行政院國家科學委員會專題研究計畫　期中進度報告

反應/分離迴流程序之設計與控制(2/3)

計畫類別：個別型計畫
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執行期間：93 年 08 月 01 日至 94 年 07 月 31 日
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計畫主持人：余政靖

計畫參與人員：陳逸航

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行政院國家科學委員會補助專題研究計畫成果報告

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計畫類別：■個別型計畫　　□整合型計畫

計畫編號：NSC93－2811－E－002－056－

執行期間：　93 年　08 月　01 日至　94 年　07 月　31 日

計畫主持人：余政靖

本成果報告包括以下應繳交之附件：

□赴國外出差或研習心得報告一份
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□國際合作研究計畫國外研究報告書一份

執行單位：國立台灣大學

中　華　民　國　九十四　年　五　月　二十七　日

行政院國家科學委員會專題研究計畫成果報告

清淨製程：反應/分離迴流程序之設計與控制(2/3)

Interaction between Design and Control for an Adiabatic Tubular Reactor Process with Recycle

]計畫編號：NSC93-2811-E-002-056-

執行期限：93 年 08 月 01 日至 94 年 07 月 31 日

主持人：余政靖　　國立台灣大學化工系

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1、中文摘要

本計劃的工作，在探討迴流系統含有絕熱塞狀式雙分子反應器之設計與控制問題。雖然本研究是利用理論的方式進行，但其化學及系統流程相當接近真實的工廠，如：異構化，甲醇，氨，苯等製程。利用簡化的 TAC 方程式求得最適的反應物分佈，以及系統之動力學及熱力學對於迴流系統所帶來的影響。並利用簡化模式，解析反應器之操作溫度對系統的操作度影響。其結果顯示，在恆溫及絕熱操作下，其產能會受到迴流量的變化而有所影響。對於可操作度分析，在此提出 2 個控制結構，及 3 種不同的產能調結的方式。此研究的結果顯示，當系統操作在反應物入料濃度相等時，應選用反應器入口溫度來作為產能調協變數，且應固定反應器入口 2 個反應物之濃度。當反應物之濃度相差較大時，則應選用迴流量來控制系統之產能。

Abstract

In this work, the design and control problem of recycle processes with a bimolecular reaction taking place in an adiabatic tubular reactor is explored. Although hypothetical components are used in this paper, the chemistry and the flowsheets are similar for a very large number of real industrial processes, e.g., production of isooctane, amines, methanol, ammonia, ethyl-benzene, etc. Optimal reactant distribution can be obtained directly form the simplified TAC equation and effects of kinetics parameters and relative volatilities on this optimality are also explored. Next the connection between reactor temperature and operability is established analytically for the simplified process. It reveals the important difference between isothermal and adiabatic operations, especially for the reversal in production rate variation as the recycle flow changes. For the operability analysis, two control structures are proposed with three different combinations of TPM. For the case of equally distributed reactant, the control structure using the reactor inlet temperature as TPM gives good control performance when the reactant distribution is held constant. For the case of biased reactant distribution, the reactant redistribution provides an extra degree of freedom and this alleviates the high T_{out} problem. The results presented in this work clearly indicate that simple material and energy balances provide useful insights in the design and control of recycle processes.

2. INTRODUCTION

The simple recycle process of Papadourakis et al. probably is one of the most studied systems [5]. It consists of a CSTR and a distillation column in a recycle structure. The reaction, A→B, is irreversible with first-order kinetics and the light reactant is separated from the product in the distillation column and recycled back to the reactor. Important recycle plant characteristics, which include slowing down process dynamics, increased sensitivity in the recycle flow (also known as the snowball effect), difference between internal and external flow dynamics, and nonlinear dynamics, can be deduced from this simple process. Subsequently, issues such as arrangement of throughput manipulator, on-demand and on-supply control structures, regulatory control structure, optimizing control structure, nonlinear behaviour for different designs, and interaction between design and control are explored. This provides the basic principles for plantwide control. From the reaction kinetics perspective, the bimolecular reaction (A+B→X) provides a feature was not been seen in the isomerization reaction. The reason is clearly stated in Tyreus and Luyben [1] that we need to "balance the reactants down to the last molecule". This stoichiometric balance has significant implication in control structure design. That is: a simple ratio of the reactants (an open-loop control) will not work and only a feedback mechanism will overcome the stochiometric imbalance. Potential stability problem of the bimolecular reaction was pointed out by Luyben et al. [2] and the tradeoff between design and control was explored by Cheng and Yu [6]. Certainly, the same principle, stiochiometric balance, applies to all the reactions with more than one reactant. Up to this point, we have focus on recycle processes with isothermal CSTR. If a tubular reactor is used in recycle processes, this gives another degree of complexity. Reyes and Luyben [3] pointed out the difference: "Unlike CSTR systems in which the feed temperature is usually unimportant, both the design and the control of tubular reactors are strong function of temperature of the inlet stream to the reactor." In this work, the design and control problem of recycle processes with a bimolecular reaction taking place in an adiabatic tubular reactor is explored. Although hypothetical components are used in this paper, the chemistry and the flowsheets are similar for a very large number of real industrial processes, e.g., production of isooctane, amines, methanol, ammonia, ethyl-benzene, etc. The objective of this work is to extend the approach of Cheng and Yu [6] to recycle plant with an adiabatic tubular reactor.

3. STEADY-STATE DESIGN

3.1 Process

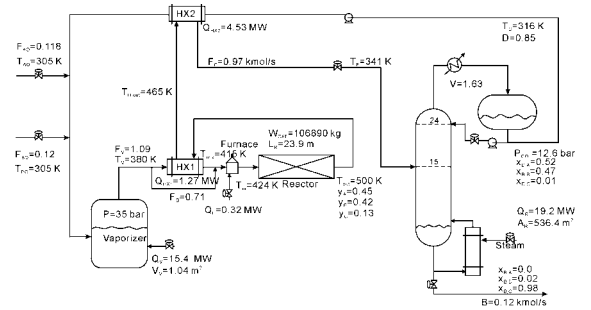

Fig. 1. Process flowsheet for the recycle process with optimal design.

Consider a recycle process where an irreversible, exothermic reaction A+B→X occurs in a gas phase, adiabatic tubular reactor. The process flowsheet consists of one tubular reactor, one distillation column, one vaporizer, and one furnace with two heat exchangers which was first studied by Reyes and Luyben [3] (Fig. 1). Two fresh feed streams $F_{0A}$and F_{0B} are mixed with the liquid recycle stream D and sent to a steam-heated vaporizer. According to the requirement of reaction temperature, the vapor from the vaporizer outlet stream is preheated first in a feed-effluent heat exchanger followed by a furnace to get proper reactor temperature as well as for the start-up purpose. The exothermic reaction takes place in the tubular reactor and the reactor temperature increases monotonically along the axial direction with the following inlet and outlet temperatures, T_{in} and T_{out}. The hot gas from the reactor preheats the reactor feed in a feed-effluent heat exchanger, HX1, and the liquid recycle stream in a second heat exchanger, HX2, as shown in Fig. 1.

Following Reyes and Luyben [3], the following process specifications are used (in Fig. 1)

3.2 Steady-state design and analysis

With the given specifications, we can complete the steady-state design for any given reactor conversion and reactant distribution.

Next, shortcut methods are applied to find the minimum number of trays (Fenske equation) for distillation columns, locate the feed tray location (Kirkbride equation), and size the column diameter. The heat transfer areas for the reboiler and condenser are also computed from the vapor flow rates.

The capital cost and operation cost of the entire plant are estimated using the correlation given in Douglas and Reyes and Luyben. Therefore, the total annual cost (TAC) model can be expressed as:

$$TAC = C_1 W_{CAT}^{0.62267} + C_2 W_{CAT} + C_3 V_S^{0.533} N_T^{0.802} + C_4 V_S^{0.775} N_T + C_5 A_V^{0.65} + C_6 V_V^{0.62267} + C_7 Q_V + C_8 Q_F^{0.76} + C_9 Q_F + C_{10} A_H^{0.65} \quad (1)$$

where W_{cat} is catalyst weight, V_s denotes vapor flow rate in the distillation column, N_T represents total number of trays in the distillation column, A_v is heat exchanger area for the vaporizer, V_v denotes volume of vaporizer, Q_v is energy supply to the vaporizer, Q_F is energy supply to the furnace. Eq.(1) gives a rigorous expression for the TAC. In Eq.(1), the TAC model consists of the following terms: the first two term represents the cost of the reactor and catalyst cost, the third and fourth terms correspond to the capital and operating costs of distillation column and trays, the fifth and seventh terms are for the vaporizer capital and operating costs, and the last three terms are for the furnace and heat exchanger costs.

3.2.1 Optimal Paths. The objective here is to find the optimal reactant distribution (y_A/y_B) for any given reactor outlet composition y_C (conversion). This locus is termed as optimal TAC trajectory. That is the optimization is carried out in a two-step procedure. First, for a given y_C, an optimal reactant distribution is located. Next, we repeat the previous step for all possible y_C and the optimal TAC trajectory can be drawn by connecting all the optimal distributions (y_A/y_B). Consider the following system parameters: production rate B = 0.12 kmol/s, product purity $x_{B,C}$= 0.98, reactor outlet temperature T_{out} = 500 K, Q_F/Q_{total} = 0.2, vaporizer outlet stream temperature T_V = 380 K, column feed temperature T_F = 336 K. For a given y_C, the optimal reactant distribution can be found by taking the derivative of the simplified TAC. First, we substitute y_B and y_C for y_A in the cost model and, then, take the derivative with respect to y_B.

Since the fractional recoveries are fixed, K_i's are constant, and C_{PA}=C_{PB}, the TAC equation can be simplified to:

$$\frac{\partial TAC}{\partial y_B} = 0 = K_1' \frac{1}{N_R B P^2 k_o} \sum_{i=N_R}^{1} \frac{F_i^2}{e^{-E/RT_i}\left[\frac{N_R - i}{N_R} + \frac{-\lambda y_A}{C_P(T-T_o)(1+z_C)}\right]\left[\frac{N_R - i}{N_R} + \frac{-\lambda y_B}{C_P(T-T_o)(1+z_C)}\right]} + 1.2\frac{L}{y_C}\left[\frac{(\frac{1}{\alpha_{BC}-1})-(\frac{1}{\alpha_{AC}-1})}{1+y_C(1-y_B-y_C)} + \frac{(\frac{y_B+y_C}{\alpha_{BC}-1}+\frac{1-y_B-y_C}{\alpha_{AC}-1})y_C}{(1+y_C(1-y_B-y_C))^2}\right] \quad (2)$$

For any given y_C, we can find the optimal y_A/y_B by solving Eq.(2) and subsequently optimal reactant distribution along the trajectory as shown in Fig. 2. Next the TACs along the trajectory are compared and the true optimum is thus obtained. Fig. 2 reveals the changes of TAC as y_C varies and the minimum TAC corresponds to y_A=0.45, y_B =0.42, y_C =0.13 with a TAC of 4.21×10^7\$/year.

3.3 Effect of process parameters on optimal path and true optimality

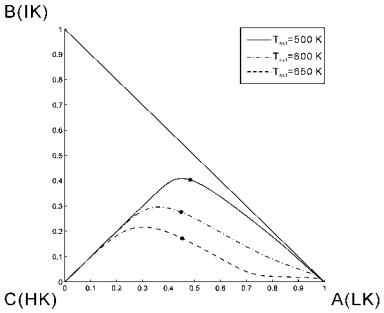

Fig. 2. Optimal TAC trajectory and design for different specifications

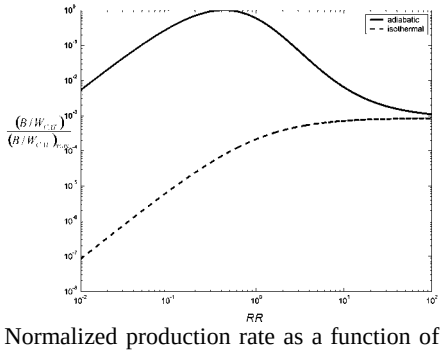

Fig. 3. Normalized production rate as a function of recycle ratio (RR) for adiabatic and isothermal operations.

The analytical expression of Eq.(2) allows us to explore the effects of kinetics parameters and vapour liquid equilibrium on the optimal trajectory and corresponding optimal design. Fig. 2 reveals that as the maximum allowable reactor outlet temperature increases, the optimal trajectory converges to the center line at a larger y_C. The reason is that a higher reactor temperature leads to a smaller reactor costs and this, in turn, reduces the relative cost of reactor (compared to the separation cost). Moreover, the reactant distribution

becomes biased (light reactant A in excess) as T_{out} increases.

3. OPERABILITY

The material and energy balances provide the basis for steady-state operability analysis [5]. For a simple isomerization reaction, the production rate in terms of recycle ratio and subsequently control structure can be devised. Similar approach is taken for the case of adiabatic tubular reactor.

Assuming perfect separation, the total production rate can be expressed as:

$$B = R = W_{cat} k_o e^{-E/RT} P_A P_B \tag{3}$$

where B is the production rate, R is the generation rate of the product X, W_{CAT} is the catalyst weight can also be interpreted as reactor length, P_i is the partial pressure of component i.

The production rate for the one-lump adiabatic tubular reactor becomes:

$$B = W_{cat} k_o P^2 \exp\left(\frac{-E}{R\left(T_{in} + \dfrac{(-\Delta H)}{(1+RR)C_P}\right)}\right) \frac{x_{D,A} x_{D,B} RR^2}{(1+RR)^2} \tag{4}$$

Comparing Eq.(3) with Eq.(4), one immediately observes a significant difference in the reaction rate constant where, for the case of adiabatic tubular, it is a function of recycle ratio (RR). Also shown in Eq.(4) is that the reactor inlet temperature (T_{in}), the reactor pressure (P), and the distribution of the reactant (x_{DA}/x_{DB}) also play visible roles in the production rate expression.

Insights can be gained by examining Eq.(4). Let us explore the effects of different design/operating variables on the production rate changes.

3.1 Recycle Rates (*RR*=*D*/B)

At low RR (corresponding to high conversion or large y_C), the production rate increases as we increase RR. However, the opposite behavior is observed at high RR region (low conversion). That is B/W_{CAT} decreases with an increase in RR and this is the typical results as seen in many of Luyben and co-worker examples [6,9]. The reason for that is the temperature effect (T_{out} of the reactor) dominates the concentration effect (at high RR region). In other words, a smaller production rate will result for an increase in RR for an adiabatic reactor at low conversion with high activation energy (E) and high heat of reaction ($-\Delta H$). This can be quantified by taking the derivative of Eq.(4) with respect to RR. After some algebraic manipulation, we have:

$$\left(\frac{\partial B/\bar{B}}{\partial RR/\overline{RR}}\right)_{P,W_{cat},y_A,y_B} = \frac{2}{1+\overline{RR}} - \frac{E}{R\bar{T}_{in}^{\,2}} \frac{\left(\bar{T}_{out} - T_{in}\right)\overline{RR}}{1+\overline{RR}} \tag{5}$$

Eq.(5) clearly indicates the competing effect between concentration and temperature. Note that, for isothermal operation, i.e., $T_{reactor}$=T_{in}, we have only the concentration effect. That is:

$$\left(\frac{\partial B/\bar{B}}{\partial RR/\overline{RR}}\right)_{P,W_{CAT},y_A,y_B} = \frac{2}{1+\overline{RR}} \tag{6}$$

Fig. 3 also shows the production rate variation for isothermal operation and the "snowball effect" is also evident at high RR region where a large change in RR leads a very small increase in the production rate ($_{(B/W_{cat})/(B/W_{cat})_{\max}}$).

3.2 Reactor Inlet Temperature (T_{in})

The reaction inlet temperature is an ideal candidate for the throughput manipulator (TPM) and this is especially true for reaction system with high activation energy where the RR is relatively ineffective. Again, the sensitivity of the production rate variation for a change in T_{in} can be derived from Eq.(4). If the reactant distribution is maintained at the nominal value, we have:

$$\left(\frac{\partial B}{\partial T_{in}}\right)_{P,W_{cat},y_A,y_B} = W_{cat} k P^2 \frac{x_{D,A} x_{D,B} RR^2}{(1+RR)^2} \frac{E}{R\bar{T}_{out}^{\,2}} \frac{\partial T_{out}}{\partial T_{in}} = \bar{B} \frac{E}{R\bar{T}_{out}^{\,2}} K_R \tag{7}$$

Eq.(7) clearly shows that from steady-state viewpoint. T_{in} is a good TPM for systems with large E. Compared to the isothermal CSTR case, the sensitivity is amplified by the reactor gain K_R which is the sensitivity between the inlet and outlet temperature (i.e., K_R=$\partial T_{out}/\ \partial T_{in}$). As pointed out by Chen and Yu [4], a heat integrated reactor via feed-effluent heat exchanger can easily become open-loop unstable for system with a high reactor gain (K_R). Therefore, controllability problem may arise when we try to recover more heat form the hot gas of the reactor effluent. Nevertheless, Eq.(7) indeed shows that T_{in} is a good candidate for TPM.

3.3 Reactor Pressure (*P*)

The problem handling capability can be quantified the taking the derivative of Eq.(4) with respect to the pressure. Thus, one obtains:

$$\left(\frac{\partial B}{\partial P}\right)_{T_{in},W_{cat},y_A,y_B,RR} = 2\bar{P} W_{cat} k_0 e^{-E/R\bar{T}} \bar{y}_A \bar{y}_B = \frac{2\bar{B}}{\bar{P}} \tag{8}$$

Steady-state analysis clearly shows the reactor pressure is a good choice for TPM.

3.4 Reactant Distribution

Let us consider the case where the reactant A is in excess. The sensitivity in the production rate variation for changes in y_B can be expressed as:

$$\left(\frac{\partial B/\bar{B}}{\partial y_B/\bar{y}_B}\right)_{P,W_{cat},T_{in},RR} = \frac{(\bar{y}_A - \bar{y}_B)}{\bar{y}_A} \tag{9}$$

Eq.(9) clearly shows that, a small change in the limiting reactant B can lead to significant change in the production rate and this is especially true when A is in large excess.

4. CONTROL

4.1 Control Structures

Two control structures are devised for these two cases. In the first case, the recycle ratio is fixed as shown in Fig. 4A, denoted as CS1 hereafter, and in the second case the reactant distribution is maintained by controlling one of the reactant in the vaporizer, called CS2 hereafter (Fig. 4B). In addition to the basic difference, the remaining loops are:

(1) Product composition $x_{B,C}$ is controlled by changing column base flow (B).

Column base level is maintained by controlling heat input (V_S >>B).

(2) Reflux is flow controlled.
(3) Reflux drum level is maintained by changing fresh feed of A (F_{OA}).
(4) Vaporizer level is controlled by steam flow rates.
(5) Outlet temperature of FEHE (T_{mix}) is controlled by changing by-pass flow.
(6) Reactor inlet temperature (T_{in}) is maintained by varying fuel flow to the furnace.
(7) Reactor pressure is controlled by the feed to the column.

(A) (B)

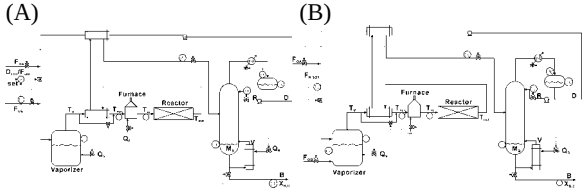

Fig. 4. Control structure fixing (A) recycle ratio (CS1) and (B) reactor exit composition (CS2).

4.2 Throughput Manipulator

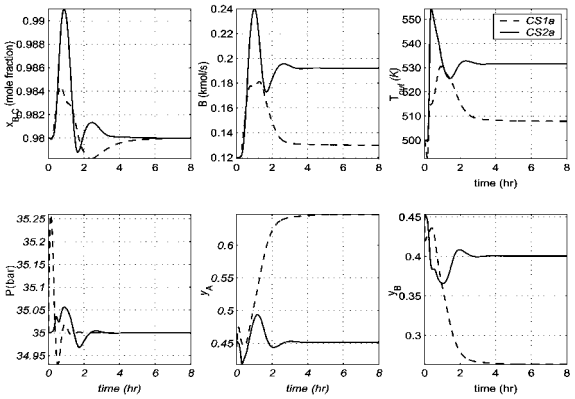

Fig. 5. Closed-loop performance using CS1 and CS2 for ΔT_{in} = +5 K (case 1).

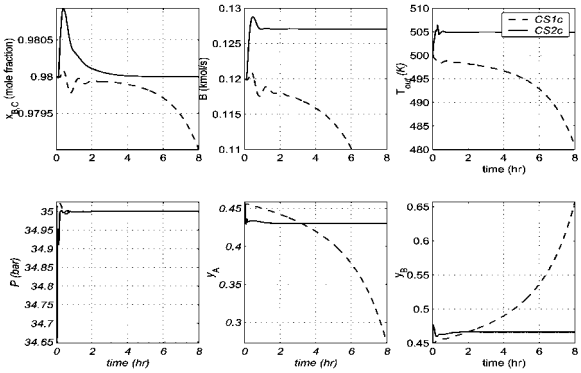

Fig. 6. Closed-loop performance using CS1 and CS2 for ΔD = +5 % (case 1).

Once the fundamental control structure is determined (Fig. 4), we can proceed to the next level. As mentioned in section 3, we have three candidate throughput manipulators. One is the reactor inlet temperature (T_{in}) which is denoted as CSia, the second one is the reactor pressure (P) which is called CSib, and the third one is the recycle flow rate which is the control structure CSic. Nonlinear dynamic simulations were performed to evaluate the effectiveness of different control structures. The modeling approach of Reyes and Luyben [3] was taken and the nonlinear recycle plant was solved numerically using FORTRAN. 0.1 minutes of measurement lags are assumed in the temperature measurements and 1 min analyzer dead time is assumed for composition analyzer. Two different designs are tested. One is the optimal design which represents the case of almost equally distributed reactant (e.g., $y_A/y_B \approx 1$) and the other case explores the scenario of biased reactant distribution (e.g., y_A/y_B=2.3). Let us compare the control performance of CS1 and CS2 for the case of equally distributed reactants. Fig. 5 shows the production rate changes for a +5 K increase in T_{in}. Despite quite similar process dynamics (e.g., settled in 4 hours), different magnitudes in production rate changes are observed. For CS2, it results in 61% production increase while, for CS1, only 8.3% production rate increased can be achieved. The reason for the smaller magnitude in production rate increase for CS2 is that the effect of T_{in} is offset by the re-distribution reactant as shown in Fig. 5. This was not seen for CS1 become the composition of B is controlled to maintain the optional reactant distribution. Similar results can also seen when the reactor pressure and recycle flow are used as TPM. CS1 simply outperforms CS2 when reactants are equally distributed as shown in Fig. 6. Also notice that significant change in T_{out} can be seen for CS1 when T_{in} is used as TPM and this may lead to potential problem in practice.

Finally, for the case when A is in excess (e.g., y_A/y_B=2.3), exactly the opposite results were obtained when comparing CS1 and CS2 (Fig. 4). Again, for a +5 K change in T_{in}, a larger production rate increase can be achieved using CS2 (67%) as compared to that of CS1 (50%) while having a lower T_{out}. The reason is obvious that the redistribution of reactants contributes to the production rate increase.

5. CONCLUSION

Interaction between design and control for gas-phase adiabatic tubular reactor with liquid recycle is studied. This generic bimolecular reaction, A+B→X, has two important features: (1) stoichimoetiric balance has to be maintained and (2) reactor temperature plays an important role in design and operability. More importantly, it represents a large class of important industrial processes. This problem presents fascinating design problems and the most important one is the tradeoff between reactor size (reactor cost) and recycle flow rate (separation cost). The total annual cost (TAC) is used to evaluate steady-state economics. The optimal TAC trajectory starts form the corner of light reactant (A) and converges to the center line toward the pure heavy product (X) edge in the triangular composition space. Unlike isothermal operation, the reactor inlet temperature limits the attainable region to low conversion range. Optimal reactant distribution can be obtained directly form the simplified TAC equation and effects of kinetics parameters and relative volatilities on this optimality are also explored. The results show that an increased reactor exit temperature leads to a more controllable optimal design while a high activation energy results in a less controllable one. Next the connection between reactor temperature and operability is established analytically for the simplified process. It reveals the important difference between isothermal and adiabatic operations, especially for the reversal in production rate variation as the recycle flow changes. Moreover, it provides insight to evaluate possible throughput manipulators (TPM). For the operability analysis, two control structures are proposed with three different combinations of TPM. For the case of equally distributed reactant, the control structure using the reactor inlet temperature as TPM gives good control performance when the reactant distribution is held constant. However, potential problem may arise as the result of high reactor exit temperature (T_{out}). For the case of biased reactant distribution, the reactant redistribution provides an extra degree of freedom and this alleviates the high T_{out} problem. The results presented in this work clearly indicate that simple material and energy balances provide useful insights in the design and control of recycle processes.

6. REFERENCES

[1] B. D. Tyreus and W. L. Luyben, Dynamics and Control of Recycle Systems. 4. Ternary Systems with One or Two Recycle Streams, Ind. Eng. Chem. Res., 32 (1993) 1154.

[2] M. L. Luyben; B. D. Tyreus; W. L. Luyben, Analysis of Control Structures for Reaction/Separation/ Recycle Processes with Second-Order Reactions, Ind. Eng. Chem. Res., 35 (1996) 758.

[3] F. Reyes and W. L. Luyben, Extension of the Simultaneous Design of Gas-Phase Adiabatic Tubular Reactor Systems with Gas Recycles, Ind. Eng. Chem. Res., 40 (2001a) 635.

[4] Y. H. Chen and C. C. Yu, Interaction between Thermodynamic Efficiency and Dynamic Controllability: Heat-Integrated Reactor. Comput. Chem. Eng., 23 (2000) 1077.

[5] K. L. Wu and C. C. Yu, Reactor/Separator Processes with Recycle-1. Candidate Control Structure for Operability, Computers Chem. Engng., 20 (1996) 1291.

[6] Y. C. Cheng and C. C. Yu, Optimal Region for Design and Control of Ternary Systems. AIChE J., 49 (2003) 682.