Design and Control of Di n-Pentyl Ether Process

Ahtesham Javaid⁴ *, Costin Sorin Bildea¹

Received 01 August 2014; accepted after revision 29 September 2014

Abstract
Recycle of un-converted reactants is a common practice in industrial chemical processes. However, the material recycle induces a non-linear behaviour of the plant which often manifests as high sensitivity of the recycle flow rates with respect to disturbances such as changes in raw material quality, production rate and uncertain design parameters. This non-linear behaviour of the system is often the source of control difficulties. Thus the importance of appropriate control structure in reactor-separation-recycle is evident. The case study of di n-pentyl ether production illustrates two control strategies that can be applied to processes involving one reactant and one recycle. The strategy based on self-regulating reactant inventory uses the plant-inlet flow rate as the dominant variables which significantly affects the production rate. The strategy based on inventory feedback control uses the reactor inlet flow rate, the reactor holdup or the reaction temperature / pressure as throughput manipulator. For the di n-pentyl ether process, both strategies are applicable, as demonstrated by rigorous dynamic simulation.

Keywords
Process design, Process control, Non-linearity, Di n-pentyl ether

1 Introduction
To make the chemical processes economical, the un-converted reactants are not allowed to leave the plant, being separated and recycled to the reaction section. The behaviour of integrated plants involving material recycles is different from the stand-alone reactors, as positive feedback due to recycling adds non-linearity to the system, which causes difficulty to control the reactants inventory. The mass balance of the plant can be understood by analysing the reactor - separation - recycle system. In general, the separation units ensure that the products and by-products are removed from the system, therefore preventing their accumulation. In contrast, the chemical reactor must convert the entire amount of reactants fed to the plant. If reactants are fed at constant rate but the reactor does not have enough capacity, reactant accumulation occurs and no steady state can be reached. Moreover, unsafe condition, like multiple steady states and high sensitivity to disturbances (known as the "snowball effect" [1]) may arise. In this context, it is the duty of the designer to ensure that the chosen steady state is grasped during start-up and can be maintained during operation.

It should be remarked that, for a given design, it is possible to assess the feasibility of a control structure implementing a certain operating procedures by taking into account a simple steady state plant model considering kinetic reactor and perfect separation. The concept of design degrees of freedom is very useful, being defined as the numbers of variables required to define the process. Similarly, the control degrees of freedom are defined as the variables (control valves) which are available to the control system. For many processes the number of design degrees of freedom is equal to the number of control degrees of freedom [2]. Therefore, there is a close relationship between process design and process control. Note that it is possible to identify un-stable operating points using the steady state model; however, the stability cannot be guaranteed based on steady state considerations, as stability is the property describing the dynamic behaviour.

We will start by presenting two different concepts behind plantwide control structures, namely control of inventory by feedback and self-regulating inventory. In the first strategy

1 Department of Chemical and Biochemical Engineering, University Politehnica of Bucharest, Strada Gh. Polizu 1-7, 011061, Bucharest, Romania
* Corresponding author, e-mail: ahteshamjavaid@hotmail.com
(Fig. 1a), the reactant inventory is measured and controlled by a level or pressure controller which acts on the system-inlet flow rate. In a reactor - separation - recycle system, the flow rate at reactor-inlet is fixed, so fresh feed is increased or decreased when material is depleted or accumulated (Fig. 2a). When the inventory is self-regulating (Fig. 1b), the liquid level increases if more fluid is fed to the vessel. As the outlet flow is proportional to the square root of the liquid level, it also increases. After some time, the equilibrium is reached when the inlet and outlet flows become equal. In a reactor - separation - recycle system, the fresh feed is set on flow control and the reactant inventory is self-regulating as conversion rate is proportional to the amount of reactant present in the plant (Fig. 2b).

Both of these strategies will be discussed in detail later by considering the case study for production of di n-pentyl ether, which is one-reactant one-recycle process.

2 One-reactant, one-recycle process

Consider a chemical process where the first order reaction $A \rightarrow P$ takes place in continuous stirred tank reactor (CSTR). We assume that the raw material ($A$) is pure and the separation section performs a perfect reactant / product split, such that only un-converted reactant ($A$) is recycled and only product ($P$) leaves the plant. Two different strategies could be the imagined. First strategy shown in Fig. 2a uses feedback for inventory control, by measuring the amount of reactant in a buffer vessel and implementing a feedback control loop. The flow rate of reactant is fixed at the reactor inlet. The increase or decrease of reactant inventory is compensated by less or more fresh reactant being added to the process. In the second control structure shown in Fig. 2b the flow rate of reactant is fixed at plant inlet. When the reactant accumulates, the consumption rate increases until it balances the feed rate. This strategy is based on the self-regulation property.

In order to analyse the feasibility of these two control strategies, let us consider the chemical reactor (CSTR), fed with pure reactant $A$. The reactant consumption rate is given by:

$$r_A = k \cdot M \cdot z_{A2} \text{ (kmol.s}^{-1}\text{)}$$  \hspace{1cm} (1)

where:

$k$ - Reaction rate constant (s$^{-1}$)

$M$ - Reactor holdup (kmol)

$z_{A2}$ - Reactant mole fraction (equal to the outlet concentration)

The reactor mass balance can be written as:

$$F_1 \cdot z_{A2} = k \cdot M \cdot z_{A2}$$  \hspace{1cm} (2)

Combining Eq. (1) and Eq. (2) gives the production rate for a fixed reactor-inlet flow rate $F_1$:

$$F_{p,2} = \frac{kM}{1+kM/F_1}$$  \hspace{1cm} (3)

Moreover, the following relationships can be easily derived:

Sensitivity of $F_{p,2}$ with respect to $F_1$:

$$\frac{\partial F_{p,2}}{F_1} = \frac{1}{(1+F_1/kM)}$$  \hspace{1cm} (4)

Sensitivity of $F_{p,2}$ with respect to $kM$:

$$\frac{\partial F_{p,2}}{\partial kM} = \frac{1}{(1+kM/F_1)}$$  \hspace{1cm} (5)
Maximum production rate:
\[
F_{p,2} = \lim_{F_1 \to \infty} F_{p,2} = kM
\]  
(6)

Reactant conversion:
\[
X_A = \frac{kM/F_1}{1 + kM/F_1}
\]  
(7)

Conversion at maximum production rate:
\[
X_A' = \lim_{F_1 \to \infty} X_A = 0
\]  
(8)

Eq. (3) shows that the production rate can be changed in two ways, either by changing the reactor-inlet flow rate \(F_1\), or the combined reactor holdup - kinetic constant \(kM\). These options are implemented as the control structure fixing the reactor-inlet flow, shown in Fig. 2a. The dependence of the production rate \((F_{p,2})\) and reactant conversion \((X_A)\) versus the reactor-inlet flow rate \(F_1\) is presented in Fig. 3. It can be observed that increasing the reactor-inlet flow rate leads to a higher production rate, but at lower conversion. Note that according to Eq. (4), \(F_1\) is an effective throughput manipulator only when \(kM\) is large (fast reaction, large reactor).

Figure 4 presents the dependence of the production rate \((F_{p,2})\) and reactant conversion \((X_A)\) versus the reactor holdup \(kM\). As expected, bigger reactors (large \(M\)) or faster reaction (large \(k\)) results in higher production rate. Note that in practice the rate constant \(k\) can be easily modified, changing the reaction temperature. According to Eq. (5), \(kM\) is an effective throughput manipulator only when \(kM\) is small (slow reaction, small reactor).

In strategy where inventory is controlled by feedback the reactor is decoupled from the whole plant and the production can be changed indirectly, by changing either the reactor-inlet flow or the reaction conditions. It can better handle non-linear phenomena such as state multiplicity or snowball effect. In addition this strategy assures the stability of the complete reactor - separation - recycle system if the individual units are stable or stabilized by local control. Feedback-control of reactant inventory can be implemented by fixing the reactor-inlet (recycle plus fresh feed) flow rate adjusting the fresh feed to keep the inventory at a constant value the reactant inventory (level, pressure or concentration) somewhere in the recycle loop.

When the whole plant (including reactant recycle) is under consideration, the overall mass balance requires that the total amount of reactant fed to the process \((F_{A,0})\) is transformed into the product. Therefore,
\[
r_A = F_{A,0} = F_{p,2}
\]  
(9)
The production rate can be set directly by implementing the self-regulatory control structure shown in Fig. 2b. The production rate \( F_{p,2} \) does not depend on reactor size \( M \) or the reaction kinetics \( k \), as the reactant inventory is self-regulating. However, Eq. (6) is still valid, meaning that the feasibility of this control structure is limited by the reactor capacity. The following relationships can be derived from Eq. (3):

Reactor-inlet flow rate for a given production rate:

\[
F_i = \frac{F_{p,2}}{1 - F_{p,2}/kM} \tag{10}
\]

Sensitivity of \( F_i \) with respect to \( F_{p,2} \):

\[
\frac{\partial F_i}{\partial F_{p,2}} = \frac{1}{(1 - F_{p,2}/kM)^2} \tag{11}
\]

The self-regulation strategy has the advantage of setting directly the production rate. However, it is recommended only if the reactor is large enough and the per-pass conversion is high. To prove this, it may be observed that on approaching maximum production rate \( F_{p,2} \rightarrow kM \), the reactor-inlet flow rate \( F_i \) and the sensitivity to production rate \( \partial F_i/\partial F_{p,2} \) becomes very large. This high sensitivity is known as snowball effect [1]. Moreover, the process is very sensitive to other process disturbances or design-parameter uncertainty and the plant could exhibit state multiplicity and closed-loop instability [3-5].

### 3 Case study: Production of di n-pentyl ether

Di n-pentyl ether (DNPE) is a linear symmetric ether that can be used as blending additive in reformulated diesel fuels. It may be produced from C4 feed stocks via n-pentanol, obtained in its turn by selective hydroformylation of linear butenes.

#### 3.1 The chemical reaction

The etherification of n-pentanol is catalysed by Amberlyst 70, Nafion NR50, NaA and H-Beta zeolites [6,7].

\[
2C_5H_{12}OH \rightarrow C_5H_{10}O_2 + C_5H_{10} + H_2O \tag{12}
\]

The reaction is exothermic and equilibrium limited, so complete conversion of reactant is not possible.

The reaction kinetic expression used in this study is derived from an Eley-Rideal mechanism for Amberlyst 70 (catalyst) [6].

\[
r = \frac{k a_n \alpha_k}{a_p} \left( \frac{1}{a_p} - \frac{a_n \alpha_D}{a_p} \right) \tag{13}
\]

where:

\[
k = 4.6 \times 10^5 \exp \left( -11595 \left( \frac{1}{T} - \frac{1}{438} \right) \right) \text{ kmol kg}_{cat}^{-1} \text{s}^{-1} \tag{14}
\]

\[
K_{eq} = 8.9229 \exp \left( \frac{778.69}{T} \right) \tag{15}
\]

#### 3.2 Physical properties

Boiling point differences among reactant and products are the basis for designing of separation section, but azeotrope formation among the components adds complexity and limitation to the separation process (Table 1). DNPE is the high-boiling component and can be easily separated. However, water is involved in several heterogeneous azeotropes (n-pentanol-water, ether-water, and n-pentanol-ether-water), so liquid-liquid split is used in the process.

| Azeotrop type | n-pentanol | DNPE | Water | \( T_{boll} \) [°C] |
|--------------|------------|------|-------|----------------|
| 1 Heterogeneous | 11.5 | 87.32 | 1.16 | 96.37 |
| 2 Heterogeneous | 12.6 | -- | 87.4 | 96.41 |
| 3 Homogeneous | -- | 4.61 | 95.39 | 98.7 |
| 4 Water | -- | -- | 100 | 100 |
| 5 n-pentanol | 100 | -- | -- | 137.8 |
| 6 DNPE | -- | 100 | -- | 186.5 |

#### 3.3 Flowsheet

Although the etherification of linear n-alcohols such as n-pentanol has been the subject of many experimental studies [6-12], design and control studies are missing from the literature. The flowsheet for the production of di n-pentyl ether proposed in this study is presented in Fig. 5. Fresh and recycled streams of n-pentanol are mixed, heated to reaction temperature (190 °C) and fed to the plug flow reactor (diameter 1.5 m, length 2 m, catalyst particle density 1400 kg/m³, void fraction 0.5) operated adiabatically. Due to the equilibrium-limited reaction the conversion of n-pentanol is about 65%. Temperature and mole fraction profiles are shown in Fig. 6. The temperature decrease is due to the partial evaporation of the water formed in the reaction.

The reactor outlet is a mixture of un-reacted reactant (n-pentanol) and products (DNPE, water), so a series of distillation columns is required to obtain high purity products. The first distillation column, operated at 1 bar and having 10 stages, separates the water from the mixture. The distillate is condensed, cooled to 30 °C and sent to liquid-liquid separation (decanter). The aqueous phase (water) is withdrawn as product (> 99.5 purity) and the organic phase is returned as reflux to the distillation column. Bottom product of distillation column 1, containing n-pentanol and DNPE, is sent to the second distillation column operating at 1 bar pressure and having 20 stages. The product (DNPE) is withdrawn as bottom product with high purity (99%) and n-pentanol (99% pure) is recycled as distillate. The plant was simulated using AspenPlus [13]. Stream table and design
of distillation columns are tabulated in Table 2 and Table 3 respectively. Temperature and mole fraction profiles along the distillation columns are presented in Fig. 7 and Fig. 8.

### 3.4 Plantwide Dynamics and Control

Two control structure strategies are proposed and evaluated: fixing the reactor-inlet flow rate (CS-1) and fixing the plant-inlet flow-rate (CS-2), shown in Fig. 9. The control structure CS-1 maintains the inventory of n-pentanol by adjusting the fresh feed in such a way that the flow rate remains same at reactor inlet (feedback). This strategy is usually recommended to avoid unfavourable behaviour in reactor-separator-recycle system as indicated in studies [3]. The control strategy CS-2, based on the self-regulating property, offers a direct way for setting the process throughput.

Heater duty is used to control the reactor inlet temperature. In first distillation column bottoms flow, vapour distillate flow and reboiler duty control the sump level, pressure and a tray temperature (stage-9). In the liquid-liquid separator (decanter), temperature is controlled by the condenser duty and organic & aqueous phase levels are controlled by the reflux and distillate flow rates. Control of the second distillation column is standard: condenser duty controls the pressure, distillate and bottoms flow rates control the levels in of the reflux drum and column sump.

| Temperature / °C | 25 | 190 | 167.1 | 145.8 | 123 | 30 | 137.5 | 189 | 30 |
|------------------|----|-----|--------|--------|-----|-----|--------|-----|-----|
| Pressure / bar   | 1  | 5   | 4.5    | 1.09   | 1   | 1   | 1      | 1.19| 1   |
| Vapor Fraction   | 0  | 0.355 | 0     | 1      | 0   | 0   | 0      | 0   | 0   |
| Mole Flow / kmol/hr | 32.01 | 50.16 | 50.16 | 34.22 | 79.86 | 63.93 | 18.15 | 16.07 | 15.93 |
| Mass Flow / kg/hr | 2821 | 4432 | 4432 | 4143 | 4626 | 4337 | 1611 | 2531 | 289 |

| n-pentanol | 32.01 | 50 | 18.21 | 18.17 | 43.04 | 43 | 17.99 | 0.182 | 0.038 |
| Water      | 0 | 0 | 5.895 | 7.36 | 19.72 | 0 | 0 | 0 | 0.15.895 |
| DNPE       | 0 | 0.161 | 16.05 | 16.05 | 1.205 | 1.20 | 0.16 | 15.895 | 0 |
The temperature on stage-18 is controlled by the reboiler duty to assure product purity, while the reflux rate is constant.

The controllers were chosen as PI and were tuned by the direct-synthesis method. Thus, for each control loop the appropriate ranges of the controlled and manipulated variable were specified, and controller gain was set to 1 %/%. The integral time was set equal to an estimated time constant of the process, i.e. 20 minutes for temperature and 12 minutes for pressure. No integral action was used for level control. Table 4 presents the details of the control loops and controller tuning.

The dynamic behaviour of the plant analysed by using AspenDynamics [14]. Results of dynamic simulation for control strategy CS-1 are given in Fig. 10. The simulation starts from steady state and a disturbance is introduced at time $t = 2$ h, when the reactor inlet flow rate (n-pentanol) is increased by 20%, from $50 \text{ kmol/h}$ to $60 \text{ kmol/h}$. As a result, the production rate of DNPE also increases. The purity of ether and water products remains practically unchanged.

The simulation is re-run by fixing the flow rate of n-pentanol at plant inlet (CS-2). On increasing inlet flow rate by 20%, the production rate of DNPE is also increased. Results obtained are similar to first case (CS-1), shown in Fig.11.

### Table 3 Data of distillation columns design

|        | Col-1 | Col-2 |
|--------|-------|-------|
| Total Stages | 10    | 20    |
| Feed Stage  | 5     | 10    |
| Reflux ratio | 1.1   | 2     |
| Distillate rate | 79.87 | 19 kmol/h |
| D/F       | 0.7   | 0.53  |
| Pressure  | 1 bar | 1 bar |
| Condenser Type | vap-liq-liq | vap-liq |
| Design specs |       |       |
| Purity (Ether) | 47%    | 99%   |
| Purity (n-pentanol) | 53% | 99% (Recycle) |
| Condenser duty | -1.3 MW | -2.1 MW |
| Reboiler duty | 1 MW   | 2.16 MW |
| Pressure | 1 bar | 1 bar |
| Condenser Type | vap-liq | vap-liq |
| Design specs | | |
| Purity (Ether) | 47% | 99% |
| Purity (n-pentanol) | 53% | 99% (Recycle) |
| Condenser duty | -1.3 MW | -2.1 MW |
| Reboiler duty | 1 MW | 2.16 MW |

Fig. 7 Profiles of distillation column-1 (a) Temperature (b) Molar

Fig. 8 Profiles of distillation column-2 (a) Temperature (b) Molar
Table 4 Plantwide control (controller tuning)

| Controller | PV / [value & range] | OP / [value & range] | $K_c$ / [%/%] | $T_i$ / [min] |
|------------|----------------------|----------------------|---------------|---------------|
| Mixer      | Level = 1.25 m       | Alcohol feed = 32 kmol/h | 1             | 60            |
|            | 0 - 2.5m             | 0 - 64 kmol/h         |               |               |
| HX-1       | Temperature = 190 °C | Duty = 0.426×10⁶ kcal/h | 1             | 20            |
|            | 180 - 200 °C         | 0 - 1×10⁶ kcal/h      |               |               |
|            | Pressure = 1 bar     | Vapour distillate = 79.9 kmol/h | 2     | 12            |
|            | 0.9 - 1.1 bar        | 0 - 160 kmol/h        |               |               |
| Col-1      | Temperature$_{op}$ = 142.6 °C | Reboiler duty = 0.85×10⁶ kcal/h | 1     | 20            |
|            | 130 - 150 °C         | 0 - 1.7×10⁶ kcal/h    |               |               |
|            | Level, sump = 1.875 m | Bottoms product = 4143 kg/h | 1     | 60            |
|            | 0 - 3.75 m           | 0 - 8286 kg/h         |               |               |
| HX-2       | Outlet temperature = 30 °C | Cooling duty = -1.11×10⁶ kcal/h | 1     | 20            |
|            | 20 - 40 °C           | -2.22×10⁶ - 0 kcal/h  |               |               |
| Col-2      | Level (organic) = 1.25 m | Reflux = 4343 kg/h     | 1             | 60            |
|            | 0 - 2.5 m            | 0 - 8672 kg/h         |               |               |
| Decanter   | Level (aqueous) = 0.14 m | Water product = 289.6 kg/h | 1     | 60            |
|            | 0 - 2.5 m            | 0 - 580 kg/h          |               |               |
|            | Pressure = 1 bar     | Condenser duty = -1.8×10⁶ kcal/h | 2     | 12            |
|            | 0.9 - 1.1 bar        | -3.6×10⁶ - 0 kcal/h   |               |               |
|            | Temperature$_{op}$ = 149.8 °C | Reboiler duty = 1.85×10⁶ kcal/h | 1     | 20            |
|            | 140 - 160 °C         | 0 - 3.7×10⁶ kcal/h    |               |               |
|            | Reflux drum level = 1.875 m | Distillate product = 1612 kg/h | 1     | 60            |
|            | 0 - 3.75 m           | 0 - 3224 kg/h         |               |               |
|            | Sump level = 2.5 m   | Bottoms product = 2531 kg/h | 1     | 60            |
|            | 0 - 5 m              | 0 - 5065 kg/h         |               |               |
4 Conclusion

This case study addresses the plantwide control DNPE plant, a one-reactant, one-recycle process. The conversion of n-pentanol is about 65% and un-converted reactant is recycled. Two different control strategies are analysed, considering fixing flow rate at: (a) reactor inlet and (b) plant inlet. Second strategy (CS-2) requires slightly more time to settle down, but both the control structure work equally well, because the DNPE reactor is designed for a rather high reactant conversion. The product purity remains same throughout the process, independent of control strategies.
References

[1] Luyben, W. L. "Snowball effects in reactor/separator processes with Recycle." *Industrial Engineering and Chemical Research*. 33 (2). pp. 299-305. 1994. DOI: 10.1021/ie00026a019

[2] Luyben, W. L. "Process Modelling, Simulation and Control for Chemical Engineers." McGraw-Hill. 1996.

[3] Bildea, C. S., Dimian, A. C. "Fixing flow rates in recycle systems: Luyben’s rule revisited." *Industrial & Engineering Chemical Research*. 42 (20). pp. 4578-4585. 2003. DOI: 10.1021/ie020982b

[4] Bildea, C. S., Dimian, A. C., Cruz, S. C., Iedema, P. D. "Design of tubular reactors in recycle systems." *Computers & Chemical Engineering*. 28. pp. 63-72. 2004. DOI: 10.1016/S0098-1354(03)00170-4

[5] Kiss, A. A., Bildea, C. S., Dimian, A. C. "Design and control of recycle systems by non-linear analysis." *Computers and Chemical Engineering*. 31. pp. 601-611. 2007. DOI: 10.1016/j.compchemeng.2006.09.002

[6] Pera-Titus, M., Llorens, J., Cunill, F. "Technical and economical feasibility of zeolite NaA membrane-based reactors in liquid-phase etherification reactions." *Chemical Engineering and Processing: Process Intensification*. 48 (5). pp. 1072-1079. 2009. DOI: 10.1016/j.cep.2009.02.006

[7] Bringué, R., Tejero, J., Ibora, M., Izquierdo, J. F., Fité, C., Cunill, F. "Thermally stable ion-exchange resins as catalysts for the liquid-phase dehydration of 1-pentanol to di-n-pentyl ether (DNPE)." *Journal of Catalysis*. 244. pp. 33-42. 2006. DOI: 10.1016/j.jcat.2006.07.035

[8] Bringué, R., Tejero, J., Ibora, M., Izquierdo, J. F., Fité, C., Cunill, F. "Experimental study of the chemical equilibria in the liquid-phase dehydration of 1-pentanol to di-n-pentyl ether." *Industrial & Engineering Chemistry Research*. 46. pp. 6865-6872. 2007. DOI: 10.1021/ie0616646

[9] Tejero, J., Fite, C., Ibora, M., Izquierdo, J. F., Bringue, R., Cunill, F. "Dehydration of 1-pentanol to di-n-pentyl ether catalyzed by a microporous ion-exchange resin with simultaneous water removal." *Applied Catalysis A: General*. 308. pp. 223-230. 2006. DOI: 10.1016/j.apcata.2006.04.036

[10] Casas, C., Bringue, R., Ramirez, E., Ibora, M., Tejero, J. "Liquid-phase dehydration of 1-octanol, 1-hexanol and 1-pentanol to linear symmetrical ethers over ion exchange resins." *Applied Catalysis A: General*. 396. pp. 129-139. 2011. DOI: 10.1016/j.apcata.2011.02.006

[11] Mohamed, M. M., Al-Esaimi, M. M. "Synergistic catalysis effect in pentanol conversion into di-n-pentyl ether on ZSM-5 supported titania catalysts synthesized by sol-gel." *Materials Chemistry and Physics*. 115. pp. 209-216. 2009. DOI: 10.1016/j.matchemphys.2008.11.057

[12] Tejero, J., Fite, C., Ibora, M., Izquierdo, J. F., Cunill, F. Bringue, R. "Liquid-phase dehydrocondensation of 1-pentanol to di-n-pentyl ether (DNPE) over medium and large pore acidic zeolites." *Microporous Mesoporous Materials*. 117. pp. 650-660. 2009. DOI: 10.1016/j.micromeso.2008.08.055

[13] ASPENTECH "Aspen Plus Getting Started Building and Running a Process Model." Burlington: ASPE Technology. 2010.

[14] ASPENTECH "Aspen Dynamics User Guide." Burlington: ASPE Technology. 2009.