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**A Case Study for Reactor Network Synthesis:
The Vinyl Chloride Process**

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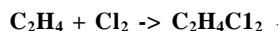
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Abstract - A key objective of the integrated reactor network synthesis approach is the development of waste minimizing process flowsheets (Lakshmanan and Biegler, 1994). With increasing environmental concerns in process design, there is a particularly strong need to avoid the generation of wasteful or harmful byproducts within the reactor network. This also avoids expensive treatment and separation costs downstream in the process. In this study, we focus on the application of integrated reactor network synthesis concepts for the vinyl chloride process. Vinyl chloride is currently produced by a balanced process from ethylene, chlorine and oxygen with three separate reaction sections: oxychlorination of ethylene, direct chlorination of ethylene and pyrolysis of ethylene dichloride, with the hydrogen chloride produced in the pyrolysis reactor used completely in the oxychlorination reactor. Each of these reaction sections generate chlorinated hydrocarbons and carbon oxides as byproducts. Detailed kinetic models for the three reaction sections are used to develop optimal reactor networks which improve the conversion of ethylene to vinyl chloride product and minimize the production of by-products. This case study presents an application of the mixed integer nonlinear programming based reactor network synthesis strategy (Lakshmanan and Biegler, 1996a). A candidate flowsheet is proposed based on these results and a set of recommendations is given to improve the selectivity of vinyl chloride production.

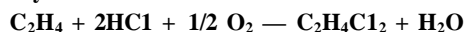
INTRODUCTION

Vinyl chloride monomer is one of the largest commodity chemicals produced in the United States. The market demand for vinyl chloride is connected to the demand for its polymers, especially polyvinyl chloride (McPherson et al., 1979). The first patented process to produce Vinyl Chloride involved reacting hydrogen chloride and acetylene in the presence of a mercuric chloride catalyst. Nowadays, it is produced commercially by pyrolytic decomposition of ethylene dichloride (EDC). EDC is produced by the direct chlorination or oxychlorination of ethylene. The EDC pyrolysis process produces hydrogen chloride as a co-product, which is one of the reactants in the oxychlorination of ethylene. Hence, the hydrogen chloride produced in the pyrolytic reactor is recycled to the oxychlorination reactor. The component processes of direct chlorination, EDC pyrolysis and oxychlorination are combined to develop a balanced process for the production of Vinyl Chloride from ethylene and chlorine with no net consumption or production of hydrogen chloride. The main reactions involved in the component processes and the overall reaction are given by:

Direct chlorination:



Oxychlorination:



Ethylene dichloride pyrolysis:



Overall reaction:

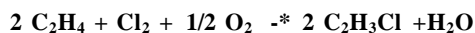


Figure 1: Principal steps in the vinyl chloride process

The three principal operating steps used in the ethylene based balanced process for the production of vinyl chloride (Cowfer and Magistro, 1983) are shown in the block flow diagram, Figure 1. Apart from the main products shown in the equations above a variety of byproducts are produced in these reactors. Some of the more significant byproducts are: 1,1,2 trichloroethane, chloral (trichloroacetaldehyde), cis- and trans- 1,2 dichloroethylenes, mono-, di- tri- and tetrachloromethanes and carbon oxides in the oxychlorination reactor; 1,1,2 trichloroethane in the direct chlorination reactor; and acetylene, ethylene, butadiene, methyl chloride, vinyl acetylene, chloroprene, vinylidene chloride, benzene, trichloroethylene, tri- and tetrachloromethane and other chlorinated products in the pyrolysis reactor. All of these by-products cause problems and their production should be minimized to improve conversion of raw materials to desired products, lower raw material costs, decrease the difficulties in the EDC purification section, prevent coking and fouling of the pyrolysis reactor and reduce waste handling and treatment costs. For example trace quantities of impurities in the pyrolysis reactor feed makes the EDC cracking process susceptible to fouling and inhibition. The feed to the pyrolysis reactor should be at least 99.5% pure EDC. Also, the EDC recovered from the exit of the pyrolysis reactor

contains an appreciable number of impurities, some of these like chloroprene polymerize to a rubbery material which can seriously foul the EDC purification section. Similarly trichloroethylene forms an azeotrope with EDC which can inhibit the pyrolysis reaction, if it is recycled into the pyrolysis reactor. Hence, there is a significant need to improve the performance of these reactors. In this paper we focus on developing optimal reactor configurations, for the three processes of direct chlorination, oxychlorination and pyrolysis, that benefit the development of the vinyl chloride monomer production process flowsheet. The proposed candidate flowsheet improves the conversion of ethylene to vinyl chloride product and minimizes the formation of byproducts. In the next section we present the mixed integer nonlinear programming (MINLP) based reactor network synthesis algorithm (Lakshmanan and Biegler, 1996a); this algorithm is augmented by the multi-objective optimization based waste minimization algorithm (Lakshmanan and Biegler, 1994). In section 3 these algorithms are applied to the vinyl chloride monomer production process and the results of this case study are presented.

ALGORITHM FOR REACTOR NETWORK SYNTHESIS

Lakshmanan and Biegler (1996a) proposed a combination of superstructure and attainable region targeting techniques to synthesize optimal reactor networks. This approach incorporates attainable region properties derived from Feinberg and Hildebrandt(1995). Some of these properties are: (i) the boundary of the attainable region in reaction and mixing consists of plug flow reactor trajectories and straight lines, (ii) recycle streams need not be considered to map the boundary, and (iii) only continuous stirred tank reactor (CSTR), plug flow reactor (PFR) and differential sidestream reactor (DSR) trajectories make up the entire boundary of the attainable region. The reactor network synthesis technique is constructive. It considers multiple reactor paths at each stage by targeting the attainable region using reactor modules. A reactor module consists of a differential sidestream reactor (DSR) and a CSTR for higher dimensional problems (the space represented by independent variables such as residence time, temperature, conversion, etc.). A separate PFR model need not be considered, since the DSR without the sidestream is a PFR. A typical reactor module is shown in Figure 2. A binary variable is associated with each reactor path in a module. If the DSR is chosen in the i th reactor module Y/d , the binary variable associated with it, is set equal to 1. Additional reactor modules are added successively and the superstructure is developed in a constructive manner by solving a sequence of improving MINLP's. The attainable region properties ensure that the MINLP is compact. The steps involved in the

constructive stagewise algorithm are: (i) Solve an isothermal segregated flow model to obtain a lower bound on the solution. This formulation is often a linear program with a global solution, (ii) Initialize the first reactor module with the solution obtained from step I and optimize it with respect to a specific objective. The inlet conditions to this reactor module are the feed conditions. This yields an initial target to the attainable region. In addition, it does not eliminate the other path; the binary variables associated with each path are set to one or zero, (iii) Extend the reactor module with an additional reactor module. The feed to the second module is the exit of the first module or a combination of the fresh feed and the exit of the first module. If the extension improves the objective then further extensions need to be considered, else the optimal network is assumed to have been found., (iv) Ensure that the feed to the i th reactor module extension may be the exit of any one or a combination of the exits of the previous $i-1$ modules or the initial feed and (v) Account for bypass streams by ensuring that the exit from the i th reactor module plus the bypasses from the exits of any one or a combination of the previous ($i-1$) reactor modules, forms the inlet to the ($i+1$)th reactor module.

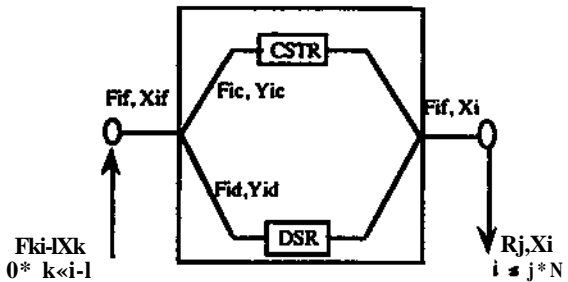


Figure 2: i th Reactor module

The problem is formulated as in (P2.1).

$$\max J(X_{\text{exit}} * x) \quad (P2.1)$$

$$q, f, T$$

$$X_{\text{CSTR}(i)} = R(X_{\text{CSTR}(i)}, T_{\text{CSTR}(i)}) + X_{0(i)} \quad (2.1)$$

$$dX_{\text{DSR}(i)} = R(X(\alpha_{(i)}), T(\alpha_{(i)})) + (q(\alpha_{(i)}) Q_{\text{side}(i)} / Q(\alpha_{(i)})) (X_{\text{side}(i)} - X(\alpha_{(i)})) \quad (2.2)$$

$$X_{\text{DSR}(i)} = X_{0(i)} \quad (2.3)$$

$$X_{\text{DSR exit}(i)} = \int_0^{t_{\text{max}}} X(\alpha_{(i)}) d\alpha_{(i)} \quad (2.4)$$

$$1 = \int_0^{t_{\text{max}}} X_{f(a w)} d\alpha_{(i)} \quad (2.5)$$

$$1 = \int_0^{t_{\text{max}}} q(\alpha_{(i)}) d\alpha_{(i)} \quad (2.6)$$

$$\tau = \int_0^{t_{\text{max}}} \int_0^{\alpha_{(i)}} (q(\alpha_{(i)}) Q_{\text{side}(i)} / Q_{\text{exit}(i)} - f(\alpha_{(i)})) d\alpha_{(i)} d\alpha_{(i)} \quad (2.7)$$

$$T_{\text{DSR exit}(i)} = \int_0^{t_{\text{max}}} f(\alpha_{(i)}) T(\alpha_{(i)}) d\alpha_{(i)} \quad (2.8)$$

$$F_{if} = \sum_{k=0}^i F_{k,i-1} \quad (2.9)$$

$$F/fX_{jf} - ZFkMX_{fc} \quad (2.10)$$

$$k=0$$

$$X_{if} = X|_c \quad i_n = X_{id} \quad i_n \quad (2.11)$$

$$F_{if} = F_{ic} + F_{id} \quad (2.12)$$

$$F/f \quad X/f = F|_c X|_c + F_{id} X_{id} \quad (2.13)$$

$$1 = Y_{ic} + Y_{id} \quad (2.14)$$

$$F_{if} \quad X_i = \sum_{j=i}^{N_{mod}} F_{ij} \quad X_j \quad (2.15)$$

$$X_{c_{ik}} = X_{N_{mod} \text{ exit}} \quad 0 \leq F_{ic} \leq UY_{ic} \\ 0 * F_{id} * </Y_{id} \quad Y_{ic} \in \{0,1\} \quad Y_{id} \in \{0,1\}$$

Equations (2.1)-(2.8) constitute the reactor module at stage i made up of a CSTR (2.1) and a DSR (2.2)-(2.8). Equations (2.9) and (2.10) may be understood by studying Figures 2. In Figure 2 the feed conditions (F/f , X/f) to i th module may be the exit conditions of any one or a combination of the previous ($i-1$) modules. Hence when the i th reactor extension is considered, bypasses from the exits of the previous ($i-2$) modules and the feed are automatically considered. Similarly, parallel reactor structures up to the ($i-1$)th module are also accounted for. This structure keeps the constructive MINLP algorithm as small as possible. In the i th reactor module either the CSTR or the DSR may be chosen and the exit conditions from the i th reactor module ($X|$) are determined appropriately. This is represented by equations (2.11), (2.12), (2.13) and (2.14). The exit stream from the i th reactor module forms the inlet stream to any one or a combination of reactor modules ($i+1$) to N_{mod} (2.15). Up to N_{mod} parallel structures may be realized where N_{mod} is the number of reactor modules or stages in the optimization. Lakshmanan and Biegler (1996a) discuss the advantages and disadvantages of this strategy. In addition, they suggest an initialization procedure, a solution technique and remedies for possible problems due to the bilinear equations (2.10) and (2.13).

WASTEMINIMIZATION ALGORITHM

The reactor network synthesis algorithm presented above gives a good reactor network configuration which optimizes a specified objective. In order to simultaneously minimize waste while maximizing the primary objective a multiobjective optimization algorithm based on the ϵ constraint technique (Haimes and Li, 1971) is proposed. The problem is formulated as in P2.2. Formulation P2.2 is used to generate the noninferior set or pareto set of solutions. The waste minimization algorithm (Lakshmanan and Biegler, 1994) first solves the primary problem, which yields the limiting points of the noninferior curve, the maximum primary objective (P) and the

minimum waste level (W) which may be achieved. The reactor network synthesis strategy described earlier is used to generate the reactor network for both cases, with the production level of the desired product fixed at the required levels and the waste constrained to remain below the maximum allowed levels, which conform to regulatory constraints. The results of the primary problem are then used to initialize the secondary problem. The objective here is to maximize the primary objective. The ϵ constraint technique is adapted to map the "noninferior curve" by using an additional constraint which varies the waste between the minimum and maximum possible levels. The solution, using this algorithm, yields the optimal reactor network, size of the reactors, maximum primary objective, waste production levels, fraction of recycle in the process and the noninferior curve between the primary objective and waste levels.

$$\min_{x,y} \{-P(x,y), W(x,y)\} \quad \min_{x,y} -P(x,y) \quad (P2.2)$$

$$\text{s.t. } h(x,y) = 0 \quad \text{s.t. } h(x,y) = 0 \\ g(x,y) \leq 0 \quad g(x,y) \leq 0 \\ W(x,y) \leq W_{max} \quad W(x,y) \leq \epsilon$$

$$x \in \text{R}^n, y \in \text{P} \quad y \in \text{PY} \in \text{R}^m \in G[W_{min}, W_{max}]$$

where x is the set of flowsheet parameters, y is the set of reaction and energy network variables, ϵ is a fixed parameter and $h(x,y)$ and $g(x,y)$ are the constraints involved in the process.

The most significant outcome of finding the noninferior curve is that, since we cannot always be sure of what the allowable waste levels will be in the future, decision makers can get an estimate of what the primary objective would be at specific waste levels. After making educated guesses as to what the future specifications and costs would be, they can decide as to whether the project should be implemented or abandoned. This represents an opportunity cost for the design of a waste minimizing plant. Also, once the noninferior curve has been plotted, a sensitivity curve between say, net profit after waste treatment, and waste costs can be plotted. In the next section we apply these algorithms to the vinyl chloride monomer production process.

VINYL CHLORIDE MONOMER PRODUCTION PROCESS - CASE STUDY

Figure 1 shows the five major sections of the vinyl chloride monomer production plant. The three reaction sections are integrated into a balanced process flowsheet with the separation sections, by recycling the hydrogen chloride recovered from the pyrolysis section to the oxychlorination section. In addition, the EDC recovered from the pyrolysis section is recycled to the EDC purification section.

The process flowsheet is modeled in GAMS (Brooke et al., 1988). The model is a MINLP with 8 binary variables (4 each in the direct chlorination and oxychlorination sections to synthesize the optimal reactor structures, for the sake of simplicity the pyrolysis reactor section was fixed to be a PFR in the process flowsheet) and 49S4 continuous variables and 4193 equations. The purification sections are modeled using split fractions, which were based on the data published in the PRO/II Casebook on the vinyl chloride monomer plant (1992). Each of the reactors in the model was initialized with profiles obtained from solving initial value problems. The results of the flowsheet optimization, which maximizes selectivity of ethylene to vinyl chloride monomer, are shown in Table 1. The waste minimization algorithm may be used to develop trade off curves between the amount of waste produced (in each of the different sections) and conversion of ethylene. Each individual reaction section and the results obtained from the optimization are discussed in detail below.

DIRECT CHLORINATION OF ETHYLENE

Direct chlorination of ethylene to EDC is a homogeneous catalytic reaction in the liquid phase. Commercially the exothermic reaction is conducted in a liquid phase reactor by intimately mixing ethylene and chlorine in liquid EDC. The reaction is catalyzed by ferric chloride catalyst. The heat produced is removed by cooling water or by operating the reactor at the boiling point of EDC and allowing the pure product to vaporize. We modeled the direct chlorination reaction using kinetics from Wachi and Morikawa, 1986. EDC is formed by an addition reaction between ethylene and chlorine. The main byproduct is 1,1,2 trichloroethane which is formed by substitution and addition reactions between chloride radicals, chlorine and EDC. The temperature range considered was 30-75 C and pressure was allowed to vary between 0-2 atm. A slight excess of ethylene is used and the optimal reactor structure was found to be a CSTR (1701.08 s) followed by a PFR (0.01 s) with 99.97% conversion of the limiting component (chlorine) and 99.41% selectivity to EDC. If the reactor network was fixed to be a single CSTR the conversion of the limiting component is 99.94%.

OXYCHLORINATION OF ETHYLENE

In the balanced oxychlorination process ethylene reacts with dihydrogen chloride gas produced from the pyrolysis of EDC. Typically, the reaction is conducted in either a fixed bed (230 - 300 C, 1.5 - 14 atm gauge pressure) or a fluidized bed (220-235 C, 1.5-5 atm gauge pressure) plug flow reactor containing a catalyst with copper chloride as the active ingredient impregnated on a porous alumina support (Cowfer and Magistro, 1983). It is a highly

exothermic reaction, good temperature control is essential. Increasing reactor temperature results in increased byproduct formation and catalyst deactivation. The reaction is modeled using kinetics obtained from a series of papers by Gel'perin et al., (1979, 1983, 1984). EDC is formed through a heterogeneous catalytic cycle where the main chlorinating agent is copper(II) chloride. The byproducts considered are trichloroethane and carbon oxides. The recycled hydrogen chloride stream from the top of the vinyl chloride monomer purification section is the limiting component in this reaction. Ethylene and oxygen are fed to the reactor in slight excess of their stoichiometric requirement. The optimal reactor network was found to be a PFR (0.09 h) followed by a CSTR (0.0067 h). The optimal temperature profile in the PFR is shown in Figure 3 and the reactor pressure was found to be 4.9 atm. 99.9% conversion of the limiting component (hydrogen chloride) was observed with a selectivity of ethylene to EDC of 99%. If the reactor network was fixed to be a PFR under the conditions in the vinyl chloride monomer plant PRO/II case study (290 C, 6.122 atm) then the amount of trichloroethane produced per kg of EDC formed is 0.016 and the amount of carbon oxides produced per kg of EDC formed is 0.03, as compared to our results of 0.0015 and 0.00036 respectively. The waste minimization algorithm was used to plot the noninferior curve between conversion of ethylene to EDC and the trichloroethane produced in the oxychlorination reactor. The optimal reactor structure was a PFR + CSTR and the curve is shown in Figure 4.

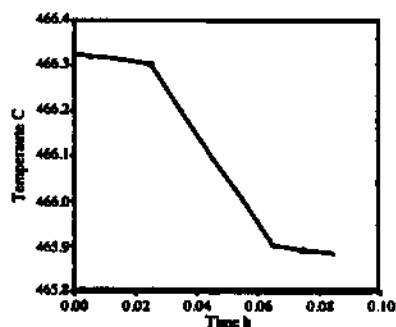


Figure 3: Temperature profile in the PFR - Oxychlorination section

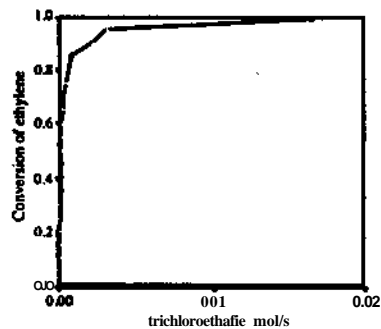


Figure 4: Noninferior curve

EDC PURIFICATION

Trace quantities of impurities in the pyrolysis reactor feed can cause fouling of the reactor. Hence, EDC from three different sources: direct chlorination, oxychlorination, and EDC recovered and recycled from the pyrolysis section must be purified to at least 99 wt % pure dry EDC. EDC produced in the oxychlorination section is washed in a caustic wash to remove unreacted hydrogen chloride. This stream is mixed with the EDC produced in the direct chlorination section and fed to a decanter, followed by two distillation columns, the first column is the lights column where 99.9 % of the water is removed as top product. The bottom product is fed into the heavies column. The top product of this column is 99.9 wt % pure dry EDC which is fed to the pyrolysis section.

	Chlorination		Pyr.	Purification	
	Direct	Oxy-		EDC	VCM
Raw* material					
C ₂ H ₄	0.514	0.499	6.1e-6	6.0e-3	6.0e-6
Cl ₂	0.511		3.1e-6	1.5e-4	1.3e-8
O ₂		0.251	3.4e-7	3.4e-4	
Inter- mediate EDC	0.506	0.494	1.85	3.8e-4	0.85
By- product					
C ₂ H ₃ Cl, CO ₂				7.0e-3 1.6e-4	1.0e-4
C ₂ H ₂ , C ₄ H ₆ , C ₂ H ₂ Cl ₂					9.8e-4
Main Product C ₂ H ₃ Cl					1

* mol/mol of vinyl chloride

Table 1: Results of the vinyl chloride case study

PYROLYSIS OF EDC

Vinyl chloride monomer is produced by thermal cracking of EDC. The endothermic reaction is carried out commercially in tubular reactors at temperatures of 480 - 530 C and reactor gauge pressures of 6 - 35 atm (Ranzi et al., 1993). The main reaction which yields vinyl chloride monomer and hydrogen chloride is a homogeneous, first-order free-radical chain mechanism. Several byproducts are produced in trace amounts through related free-radical and molecular mechanisms. The EDC pyrolysis process is very selective to vinyl chloride. It is difficult to verify the formation and amount of the

byproducts. Also, it is very difficult to obtain kinetic parameters of the reactions involved. The pyrolysis reaction kinetics were compiled from various literature sources (Ranzi et al., 1990, Benson and Weissmann, 1984, Kurtz, 1972, Kara and Senkan, 1988). The byproducts considered in the kinetic model include acetylene, ethylene, butadiene, trichloroethane and vinyl acetylene. Each of these byproducts are harmful and could foul the reactor, if recycled. A plug flow reactor with the temperature fixed at 500 C and a reactor pressure of 20 atm was used to model the pyrolysis section. Orthogonal collocation on finite elements is used to discretize the reactor into finite elements. The results are summarized in Table 1. Vinyl chloride selectivity was found to be 99.9% at a single pass conversion of 54 % of the EDC fed to the pyrolysis reactor.

CONCLUSION

The reactor network synthesis algorithm has been successfully applied to the three reaction sections (oxychlorination, direct chlorination and pyrolysis) of the vinyl chloride monomer production process. The reactor models developed were integrated into a balanced flowsheet and the selectivity of the ethylene entering the process to vinyl chloride has been maximized. The optimal reactor structures for the three reactor sections were found to be: Oxychlorination: PFR + CSTR; Direct chlorination: CSTR + PFR and a PFR for the pyrolysis section. These reactor structures perform better than the conventional reactors used for these processes and enhance the conversion of raw materials to the desired products while minimizing waste production. The waste minimization algorithm was applied to the oxychlorination section and the noninferior curve between one of the main waste products and the conversion of ethylene was plotted.

Research work is in progress to study the effect of mass integration on this candidate flowsheet. The streams in the process are characterized as rich and lean streams. The reaction-mixing-separation model (Lakshmanan and Biegler, 1996b) is incorporated into the MINLP approach for reactor network synthesis by replacing the DSR in the module by the reaction-mixing-separation model and the CSTR with a steady state model of a CSTR with separation. The problem is formulated as:

$$\begin{aligned}
 & \max_{x,y} J(x,y) - I_m CO_m L_m \\
 & \text{s.t.} \quad (x,y) = 0 \\
 & \quad g(x,y) \neq 0 \\
 & \quad m_p(rx,ly) = 0 \\
 & \quad z_p(rxJy)s_0 \\
 & \quad x \in P, x \in R^m, y \in PYGRQ, rx, ry \in G, PY
 \end{aligned}$$

where CO_m is the utility cost of the m th lean stream, x is the set of flowsheet parameters, y is the set of reaction and separation network variables, rx is the mass composition of the key component being separated (kg key/kg inert) from the rich reactor streams and ly is the mass composition of the same component in the lean stream. $h(x,y)$ and $g(x,y)$ are the constraints involved in the reaction-mixing section and the process, and $mp(rx^y)$ and $z_p(rx,ry)$ are mass balance and thermodynamic feasibility constraints involved in the mass integration of the process. This integrated reactor network and mass exchanger approach derives networks that can remove products as they are formed without further degradation. Moreover, a tighter integration of reaction and separation has led to more profitable and efficient processes. Results of this approach will be reported in a future study.

NOMENCLATURE

$f(a(t))$ = residence time distribution in the PFR or DSR in module i
 F/f = inlet flowrate to the i th reactor module
 F/c = flowrate through the CSTR and DSR in the i th reactor module
 Pk_{i-1}^{exit} = flowrate from module k which is an inlet to module $i-1$, $k=0, i-1$
 $q(o(t))$ = fraction of Q_{side} entering the DSR at a in module i
 $Q(ct(t))$ = Volumetric flowrate through the PFR or DSR at a in reactor module i
 Q_{side} = feed stream flowrate to the DSR
 $R(X(ct), T(a))$ = rate vector at a
 x = residence time
 $T(a)$ = temperature inside the reactor at a
 T_{CSTR} = temperature inside the CSTR
 $T_{DSR exit (i)}$ = temperature at exit of the DSR in module i
 $X(o(t))$ = concentration vector at point a inside the DSR in module i
 $X_{CSTR (i)}$ = concentration vector inside the CSTR in module i
 $X_{DSR (i)}$ = concentration vector inside the DSR in module i
 X/c_{in} = concentration vector at the inlet to the CSTR in module i
 X/d_{in} = concentration vector at the inlet to the DSR in module i
 X/f = concentration vector at the feed to module i
 $Y|_c$ = Binary variable denoting the existence / nonexistence of the CSTR in module i
 $Y|_d$ = Binary variable denoting the existence / nonexistence of the DSR in module i

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