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PROCESS OPTIMIZATION OF A BUTANE-BUTENE ALKYLATION PLANT

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This paper presents the optimization of a butane-butene alkylation unit, where the recycle flowrate is the objective function to be minimized. A simple Reactor-Separation-Recycle model of the plant is developed. Two control structures are suggested and analyzed, showing the influence of reactor volume and reaction temperature on conversion, selectivity and recycle flowrate. State multiplicity and unfeasible operating regions are revealed. The minimum recycle flowrate is obtained for a series of large reactors operated at the lowest economically achievable temperature, with the reactants fed to the first reactor from the series.

Keywords: alkylation, process design, process optimization

1. Introduction

In chemical process industries the manufacturing of a certain product can pass very quickly from being cost competitive to non-saleable. The competition is often very high and small changes in the market prices could be vital. The cost of the products depends both on the cost of raw materials and the production cost. Unfortunately, the cost of raw materials is not a controllable parameter, but the production cost is. In order to get the best process (providing the lowest production cost), the behavior of different alternative flowsheets should be analyzed. Moreover, the parameters that have the most important influence on the operability of the unit must be determined.

In this paper, the modeling and optimization of an alkylation process will be considered. In the petroleum industry, alkylation is the reaction of an olefin with a paraffinic hydrocarbon carried on with the goal of obtaining a product with a higher octane rating and no olefin content (alkylate) [1], [2]. Alkylation is accomplished by using a liquid acid catalyst [1]-[4], [7], sulfuric acid being the most widely used. The alkylate is a mixture of saturated, stable iso-paraffins distilling in the gasoline range, which is the most desirable component of many high-octane fuels. However, higher paraffins, which have low added value, are

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also obtained as by-products. Therefore, the selectivity of the process is of outmost importance.

A typical alkylation plant consists of reaction section, spent acid removal and purification, product-reactant separation and recycle of the unconverted raw materials [1]-[3]. Lower reaction temperature and higher recycle flowrate improve the selectivity [1], but at the expense of larger operating costs. Therefore, an optimum exists. In this article we analyze these competing effects with the goal of finding the best operating conditions for the alkylation plant.

The article is organized as follows. First, the reaction stoichiometry and kinetics are presented followed by the description of process flowsheet, feed streams quality, product specifications and the design constraints. Then, a simple mathematical model of the process is derived. The model is solved in order to get an initial mass balance of the plant and to assess the influence of the key parameters (reaction temperature, recycle size) on the reactor performance (conversion, selectivity). Further on, the optimal design of the process is achieved, with minimum recycle as objective function, considering the complex composition of the raw materials and a multi-reactor setup. The article ends with discussion of the main results and conclusions.

It should be remarked that the alkylation consists of two consecutive reactions, where the intermediate product is of interests. Examples of similar processes are: ethylene oxide production by direct oxidation of ethylene and phthalic anhydride production by o-xylene oxidation. Therefore, the results obtained for the alkylation process can be also extended to other process: two exothermic, parallel-consecutive reactions, with the desired product obtained in an intermediate step and the activation energy of first reaction lower than of the second one.

2. Initial data

The alkylation reaction between the paraffin (isobutane) and olefin (butene) takes place at low-temperature, in the presence of a second liquid phase consisting of the sulfuric acid catalyst [1]-[3], in a stirred reactor [1]-[5]. The alkylate (which is also a mixture of paraffins) can also react with the olefin leading to formation of byproducts. The stoichiometry of alkylation process is well described by the following two irreversible main reactions [6]:

$$C_4H_8 + C_4H_{10} \rightarrow C_8H_{18} \tag{R1}$$

$$C_4H_8 + C_8H_{18} \rightarrow C_{12}H_{26} \tag{R2}$$

The components will be shortly referred as: A (butene), B (isobutane), P (isooctane), and R (heavier by-products, modeled as dodecane). The raw materials streams are not pure. They contain high amounts of inert components such as: propane (I) and n-butane (N). These must be separated from the product in order to reach the product quality specifications and purged from the system to avoid their accumulation.

The reactions are exothermic and irreversible [6]. The heat generated due to reaction is transferred to a cold source (refrigerant) in order to keep the temperature constant inside the reactor.

The reaction rates are second-order and follow an Arrhenius type dependence on temperature [5], [6].

$$v_{R1} = k_1 \cdot C_A \cdot C_B \qquad (1)$$

$$v_{R2} = k_2 \cdot C_A \cdot C_P \qquad (2)$$

The pre-exponential factors, activation energies and heats of reaction are provided in *Table **1***.

Table 1.

Kinetic parameters

Parameter	Reaction 1	Reaction 2
k_0 / [m^3/kmol·s]	1.66×10^9	4.16×10^{12}
E_a / [kJ/kmol]	6.5×10^4	8.1×10^4
ΔH_r / [kJ/kmol]	-9.07×10^4	-6.51×10^4

It should be remarked that the activation energy of the second reaction is higher than of the main reaction; therefore, low reaction temperature improves selectivity, but decreases the conversion. Moreover, low concentration of butene (A), obtained by large isobutane (B) recycle, decreases the contribution of the second reaction, since less A is available for the reaction [1].

3. Preliminary analysis

An important trade-off in design of chemical processes is between reactor size and recycle flowrate [1]. Small reactors are cheap but lead to low reactant conversion and therefore high recycle flowrates. Increasing the reactor volume, the conversion of reactants increases, leading to smaller recycles. Finally, an economic analysis of the whole system, reactor, separator and recycle, reveals the optimum design / operating point.

For a preliminary analysis of the inter-dependence between reactor volume, reaction temperature, recycle flowrate, selectivity and conversion, a simple model of the plant will be considered. Thus, the separation section is considered as a ‘black box” unit, assuming that it achieves perfect separation between the components ($\beta_i = 1$). Therefore the unconverted reactants are recycled back to the reactor and the products are completely withdrawn from the system. Because the reactants (isobutane and butene) are the lightest components they can be separated in a single distillation column and recycled together. Moreover, the impurities that are present in the fresh streams (I, N) are neglected and issues related to the separation, recycle and make-up of the sulfuric acid were not taken into account.

The following notation will be used: the flowrate of a component C in stream *j* will be denoted by $F_{C,j}$, where the second subscript $j = 0, 1, 2, 3, 4$ will generally refer to the process inlet, reactor inlet, reactor outlet, recycle and product, respectively (see Fig. 1 and Fig. 2). For example, $F_{A,3}$ is the mole flow of component *A* (butene) in stream 3 (recycle).

We aim to design and optimize a process which produces $F_{P,4} = 47.5$ kmol/h isooctane (P) with the process selectivity selectivity $\sigma_{P/A} \approx 0.9$ kmol P/ kmol of A. The quantity of reactants required to achieve the product quantity can be easily determined from the main reactions stoichiometry and the definition of selectivity.

$$F_{A,\mathbf{0}} = \frac{F_{P,\mathbf{4}}}{\sigma_{P/A}} = 52.5\frac{kmol}{h} \tag{3}$$

$$F_{B,\mathbf{0}} = 50\frac{kmol}{h} \tag{4}$$

Since the alkylation process is strongly influenced by a good contact between the organic phase and catalyst [1], a CSTR reactor is used for the reaction between the butene and isobutane.

The mathematical model of the process consists of the material balance equations describing the reaction section, the separation section and the mixing point of recycle stream with the fresh feed [5]:

Reactor (9 equations):

$$F_{i,1} - F_{i,2} = -\left(\sum_{j=1}^{R} \nu_{ij} \cdot r_j \cdot V\right) \tag{5}$$

$$C_{i,2} = \frac{F_{i,2}}{D_v} \tag{6}$$

$$D_v = \sum_{i=1}^{NC} F_{i,2} \cdot V_{\mu i} \tag{7}$$

Separation section (8 equations):

$$F_{i,2} = F_{i,3} + F_{i,4} \tag{8}$$

$$F_{i,3} = \beta_i \cdot F_{i,2} \tag{9}$$

Recycle (4 equations):

$$F_{i,1} = F_{i,0} + F_{i,3} \tag{10}$$

Reaction rates (4 equations):

$$v_{R1} = k_1 \cdot C_A \cdot C_B \tag{11}$$

$$v_{R2} = k_2 \cdot C_A \cdot C_P \tag{12}$$

$$k_1 = k_{01} \cdot \exp\left(-\frac{E_{a1}}{R \cdot T}\right) \tag{13}$$

$$k_2 = k_{02} \cdot \exp\left(-\frac{E_{a2}}{R \cdot T}\right) \tag{14}$$

ν – stoichiometric coefficient;
V_μ – molar volume, m^3/kmol;

The model contains 25 equations and a total of 35 variables: 20 flowrates ($F_{i,k}$, kmol/h), 2 reaction rates (r_j, kmol/m^3/h), 2 reaction rate constants (k_j, m^3/kmol/h), 4 concentrations (C_i, kmol/m^3), 4 component recoveries in the recycle stream (β_i), volumetric flowrate (D_v, m^3/h), reactor volume (V, m^3) and temperature (T, K). Therefore, the values of 10 variables should be specified.

In this study, two different reactor feed policies will be analyzed, each corresponding to a different control structure. The following eight specified variables are common for both control structures: $F_{P,0}$, $F_{R,0}$ β_i, V, T.

The two control structures are different with respect to the remaining specifications:

- Control structure 1: both reactants flowrates at process inlet are fixed (Fig. 1).

$$F_{A0} = SP_A \tag{15}$$

$$F_{B0} = SP_B \tag{16}$$

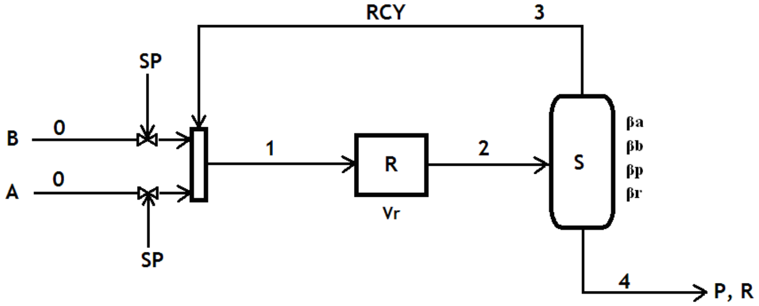

Fig. 1. Reaction-Separation-Recycle system, fixed fresh reactants

- Control structure 2: butene flowrate at process inlet and combined fresh isobutane - recycle are fixed (Fig. 2).

$$F_{A0} = SP_A \tag{17}$$

$$F_{B0} + F_{B3} + F_{A3} + F_{P3} + F_{R3} = SP_B \tag{18}$$

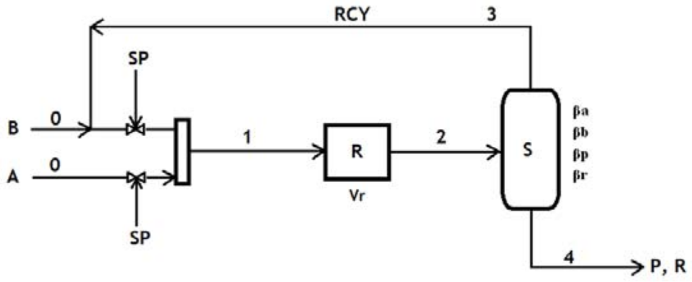

Fig. 2. Reaction-Separation-Recycle system, fixed flowrates at reactor inlet

Control structure 1

The system of nonlinear equations is solved using the “fsolve” function from Matlab. The mass balance of the process, calculated for a total reactor volume of 30 m^3 and a reaction temperature of 263 K, is presented in *Table* ***2***.

Table 2

Material balance

Stream / Component	F_0 [kmol/h]	F_1 [kmol/h]	F_2 [kmol/h]	F_3 [kmol/h]	F_4 [kmol/h]
A	52.5	94.7	42.2	42.2	0
B	50	1663.9	1613.9	1613.9	0
P	0	0	47.5	0	47.5
R	0	0	2.5	0	2.5

It should be remarked that the products flowrates, $F_{P,4}$ and $F_{R,4}$, are solely determined by the process-inlet flowrates $F_{A,0}$ and $F_{B,0}$. This is an advantage of this control structure, because both production rate and selectivity can be directly set.

The influence of the reactor volume on butene conversion and recycle flowrate, at different reactor temperatures, is presented in Fig. 3.

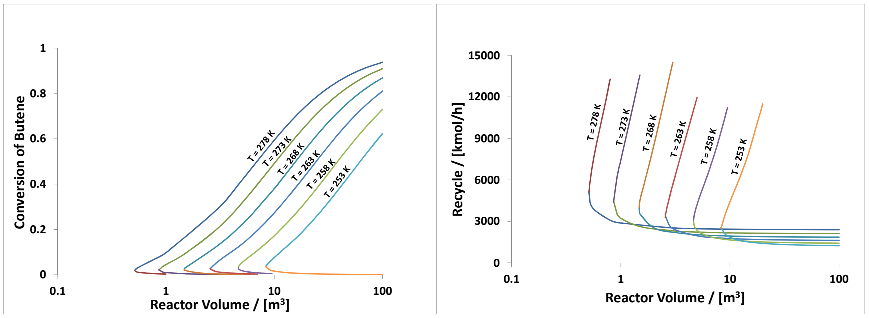

Fig. 3. Influence of reactor volume, at different temperatures, on conversion and recycle flowrate

Fig. 3 shows that, depending on the reaction volume, either two or no steady state solutions exist, at large volumes or small volumes, respectively. Of course, the preferred state is the high-conversion one, which gives the lowest recycle. Choosing a reactor close to the minimum volume is risky since the system may become unstable if the process is disturbed.

On the high-conversion / low-recycle branch, if the temperature is kept constant, the recycle decreases with the increase of reactor volume; an infinite-volume reactor would provide the minimum recycle. At constant and large values of the reactor volume, lower temperature leads to lower conversion but also to smaller recycle rate. This unusual behavior can be explained as follows: the second reaction has higher activation energy; therefore it is favored by high temperature. However, because the selectivity is fixed by process-inlet reactant flowrates, the recycle flowrate must increase to compensate the effect of the temperature. This observation has an important implication on designing the minimum-recycle plant: if the operation is constrained by the refrigerant temperature and the reactor volume is large enough, the optimum temperature that provides the minimum recycle always corresponds to the minimum temperature.

In conclusion, the advantage of this control structure is that the selectivity can be maintained constant, set by the ratio of the reactants flow at the inlet of the unit. However, the equipment must be designed to cope with the variations of recycle flow. For example, a 10^{o}C change of reaction temperature leads to a 25% increase of the recycle flow, which should be tolerated by the separation section.

Control structure 2

The second control structure considers a different reactant feed policy: the reactant streams at the reactor inlet are fixed, as shown in Fig. 2. The fresh butene is fed under flow control and the fresh isobutane balances the recycle flow in order to keep constant the combined flow at the reactor inlet. The mathematical model contains the same equations as for the previous control structure, the only difference being the variables that are specified.

The disadvantage of this control structure is that the selectivity cannot be directly set. Fig. 4 shows the influence of the reactor volume on selectivity at different temperature levels and different values of SP_B. For each temperature level and a given SP_B, a minimum reactor volume exists, below which no solution is found; (similarly, for a given reactor volume there is a minimum temperature below which no solution is found). Far away from the minimum volume, (for large reactors) lower temperature means higher selectivity. Moreover, when the selectivity is imposed (for example 90%) the reactor volume must exceed a minimum (critical) value (e.g. 1.9 m^3 for a given SP_B of 2500 kmol/h). Below this volume, there is no temperature that can bring the selectivity to the required value.

In general, the selectivity increases with the increase of SP_B value. However, for large reactors, the selectivity is not sensitive to reaction volume.

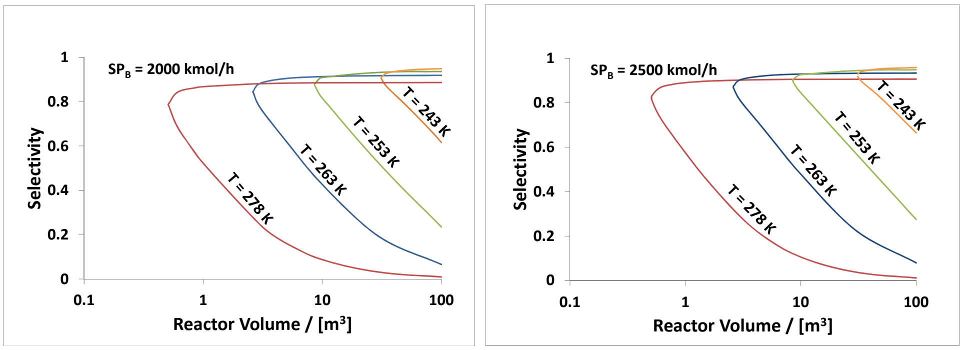

Fig. 4. The influence of temperature on selectivity

Fig. 5 presents the recycle flowrate versus the reactor volume at different temperatures. For each temperature, there is a minimum reactor volume for which two steady states exist. For constant reaction temperature, large reactor leads to low recycle flow (Fig. 5) and high conversion (Fig. 6). In contrast to the previous control structure, the recycle flowrate is less sensitive to changes of the reactor volume or reaction temperature.

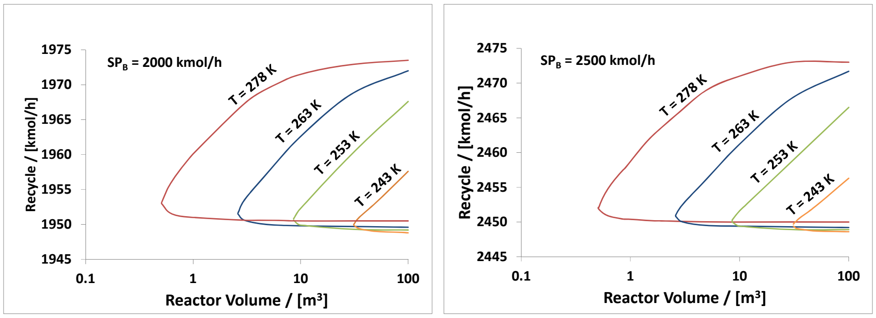

Fig. 5. Influence of Reactor Volume on Recycle Flow

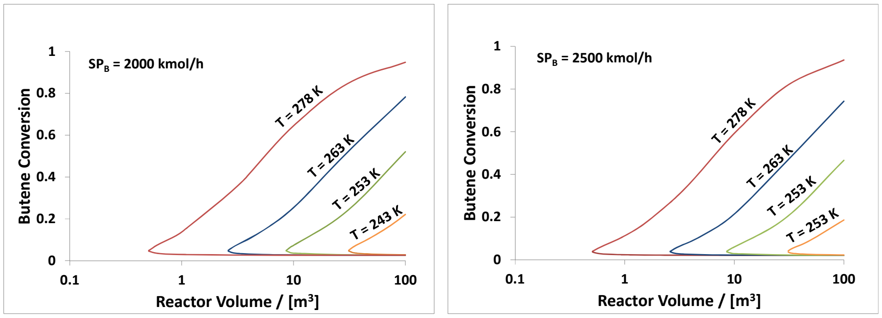

Fig. 6. Influence of Reactor Volume on Conversion

The advantage of this operating scheme is that the flows at the inlet of the reactor and separation section are almost constant. This provides more flexibility to the process, since the separation section is not exposed to large disturbances of the inlet flow. But, the selectivity cannot be controlled and the product can be off-spec.

4. Process optimization

Optimization problems in process design are usually concerned with maximizing or minimizing an objective function [8].

Typical objective functions are the economic potential, the cost of investment and/or operation, or any other key variable that strongly influences the efficiency of the process.

In this article we chose the recycle flowrate as the objective function. Low recycle flowrate means lower cost (operating and capital) of the products-reactants separator and of the recycle pump/compressor. Often (but not always), low recycle flowrates are obtained in large reactors operated at high temperatures. Because the cost of the separation (operation and investment), which increases with the recycle flow, usually exceeds the cost of reactor, the minimum recycle leads to the most economical flowsheet.

The use of recycle flowrate as objective function to be minimized is more convenient compared to a cost function, because the later requires detailed sizing of the units, cost relationships and values of the cost factors and parameters, which are seldom available during the conceptual design [5]-[9].

In this section, the process configuration previously described is extended by considering a series of three reactors and the possibility to split the feed of reactant A between them (Fig. 7); this type of reactor configuration is also known as "*semi-plug-flow model*" [8].

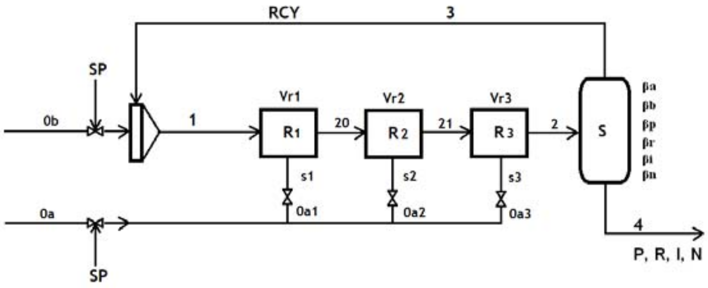

Fig. 7. Reactor-Separator-Recycle system with three reactors in series

Moreover, two more components are added in the system: n-butane (N) and propane (I), impurities that are present in the raw materials (*Table* ***3***). These components are removed from the process by the separation section, therefore they are not found in the recycle. Although n-butane and propane are inert, they influence the reaction rate by diluting the reaction mixture.

The analysis will focus on the behavior of the plant when control structure CS1 is applied, because this ensures constant selectivity.

The composition and flow of the fresh feeds, *0a* and *0b* are known from the initial material balance calculation: they are the stoichiometric flows required to reach 47.5 kmol/h of alkylate with a selectivity of ≈ 90%. Since the selectivity remains constant due to the constant reactant ratio at the inlet of the process (and no loss of reactants with products), the flowrate and ratio of the product and byproduct are also constant.

Table 3

Feed streams

Component	Stream 0a [kmol/h]	Stream 0b [kmol/h]
Butene	52.5	0
Isobutane	20	30
Isooctane	0	0
Dodecane	0	0
Propane	5.5	3
n-butane	27	27
Total	105	60

The model was extended to include all reactors, the split feed and all the six components (NC = 6; A, B, P, R, I, N). The equations for the split of the fresh reactant to the reactors are given below:

$$F_{i0a} = F_{i0a1} + F_{i0a2} + F_{i0a3} \tag{19}$$

$$F_{i0a1} = s_1 \cdot F_{i0a} \tag{20}$$

$$F_{i0a2} = s_2 \cdot F_{i0a} \tag{21}$$

The extended model contains 78 equations and 101 variables. After fixing 17 variables, six degrees of freedom are left: V_1, V_2, V_3, s_1, s_2, T. The values of these variables should be determined in order to reach the *minimum of the objective function*.

The problem represents a multivariable optimization problem. One method used for solving this kind of problems, is the "*direct search method*", which starts fixing all the variables except one, which is optimized. When the optimum value of this variable is reached, the algorithm fixes it and starts a new trial finding the best value of another variable and so on, until no improvement of the objective function is reached [8]. The optimization problem is solved in Matlab using "*fmincon*" optimization function. In order to provide feasible and meaningful solutions, lower and upper bounds for the decision variables are given. To avoid reaching local optimum of the objective function, it is recommended to run the program starting from different initial values of decision variables. The results and the discussions regarding different optimization aspects of the unit will be presented in the next chapter.

5. Results

The purpose of the study is to find out the optimum reactors volume (for bounded and unbounded total reactor volume), the split of butene and the temperature that provides the minimum recycle.

Several optimization trials were performed and compared, using different sets of decision variables.

First, the optimum parameters for the flowsheet with one reactor are calculated. For this case, there are no alternatives for the split; the only decision variable is the reactor temperature. The calculation was performed considering different (upper) limits of the reactor volume and a wide range of reactor temperature. For each reactor volume, the optimum temperature was calculated.

Further on, trials for different configurations of the flowsheet and different total reactor volumes are performed; these are detailed below:

- Equal volumes of reactors and fresh reactant equally split between the reactors. The decision variable is the reactors temperature.
- Equal volumes of reactors; the decision variables are the fresh reactant split s_1, s_2 and the reactor temperature;
- Equal fresh reactant split; the decision variables are the reactors volume and the reactors temperature;
- All parameters, the fresh reactant splits, the reactors volume and the reactors temperature are considered as decision variables.

The following figures present the dependence of minimum recycle flow on reactor volume for the cases presented above (different sets of decision variables). Fig. 8a shows the difference between the curves for different series of reactors (cases 1, 2, and 3, with fewer number of decision variables) and the optimum curve (case 4, all decision variables considered). Fig. 8b presents the difference between the optimum curve for a flowsheet with one reactor and the curve when all decision variables are considered.

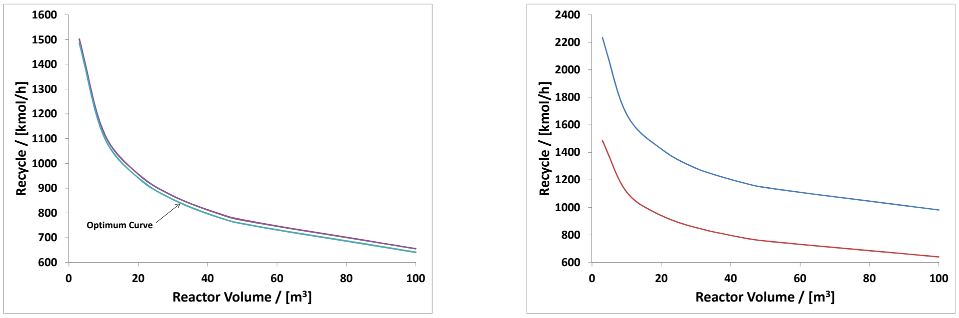

Fig. 8. Min. recycle flow vs. reactor volume a) three reactors b) one/three reactors

The difference between the minimum recycle for the cases with three reactors (different configurations) is not big, as the curves are very close to each other. For the same volume, the optimum temperature is almost the same for all flowsheets regardless the number of reactors. From the point of view of minimum recycle, the fresh butene should be all fed in the first reactor.

For the control structure of constant selectivity, it was also observed that at constant total reactor volume, higher temperature leads to higher conversion but also to larger recycle flow. This unusual behavior, (higher conversion and smaller recycle being expected) is due to the fact that high temperature tends to decrease the selectivity. In order to compensate this effect, a larger recycle (leading to larger isobutane excess) is necessary. Therefore, for multiple reactions, there is a strong dependence of recycle on the selectivity as well, compared to the single reactions where the dependence is only recycle flow-conversion.

If large reactors are allowed, the optimum temperature decreases, reaching very low values (for example, 240 K at V_{total} = 100 m^3). In practice, this is both difficult and expensive to achieve. A reasonable reactor temperature range that can be reached easier and cheaper with the commercial refrigerants shall be used. The range of 258-278 K is chosen and the optimum parameters are recalculated. This time, the reactors volumes are not constrained. The total reactor volume reaches high values (and it is dictated mainly by reactor 3) and the temperature goes always to the minimum.

Fig. 9 presents the dependence of recycle flow on minimum allowable operating temperature (constrained by the minimum cooling temperature of the refrigerant and set in the model by the lower bound value) at different volumes of reactor 3. The reason that the curves were drawn considering reactor 3 was that, during optimization trials, it had been observed that the volume of reactor 3 always had values corresponding to the upper bound, whereas the first two reactors got intermediate values; so, for different upper bounds of V_3, the volume of reactor 1 and 2 were optimized (Fig. 10) together with the temperature and reactant splits. For large reactors (V_{total}>15 m^3), the operating temperature went always to the minimum allowed temperature.

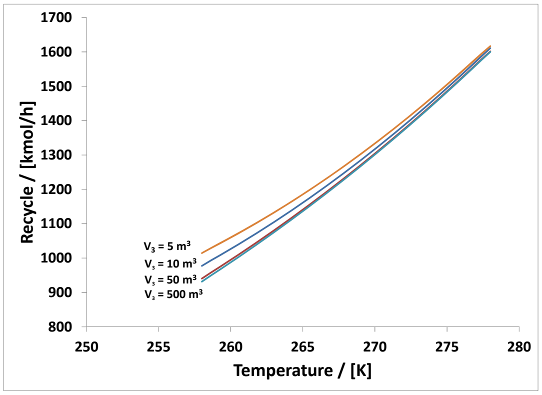

Fig. 9. Minimum recycle flow vs. reactor temperature

Fig. 9 also proves that above a certain reactor volume (V_3), the recycle flow does not change too much and there is no reason to further increase it; at $V_3 = 30$ m^3, the recycle flow is 947 kmol/h compared to 932 kmol/h at 500 m^3. A further increase of the reactor volume increases the investment cost, while minor changes in the operating costs occur. The optimized volumes of V_1 and V_2 at $V_3 = 30$ m^3 are 11 m^3 and 17 m^3 (see Fig. 10).

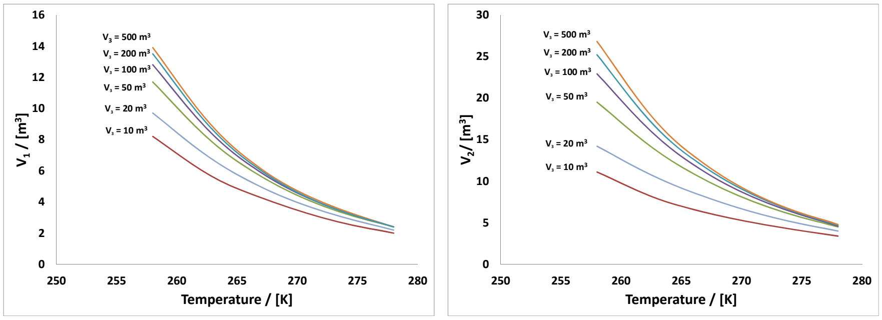

Fig. 10. Optimum reactor volume at different temperatures a) V_1; b) V_2

The most important process variable for reaching the minimum recycle remains the operating temperature. The lower the temperature is, the lower the recycle.

For the flowsheet with 3 reactors, the influence of butene feed distribution to the reactors on recycle flowrate was analyzed. The results showed that the best feed policy (for a series of CSTR reactors) was to add all the fresh butene in the first reactor rather than splitting it to all three reactors (in parallel).

6. Conclusions

The analyzed system of reactions (parallel consecutive exothermic reactions), where the product of interest is obtained within an intermediate step, presents a high interest due to its applicability to similar systems such as ethylene oxide or phthalic anhydride production.

The purpose of this article was to model and analyze the behavior of an alkylation unit consisting of a Reaction-Separation-Recycle system. The target was to find out the optimum value of several parameters in order to reach the minimum recycle. The influence of important variables and two process control structures regarding the feed of reactant were also discussed.

1. Control structure CS1 fixes the plant-inlet flowrates. It ensures constant selectivity. Control structure CS2 fixes the reactor-inlet flowrates. It leads to constant flow to the separation section. Both CS1 and CS2 show multiple steady states and the operation is unfeasible at low temperature or small reactors.
2. For both control structures there is a set of critical values (temperature-volume), close to which the operation is unfeasible;
3. Optimization of CS1: when the temperature is constrained by a minimum allowed value, and the reactor is large, the optimum temperature is always at the constraint (not true for small reactors);
4. A series of 3 reactors performs better than a single reactor (smaller recycle). The best policy is to feed all reactants to R1;
5. The optimum is achieved for the maximum allowed value of third reactor volume (V_3). The optimum is unconstrained with respect to V_1 and V_2.

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