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Optimal design and plantwide control of novel processes for di-n-pentyl ether production

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Abstract

BACKGROUND: Di-n-pentyl ether (DNPE) is a good candidate for diesel fuel formulations due to its blending cetane number, good cold flow properties and effectiveness in reducing diesel exhaust emissions, particulates and smokes. However, novel processes are required in order to drive the production costs down and to increase the efficiency at industrial scale.

RESULTS: The dehydration of 1-pentanol to yield DNPE is catalyzed by thermally stable resins, such as Amberlyst 70 which has high activity and selectivity at temperatures up to 190 °C. Two process options are proposed for a plant capacity of 26.5 ktpy: a reaction-separation-recycle (R-S-R) system based on an adiabatic tubular reactor and a catalytic distillation process. Both processes were optimized in terms of total annual costs (481 and 523 k\$/year), leading to specific energy requirements of 225 and 256 kWh/ton DNPE, respectively. The controllability was assessed by dynamic simulation performed in Aspen Dynamics.

CONCLUSION: Compared with the membrane reactor reported earlier, the new DNPE process alternatives (i.e. conventional reaction-separation-recycle system and catalytic distillation) are better process candidates, requiring simpler units leading to much smaller investment costs, while also having good controllability.

Keywords: reaction-separation-recycle system, reactive distillation, design and control

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1 Nomenclature

2	a	Activity, –
3	A	Area, m ²
4	C	Cost, US \$
5	D	Distillate flow rate, kmol/h
6	F	Feed flow rate, kmol/h
7	F_i	Correction factor (i=d,p,m / e.g. design, pressure, material), –
8	k	Reaction constant, kmol/kg _{cat} ·s
9	K_{eq}	Equilibrium constant, –
10	L	Length, m
11	m	Mass, kg
12	N_T	Number of trays, –
13	P	Pressure, bar
14	Q	Heat duty, kW
15	t	Time, min
16	T	Temperature, K
17	x	Liquid mol fraction, –
18	ω	Volume fraction, –
19	<i>Subscripts</i>	
20	cat	Catalyst
21	D	Di-n-pentyl ether
22	eq	Equilibrium
23	max	Maximum
24	P	1-Pentanol
25	R	Reactive
26	W	Water
27	<i>Abbreviations</i>	
28	CAPEX	Capital expenditures
29	COM	Component object model
30	DIPE	Di-isopropyl ether
31	DNPE	Di-n-pentyl ether
32	ETBE	Ethyl tert-butyl ether
33	FEHE	Feed-effluent heat exchanger
34	HP	High pressure
35	LP	Low pressure
36	MP	Medium pressure
37	M&S	Marshall and Swift index
38	MTBE	Methyl tert-butyl ether
39	OPEX	Operating expenditures
40	PID	Proportional integral derivative
41	RD	Reactive distillation
42	RDC	Reactive distillation column
43	R-S-R	Reactor-separation-recycle
44	SQP	Sequential quadratic programming
45	TAC	Total annual cost
46	TAME	Tert-amyl ether
47	TAEE	Tert-amyl ethyl ether
48	THEME	Tert-hexyl methyl ether

1

2 **1. Introduction**

3 Along with the design of the diesel engines, the fuel quality is also a key factor controlling the
4 composition of the exhaust gases. Low quality diesel fuels cause greater gaseous and smokes
5 emissions, higher noise levels and more difficult cold start-up. Improving the diesel fuels
6 quality in a cost-effective manner is therefore an important issue for industry.¹ The possible
7 options from a technical and economical viewpoint include upgrading of refining processes,
8 selective blending and using cetane improvers. The use of oxygenated additives for biofuels
9 has been reported as a method to improve the quality of fuels obtained from renewable
10 sources.²⁻⁵ Oxygenates (e.g. ethers) are usually employed as additives to reduce the CO
11 emissions, soot and soot-related compounds (poly-aromatic hydrocarbons and their nitrated
12 derivatives). Commonly used oxygenated additives include alcohols (e.g. methanol, ethanol,
13 isopropyl alcohol, n-butanol and t-butanol) or ethers, such as MTBE, ETBE, TAME, TAEE,
14 THEME, and DIPE. However, during the past decade some of these ethers (e.g. MTBE) have
15 been banned in various states, hence the quest for more sustainable alternatives. There is also
16 an intensive discussion about using linear ethers containing a significantly higher fraction of
17 oxygen, so called oxymethylene dimethylethers, which are high molecular and thus liquid
18 ethers that could be easily produced from methanol.⁶⁻⁸ Previous literature reports that linear
19 ethers with over nine carbon atoms showed the best balance between blending cetane number
20 and cold flow properties.¹ Among them, di-n-pentyl ether (DNPE) is an excellent candidate
21 for diesel fuel formulations due to its high blending cetane number, good cold flow properties
22 and effectiveness in reducing diesel exhaust emissions, particulates and smokes. Moreover, 1-
23 butene is an appropriate feedstock for DNPE production, as it can be selectively
24 hydroformylated and hydrogenated to 1-pentanol, which can then be dehydrated to DNPE.
25 Although the literature review reveals several reports on equilibrium and kinetics of DNPE
26 formation by dehydration of 1-pentanol,⁹⁻¹² to the best of our knowledge there is only one
27 study describing a process for DNPE synthesis, based on a membrane reactor.¹³
28 The present work proposes two new feasible process options for the DNPE production: 1)
29 reaction-separation-recycle process based on an adiabatic reactor, 2) catalytic distillation
30 process. The key design parameters are identified and steady state optimization is performed
31 in Aspen Plus. The objective function is the total annual cost (TAC), which is minimized
32 using key decision variables, such as: reactor size, number of distillation trays, reflux ratio,
33 feed location, and stage catalyst loading. The process alternatives are analyzed in terms of

1 energy requirements, total investment, operating cost and annual costs. Furthermore, the
2 controllability is assessed by rigorous dynamic simulation performed in Aspen Dynamics.

4 **2. Problem statement**

5 The dehydration of 1-pentanol to yield DNPE is equilibrium limited hence complete reactant
6 conversion is not possible.¹³ As a consequence, reactant separation and recycle are necessary
7 but this should be carried out in an economically efficient manner. Alternatively, the
8 equilibrium displacement can be achieved by removing at least one product from the reaction
9 mixture. The use of a membrane reactor was suggested as a feasible option for in-situ water
10 removal.¹³ Although high reactant conversion is possible, such an option is plagued by the
11 high cost and the reduced service life of the membrane. Moreover, one distillation unit is still
12 necessary for the separation of 1-pentanol and DNPE. As a result, the production cost per unit
13 of DNPE product is currently rather high – about 2.16 \$/L, excluding raw materials¹³ –
14 mainly due to the high costs of membrane replacement (25.4 M\$/year) and refrigeration water
15 (13.3 M\$/year). To avoid these problems, we propose here two novel process alternatives for
16 DNPE synthesis, based on reaction-separation-recycle and catalytic distillation, respectively.

18 **3. Simulation results**

19 A plant capacity of 26.5 ktpy DNPE is considered in this work. The steady state process
20 simulations and optimization were performed in Aspen Plus, while the controllability was
21 assessed by rigorous dynamic simulation performed in Aspen Dynamics. Both processes (R-
22 S-R and catalytic distillation) were optimized using the same approach. The optimal values
23 for the real-valued decision variables (such as mass of catalyst, pressure, flow rate, etc.) were
24 found in Aspen Plus using the SQP method. No integer-valued variables are used in the R-S-
25 R case, whereas in case of the catalytic distillation process, a direct search algorithm was used
26 to determine the optimal values for the number of trays, feed tray location, first reacting and
27 last reacting trays.

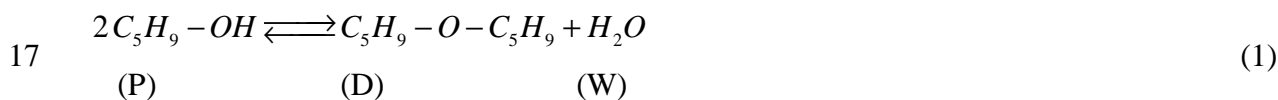
29 **3.1. Physical properties and kinetics**

30 The physical properties (such as boiling points, enthalpy of formation, ideal gas heat capacity,
31 Antoine parameters, molar density, etc) of all components are available in the pure component
32 database of Aspen Plus v8.4. As the process takes place at moderate pressure and involves
33 polar chemical species, only the non-ideality of the liquid phase has to be taken into account.

1 Accordingly, UNIQUAC was used as a suitable property model for this system.¹⁴ The Aspen
 2 Plus database contains UNIQUAC binary interaction parameters for the water – 1-pentanol
 3 pair. The binary interaction parameters for water – DNPE and 1-pentanol – DNPE pairs were
 4 estimated by the UNIFAC group contribution method. Estimation of binary interaction
 5 parameters by the UNIFAC method was also employed by several other kinetic and
 6 thermodynamic studies.^{1,9-13,17}

7 In order to design the reaction and separation sections of a plant, one needs to consider the
 8 boiling points of pure components and azeotropes that can be found in the ternary system 1-
 9 pentanol – water – DNPE (Table 1). DNPE is the high-boiling component hence it can be
 10 easily separated. Water is involved in several heterogeneous azeotropes, which suggest the
 11 use of a liquid-liquid split in order to cross the distillation boundary. Figure 1 presents the
 12 residue curve map (RCM) and the ternary diagram of this ternary system. Besides the
 13 presence of azeotropes, the system also exhibits a liquid-liquid split envelope, which must be
 14 accounted for in the design of the separation sequence – as two liquid phases should be
 15 avoided inside distillation columns, but a separate decanter could be used for phase splitting.

16 Note that the dehydration of 1-pentanol to yield DNPE is an equilibrium limited reaction:



18 The etherification of 1-pentanol was reported to be catalysed by NaA, H-Beta and ZSM-5
 19 zeolites, eta-alumina, Amberlyst 70 (and other types), Dowex 50Wx4-50, Nafion NR50.^{1,9-12,}
 20 ¹⁵⁻¹⁷ When Amberlyst 70 is used as catalyst, the reaction kinetics is described by the following
 21 expression, derived from an Eley-Rideal mechanism:^{10,13}

$$22 \quad r = \frac{ka_p^2 \left(1 - \frac{1}{K_{eq}} \frac{a_W a_D}{a_p^2} \right)}{a_p (1 + K_W a_W^{1/2})} \quad (2)$$

23 where:

$$24 \quad k = 4.6 \times 10^{-6} \exp \left(-11595 \left(\frac{1}{T} - \frac{1}{438} \right) \right) \frac{\text{kmol}}{\text{kg}_{cat} \cdot \text{s}} \quad (3)$$

$$25 \quad K_{eq} = 8.9229 \cdot \exp \left(\frac{778.69}{T} \right) \quad (4)$$

$$26 \quad K_W = 4.306 \cdot \exp \left(-6616 \left(\frac{1}{T} - \frac{1}{438} \right) \right) \quad (5)$$

1 with temperature (T) expressed in K. This kinetics is used in the present study to allow for a
2 fair comparison of the newly proposed processes against the previously reported membrane
3 reactor for the production of DNPE by etherification in liquid phase.¹³

4 Note that the kinetic experiments performed at temperatures below 150 °C and involving
5 catalyst particles of different sizes proved that mass transfer does not affect the reaction rate.¹⁰
6 Moreover the Arrhenius plots of initial reaction rates are straight lines for temperatures up to
7 180 °C.¹⁰ Thus, it can be concluded that diffusion does not influence the process kinetics over
8 the entire temperature range of interest. This can be explained by the fact that the resin beads
9 swell sufficiently in aqueous medium, allowing good accessibility to inner active centers.¹⁰

11 **3.2. Reaction-separation-recycle process**

12 The reaction is only slightly exothermic and it can be performed in an adiabatic plug-flow
13 reactor. Because the reaction is equilibrium limited, complete reactant conversion is not
14 possible^{9,13} hence the use of a reaction-separation-recycle process can be considered.^{18,19}

15 In a reaction-separation-recycle (R-S-R) plant – flowsheet shown in Figure 2 – the fresh and
16 recycled reactant (1-pentanol) are brought to reaction temperature by means of a process-
17 process heat exchanger (FEHE), and a heater. The reaction takes place in a catalytic reactor
18 that is operated adiabatically, in a single-phase (liquid). A multi-tubular reactor configuration
19 (with only 25 large tubes) was chosen, as it allows better control of the flow pattern, uniform
20 catalyst arrangement, and better mechanical resistance at the operating pressure (12 bar),
21 when compared with a single large tube. In particular, the multi-tube arrangement leads to a
22 large value of the length-to-diameter ratio, therefore minimizing the axial dispersion.²⁰ Note
23 that, through the entire reactor length, the mixture is a one-phase system due to the limited
24 amount of water and high pressure and temperature (exceeding 160 °C). Therefore, the
25 kinetics described by equation (2) is applicable.

26 The pressure of the reactor effluent is reduced to 1.1 bar. The partially vaporized stream is fed
27 to the first distillation column. The distillate, containing the 1-pentanol – water heterogeneous
28 azeotrope is condensed at the boiling temperature of the mixture, then sub-cooled to 30 °C,
29 and sent to the liquid-liquid separation. The low limit of temperature is considered 30 °C for
30 operating reasons, since cheap cooling water (at 20 °C) can be used instead of expensive
31 refrigeration. Obviously, during summer time the temperature could be increased with little
32 impact on the phase splitting. The aqueous phase is withdrawn as product, while the organic
33 phase is returned as reflux to the distillation column. Compared with the membrane process

1 from literature,¹³ the purity of water is higher: 99.8 %mol for R-S-R and catalytic distillation
 2 (see next section) versus 94.75 %mol in the membrane process. Note that the purity of the
 3 water product stream is set by the LLE which is only slightly influenced by the operating
 4 temperature in the decanter – if the decanting temperature increases to 60 °C, the water purity
 5 is 99.7 %mol. The bottom product of the column contains 1-pentanol and DNPE, and it is sent
 6 to the second distillation column. The distillate and bottoms are the 1-pentanol recycle and the
 7 DNPE product.

8 After developing the base case design based on heuristics, the plant design was further
 9 optimized using the minimization of the total annual cost (TAC) as objective function:

$$10 \quad TAC = OPEX + \frac{CAPEX}{\text{payback period}} \quad (6)$$

11 A payback period of 3 years was used,²¹ and it was assumed that the plant is running 8000
 12 hours/year. In addition, the following heating and cooling costs were taken into account: high-
 13 pressure (HP) steam (42 bar, 254 °C, \$9.88/GJ), medium-pressure (MP) steam (11 bar, 184
 14 °C, \$8.22/GJ), low-pressure (LP) steam (6 bar, 160 °C, \$7.78/GJ), and cooling water
 15 (\$0.72/GJ). Note that the costs of utilities used here are typical for a US plant.²¹ However, the
 16 reader must be aware that the costs of utilities might differ, being dependent on the plant
 17 location. In case of the reaction-separation-recycle process, MP steam is used for heating the
 18 reactor feed to reaction temperature (duty Q_H), LP steam is used for the reboiler of column 1
 19 (duty Q_{R1}), HP steam is used for the reboiler of column 2 (duty Q_{R2}), and cooling water is
 20 used for the condenser of column 1 (duty Q_{C1}).

21 The total investment costs (CAPEX) include the reactor, distillation columns, FEHE and
 22 heater. The cost of the multi-tubular chemical reactor (tubes with diameter 0.3 m) and the cost
 23 of the heat exchangers (reboiler, condenser, FEHE, heater) are given by:²²

$$24 \quad C_{\text{reactor/HEX}} (\text{US\$}) = (M \& S / 280) \cdot (474.7 \cdot A^{0.65}) (2.29 + F_m (F_d + F_p)) \quad (7)$$

25 where $M\&S$ is the Marshall & Swift equipment cost index ($M\&S=1536.5$ in 2012), A is the
 26 area (m^2), $F_m = 1$ (carbon steel), $F_d = 0.8$ (fixed-tube), $F_p = 0$ (less than 20 bar). To calculate
 27 the heat transfer area, a heat transfer coefficient $U=500 \text{ kcal/m}^2/\text{h/K}$ was assumed. For the
 28 reboilers, the design factor was taken as $F_d = 1.35$. For the solid catalyst (ion exchange resin,
 29 with a bulk density of 770 kg/m^3), a purchased cost of 50 \$/kg was considered. Clearly, the
 30 price of catalyst differs per country and manufacturer. While Pera-Titus et al.¹³ used a price of
 31 \$20/kg for a very large amount of catalyst, in this work we consider a higher cost due to
 32 inflation and significantly smaller amount of catalysts used (no bulk discounts included). This

1 price is also in line with other literature references citing up to \$50/kg catalyst.²¹

2 The distillation columns diameter (D) were obtained by the tray sizing utility from Aspen
3 Plus, while the height was evaluated as $H = 0.6 \cdot (NT-1) + 2$ (m). Afterwards, the cost of the
4 columns shell was calculated as:²²

$$5 \quad C_{shell} (US\$) = (M \& S / 280) \cdot (957.9 \cdot D^{1.066} \cdot H^{0.82}) \cdot (2.18 + F_c) \quad (8)$$

6 where $F_c = F_m \cdot F_p$, $F_m = 1$ (carbon steel) and $F_p = 1 + 0.0074 \cdot (P - 3.48) + 0.00023 \cdot (P - 3.48)^2$

7 The cost of the trays was given by:

$$8 \quad C_{trays} (US\$) = N_T \cdot (M \& S / 280) \cdot 97.2 \cdot D^{1.55} \cdot (F_t + F_m) \quad (9)$$

9 with $F_t = 0$ (sieve trays) and $F_m = 1$ (carbon steel)

10 The optimization was carried out using the state of the art sequential quadratic programming
11 (SQP) method available in Aspen Plus. Backed by a solid theoretical and computational
12 foundation, the SQP method has become one of the most successful methods for solving
13 nonlinearly constrained optimization problems.²³ The decision variables considered for the
14 optimization procedure are:

- 15 • Reactor length, L 3 m < L < 6 m
- 16 • Temperature at the HEATER outlet / reactor inlet, $T_{r,in}$: 100 °C < $T_{r,in}$ < 190 °C
- 17 • Distillate to feed ratio (D/F) of column COL-1 0.2 < D/F < 0.95

18 A design-specification block was implemented, in which the controlled variable was the mole
19 purity of the DNPE product stream, $x_{DNPE} = 0.999$ and the manipulated variable was the
20 column COL-2 distillate rate, $10 \text{ kmol/h} < D_2 < 100 \text{ kmol/h}$. Additionally, an inequality
21 constraint set an upper limit on the reaction temperature (required to avoid catalyst
22 deactivation), $T_{\max, REACTOR} < 180 \text{ °C}$. The number of trays for the two columns was set to 9,
23 with feed on tray 5 and 1, respectively. By performing several optimization runs, it was found
24 that the total annual cost (TAC) is practically insensitive to these values, the cost of using
25 more trays being compensated by smaller reboiler duties. Moreover, adding a condenser to the
26 last distillation column (COL-2) does not improve the objective function, as the additional
27 equipment and energy costs overcome the positive effect that the high-purity recycle has on
28 the reaction rate. Because COL-2 has only one degree of freedom (the vapor boilup, or
29 equivalently, the distillate rate) - which was used to ensure that the DNPE product has the
30 required purity - the recycle flow rate (same as the distillate) is not available for optimization.
31 Note that using more trays in the columns leads to slightly reduced energy costs but larger
32 investment costs. The feed location stage of Column 1 was determined by matching the stage

1 composition with the feed stream. Column 2 is operated as a stripping column with no
2 condenser and no reflux hence the feed location stage is stage 1. Figure 2 presents the detailed
3 stream results, together with a summary of the units design, whereas Table 2 provides the
4 optimal design parameters. The reactor accounts for the main investment cost (533 k\$,
5 including 352 k\$ for the catalyst), while the costs of distillation columns COL-1 and COL-2 are
6 151 k\$ and 89 k\$, respectively. Note that the main cost of the reactor (over 75%) is
7 represented by the catalyst and not by the (low number of) tubes, as it can be inferred from
8 Table 2. The operating costs are mainly given by the steam used in the two reboilers and
9 heater: 40.7 k\$/year, 102 k\$/year and 48.9 k\$/year, respectively.

10 The control structure (shown in Figure 2, details in Table 3) fixes the plant-inlet flow of 1-
11 pentanol, allowing the direct manipulation of the plant throughput.²⁴ The heater duty controls
12 the reactor-inlet temperature. Control of the first distillation column involves sump level,
13 pressure and a temperature on the stripping section (stage 8), by means of bottoms flow,
14 vapour distillate flow and reboiler duty. Condenser duty sets the temperature of the liquid-
15 liquid separator. Finally, the organic reflux and water product flow rates control the levels of
16 the organic and aqueous phases. Control loops of the second distillation column are: distillate
17 rate - pressure, bottoms flow rate - level of the column sump, and reboiler duty - temperature
18 on the lower part of the column (stage 8). Note that stage 8 was determined as the sensitive
19 stage, based on the temperature profile in the column. For both distillation columns, the
20 control structures (pairing of the controlled and manipulated variables) are standard and
21 widely used in industry.²⁵ A dynamic simulation was built in Aspen Dynamics. All vessels
22 were sized assuming a residence time of 15 minutes. This value is in line with the rules of
23 thumb accepted industrially (5-20 min) and suggested in numerous references.^{14,20,25} The
24 controllers were chosen as PI and were tuned by the direct-synthesis method. According to
25 this method, the desired closed-loop response for a given input is specified. Then, with the
26 model of the process known, the required form and the tuning of the feedback controller are
27 back-calculated. For all controllers, the acceptable control error ($\Delta\epsilon_{\max}$) and the maximum
28 available control action (Δu_{\max}) were specified. Then the controller gain, expressed in
29 engineering units, was calculated as $K_c = \Delta u_{\max} / \Delta\epsilon_{\max}$ and translated into percentage units.
30 First order open-loop models were assumed, in order to calculate the reset time of the pressure
31 and temperature control loops. As rough evaluations of the process time constants (τ), 12 min
32 and 20 min were used, respectively. It can be shown that the direct synthesis method requires
33 that the reset time of a PI controller is equal to the time constant of the process ($\tau_i = \tau$).²⁶ For

1 the level controllers, a large reset time $\tau_i = 60$ min was chosen as no tight control is required.
2 Table 3 presents the details of the control loops and controller tuning, while the results of
3 dynamic simulation are given in Figure 3. The simulation starts from steady state. At time $t =$
4 2 h, the plant inlet flow rate is increased by 20 %, from 42 kmol/h to 50 kmol/h. As more
5 reactant is fed to the plant, the production rate increases from 21 kmol/h to 25 kmol/h in about
6 6 hours. The purities of DNPE and water products remain practically unchanged. Only one
7 case is presented here due to space limitations. Other disturbances were tested as well, with
8 similar performance: 20% decrease of the production rate, 10% decrease of the FEHE heat
9 transfer coefficient (for example due to fouling), increase of the distillation columns operating
10 pressure from 1 bar to 1.1 bar.

11

12 **3.3. Catalytic distillation process**

13 The use of advanced distillation technologies – including reactive and catalytic distillation –
14 in the production of biofuels and additives have been recently reported in the case of
15 esterification and etherification reactions.²⁷⁻³¹ In this work we propose a process for DNPE
16 production based on catalytic distillation, as a process intensification method that is used to
17 perform both reaction and separation in the same unit. According to the feasibility framework
18 proposed in literature,³² reactive distillation is a good candidate for DNPE synthesis, as the
19 reactant is the middle boiling component in the water / 1-pentanol / DNPE mixture.

20 The process flowsheet is schematically shown in Figure 4. The reactant is fed at the top of the
21 reactive section, as saturated liquid stream. High purity (over 99.9%) DNPE is obtained as
22 bottom product, while the vapor distillate is condensed and sent to liquid-liquid separation,
23 which gives the water product and the organic reflux. It is worth noting that the same ion-
24 exchange resin catalyst is used in the catalytic distillation, just as in the R-S-R process and the
25 membrane reactor reported earlier.¹³ MellaPak structured packing is used to enclose the solid
26 catalyst in between the sandwiched sheets of packing – similar to the KataPak-SP structured
27 packing especially developed by Sulzer for reactive distillation systems.

28 After developing the base case design, the reactive distillation column was further optimized
29 using the minimization of the total annual cost as objective function (as described earlier).
30 The investment cost (CAPEX) included the cost of the column shell, reboiler and condenser
31 (as described earlier), as well as the structured packing (MellaPak, cost 10,000 \$/m³) and the
32 solid catalyst. The operating cost (OPEX) included the cost of high-pressure steam and
33 cooling water. The decision variables considered for the optimization procedure are:

- 1 • Total column stages, N_T
- 2 • Feed stage, N_F
- 3 • First reactive stage, N_{R1}
- 4 • Last reactive stage, N_{R2}
- 5 • Vapor distillate rate, D $10 < D < 100$ kmol/h
- 6 • Operating pressure, P $1 < P < 5$ bar
- 7 • Amount of catalyst on each reactive stage, m_{cat} $20 < m_{cat} < 200$ kg

8 The problem constraints are related to the minimum product purity ($x_{DNPE} > 0.999$), the
 9 maximum temperature of the reactive stages ($T_k < 180$ °C, $k = N_{R1}, \dots, N_{R2}$), and the volume
 10 fraction of the catalyst per stage ($\omega < 0.2$). An inner loop used the *Optimization* tool of
 11 AspenTech Aspen Plus to find the real-valued decision variables (D, P, m_{cat}), while ensuring
 12 that the constraints are satisfied. The integer-valued variables (N_T, N_F, N_{R1}, N_{R2}) were found in
 13 an outer loop, where a direct search algorithm was implemented in MathWorks Matlab.
 14 Aspen Plus and Matlab exchanged data via a COM interface. It is also worth noting that
 15 optimizing a chemical process is typically a mixed-integer nonlinear problem that is non-
 16 convex and likely to have multiple locally optimal solutions. Such problems are intrinsically
 17 very difficult to solve, and the solution time increases rapidly with the number of variables
 18 and constraints. A theoretical guarantee of convergence to the globally optimal solution is not
 19 possible for non-convex problems.

20 Figure 4 presents the process flowsheet, mass balance, as well as the process control structure,
 21 while Table 4 provides the key parameters of the optimized RD design. The catalytic
 22 distillation column has an investment cost of 816 k\$, and operating costs of 251 k\$/year,
 23 leading to a total annual cost of 523 k\$/year. In addition, Figure 5 shows the composition, as
 24 well as temperature and reaction rate profiles along the catalytic distillation column – for the
 25 optimal design case. It can be observed that the high purity DNPE is obtained as bottom
 26 product, while a mixture of 1-pentanol and water is removed as top product of the column.
 27 According to the VLE, the range of temperature values on reactive stages is 140-180 °C. The
 28 reaction rate is quite low on the top 10 reactive stages, but increases towards the bottom of the
 29 column. On the reactive stages, the liquid phase mole fraction of 1-pentanol is quite high
 30 exceeding 0.6.

31 Furthermore, Figure 6 presents the key results of the dynamic simulations for the DNPE
 32 production in a catalytic distillation column. Details of the control loops and controller tuning
 33 are given in Table 5. At time $t = 2$ h, the flow rate of fresh 1-pentanol is increased by 20%,

1 from 42 kmol/h to 50 kmol/h. As more reactant is fed to the plant, the production rate
2 increases to the setpoint while the purities of DNPE and water products remain practically
3 unchanged. Remarkable, the system is able to reject the disturbance, with short response time
4 and low overshooting. Note that similar results were obtained when the reactor-inlet flow rate
5 of fresh 1-pentanol was decreased, with the result of lower production rate (-20%).

7 **4. Process comparison**

8 Table 6 presents the key performance indicators of the two processes proposed. Compared
9 with the reported process based on membrane reactor,¹³ both processes described here have
10 greatly reduced total investment and operating costs. Remarkably, the R-S-R process appears
11 to be slightly more attractive than the RD process alternative. This result can be explained by
12 the fact that catalytic distillation is somewhat limited by constraints, such as a common
13 operation range for distillation and reaction (similar temperature and pressure). Working in
14 the limited overlapping window of operating conditions (reaction and separation) is not
15 always the optimal solution, but merely a trade-off. On the contrary, in a conventional multi-
16 unit flowsheet (such as a R-S-R process), the reactors can be operated at their optimum
17 parameters that are most favorable for the chemical kinetics, while the distillation columns
18 can be operated at their optimal pressures and temperatures where the vapor-liquid
19 equilibrium (VLE) properties are the most favorable for separation.

20 Having said that, in case of the DNPE process the operating window for reaction is limited to
21 the temperature range 120-180 °C due to minimum acceptable reaction rate and maximum
22 temperature at which the solid catalyst is active and stable, while pressure must have values
23 that allow a liquid or vapor-liquid operation. These limits are shown in Figure 7 by the
24 REACTION area. The optimal reaction conditions are at 180 °C and min. 2.1 bar, where the
25 reaction rate is highest and maximum conversion is possible. Similarly, the separation by
26 distillation is limited by the temperature range of 45-245 °C which allows condensation with
27 cooling water and heating with high-pressure steam. The corresponding pressure range is
28 therefore 0.1-3.6 bar – according to the VLE, such that vapor-liquid phases exist. The
29 temperature limits are shown in Figure 7 by the DISTILLATION area. As vacuum distillation
30 incurs additional costs, the optimal separation should be performed at atmospheric pressure,
31 when the range of boiling points is 100-187 °C. As the reaction is only slightly exothermic, in
32 the R-S-R process the reactor feed can be at a rather high temperature (160 °C), without
33 violating the maximum temperature constraint (180 °C). Therefore, the reaction takes place in

1 the range 160-180 °C which ensures a reaction rate close to the maximum achievable one. On
2 the other hand, the separation is performed at atmospheric pressure, therefore at the optimal
3 conditions. In the Reactive Distillation process, operation at a higher pressure is necessary in
4 order to have a temperature range for which the reaction rate is high. However, the higher
5 pressure has a detrimental effect of relative volatilities, and therefore on separation efficiency.
6 Moreover, as water mole fraction increases towards the top of the column, the temperature
7 range on the reactive stages is 140-180 °C, with the result of rather low reaction rate on the
8 first 10 reactive stages (Figure 5).

9 In conclusion, there is no clear overlap of the *optimal conditions* for both reaction and
10 distillation. As a convenient visual aid, Figure 7 illustrates graphically the overlapping
11 window of operating parameters (temperature and pressure) for both reaction and distillation
12 operations – the optimal operating range is the area marked by REACTIVE DISTILLATION.

14 **5. Conclusions**

15 Compared with the membrane reactor previously reported in literature, both alternatives
16 (conventional reaction-separation-recycle process and compact catalytic distillation) proposed
17 here are better DNPE process candidates, requiring lower operating costs and simpler units
18 leading to much smaller investment costs, while also having good controllability.

19 The reaction-separation-recycle process allows designing both the reactor and the separation
20 units to operate close to the optimal conditions of reaction and distillation, respectively.
21 Hence the reaction-separation-recycle process appears to be slightly more attractive than the
22 catalytic distillation process, which operates in the overlapping window of process conditions
23 for reaction and distillation, and thus suffering from this inherent trade-off.

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- 12

1 **Tables**

2

3 **Table 1.** Singular points in the 1-pentanol – water– DNPE system (UNIQUAC)

Component / azeotrope (mol fraction composition)	Boiling point (at 1.0 bar)	Boiling point (at 1.5 bar)	Node type
Ternary azeotrope, heterogeneous: 1-pentanol (0.115); Water (0.8732); DNPE (0.0116)	96.37 °C	107.36 °C	unstable node
Binary azeotrope, heterogeneous 1-pentanol (0.126); Water (0.874)	96.41 °C	107.40 °C	saddle
Binary azeotrope, heterogeneous Water (0.9539); DNPE (0.00461)	98.7 °C	109.93 °C	saddle
Water	100 °C	111.4 °C	stable node
1-pentanol	137.8 °C	150.34 °C	saddle
Di-n-pentyl ether (DNPE)	186.75 °C	202.39 °C	stable node

4

5

1
2 **Table 2.** Design of the DNPE plant (reaction-separation-recycle). The optimal values of the
3 decision variables are presented in **bold**.
4

Reactors	REACTOR	
Inlet temperature / [°C]	161.0	
Pressure / [bar]	12	
Number of tubes (0.3 m diameter)	25	
Length / [m]	5.04	
Amount of catalyst / [kg]	7760	
Installed cost / [k\$]	522.03	
Separation columns	COL-1	COL-2
Number of trays	9	9
Feed tray	5	1
Reflux rate / [kmol/h]	10.41	-
Distillate : Feed ratio	0.4207	0.517
Diameter / [m]	0.44	0.66
Reboiler duty / [kW]	118.40	408.29
Condenser duty / [kW]	411.75	-
Installed cost / [k\$]	163.81	99.43
Utilities / [k\$ / year]	50.3	10.26
Heat exchangers	FEHE	HEATER
Pressure / [bar]	1	1
Heat duty / [kW]	296.5	206.7
Heat transfer area / [m ²]	9.47	8.38
Installed cost / [k\$]	31.95	31.95
Utilities / [k\$ / year]	-	47.34

1

2 **Table 3.** Controller tuning parameters for the plantwide control of a DNPE plant (R-S-R)

<i>Controller</i>	<i>PV, value & range</i>	<i>OP, value & range</i>	<i>K_c, %/%</i>	<i>T_i, min</i>
HEATER				
TC	Temperature = 161 °C 150 ... 170 °C	Duty = 0.173×10 ⁶ kcal/h 0 ... 1×10 ⁶ kcal/h	1	20
COL-1				
PC	Inlet pressure = 1.1 bar 0.9...1.1 bar	Valve opening = 50% 0...100%	1	5
PC	Pressure = 1 bar 0.95 ... 1.05 bar	Vapour distillate = 31.28 kmol/h 0 ... 62.5 kmol/h	1	12
TC	Stage 9 temperature = 123.4 °C 1110 ... 140 °C	Reboiler duty = 0.151×10 ⁶ kcal/h 0 ... 0.3×10 ⁶ kcal/h	1	20
TC	Condensate temperature = 30 °C 20 ... 40 °C	Cooling duty = -0.37×10 ⁶ kcal/h -0.74×10 ⁶ ... 0 kcal/h	1	20
LC	Level, organic phase = 0.94 m 0.4 ... 1.8	Reflux = 714.3 kg/h 0 ... 1430 kg/h	1	60
LC	Level, aqueous phase = 0.35 m 0 ... 0.8 m	Water product = 382 kg/h 0 ... 765 kg/h	1	60
LC	Level, sump = 1.375 m 0 ... 2.75 m	Bottoms product = 5594 kg/h 0 ... 11200 kg/h	1	60
COL-2				
PC	Pressure = 1 bar 0.95 ... 1.05 bar	Vapour distillate = 22.47 kmol/h 0 ... 80 kmol/h	1	12
LC	Sump level = 1.375 m 0 ... 2.75 m	Bottoms product = 3321 kg/h 0 ... 6640 kg/h	1	60
TC	Stage 8 temperature = 178.11 °C 160 ... 190 °C	Reboiler duty = 0.321×10 ⁶ kcal/h 0 ... 1×10 ⁶ kcal/h	1	20

3

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- 1
2 **Table 4.** Design of the DNPE plant (catalytic distillation). The optimal values of the decision
3 variables are presented in **bold**.

Parameter [unit]	RDC
1-pentanol temperature / [°C]	25
Condenser pressure / [bar]	2.82
Bottoms pressure / [bar]	2.93
Number of trays	58
Feed tray number	4
First reactive tray	4
Last reactive tray	53
Diameter / [m] diameter)	0.94
Amount of catalyst / [kg/stage]	63.15
Reboiler duty / [kW]	29.575
Condenser duty / [kW]	425.4
Installed cost / [k\$]	816.35
Utilities / [k\$ / year]	251.23

Table 5. Controller tuning parameters for the DNPE plant based on catalytic distillation

<i>Controller</i>	<i>PV, value & range</i>	<i>OP, value & range</i>	<i>K_c, %/%</i>	<i>T_b, min</i>
PC	Pressure = 2.82 bar	Vapour distillate = 34.67 kmol/h	2	12
	2.5 ... 3.0 bar	0 ... 57.19 kmol/h		
TC	Stage 56 temperature = 219 °C	Reboiler duty = 0.866×10 ⁶ kcal/h	1	20
	210 ... 230 °C	0 ... 1.4×10 ⁶ kcal/h		
TC	Condensate temperature = 30 °C	Cooling duty = -0.428×10 ⁶ kcal/h	1	20
	20 ... 40 °C	-0.7×10 ⁶ ... 0 kcal/h		
LC	Level, organic phase = 1.87 m	Reflux = 638.9 kg/h	10	60
	0.0 ... 3.75	0 ... 1046 kg/h		
LC	Level, aqueous phase = 0.79 m	Water product = 454.8 kg/h	10	60
	0 ... 3.75 m	0 ... 752 kg/h		
LC	Level, sump = 2.175 m	Bottoms product = 3953.1 kg/h	1	60
	0 ... 4.35 m	0 ... 6650 kg/h		

Table 6. Process comparison in terms of key performance indicators

Key performance indicator	R-S-R process	Catalytic distillation
Total investment costs, TIC (k\$)	842.02	816.34
Total operating costs, TOC (k\$/yr)	200.7	251.2
Total annual costs, TAC (k\$/yr)	481.4	523.3
Specific production cost (\$/ton DNPE)	18.2	19.7
Energy requirements (kWh / ton DNPE)	225	256.6

Note: The following economic figures were reported for the membrane reactor in Pera-Titus et al.,¹³ OPEX includes: 25.4 M\$/yr for membranes, 13.3 M\$/yr for refrigeration, 1.3 M\$/yr for cooling water, and 3.8 M\$/yr for steam, and 0.2 M\$/yr for the catalyst. The equipment costs (CAPEX) are evaluated at 9.0 M\$, with 7.7 M\$ being ascribed to the membrane reactor.

1 **Figure captions (auto-updated)**

2

3 **Figure 1.** Residue curve map (RCM) and ternary diagram for the ternary mixture n-pentanol –
4 water – DNPE (at 1.5 atm)

5

6 **Figure 2.** Flowsheet and plantwide control of a DNPE plant (reaction-separation-recycle)

7

8 **Figure 3.** Results of the dynamic simulations for the DNPE production in a reaction-
9 separation-recycle process (at time $t = 2$ h, the flow rate of fresh 1-pentanol is increased by
10 20%, from 42 kmol/h to 50 kmol/h) – Labels represent stream names from Figure 2.

11

12 **Figure 4.** Flowsheet and control of a catalytic distillation process for DNPE production

13

14 **Figure 5.** Profiles along the catalytic distillation column

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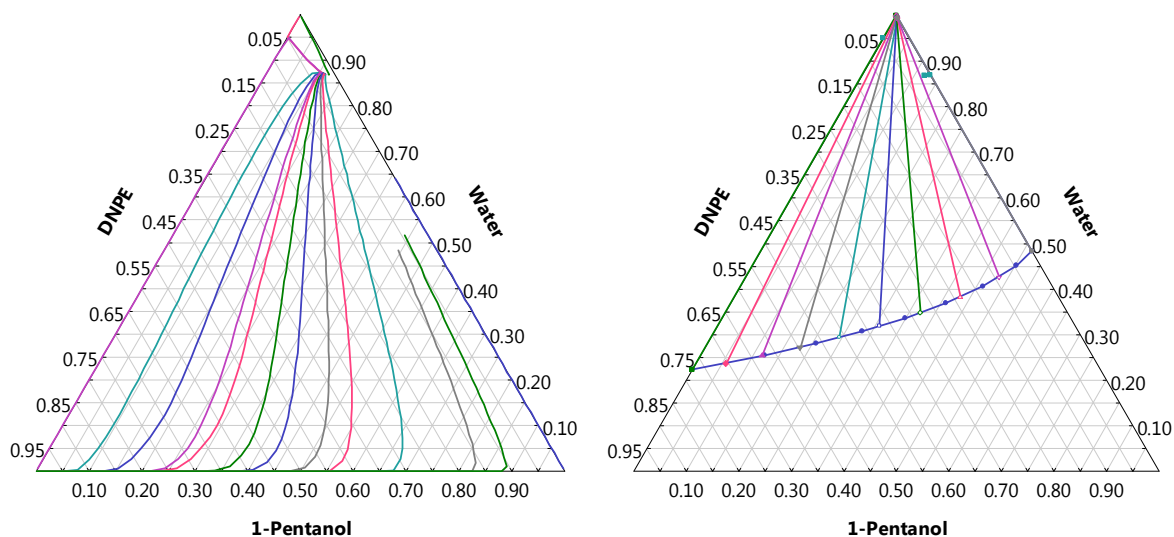
16 **Figure 6.** Results of the dynamic simulations for the DNPE production in a catalytic
17 distillation column: at time $t = 2$ h, the flow rate of fresh 1-pentanol is increased by 20%, from
18 42 kmol/h to 50 kmol/h – Labels represent stream names from Figure 4.

19

20 **Figure 7.** Overlapping window of operating conditions (pressure and temperature) for
21 reaction and distillation, for the DNPE system

22

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3 **Figure 1.** Residue curve map (RCM) and ternary diagram for the ternary mixture n-pentanol –
 4 water – DNPE (at 1.5 atm), based on molar fractions of components

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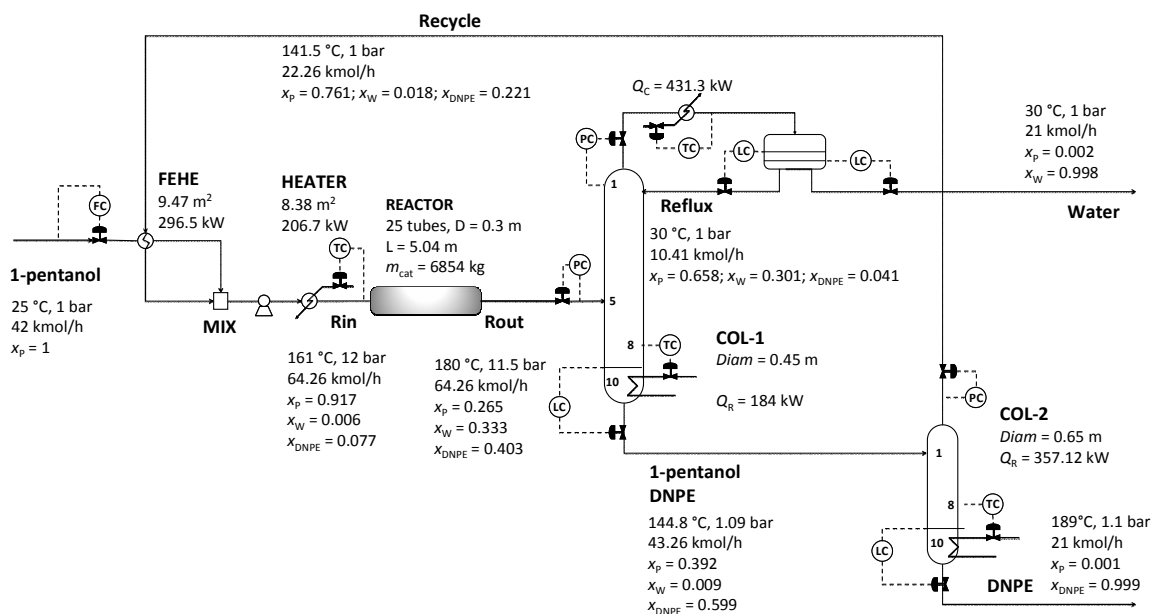
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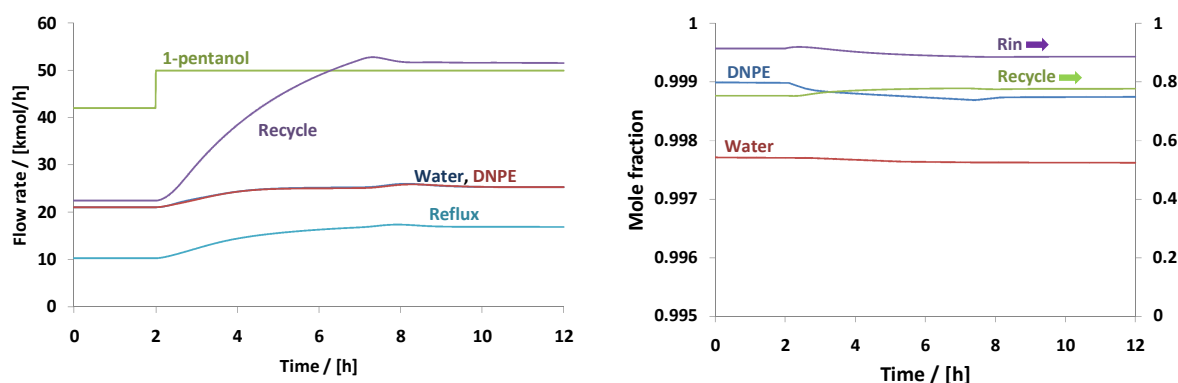


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13 **Figure 2.** Flowsheet and plantwide control of a DNPE plant (reaction-separation-recycle)

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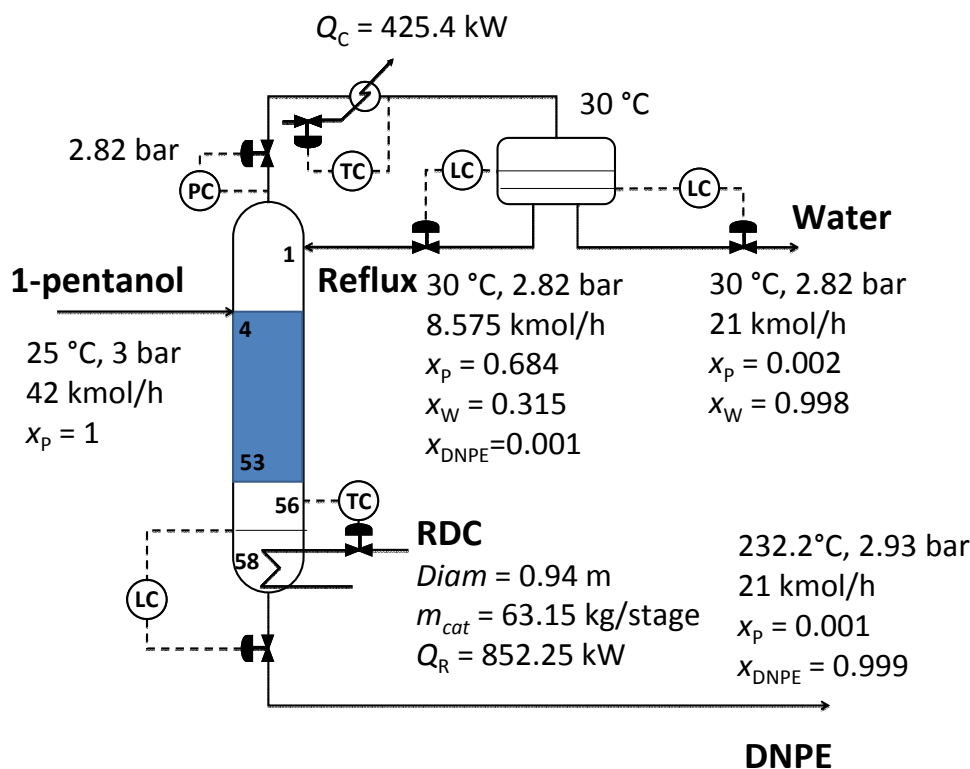
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Figure 3. Results of the dynamic simulations for the DNPE production in a reaction-separation-recycle process (at time $t = 2$ h, the flow rate of fresh 1-pentanol is increased by 20%, from 42 kmol/h to 50 kmol/h) – Labels represent stream names from Figure 2.



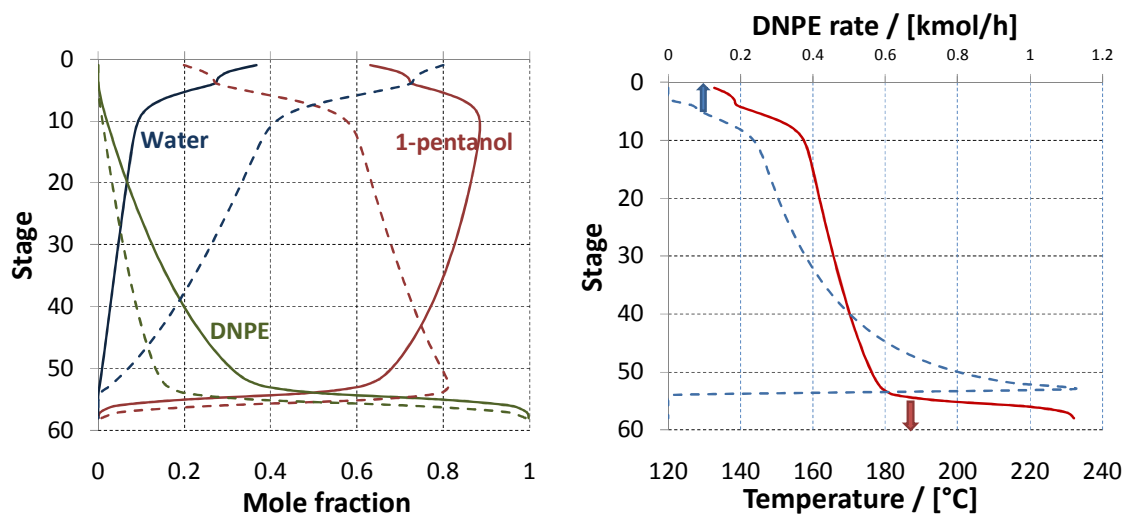
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Figure 4. Flowsheet and control of a catalytic distillation process for DNPE production

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3 **Figure 5.** Profiles along the catalytic distillation column: molar composition (left),
 4 temperature and reaction rate (right)

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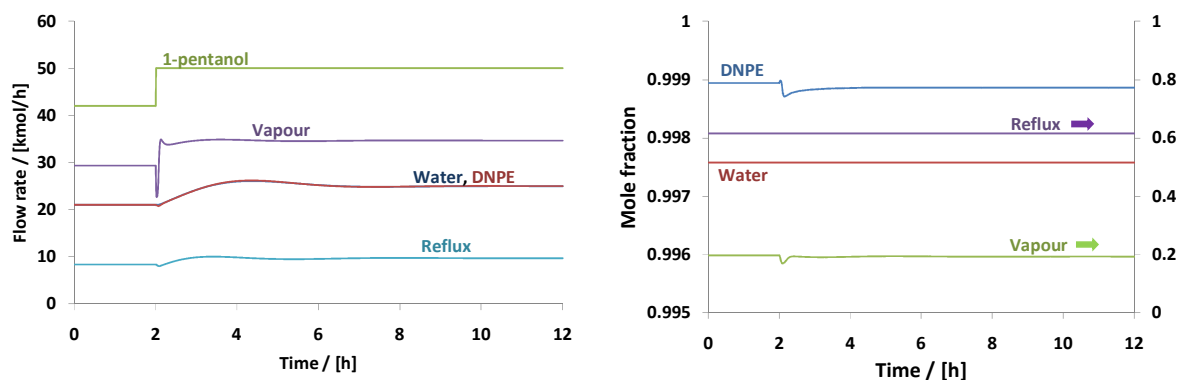
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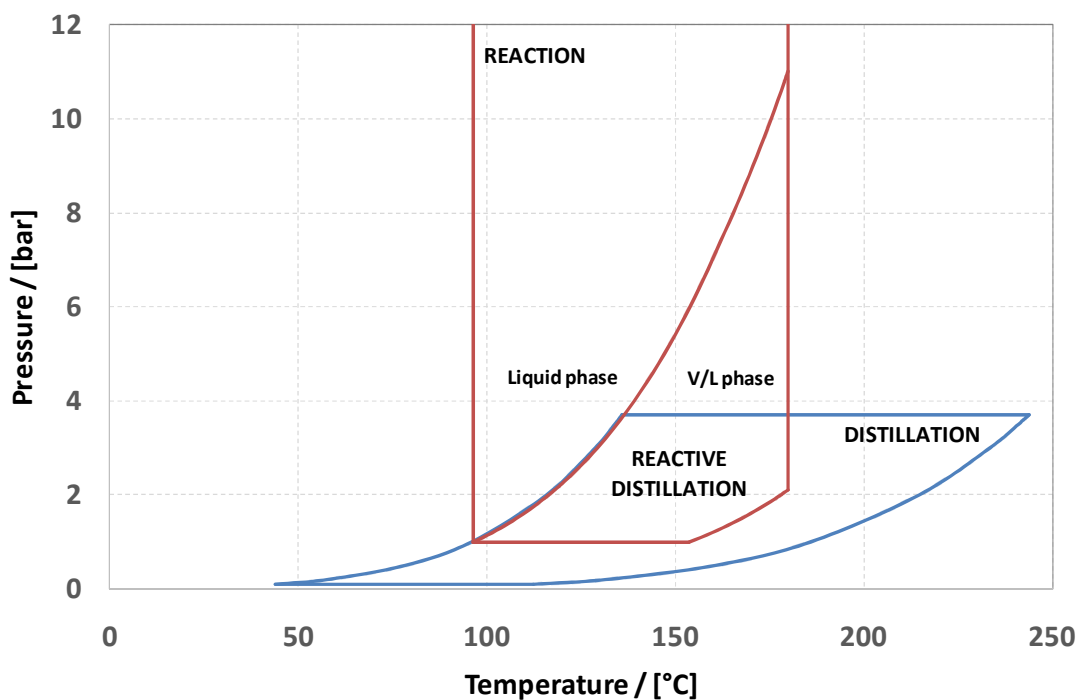
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14 **Figure 6.** Results of the dynamic simulations for the DNPE production in a catalytic
 15 distillation column: at time $t = 2$ h, the flow rate of fresh 1-pentanol is increased by 20%, from
 16 42 kmol/h to 50 kmol/h – Labels represent stream names from Figure 4.

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Figure 7. Overlapping window of operating conditions (pressure and temperature) for reaction and distillation, for the DNPE system

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