Optimization of Van de Vusse Reaction Kinetics Using Semibatch Reactor Operation

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Methods of semibatch or periodic reactor operation needed to maximize the yield of the desired intermediate species in the Van de Vusse chemical reactions are presented. The operating parameters of the stirred-batch reactor in the kinetic region where semibatch operation is superior to both plug-flow and continuous operation are determined and are given as a function of the ratios of the associated kinetic rate constants. Digital simulation techniques are employed to investigate the range of operating and kinetic conditions likely to be encountered. The methods employed are easily extendable to other reaction schemes.

Cyclic operation of a stirred tank chemical reactor in such a manner that the input and output flows are periodically varied results in a type of variable-volume operation known as semibatch. Under this procedure, the reactor is charged with feed until full, allowed to remain at a constant volume for a predetermined period of time (a variable used in optimizing yield), and emptied to a specified minimum level (another variable used in optimizing yield). The cycle then starts over immediately, unless downtime is inserted as another segment in the cycle.

A generalized depiction of semibatch operation using periodically adjusted flow rates is shown in Figure 1. The cycle is divided into four parts: filling, batch, emptying, and down. The simplest case of semibatch operation (used in this work) operates with no downtime, and with equal filling and emptying rates. This type of cyclic operation has been shown to result in increased yield relative to both the CSTR and the batch reactor in a number of cases.
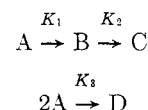
Lund and Seagrave (1971a) analytically demonstrated an increase in yield using a variable-volume reactor with an isothermal first-order reaction and an adiabatic first-order exothermic reaction. Fang and Engel (1967) showed increases in the cases of isothermal first- and second-order reactions. Codell and Engel (1971) showed that for cases in which the reaction rate passes through a maximum, semibatch operation can give improved yields relative to the CSTR and plug flow reactors when compared on a residence time basis.

Lund (1970) has shown that when the batch fraction, σ_B, and the dimensionless minimum volume, V_0^*, approach unity, the semibatch reactor approaches batch or plug flow performance. This result implies one can also simulate different levels of mixing, given a stirred tank reactor and a semibatch mode of operation. This adaptability becomes particularly advantageous when consecutive reactions with higher order side reactions occur in a reactor and an intermediate product is desired.

The plug flow and the CSTR reactors represent two conceptual extremes in reactor operation. The plug flow reactor, in which ideally there is no backmixing of reactants of different concentrations, shows a higher yield of intermediate product in consecutive reactions. The CSTR, in which there is supposedly perfect backmixing, has the advantage of suppressing side reactions that are of a higher order than the one producing the desired intermediate product. It is expected then that there will be cases in which an intermediate level of mixing will be desired, whenever both consecutive and higher order side reactions are occurring simultaneously. Van de Vusse (1964) investigated such a reaction scheme and compared plug flow to CSTR operation.

Van de Vusse Reactions

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C$$

$$2A \xrightarrow{K_3} D$$

His findings enable one to choose between the two extremes in mixing.

Gillespie and Carberry (1966), using Van de Vusse's (1964) reaction scheme, extended their analysis to show that in some cases an intermediate level of mixing would produce a yield of intermediate higher than either plug flow or CSTR operation. Intermediate levels of mixing were simulated using a plug flow reactor model with recycle.

Lund and Seagrave (1971b) also investigated the Van de Vusse reactions and simulated intermediate levels of mixing using semibatch operation. They presented their findings along with part of the original work done by Van de Vusse (1964) on a graph whose two coordinates are formed from ratios of the feed composition and reaction rate constants of the three reactions.

They compared the yield of B, the intermediate, using one semibatch policy, to the yields from both standard reactors over a range of points on the graph to determine the region where the semibatch policy was superior. It was recommended that the area of the region where semibatch operation gave the maximum yield be maximized and also that the different semibatch cycles which optimize the yield of B for each specific set of coordinates could be determined for points within this region. This work presents the results of the subsequent investigation to optimize the yield of B and is of particular interest in cases where the intermediate is of great value.

Analysis of Variable-Volume Operation

General Working Equations. The starting point in the investigation of the Van de Vusse reaction scheme using a semibatch mode of reactor operation is the derivation of the material balance equations. These equations are then put into dimensionless form suitable for solution on a digital com-
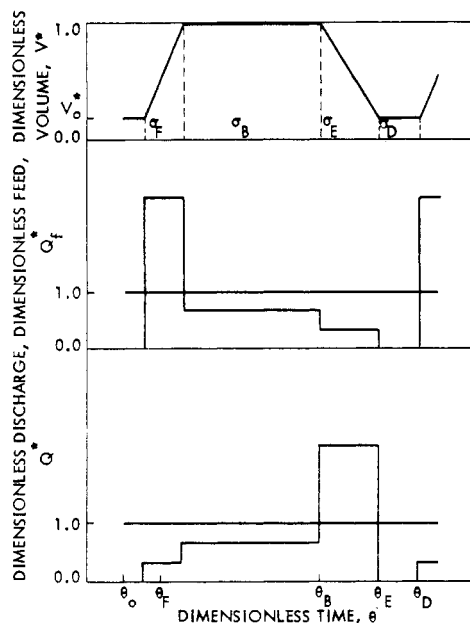
Figure 1. The generalized semibatch cycle

Figure 2. The specialized semibatch cycle

puter using a numerical integration technique. The method is illustrated below and can be extended to other reaction schemes.

The semibatch policy depicted in Figure 1 was further specialized in that input and output flows were never simultaneous and were always of constant magnitude. Figure 2 depicts this specialized semibatch cycle.

For Component A. Filling

$$\frac{d}{dt}(VC_A) = Q_fC_{Af} - K_1VC_A - K_3VC_A^2 \tag{1}$$

$$V\frac{dC_A}{dt} + C_AQ_f = Q_fC_{Af} - K_1VC_A - K_3VC_A^2 \tag{2}$$

Substituting

$$C_A^* = C_A/C_{Af} \tag{3}$$

$$P1 = K_1V_m/Q_f \tag{4}$$

$$P3 = K_3C_{Af}V_m/Q_f \tag{5}$$

$$V_0^* = V_0/V_m \tag{6}$$

$$\theta = t/(V_m/Q_f) \tag{7}$$

$$V = V_0 + Q_ft \tag{8}$$

into eq 2 leads to a dimensionless material balance for component A during the filling of the reactor.

$$\frac{dC_A^*}{d\theta} = -P1 \cdot C_A^* - P3 \cdot C_A^{*2} - \frac{C_A^*}{(V_0^* + \theta)} + \frac{1}{(V_0^* + \theta)} \tag{9}$$

It has been assumed that there is no volume change due solely to chemical reactions, and that the reactor operates isothermally. In addition, perfect mixing has been assumed; that is, the exit stream exactly represents the reactor contents at every location at any point in time. The remaining two parts of the semibatch cycle (batch and emptying) are described by the same material balance equation.

Batch

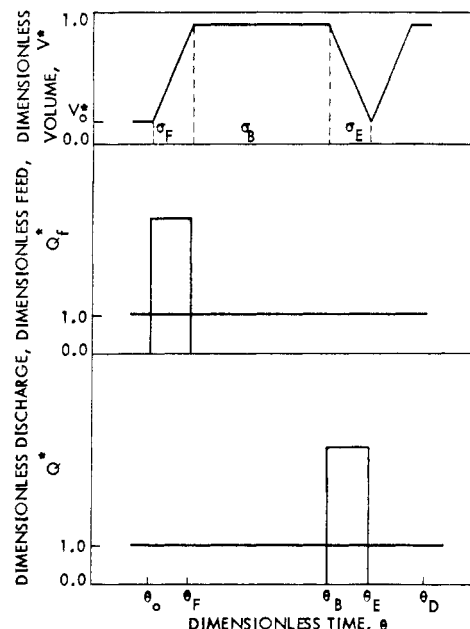$$\frac{d}{dt}(VC_A) = -K_1VC_A - K_3VC_A^2 \tag{10}$$

Dividing both sides of the equation by V

$$\frac{dC_A}{dt} - = K_1C_A - K_3C_A^2 \tag{11}$$

Substituting the same dimensionless quantities as before, the material balance expression for component A is obtained for both the batch and emptying parts of the cycle.

$$\frac{dC_A^*}{d\theta} = -P1 \cdot C_A^* - P3 \cdot C_A^{*2} \tag{12}$$

The same procedure is used in deriving the material balance equations for component B and yields eq 13 and 14.

Component B. Filling

$$\frac{dC_B^*}{d\theta} = P1 \cdot C_A^* - P2 \cdot C_B^* - \frac{C_B^*}{(V_0^* + \theta)} \tag{13}$$

Batch and Emptying

$$\frac{dC_B^*}{d\theta} = P1 \cdot C_A^* - P2 \cdot C_B^* \tag{14}$$

$$P2 = K_2V_m/Q_f \tag{15}$$

Equations 13 and 14 must be solved simultaneously with eq 9 and 12, respectively, and this was done using a fourth-order Runge-Kutta numerical integration. Copies of the program are available on request.

Computational Strategy

The objective of this study is to find that policy which maximizes the yield of component B. Obviously, the only time B will be flowing from the reactor will be during the emptying segment of the cycle. During this interval, the concentration of B will be a function of time. For this reason, two new symbols are introduced to denote the time-average outlet concentrations during the emptying segment of the cycle: $\bar{C}_A^*$ and $\bar{C}_B^*$.

At this point, there appear to be seven parameters involved in the solution of eq 9, 12, 13, and 14: $P1$, $P2$, $P3$, σ_B, σ_F, σ_E, and V_0^*. However, since the ratios $P3/P1$ and $P2/P1$ are presumed known, that is, the kinetic rate constants are known,
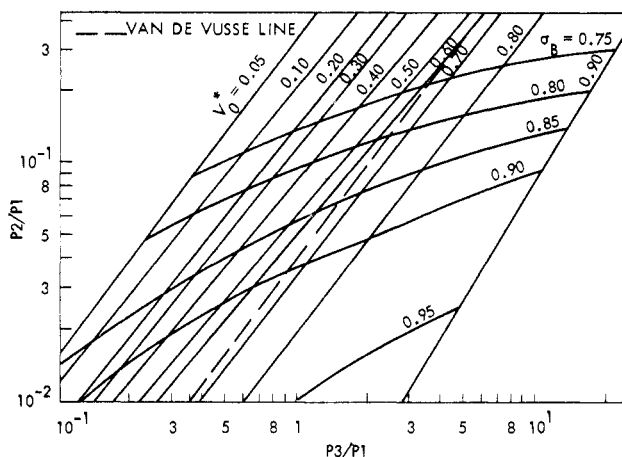
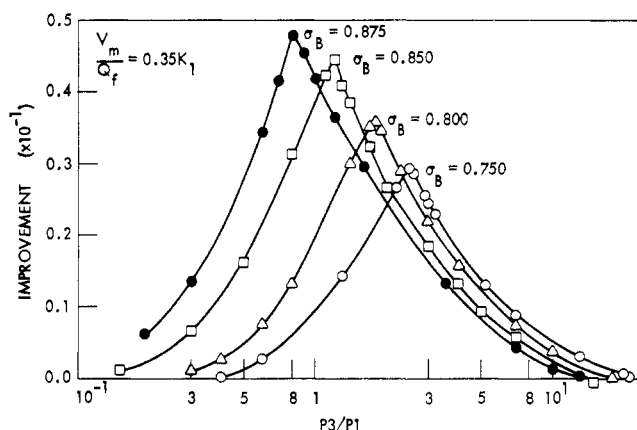Figure 3. An interpolated plot of optimal policy

Figure 4. Maximum improvement as a function of rate constant ratio

only $P1$ need be specified to fix $P2$ and $P3$. The system is additionally constrained by the restrictions that σ_B, σ_F, and σ_E must add to one, and that σ_E must equal σ_F for equal feed and discharge flow rates. Lund (1970) has demonstrated the advantages of maintaining this equality between the input and output flow rates. Therefore, specifying one semibatch parameter fixes the other two. The three remaining parameters are: $P1$, σ_E (or σ_F), and V_0^*.

These three parameters can be reduced to two by making use of the concept of a reference reactor. The mean residence time of this reference reactor will be given the symbol τ_{Ref}. The reference reactor will be a continuous-flow stirred tank reactor and will have a volume equal to the maximum volume of the semibatch reactor (V_m). The reference and semibatch reactors will have the same time-average throughput of process material. Since the reference reactor is operated continuously the flow rate into the semibatch reactor must be multiplied by σ_F in order to give the flow rate of the reference reactor. This leads to the expression for the mean residence time of the reference reactor.

$$\tau_{Ref} = V_m/\sigma_F Q_f \qquad (16)$$

The expression for $P1$ also contains the grouping V_m/Q_f and since the reaction rate constant (K_1) is presumed known, varying V_m/Q_f is the only means left of varying $P1$.

Thus, τ_{Ref} combines two of the previous three parameters ($P1$ and σ_F) into one. The validity of this step was determined

by varying both V_m/Q_f and σ_F, but doing it in such a way that τ_{Ref} always remained constant. The results showed that given a value for τ_{Ref} and V_0^*, the conversion in a semibatch reactor would be fixed regardless of the values V_m/Q_f and σ_F took on individually (see Appendix for demonstration).

Because of this, V_m/Q_f could be fixed at some arbitrary convenient value and the magnitude of τ_{Ref} could be varied by adjusting the value of σ_F (fixing σ_F and varying V_m/Q_f by varying $P1$ would also be acceptable). Subsequent calculations were carried out with the value of V_m/Q_f set at $0.35/K_1$. This then leaves two adjustable parameters, V_0^* and σ_F, with which to optimize the conversion of component A to the intermediate component B in a semibatch reactor.

Note that assigning V_m/Q_f an arbitrary value in no way constrains the semibatch system. Once the optimal values for σ_F and V_0^* are determined, different values for V_m/Q_f can be used by adjusting σ_F accordingly (see Appendix).

Results and Discussion

As stated previously, there are two variables that characterize the semibatch cycle. They are V_0^*, the dimensionless minimum volume, and τ_{Ref}, the holding time of the reference CSTR. The calculations were performed, and the results are presented in terms of V_0^* and σ_B in Figure 3. Keep in mind that the values of σ_B, σ_F, and σ_E are applicable only for the value of V_m/Q_f specified previously $(0.35/K_1)$. It is likely that different values for V_m/Q_f may be more convenient to use in particular cases. This presents no problem, and the technique for carrying out the necessary transformation is presented in the Appendix. The change will have no effect on V_0^* but will result only in a reapportionment of the semibatch cycle among the three segments, batch, filling, and emptying in such a way that τ_{Ref} remains constant.

In reference to Figure 3, it should be emphasized that there was no a priori connection between the semibatch cycle parameters that optimized the yield of intermediate. Optimization of the semibatch cycle was performed for 57 points on the graph. The two sets on contour lines resulted from interpolation.

Using Figure 3, a choice can be made between one of the three reactor types: plug flow, semibatch, or CSTR. This choice will be determined by the ratios of the reaction rate constants K_2/K_1 and K_3C_{Af}/K_1. (Note that $P2/P1$ equals K_2/K_1 and $P3/P1$ equals K_3C_{Af}/K_1. Different notation is used as a reminder that the P's contain the grouping, V_m/Q_f in addition to the reaction rate constants.)

The contour line for $V_0^* = 0.05 \pm 0.01$ forms the boundary between plug flow and semibatch operation, and $V_0^* = 0.90 \pm 0.01$ forms the boundary between CSTR and semibatch operation. They serve the same purpose as the Van de Vusse line does when the choice is restricted to plug flow or CSTR operation. The Van de Vusse line is shown as a reminder that semibatch yields must be compared to plug flow yields for points to the left and CSTR yields for points to the right.

As an example in using Figure 3, take the case in which $K_2/K_1 = 0.12$ and $K_3C_{Af}/K_1 = 7.0$. This point lies within the semibatch region at the intersection of the contour lines $V_0^* = 0.85$ and $\sigma_B = 0.85$. The reactor would cycle between 85 and 100% capacity, spending approximately $^{11}/_{13}$ of each cycle as a batch reactor with $^1/_{13}$ of the cycle spent in filling and $^1/_{13}$ in emptying.

Figure 4 is a plot of improvement (semibatch yield minus steady-state reactor yield) in the dimensionless concentration of B vs. $P3/P1$, the abscissa of Figure 3, for each of the four values of σ_B.

Summary

Semibatch operation differs from plug flow, CSTR, and plug flow with recycle operation in that it incorporates reactor filling as part of its process. A comparatively minor segment of the semibatch cycle spent in reactor filling changes reactor performance radically. Lund and Seagrave (1971b) discuss these effects for first-order reactions. Since the semibatch cycle simulates a level of mixing between the plug flow and CSTR reactors, it is similar in some respects to a plug flow reactor with recycle. When the yield of intermediate in the Van de Vusse reaction scheme is compared to the yield in the CSTR or in the plug flow reactor, depending on which side of the Van de Vusse line the reaction coordinates fall, a region is found in which the yield is superior to either. It is then possible to optimize the semibatch cycle for each set of reaction coordinates $(P3/P1, P2/P1)$ so that the yield of intermediate is maximized.

For the area studied, semibatch improvement over plug flow and CSTR performance increased as the reaction coordinate $P2/P1$ decreased and roughly as the Van de Vusse line was approached. It is recommended that more of the reaction surface be studied so that the above trends can be tested.

It is also suggested that the work of Gillespie and Carberry (1966) using a plug flow reactor with recycle be investigated further to see if general relationships exist between recycle ratio and the parameters that characterize the semibatch cycle. A further question is whether there are conditions under which the optimal yield of intermediate using semibatch operation is better than the corresponding maximum using a plug flow reactor with recycle.

Appendix

The Validity of τ_{Ref} as a Characteristic Semibatch Parameter. Case 1

$$t_{BAT} = 14; t_{EMP} = t_{FIL} = 1$$

$$\sigma_F = 1/(14 + 1 + 1) = 1/16$$

$$\tau_{Ref} = V_m/(\sigma_F Q_f)$$

$$\tau_{Ref} = (0.35/K_1) \cdot 1/(1/16)$$

$$\tau_{Ref} = 5.6/K_1$$

$$\sigma_F = 1/16 \text{ and } V_0^* = 0.67 \text{ result in } \bar{C}_B^* = 0.674418$$

Case 2. Let

$$V_m/Q_f = 0.2/K_1$$

$$\tau_{Ref} = 5.6/K_1 = (0.2/K_1)1/\sigma_F$$

$$\sigma_F = 0.03572 = 1/28$$

Computer calculations show that $t_{BAT} = 26$, $t_{EMP} = t_{FIL} = 1$, and $V_0^* = 0.67$ gives the same yield to the fourth decimal place. $\bar{C}_B^* = 0.674402$.

Nomenclature

C_{Af}	= concentration of component A in the feed
C_j^*	= dimensionless concentration of component j, C_j/C_{Af}
$\bar{C}_j^*$	= dimensionless flow average concentration of component j in the discharge stream
Q	= discharge flow rate
Q_f	= feed flow rate
Q_R	= feed and discharge flow rate for the reference reactor
Q^*	= dimensionless discharge flow rate, Q/Q_R
Q_f^*	= dimensionless feed flow rate, Q_f/Q_R
V	= volume of reactor contents
V_m	= maximum volume of contents
V_0	= minimum volume of contents
V_0^*	= dimensionless minimum volume, V_0/V_m
K_i	= reaction rate constant of reaction i
P_i	= dimensionless reaction rate constant of reaction i, $K_i \cdot (C_{Af})^{n-1} \cdot (V_m/Q_f)^n$, where n is the order of the reaction
t	= time

GREEK LETTERS

θ	= dimensionless time, $t \cdot (Q_f/V_m)$
τ_{Ref}	= mean residence time of the reference reactor (defined by eq 16)
$\sigma_B, \sigma_F, \sigma_E$	= dimensionless reactions representing the proportion of the semibatch cycle occupied by batch, filling, and emptying segments, respectively

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