

A Sequential Synthesis Framework for Heat-Integrated Complex Reactor Network

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Reactor network synthesis plays an important role in finding green and sustainable chemical production flowsheet. Previous researches were usually optimized under specific reaction path, leading to a suboptimal network structure, and less attention has been paid to heat integration between reactors. However, simultaneously optimizing these two problems with multiple reaction paths involved inevitably leads to a combinational explosion of computational complexities. Therefore, a hierarchical optimization approach for the heat-integrated complex reactor network is proposed in this work. In the first step, the reaction paths tree and its relationship with reactor networks are discussed by embedding different reaction pathways into reactor network superstructure. The corresponding mathematical model is formulated as a mixed integer non-linear programming (MINLP) problem and a number of alternative reactor networks with specified catalysts arrangement are obtained by the interactive iteration solving strategy. In the second step, heat integration between reactors is achieved by the synthesis of heat exchanger network, which leads to a significant decrease in the total energy consumption. Ultimately, a case study for p-xylene production is introduced to demonstrate the effectiveness of the proposed method.

1. Introduction

The discharge of contaminants in a chemical process is primarily decided by the condition of reactions, which mainly depend on the design of reactor network, and the energy consumption indicates the sustainability of a chemical process. Optimization of reactor network is to address the problem of reactor network synthesis, whose solution approaches can be classified as heuristic, attainable region and superstructure-based methods (Peschel et al., 2010). While the most common optimization methods rely on superstructure approaches, which have shown great success in reactor network synthesis. Jin S. et al. (2012) proposed a double-level optimization method, according to the character of the reactor network model based on CSTR, combining linear programming and stochastic optimization approach. Soltani H. and Shafiei S. (2015) applied genetic algorithm coupled with quasi linear programming (LP) method for the synthesis of adiabatic reactor networks, which converted the MINLP model to a quasi LP. Zhao X. and Marquardt W. (2016) proposed a systematic superstructure-based approach to design reactor networks with guaranteed robust stability. However, reactor networks were all optimized under a specific reaction path in aforementioned researches, usually leading to a suboptimal network structure. Furthermore, heat integration should also be taken into consideration for the opinion of energy-saving and emission reduction, while previous researches pay less attention to the effect of heat integration on reactor network synthesis (Lavric et al., 2005; Zhang D. and Liu G., 2016). In most cases both reactor network synthesis and heat exchanger network synthesis lead to MINLP problems. Simultaneously optimizing the two problems inevitably causes a serious increase in computational complexities. Hence, a hierarchical optimization approach for heat-integrated complex reactor network is proposed in this work. Since the chemical reactors are the very core of any chemical process, reaction paths tree and its relationship with reactor network is discussed in the first step. By introducing functional catalysts arrangement, the reaction paths and reactor network could be incorporated in the modified state space superstructure simultaneously. The corresponding mathematical model is formulated as a MINLP problem by coupling kinetics in reaction paths and mass/energy balance equations in reactor networks. A number of alternative reactor networks with specified catalysts arrangement are obtained by the interactive iteration

solving strategy. Then, heat integration between chemical reactors through heat exchangers is employed, reactor networks seen as a part of the heat exchanger network, significantly decreasing the total energy consumption and preserving their performances in terms of chemical transformation ratios. Finally, a case study for p-xylene production is introduced to demonstrate the applicabilities of the proposed sequential method.

2. Problem statement

2.1 Reactor network

It was common that the former works considered all reactor units loaded with the same catalysts and just maximized the objective function of a single production technology. Through the synthesis of reactor network we can finally obtain: (1) the number, type and residence time of reactors; (2) the configuration of reactor networks; (3) maximum objective function value. However, in this work simultaneous synthesis has been performed. This methodology can be applied to both single reaction path and multiple reaction paths. In the later case, important information can also be gained: (1) feasible and activated reaction paths and their interconnections; (2) corresponding catalysts arrangement.

2.2 Heat exchanger network for reactor networks

When alternative reactor networks are obtained, process streams and activated reactors are identified whether they need to be cooled or heated. In this work, reactors are perceived as virtual streams, of which the temperature difference between inlet and outlet is tiny, exchanging heat with process streams or hot/cold utility through heat exchangers. Thus, the heat capacity flow rates of the process streams and reactors can be calculated. Utilities are available and their corresponding temperatures together with costs are given. Also given are the heat transfer coefficients for the process streams, reactors, and the hot and cold utilities. Furthermore, given are the fixed cost charge for each heat exchanger and the charge coefficients in order to calculate the investment of each heat exchanger according to its area. Stage-wise superstructure is adopted (Yee and Grossmann, 1990) and the objective of the problem is to achieve economic-optimal heat exchanger network, by determining the number of heat exchangers and their respective areas as well as the utility consumption. Note that the way heat transfers in reactors and the effects in heat transfer caused by phase transformation are ignored.

3. Superstructure

The synthesis strategy is based on such a proposition that the key to couple reaction path synthesis and reactor network synthesis is interconnections of reactor modules with different catalysts loaded. Each reactor module corresponds to a single production technology and each main reaction takes place only in the reactor module with specific functional catalyst loaded.

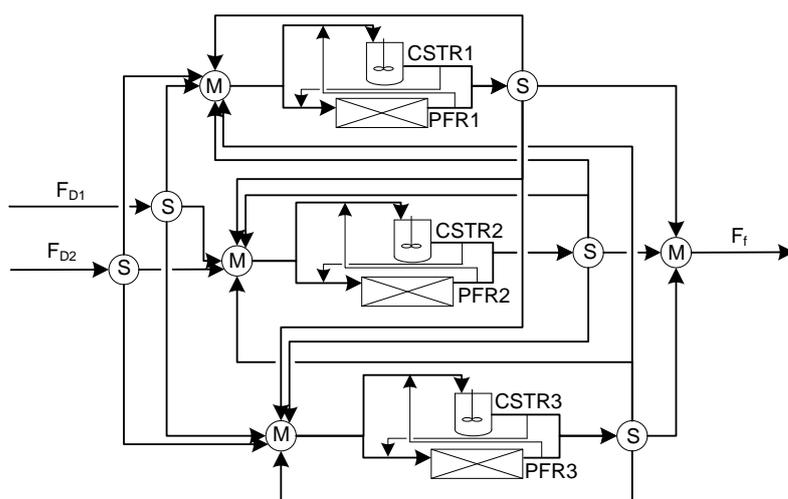


Figure 1: Schematic initial superstructure of functional catalysts arrangement.

Basic types of reactors embedded in this superstructure are: ideal CSTRs and ideal PFRs. Every reaction path is guaranteed by a reactor module consisting of a CSTR and a PFR with corresponding functional catalyst loaded. Binary variables are introduced and equal to one when CSTR/PFR is activated in the reactor module. Considering the differential properties of PFR design equation which in mathematical formulation will result in a non-linear programming (NLP) with both algebraic and differential equations, collocation with orthogonal polynomials method (Biegler, 2010) is applied to approximate the PFR model. Such approximation greatly reduces the complexity of mathematical formulation. Finally the model would be a MINLP problem with only algebraic equations.

The key to build a proper superstructure is that network of reactors and streams must embed all possible interconnections both in single unit and among various units. We built a schematic initial superstructure shown in Figure 1. From Figure 1, the schematic initial superstructure contains three reactor modules, which means desired products can be directed by three kinds of functional catalysts. The interconnections of three modules include all possible reaction sequences. In a reactor module, a CSTR and a PFR are interconnected. Besides, mixers and splitters are designed in the reactor modules to guarantee the interconnection and self-circulation.

4. Mathematical model

I: Equations

a). Total mass balance

$$\sum_n FD_n = FPRO \quad (n \in N) \quad (1)$$

$N = \{n\}$, n stands for each component in reaction system. FD_n is the pure feed stream of each reactant in mass flow, while $FPRO$ is the final product stream in mass flow.

b). Splitter of each feed stream

$$FD_n = \sum_i FR_{n,i} \quad (n \in N, i \in I) \quad (2)$$

$I = \{i\}$, i stands for number of reactor module. $FR_{n,i}$ is the feed stream of component n from outlet of splitter to mixer before each reactor module.

c). Mixer and splitter prior to each reactor module

$$FR_{n,i} + \sum_j (RR_{j-i} AFIN_{j,n}) = FRP_i AIN_{i,n} \quad (i, j \in I, n \in N) \quad (3)$$

$$FRP_i = FRP_i^C + FRP_i^P \quad (i \in I) \quad (4)$$

C in superscripts stands for variables in CSTR reactor. P in superscripts stands for variables in PFR reactor. FRP_i stands for the mass flow in reactor module i . RR_{j-i} stands for recycle flow from outlet of splitter of reactor module j to mixer before reactor module i . $AFIN_{j,n}$ is the mass fraction of recycle flow from splitter after reactor module j . $AIN_{i,n}$ is the inlet mass fraction of reactor module i . FRP_i^C and FRP_i^P stand for the mass from feed and other reactor module flow in CSTR and PFR respectively.

d). Mixer prior to each reactor

$$FRP_i^C AIN_{i,n} + FPC_i AOUT_{i,n}^P = F_i^C AIN_{i,n}^C \quad (i \in I, n \in N) \quad (5)$$

$$FRP_i^P AIN_{i,n} + FCP_i AOUT_{i,n}^C = F_i^P AIN_{i,n}^P \quad (i \in I, n \in N) \quad (6)$$

FPC_i and FCP_i stand for the mass from PFR in the same reactor module flow in CSTR and mass from CSTR in the same reactor module flow in PFR respectively. F_i^C and F_i^P stand for the total mass flow in CSTR and PFR respectively. $AIN_{i,n}^C$ and $AIN_{i,n}^P$ are the inlet mass fraction of CSTR and PFR in reactor module i , respectively. $AOUT_{i,n}^C$ and $AOUT_{i,n}^P$ are the mass fraction of outlet of CSTR and PFR after reaction respectively.

e). Splitter after each reactor

$$F_i^C = FCP_i + FF_i^C, \quad F_i^P = FPC_i + FF_i^P \quad (i, j \in I) \quad (7)$$

FF_i^C and FF_i^P stand for the mass flow outlet of reactor module i from CSTR and PFR respectively.

f). Splitter after each reactor module

$$FF_i^C AOUT_{i,n}^C + FF_i^P AOUT_{i,n}^P = \sum_j (RR_{i-j} AFIN_{i,n}) + RM_i AFIN_{i,n} \quad (i, j \in I, n \in N) \quad (8)$$

RM_i stands for the stream from reactor module i to final mixer.

h). Final mixer

$$\sum_i (RM_i AFIN_{i,n}) = FPRO \cdot APRO_n \quad (i \in I, n \in N) \quad (9)$$

$APRO_n$ is the mass fraction for component n in final product stream $FPRO$.

h). Kinetic equations

Reaction rate expressions:

$$R_{rp,i} = f(A_{i,n}, T_i) \quad (i \in I, n \in N, rp \in RP) \quad (10)$$

$RP = \{rp\}$, rp stands for every feasible reaction path. This equation expresses a general reaction rate. $R_{rp,i}$ is mass based general reaction rate for reaction path rp in reactor module i . Similarly, $A_{i,n}$ and T_i are general outlet mass fractions and outlet temperature of CSTR and PFR.

Arrhenius equation:

$$k_{rp} = k0_{rp} \cdot \exp[-Ea_{rp} / (RT_{rp})] \quad (rp \in RP) \quad (11)$$

T_{rp} is the temperature of reaction rp . In the same reactor module there will be different reactions in progress, but we want the temperature to be the optimal only for main reaction. Consequently, the value of T_{rp} should be equal to the suitable value for main reactions. In other words, $T_{rp} = T_i$ in the same reaction module.

j). Mass balance for reactors

Mass balance for CSTR:

$$AOUT_{i,n}^C - AIN_{i,n}^C = t_i^C \sum_{rp} R_{rp,i,n} \quad (i \in I, n \in N, rp \in RP) \quad (12)$$

Mass balance for PFR:

$$\sum_{sk} t_{i,sk} = t_i^P \quad (i \in I, sk \in SK) \quad (13)$$

$$AOUT_{i,n,sk} - AIN_{i,n,sk} = t_{i,sk} \sum_k \Omega_k R_{rp,i,n,sk,k} \quad (rp \in RP, i \in I, n \in N, sk \in SK, k \in K) \quad (14)$$

$SK = \{sk\}$, sk is the number of finite element of a PFR. $K = \{k\}$, k is the number of internal collocation point in a finite element. $t_{i,sk}$ stands for the residence time of reactants in element sk of reactor module i . Ω_k is a orthogonal polynomial to approximate the PFR.

II. Objective function

$$TAP = \max a FPRO \cdot APRO_{tp} - b \sum_i (z_i^P + z_i^C) - \sum_i c_i (V_i^P + V_i^C) - ACHEN \quad (tp, i \in N) \quad (15)$$

Maximum Total Annualized Profit (TAP) is set as objective function in this work. a and c_i stand for the profit coefficient of target product (tp) and cost charge coefficient of reactor respectively. b stands for the fixed cost charge of each reactor, while z_i^P and z_i^C are binary variables. V_i^P and V_i^C stand for the reactants mass in PFR and CSTR respectively. $ACHEN$ is the annualized cost of heat exchanger network.

III. Heat balance

$$QF_n = FD_n / MW_n \cdot CP_n \cdot (T - T_0) \quad (n \in N) \quad (16)$$

$$Q_i^C = F_i^C t_i^C \cdot \sum_n \sum_{rp} (R_{rp,i,n} \Delta H_{rp,n}) \quad (i \in I, n \in N, rp \in RP) \quad (17)$$

$$Q_i^P = F_i^P \sum_{sk} t_{i,sk} \cdot \sum_n \sum_{rp} \sum_k (\Omega_k R_{rp,i,n,sk,k}) \cdot \Delta H_{rp,n} \quad (rp \in RP, i \in I, n \in N, sk \in SK, k \in K) \quad (18)$$

QF_n is the energy needed by feed component n , while Q_i^C and Q_i^P stand for the heat generated in CSTR and PFR in reactor module i . MW_n and CP_n are the molecular weight and heat capacity of component n . T is the temperature of reactor modules, while ΔH_{rp} stands for the heat of reaction rp .

IV. Solving strategies

Both of the reactor network model and heat exchanger network model result in MINLP problems. In solving steps we combined deterministic algorithm with random disturbance. In order to improve the global optimality of solutions, we followed the strategy of random disturbance initializations as well as multi-iteration and screened local optimal solutions.

5. Case study

P-xylene is an important intermediate of chemical manufacture process. Two core reaction units are xylene isomerization and toluene selective disproportionation. However, compared with toluene disproportionation and xylene isomerization, alkylation is an irreversible reaction so that by this reaction path we can achieve higher utilization ratio of aromatic rings. Besides, disproportionation of toluene generates equimolar products of benzene and xylene, which shows a larger optimization space of benzene utilization. An extra reactor module of benzene conversion can be added to joint production technology. Thus we have constructed a reactor network superstructure containing four reaction pathways: toluene alkylation, toluene disproportionation, xylene isomerization and benzene alkylation. Note that different reaction path belongs to different reactor module. Module 1: isomerization (Xu O. and Su H., 2007); Module 2: disproportionation (Xu O. and Su H., 2007); Module 3: toluene alkylation (Wang T. et al., 2011); Module 4: benzene alkylation (Zhao B. and Guo X., 2013).

Feed conditions (mass flow) : 46 t/h for toluene; 32 t/h for methanol; 39 t/h for benzene.

Reaction temperature: 623.15 K

Profit of p-xylene: 200 \$/t

Working time: 8000 h/y

Cost of Reactors (\$/y) = 5000+c[Reactants mass (t)]. (c=250 for module 1, 2, 4; c=300 for module 3)

Cost of Heat Exchangers (\$/y) = 5000+150[Area (m²)]

Cost of Cooling/ Heating Utility = 20/ 100 \$(/kW·y)

Temperature of Cooling/ Heating Utility: inlet 300 K, outlet 320 K/ inlet 680 K, outlet 680 K.

heat transfer coefficient: 1 kW/(m²·K) for feed, cold utility; 5 kW/(m²·K) for hot utility; 2 kW/(m²·K) for reactors.

After computation and iteration the maximum objective function value is TAP=12,072,200 \$/y, which saves 1,381,269 \$/y compared with the reactor network without heat-integration. The corresponding reactor network configuration and heat exchanger network configuration are shown in Figure 2. All the reactors activated are PFR with residence time 0.133 h (disproportionation, PFR2), 500 h (toluene alkylation, PFR3), 32 h (benzene alkylation, PFR4) respectively. In this structure, (1) isomerization is not activated because of the feed condition and the cost of the reactors; (2) toluene alkylation is activated because of its irreversibility and high selectivity for P-xylene, although its reaction rate is much smaller than that of disproportionation (shown in Table 1); (3) disproportionation and benzene alkylation connects with each other because either product of one module serves as the reactant of the other module; (4) From Table 1, we can see the optimal reactor network has smaller heat-integration cost than that of suboptimal reactor networks, which proves we can carry out reactor network synthesis and heat-integration sequentially in cases like this.

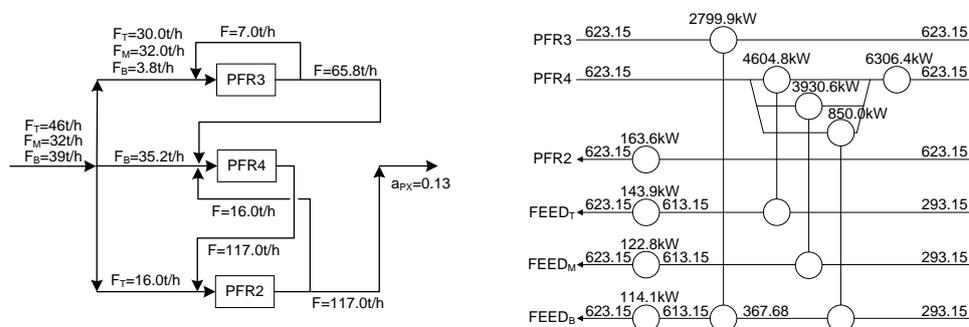


Figure 2: Resulting process flowsheet for the case

Table 1: Comparison between different reactor networks

	Optimal reactor network	Suboptimal reactor network	Optimal reactor network without module 3
Annualized profit (\$/y) (with utilities free)	12,333,732	12,330,104	11,194,016
Annualized profit (\$/y) (without heat-integration)	10,690,931	10,687,123	9,586,977
Heat integration cost (\$/y)	261,532	261,722	219,481
Total Annualized Profit (\$/y)	12,072,200	12,068,382	10,974,535

6. Conclusion

In this contribution we considered a methodology for simultaneous optimization of reactor network synthesis and reaction paths synthesis with heat integration. An initial reactor network superstructure without heat exchanging units is constructed. In each reactor module within superstructure a CSTR and a PFR are interconnected and are selectively activated by binary variables. A number of alternative reactor networks with specified catalysts arrangement can be obtained from the superstructure. Then, heat integration of chemical reactors through heat exchangers is employed, trying to decrease the total energy consumption, while preserving their performance. This methodology is tested by a p-xylene production scenario and final result proves the feasibility of the sequential solving strategy with total annualized profit for more than 12 M\$/y and 1.4 M\$/y decrease in the total energy consumption.

Acknowledgments

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