is reached, further reactant conversion can produce undesired products. It can also be shown that $\frac{\partial P'_{\mathrm{D}j}}{\partial R'_i} < 0$ for all i over some range of operating conditions, thus resulting in a nonbounded classification for this chemistry. Therefore, when the main reaction is reversible, the chemistry is always classified as nonbounded; however, the chemistry will approximate the optimal operating policy of the irreversible chemistry when the equilibrium constant is large (near the limit of irreversibility).

Summing up this section, whenever a process chemistry involves a reversible desired reaction, the chemistry is classified as nonbounded and will operate optimally with a variable reactor holdup that depends on the value of the equilibrium constant. If the main reaction is irreversible and any or all side reactions are reversible, the chemistry is classified just the same as if all reactions were irreversible.

Procedure for Process Chemistry Classification

The development in this article results in a methodology that can be used to classify process chemistries of parallel, series, series/parallel, irreversible, and/or reversible reactions of equal or unequal overall order. Rules for bounded/nonbounded species and chemistries have been presented, and a classification system was developed to classify these reactant species, with the results being summarized in Table 4. These results have been turned into an algorithmic procedure to classify each reactant species that is shown in Figure 3.

Beginning at the top of Figure 3, first determine the overall reaction order of the main reaction, α^T, and then the stoichiometric coefficient, α_i, of each reactant species in the main reaction. Then determine the overall reaction order for the jth undesired reaction, α_j^T, and the stoichiometric coefficient of species i in the jth side reaction, α_{ij}. Next, evaluate the quantities, $\alpha^T - \alpha_j^T$ and $\alpha_i - \alpha_{ij}$ to classify species i in the jth side reaction by Table 4. If the species is classified as nonbounded, then repeat the procedure with the next reactant species i+1. If the species is classified as bounded, then continue onto the next undesired reaction, j+1, and evaluate $\alpha^T_{(j+1)}$ and $\alpha_{i(j+1)}$. Repeat this process on j for any species i that is bounded, until it has been classified as bounded in every side reaction up to $j = N_{\mathrm{R}}$, which classifies species i as bounded overall; or until a side reaction is reached where species i is classified as nonbounded, which terminates the loop for species i. This procedure should be repeated until all N reactant species are classified; then, the overall chemistry is classified by Rules 4 and 5.

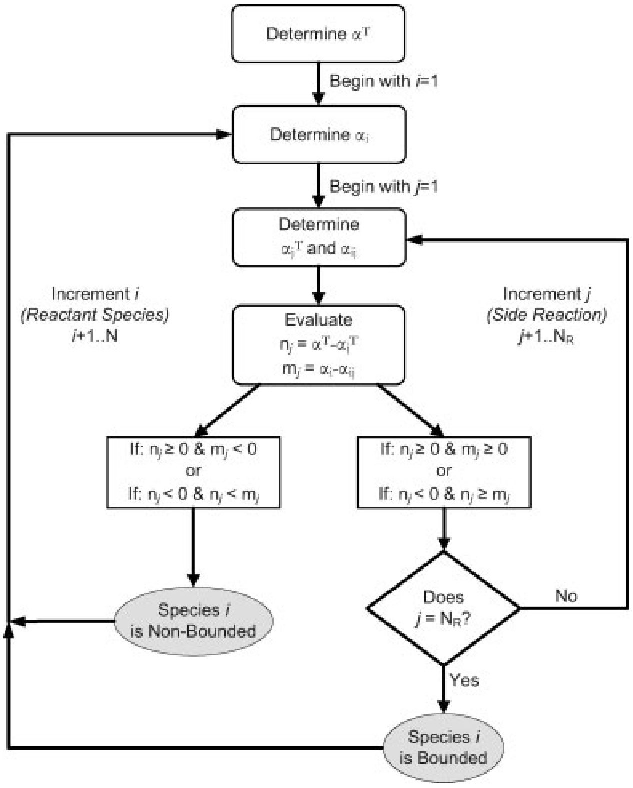

Figure 3. Reactant species classification procedure.

The special case of all parallel reactions of equal overall order inevitably results in a bounded chemistry. For reversible chemistries it can be helpful to classify the process chemistry first as if it were irreversible, and then consider which reaction(s) are reversible and the magnitude of the equilibrium constant(s) to determine what effect, if any, the reversibility has on the operating policy. The decision tree for this process chemistry classification is shown in Figure 4. Note that, for the case of a single desired reaction with no selectivity issues, it is always desirable to operate at maximum reactant conversion to lower fresh feed and separation costs (corresponding to a bounded chemistry). This result is now well established in the operations literature.

Salicylic Acid Nitration Case Study

This case study investigates the nitration of salicylic acid (SA) to produce 5-nitrosalicylic acid (5-NS), an important and

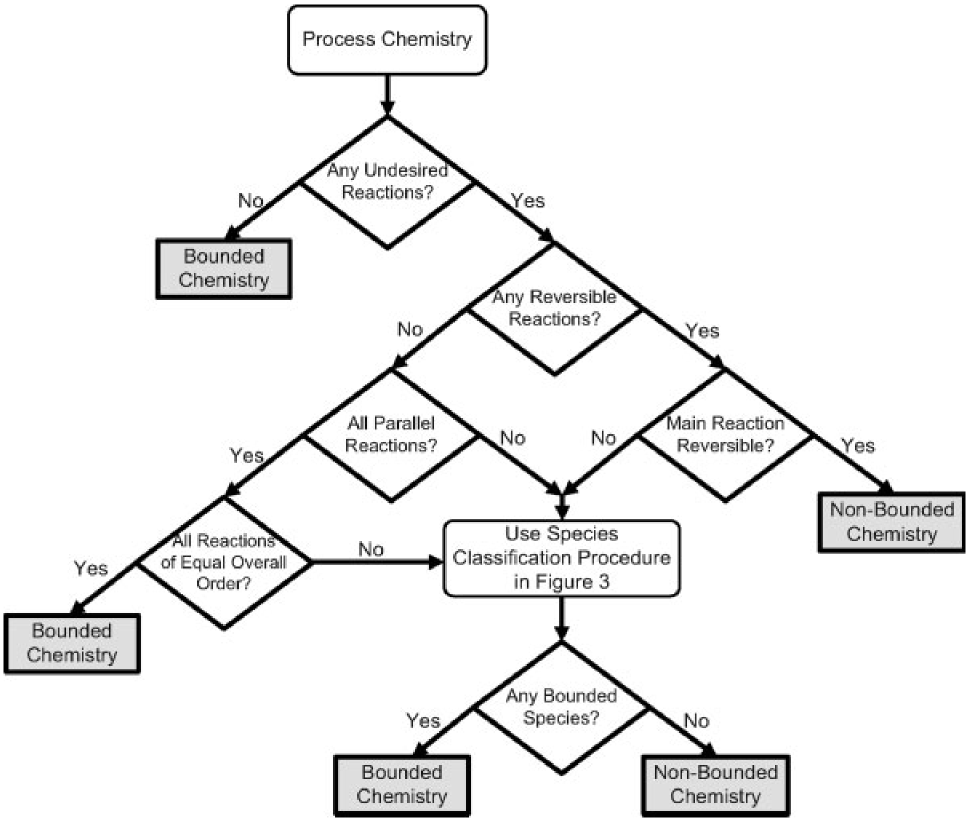

Figure 4. Process chemistry classification decision tree.

valuable pharmaceutical intermediate. Upon hydrogenation, 5-NS is converted to 5-aminosalicylic acid, which is the active ingredient in the treatment of Crohn's disease and ulcerative colitis. Several nitrating systems have been used to produce 5-NS, including nitric acid/sulfuric acid/water (mixed acid), nitric acid/acetic anhydride/acetic acid, and aqueous nitric acid; however, Andreozzi et al.[15–17] have recently proposed a nitric acid/acetic acid mixture for the nitration of SA. This system has several potential advantages such as higher selectivity and yield, ease of product separation, improved process safety, and lower waste disposal costs.

Andreozzi et al.[16] consider the following set of reactions with second-order kinetics shown in Eq. 18, the kinetic parameters are given in Table 5. The reaction order of each reactant species is equal in every reaction, resulting in constant selectivity for this system. The production rate of each undesired product, 3-nitrosalicylic acid (3-NS) and 2-nitrophenol (2-NP), is fixed by a ratio of kinetic constants; $P_{3-\mathrm{NS}} = \frac{k_1}{k_0} P_{5-\mathrm{NS}}$ and $P_{2-\mathrm{NP}} = \frac{k_2}{k_0} P_{5-\mathrm{NS}}$. A significant amount of water is produced as a byproduct, causing nitric acid to dissociate to nitrate (NO_3^-) and hydronium ions ($\mathrm{H_3O^+}$). The water concentration is not included in the equilibrium expression given in Eq. 18 as a result of the presence of an excess of water, and so the acid dissociation constant, K_A, can be considered a modified equilibrium constant. This undesired equilibrium is achieved instantaneously (relative to the other reactions) and consumes nitric acid molecules, thus increasing the required recycle flow rate of that reactant species.

$$
\begin{aligned}
&\mathrm{SA} + \mathrm{HNO_3} \xrightarrow{k_0} 5-\mathrm{NS} + \mathrm{H_2O} \\
&\qquad\qquad r_0 = k_0[\mathrm{SA}][\mathrm{HNO_3}] \quad k_0 = k_{0,0}\, e^{-E_{\mathrm{A},0}/RT} \\
&\mathrm{SA} + \mathrm{HNO_3} \xrightarrow{k_1} 3-\mathrm{NS} + \mathrm{H_2O} \\
&\qquad\qquad r_1 = k_1[\mathrm{SA}][\mathrm{HNO_3}] \quad k_1 = k_{1,0}\, e^{-E_{\mathrm{A},1}/RT} \\
&\mathrm{SA} + \mathrm{HNO_3} \xrightarrow{k_2} 2-\mathrm{NP} + \mathrm{H_2O} + \mathrm{CO_2} \\
&\qquad\qquad r_2 = k_2[\mathrm{SA}][\mathrm{HNO_3}] \quad k_2 = k_{2,0}\, e^{-E_{\mathrm{A},2}/RT} \\
&\mathrm{HNO_3} \overset{\mathrm{H_2O}}{\underset{\longleftarrow}{\longrightarrow}} \mathrm{NO_3^-} + \mathrm{H_3O^+} \\
&\qquad\qquad K_\mathrm{A} = \frac{[\mathrm{NO_3^-}][\mathrm{H_3O^+}]}{[\mathrm{HNO_3}]},\ F_{\mathrm{NO_3^-}} = \sqrt{K_\mathrm{A} q R_{\mathrm{HNO_3}}}
\end{aligned}
\tag{18}
$$

Employing the classification procedure described in this article to the reactions in Eq. 18, both reactant species are classified as bounded, making the overall chemistry bounded. The previous article by Griffin et al.[14] could not be used to classify this chemistry because of the reversible reaction that does not have the same overall reaction order as the other reactions.

Process design

This process is to be carried out in a well-mixed, isothermal reactor at 25°C. At higher temperatures, polynitration reactions occur that further produce undesired byproducts leading to the possible formation of picric acid, an explosive

Table 5. Process Chemistry Kinetic Parameters

$k_{0,0} = 2.53 \times 10^{21}$ L/(mol min)	$E_{A,0} = 124.4$ kJ/mol	$\Delta H_{R,0} = -145.9$ kJ/mol
$k_{1,0} = 8.28 \times 10^{20}$ L/(mol min)	$E_{A,1} = 123.9$ kJ/mol	$\Delta H_{R,1} = -145.9$ kJ/mol
$k_{2,0} = 3.22 \times 10^{20}$ L/(mol min)	$E_{A,2} = 124.7$ kJ/mol	$\Delta H_{R,0} = -115.5$ kJ/mol
	$K_A = 28$ at 25°C	

species that can lead to a runaway reaction. The products 5-NS, 3-NS, and 2-NP have poor solubility in the reacting medium at this temperature, and it is assumed they precipitate out of solution to be separated by filtration. The remaining liquid phase species are separated by distillation. The distillate from the first column is a water/acetic acid mixture near the tangent pinch which is then separated in column 2, a heterogeneous azeotropic distillation column using *n*-butyl acetate as the entrainer. The bottom stream from column 1 contains SA, nitric acid, water, and acetic acid which is recycled to the reactor; thus, only one degree of freedom is available, chosen as the recycle flow rate of SA. The columns were designed using the simulation programs incorporated in AspenTech's Aspen Plus® and DISTIL® and then costed and sized by the methods of Doherty and Malone.[18] A proposed flowsheet for this process is shown in Figure 5.

Optimal process operation

The process is designed to produce 100 kg/h (546.1 mol/h) of 5-NS at a reactor temperature of 25°C and a pressure of 1 atm. To make this process operable with sufficient flexibility, the equipment is sized to handle a 25% increase in the desired production rate. The base case design of 100 kg/h of 5-NS corresponds to a recycle flow rate of SA of 51.2 mol/h and a reactor holdup of 80%. For this process, the fresh feed flow rates are constant; the reactor heat load is constant; and the flow rate and composition to column 2 are fixed. Thus, the only remaining costs to optimize are the operating/utility costs of column 1. Increasing the reactor holdup decreases the formation of nitrate ion and the total flow to the separation system, lowering the utility costs for column 1. The result is that the economic optimal operating point falls on the maximum reactor holdup constraint as predicted for this bounded chemistry. The results of an economic optimization study are shown in Figure 6, where a 10 percentage point increase in reactor holdup is found to save 2.82% of the energy costs of column 1, and a 20 percentage point increase (i.e., the reactor is operated 100% full) saves 5.58%.

This case study provides an example of a chemistry with multiple undesired reactions, including an undesired equilibrium that do not all exhibit the same overall reaction order. The methodology classifies this chemistry as bounded with a predicted optimal operating policy to maintain the reactor completely full at all times. It is shown that for the nominal production rate it is in fact economically optimal to operate on the maximum holdup constraint, resulting in lower energy costs for the separation system and minimum operating costs for the overall process. This reactor-full operating policy remains optimal for any production rate increase or decrease as a consequence of the chemistry being classified as bounded.

A more detailed description of the case study is available in the Supplementary Material.

Relaxation of Assumptions

Several assumptions were made in the development of the general methodology presented in this article. Not all of them are stringent, and many can be relaxed as follows:

Nonelementary mass–action kinetics

For simplicity and convenience, this work focuses on elementary homogeneous kinetics where the reaction order of a reactant species is equal to its stoichiometric coefficient in that reaction. However, the methodology for classifying reactant species and process chemistries is easy to modify for nonelementary (pseudo) homogeneous kinetics, provided the reaction orders in the rate expressions are known.

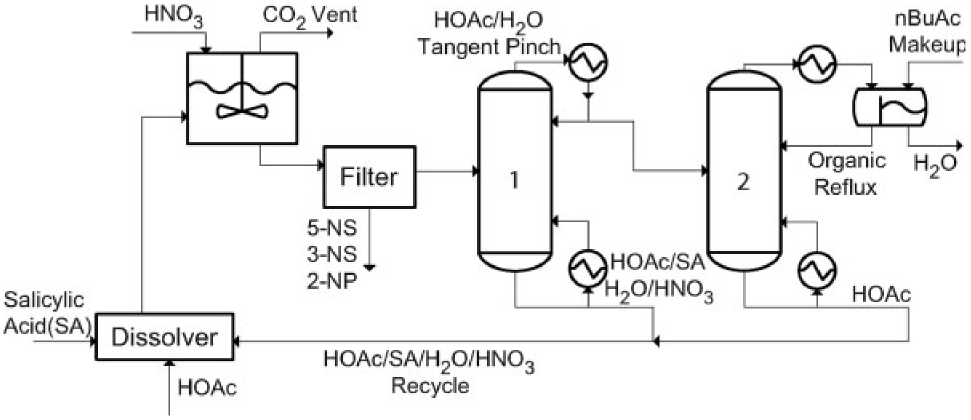

Figure 5. Salicylic acid nitration flowsheet.

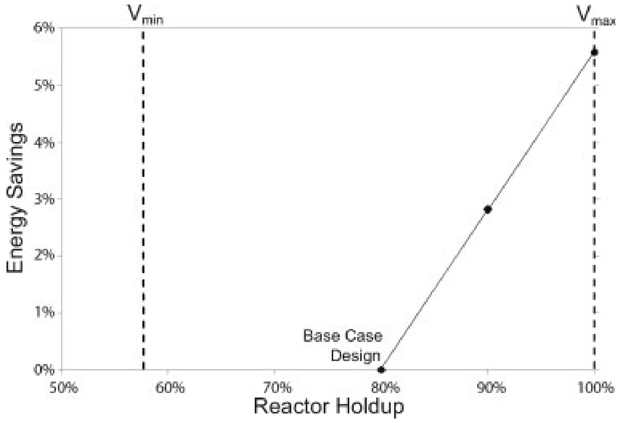

Figure 6. Economic optimization of the salicylic acid nitration process with additional equipment capacity.

Recycling all reactants

The methodology assumes there is one recycle stream per reactant species, so that the number of degrees of freedom is the same as the number of reactant species. The number of degrees of freedom is reduced by the number of reactants that are not recycled. However, such unrecycled species can still be classified as bounded or nonbounded using the rules and methodology developed in this article. If an unrecycled reactant species is classified as bounded, then maximum reactor holdup will minimize the concentration of that bounded reactant species and minimize all operating costs associated with that species.

Recycling pure reactants

Recycle streams do not need to consist of pure species as long as the desired optimal recycle flow rate of each reactant species can be achieved by that stream or by a combination of recycle streams. Impurities in a recycle stream can consist of other unreacted reactant species, product species, or inert species present in the process. Impurities present in a recycle stream increases the separation costs because of the higher flow rate of the recycle. However, if a large amount of impurities are present such that the separation system cannot achieve the desired recycle flow rate of reactant species, then a new physical constraint on a recycle flow rate is imposed on the system that can affect optimal economic performance. Impure recycle streams can alter the optimal operating point but will not affect the overall reactor operating policy.

Equal separation costs for reactants/equal byproduct production costs

The formulation of the cost-objective function in Eq. 4 assumes that the cost of separating each reactant species, C_{Ri}, is equal for all species i, and the cost of producing one mole of each undesired byproduct, $C_{\mathrm{D}j}$, is also equal for all undesired byproducts. The methodology is easily extended to cases with different C_{Ri} and $C_{\mathrm{D}j}$, but the cost function in Eq. 4 becomes more complicated. Optimal molar ratios of reactants may be such as to minimize the production rate of the more costly undesired byproducts, while high recycle flow rates may be favored for those reactants with lower separation costs. Calculating optimal recycle flow rates is generally part of a more detailed numerical optimization that would include the appropriate separation costs. In this analysis, the magnitude of the constants C_{Ri} and $C_{\mathrm{D}j}$ can only change the optimal operating point but not the operating policy.

Extensions to the Methodology

The general methodology, concepts on selectivity vs. conversion, and the resulting classification procedure can be extended to study other chemical systems that the authors have considered but not investigated in detail.

Undesired byproducts as reactants

The chemistry in Eq. 1 assumes that no undesired byproducts appear as reactant species in subsequent consecutive reactions. Consider the following kth undesired reaction where a single undesired byproduct, D_j, is now a reactant species.

$$\alpha_{1k}\mathrm{A}_1 + \alpha_{2k}\mathrm{A}_2 + \cdots + \alpha_{Nk}\mathrm{A}_N + \alpha_{\mathrm{C}k}\mathrm{C} + \alpha_{\mathrm{D}k}\mathrm{D}_j \xrightarrow{k_k} \mathrm{D}_k$$

$$r_k = k_k[\mathrm{C}]^{\alpha_{\mathrm{C}k}}[\mathrm{D}_j]^{\alpha_{\mathrm{D}k}} \prod_{i=1}^{N} [\mathrm{A}_i]^{\alpha_{ik}} \quad (19)$$

Following the methodology presented in the Appendix, the dimensionless form of the production rate of D_k in Eq. 19 can be shown as

$$\begin{aligned} P'_{\mathrm{D}k} &= k'_k \frac{\left(1 + \sum_{i=1}^{N} R'_i v'_i\right)^{n_k}}{\prod_{i=1}^{N} R'^{m_k}_i} (P'_{\mathrm{D}j})^{\alpha_{\mathrm{D}k}} \\ &= k'_k \frac{\left(1 + \sum_{i=1}^{N} R'_i v'_i\right)^{n_k}}{\prod_{i=1}^{N} R'^{m_k}_i} \left(k'_j \frac{\left(1 + \sum_{i=1}^{N} R'_i v'_i\right)^{n_j}}{\prod_{i=1}^{N} R'^{m_j}_i} \right)^{\alpha_{\mathrm{D}k}} \end{aligned} \quad (20)$$

The sign of the first derivative for the expression in Eq. 20, $\frac{\partial P'_{\mathrm{D}k}}{\partial R'_i}$, now depends on several parameters (n_j, m_j, n_k, and m_k) that involve the desired reaction, the jth undesired reaction that produces D_j, and also the kth undesired reaction that produces D_k. This complexity results in many combinations of these parameters for the classification of a reactant species; the possible number of combinations increases when multiple undesired byproducts appear as reactant species in a single side reaction.

Alternate rate laws

The chemistries investigated in this article consist of liquid-phase, homogeneous reactions that have power-law rate expressions. One could consider gas-phase reactions or heterogeneously catalyzed reactions in which these types of chemistries generally obey a different rate law, e.g., Langmuir–Hinshelwood, Ely Rideal, etc. If byproduct and profit functions can be developed for these alternate reaction schemes and rate laws, then the concepts presented in this article can be used in principle.

Nonisothermal chemistries

When nonisothermal chemistries are considered, another degree of freedom, reactor temperature, is introduced through the temperature dependency of the Arrhenius equation. Ward et al.[19] studied nonisothermal chemistries that have a single undesired reaction. It was found that the optimal operating policy, which now includes optimal reactor temperature, depends not only on the reaction orders of reactant species but also on the ratio of activation energies between the desired reaction and each undesired reaction. The methodology developed in the current article for chemistries with multiple undesired reactions can be extended to nonisothermal chemistries to determine the selectivity vs. temperature relationship using a first partial derivative test, $\frac{\partial P_{\mathrm{D}j}}{\partial T}$, similar to that developed in previous sections.

Reactor type

The analysis presented in this work applies to any well-mixed reactor, such as a continuous stirred-tank reactor or fluidized bed, etc., where it can be assumed that the exit concentration of a species is equal to the concentration in the reactor. In principle, the methodology can be extended to any other reactor type although it may be nontrivial to establish analytical results comparable to those presented here.

Implications for Process Operation and Control

The process chemistry classification procedure developed in this article determines how the excess reactor capacity should be used under nominal operating conditions; this classification has further implications for potential plantwide control structures. When a process chemistry is classified as bounded, it is immediately known that the reactor should be operated completely full at all times and under all operating conditions. No reactor optimization is ever required! Then, if further optimization efforts are required for the separation system, one degree of freedom (reactor holdup/reactant conversion) has been eliminated from the analysis. This result further indicates that for a bounded chemistry a simple self-optimizing control structure can be designed around the reactor to maintain its holdup (level) setpoint at the maximum value. On the other hand, if a chemistry is classified as nonbounded, then numerical optimization is required to determine the optimal reactor holdup and recycle flow rate(s) during process operation, because they depend on all of the parameters of the system such as kinetic rate data, molar volumes, and production rate. Thus, plants operating with nonbounded chemistries require a more complicated supervisory control structure incorporating continuous optimal reactor level and recycle flow rate set-point calculation and regulation in order to achieve optimal operation.

For both classes of chemistries, the recycle flow rate(s) need to be optimized for any system throughput change, thus it is helpful to have an estimate of the relative magnitudes of recycle flow rates. Bounded chemistries are characterized by having at least one bounded species, and the optimal recycle flow rate of a bounded species is generally small because of the improved selectivity and lowered operating costs. However, a bounded chemistry can also contain a nonbounded species that will have a larger optimal recycle flow rate because of the tradeoff between selectivity and operating costs. A nonbounded chemistry has all nonbounded species, each of which will have relatively large optimal recycle flow rates.

Kumar and Daoutidis[20] have noted that a process with a large recycle flow rate can exhibit multiple dynamic time scales that can affect possible plantwide control configurations. They proposed that the process model be partitioned into fast and slow subsystems, and showed that a suitable pairing of manipulated variables could effectively be used to control each subsystem and the overall plant. Earlier, Ward et al.[21] have considered the dynamic implications of the steady-state operating policies for bounded and nonbounded chemistries discussed earlier and has successfully designed and implemented control structures for both classes of chemistries. In their study, plant dynamics were handled effectively by using traditional decoupled controllers, with manipulated variable pairings based substantially on physical arguments.

Conclusions

This article provides a classification procedure and decision tree that allow for the classification of complicated reversible or irreversible process chemistries having multiple undesired reactions of arbitrary reaction order. By simply inspecting and comparing the reaction orders of all reactant species in the main reaction to those in each undesired reaction present, a process chemistry can be classified as bounded or nonbounded. This classification provides not only a quick method to determine selectivity vs. conversion relationships but also immediate insight into the optimal operation of a chemical plant designed to carry out the reaction(s) commercially. Thus, with the rules and simple inequalities reported in this article, one can quickly determine the strategy required to operate the reactor optimally at all times.

Acknowledgments

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Notation

r = specific reaction rate [mol/(L h)]
$\tilde{r}$ = overall reaction rate (mol/h)
k = reaction rate constant
K = equilibrium constant
P = production rate (mol/h)
R = recycle flow rate (mol/h)
V = reactor volume (L)
q = reactor effluent volumetric flow rate (L/h)
C' = dimensionless operating costs
α_i = stoichiometric coefficient of species i in desired reaction
α_{ij} = stoichiometric coefficient of species i in jth undesired reaction

α^T = overall forward reaction order of desired reaction
α_j^T = overall forward reaction order of jth undesired reaction
N = total number of reactant species
N_R = total number of undesired reactions
v = molar volume (L/mol)

Subscripts

0 = reference to desired reaction
− = reference to the back reaction
i = reactant species 1,. . ., i,. . ., N
j = undesired reaction 1,. . ., j,. . ., N_R
A,. . ., E = species A,. . ., E

Superscript

′ (prime) = dimensionless quantity

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Appendix

The old methodologies were not generalized for chemistries with multiple reactant species and multiple reactions. The following derivation is an original development that yields a general expression for the production rate of any undesired byproduct, P_{Dj}.

For the chemistry shown in Eq. 1, the overall rate of reaction $\tilde{r}$ is first expressed in units of moles per time. Concentrations at the reactor outlet are replaced by the flow rate of the individual species divided by the reactor effluent volumetric flow rate q: $[C] = P_C/q$ and $[A_i] = R_i/q$. This approach is valid for a perfectly mixed reactor where the exit concentration is equal to the concentration everywhere in the reactor such as a continuous stirred-tank reactor but not, for example, a plug-flow reactor.

The overall production rate of C based on the kinetics of the desired reaction in Eq. 1 gives $\tilde{r}_{\text{kin},0} = k_0 V \left(\frac{P_C}{q}\right)^{\alpha_C} \prod_{i=1}^{N} \left(\frac{R_i}{q}\right)^{\alpha_i}$. Now based on stoichiometry and an overall material balance of this chemistry, the overall production rate of C is the total amount of C produced in the desired reaction in addition to all byproducts that are formed by C $\tilde{r}_{\text{stoich},0} = P_C + \sum_{j=1}^{N_R} \alpha_{Cj} P_{Dj}$. For each species, $\tilde{r}_{\text{stoich}} = \tilde{r}_{\text{kin}}$, thus setting the stoichiometric and kinetic rate expressions equal for species C gives

$$P_C + \sum_{j=1}^{N_R} \alpha_{Cj} P_{Dj} = k_0 V \left(\frac{P_C}{q}\right)^{\alpha_C} \prod_{i=1}^{N} \left(\frac{R_i}{q}\right)^{\alpha_i} \tag{A1}$$

And likewise for species D,

$$P_D = k_j V \left(\frac{P_C}{q}\right)^{\alpha_{Cj}} \prod_{i=1}^{N} \left(\frac{R_i}{q}\right)^{\alpha_{ij}} \tag{A2}$$

The volumetric flow rate out of the reactor, q, is the molar flow rate of each species times its molar volume, v, summed over all species.

$$q = P_C v_C + \sum_{i=1}^{N} R_i v_i + \sum_{j=1}^{N_R} P_{Dj} v_{Dj} \tag{A3}$$

The overall forward reaction order of the desired reaction, α^T, and that of the undesired reaction, α_j^T, can be expressed as

$$\begin{aligned} \alpha^T &= \alpha_C + \sum_{i=1}^{N} \alpha_i \\ \alpha_j^T &= \alpha_{Cj} + \sum_{i=1}^{N} \alpha_{ij} \end{aligned} \tag{A4}$$

Thus, the volumetric flow rate terms in Eq. A1 can be grouped and simplified as $q^{\alpha_C}\prod_{i=1}^{N} q^{\alpha_i} = q^{\alpha_C+\sum\limits_{i=1}^{N}\alpha_i} = q^{\alpha^T}$ and similarly for the undesired reaction in Eq. A2: $q^{\alpha_{Cj}}\prod_{i=1}^{N} q^{\alpha_{ij}} = q^{\alpha_j^T}$.

It is desirable to work with dimensionless parameters; since the production rate of the desired product is fixed, the expression for the undesired reaction, Eq. A2, is divided by that for the desired reaction, Eq. A1, giving

$$\frac{P_{Dj}}{P_C + \sum\limits_{j=1}^{N_R} \alpha_{Cj} P_{Dj}} = \frac{k_j}{k_0} \frac{P_C^{\left(\alpha_{Cj}-\alpha_C\right)} q^{\left(\alpha^T-\alpha_j^T\right)}}{\prod\limits_{i=1}^{N} R_i^{\left(\alpha_i-\alpha_{ij}\right)}} \tag{A5}$$

All flow rates are nondimensionalized by dividing by the fixed production rate P_C: thus $R'_i = R_i/P_C$ and $P'_{Dj} = P_{Dj}/P_C$. Molar volumes are nondimensionalized by the molar volume of the desired species: thus $v'_A = v_A/v_C$. Reaction rate constants are made dimensionless as follows:

$$k'_j = \frac{k_j}{k_0} v_C^{\left(\alpha^T-\alpha_j^T\right)} \tag{A6}$$

where k_0 is the reaction rate constant for the desired reaction, k_j is the reaction rate constant for the undesired reaction in question, and v_C is the molar volume of the desired species.

An analytical expression for the reactor volume can be derived from Eq. A2. This yields the required reactor volume to produce the desired production rate as a function of the chosen degrees of freedom, the recycle flow rates.

$$V = \frac{P_{Dj} q^{\alpha_j^T}}{k_j P_C^{\alpha_{Cj}} \prod\limits_{i=1}^{N} R^{\alpha_{ij}}} \tag{A7}$$

Summarizing these steps, the dimensionless expressions for the byproduct production rate, the reactor effluent volumetric flow rate, and the required reactor volume are given by

$$\frac{P'_{Dj}}{1 + \sum\limits_{j=1}^{N_R} \alpha_{Cj} P'_{Dj}} = k'_j \frac{q'^{\left(\alpha^T-\alpha_j^T\right)}}{\prod\limits_{i=1}^{N} R_i'^{\left(\alpha_i-\alpha_{ij}\right)}} \tag{A8}$$

$$q' = \frac{q}{P_C v_C} = 1 + \sum_{i=1}^{N} R'_i v'_i + \sum_{j=1}^{N_R} P'_{Dj} v'_{Dj} \tag{A9}$$

$$V' = \frac{P'_{Dj} q'^{\alpha_j^T}}{k'_j P_C'^{\alpha_{Cj}} \prod\limits_{i=1}^{N} R_i'^{\alpha_{ij}}} \tag{A10}$$

For the case of low byproduct production (which is the only realistic case of interest), $P_C >> \sum_{j=1}^{N_R} \alpha_{Cj} P_{Dj}$ (in dimensionless terms, $\sum_{j=1}^{N_R} \alpha_{Cj} P'_{Dj} << 1$) and Eq. A8 can be approximated as

$$P'_{Dj} \approx k'_j \frac{q'^{\left(\alpha^T-\alpha_j^T\right)}}{\prod\limits_{i=1}^{N} R_i'^{\left(\alpha_i-\alpha_{ij}\right)}} \tag{A11}$$

The low byproduct approximation can also be used in the expression for the reactor effluent volumetric flow rate in Eq. A9 to give $q' \approx 1 + \sum_{i=1}^{N} R'_i v'_i$. Inserting this expression into Eq. A11 gives

$$P'_{Dj} \approx k'_j \frac{\left(1 + \sum\limits_{i=1}^{N} R'_i v'_i\right)^{\left(\alpha^T-\alpha_j^T\right)}}{\prod\limits_{i=1}^{N} R_i'^{\left(\alpha_i-\alpha_{ij}\right)}} \tag{A12}$$

This general expression for byproduct formation is given in Eq. 2 and is used throughout the article.

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