Process Optimization of a Butane/Butene Alkylation Unit

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The paper presents the optimization of an isooctane production unit by butane – butene alkylation, for which a Reactor-Separation-Recycle model of the plant is developed and solved in Matlab. Equipment design is performed and utilities consumption is evaluated. The objective function is the total annual cost (TAC), consisting of capital and operating expenditures. The decision variables are the reactors size, the distribution of raw materials to reactors, the reaction temperature and the component recoveries in the distillation columns. The minimum cost is obtained for a series of reactors operated at the lowest temperature allowed by the coolant availability, reactants fed to the first reactor of the series, and low recoveries of the inert impurities. Use of the TAC as objective function leads to a much lower cost, compared to the optimization aiming recycle minimization. The results of the rigorous process simulation performed in Hysys differ by less than 10% from the prediction of the Reactor – Separation – Recycle model.

Keywords: Alkylation, isooctane, process design and optimization

Optimization represents a key element of process design, leading to economical and reliable plants. Applied to existing or new units, the outcome can help many players in the chemical (and not only) industry market to take the right decisions at the right moment (e.g. searching for new utility types/sources if the currently used ones provide a too high operational cost). Since the concerns regarding the environment protection are higher and higher and the regulations become more severe, the requirements for cleaner burning fuels have gradually increased. Isobutane alkylate has proved to be a suitable blending component of gasoline for matching the required properties [1]: low content of aromatics, olefins, sulphur and nitrogen compounds, in order to make the fuel more environmental friendly. It has a low vapour pressure and a high octane number. It is a key component in replacing some of the octane number lost when the level of the high-octane banned components (e.g. aromatics) is reduced [2]. The alkylation of an olefin with a paraffinic hydrocarbon takes place in the presence of a strong acid, leading to a product (called alkylate) with a higher octane rating and no olefin content [3, 4]. Reacting the isobutane with C3 – C5 olefines produces alkylates that are the highest quality and cleanest burning gasolines [5]. The most used catalysts have been hydrofluoric or sulphuric acid, each of them with its shortcomings and benefits. Hydrofluoric acid (HF) proved to be a good (from a chemical point of view) and cheap catalyst [1]. However, because of HF high toxicity level, most of the technologies switched to sulphuric acid (40% in 1996 and almost 50% in 2009, [6]), which is considered relatively safe compared to HF. Alkylation reactions are highly exothermic; therefore, the heat of reaction should be removed from the system. There are two ways of removing the heat generated by the alkylation reactions, as follows: by means of an internal tube bundle and a suitable refrigerant, and by using auto-refrigerated reactors where the heat is removed by vaporizing a part of the acid / hydrocarbon mixture (evaporative cooling) [7]. Both technologies gained the attention of many researchers. Luyben [3] published a study regarding the optimization of an auto-refrigerated alkylation unit (based on Kellogg process) consisting of a reactor / separation / recycle system, with gaseous recycle. The approach, as was mentioned in the paper [3], was heuristic, and the optimization was performed using a trial and error procedure, from equipment to equipment, trying to minimize the total annual cost (TAC). Luyben claimed that the simulation of the plant could not be converged in steady state with the recycle connected. Dimian and Bildea [8] also performed a study on *cooled* reactor technology; the sensitivity of the flowsheet to different process variables was analysed and an optimization was also performed for reaching the reactor of minimum volume that ensured feasible operation of the reactor / separation / recycle system, for a range of temperature, and kinetic uncertainties.

This paper aims to design and optimize an alkylation plant considering the sulphuric acid process, (which proved to be more environmentally friendly than hydrofluoric acid) using a refrigerant (chilled water or other, depending on the optimization results) as the cooling medium for the reactors.

In a previous article [9], the plant flowsheet was developed based on simplified mathematical models of the units: the separation unit was considered a black-box and the heat exchangers and the stream properties were neglected. An optimization was performed assuming that a minimum recycle (as objective function) would provide the lowest cost of the plant, based on the fact that the separation columns and the recycle would be cheaper, as smaller inlet flow means less heat required in the reboiler, smaller distillate flow and also a lower column diameter. In the present article, further development of the model (consisting of the reactor, separator and recycle) is performed based on rigorous models. Equipment sizing is performed and relations for cost estimations are used, with the result of a rigorous optimization of the entire plant considering the total annual cost as objective function to be minimized. In the last part of the article, a comparison between the two approaches (namely, minimum cost and minimum recycle) is performed.

Experimental part

Typical industrial alkylation plants consist of three sections: (i) reaction and refrigeration; (ii) catalyst separation and recycle (acid settler); (iii) effluent treating and fractionation [4, 7].

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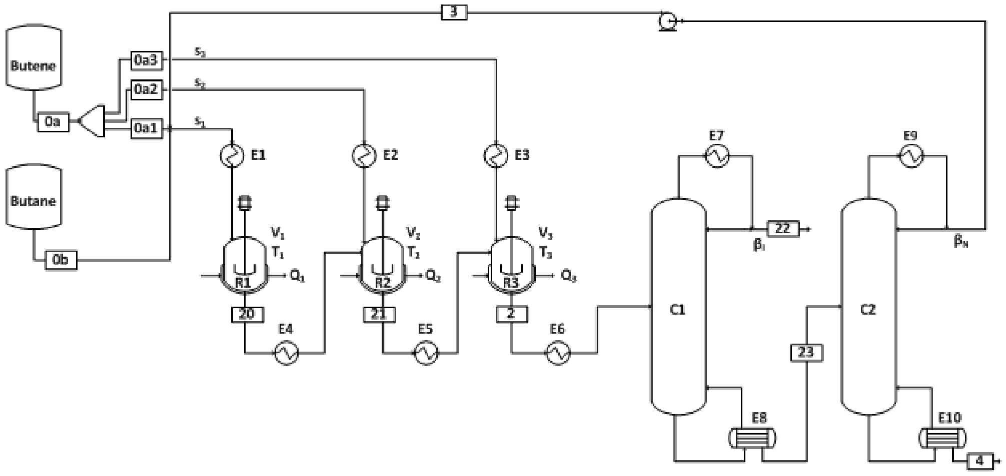


Fig. 1. Process flow scheme

Since the purpose of this study is to build and analyse the flowsheet from the conceptual point of view, only a brief description of each unit will be provided. Details about different types of equipment used in alkylation units and the features of different production licences can be easily found in the literature [7].

In the reaction section, the fresh streams coming from storage, consisting of isobutane, butene and impurities (mainly propane and n-butane) are mixed with the liquid recycle coming from the separation section consisting of high amounts of isobutane. The mixture is contacted with the liquid acid catalyst in a series of stirred reactors (R1, R2 and R3, Figure 1). Then, an acid settler (not shown in Figure 1) separates the acid catalyst and recycles it back to the reactor, while the effluent treating section removes the traces of free acid and alkyl sulphates formed by the reaction of acid with olefins. In order to simplify the model, the catalyst together with the process units related to it (the acid settler and the effluent treating section) are intentionally skipped from this study.

Before mixing the isobutane with butene and recycle stream, the butene feed stream could be distributed to all three reactors used in the flowsheet, so that the isobutane and recycle are mixed with only a part of the fresh butene feed. The amount of butene fed to each reactor is to be determined during the optimization process.

The fresh reactant streams and the recycle mixture are cooled down to the optimum reactor temperature before entering the reactors; downstream of the coolers (E1, E2, E3), the reactants are fed into a series of three continuously stirred (CSTR) reactors. Good mechanical mixing is required to form a reactive acid / hydrocarbons emulsion and to overcome the difference in solubility of the reactants in sulphuric acid (olefins are much soluble than isobutane) [4]. Since the reactors could operate at different temperatures, depending on the results provided by the optimization, coolers / heaters (E4 and E5) are provided in between the three reactors. Recommended reaction temperatures for the sulphuric acid process are in the range of -4 ÷ 15^{o}C; lower temperatures make the liquid catalyst more viscous and slow down the mixing, while higher temperatures promote polymerization of the olefin to acid soluble oils (ASO) that remain dissolved in the acid phase. The catalyst consumed in reactions with the olefins also decreases at lower temperatures and the octane number of the alkylate is higher [4]. The heat of reaction is removed from the system using either refrigerant or chilled water. Although details of the refrigeration system are not considered here, its cost is taken into account when calculating the total cost of the plant.

Skipping the catalyst from the study does not bring any inconsistencies: as the catalyst consumption per cubic meter of alkylate is constant [8] the cost of sulphuric acid depends only on the (constant) product flowrate.

Downstream the reaction section, the effluent is routed to the fractionation unit. Before entering the first separation column (C1, the depropanizer), the liquid reactor effluent is heated up to the boiling temperature (in E6). In the depropanizer, the light inert propane impurity is removed by distillation from the reactors effluent mixture. The operating pressure of this column is high (10 bar), in order to allow the use of water as cooling agent for the condensation of the overhead vapour. The propane is removed as distillate at the top and the bottom product is routed to the second distillation column (C2) that separates the unconverted reactants from the products. The overhead stream of this column contains the unconverted reactants (recycle) and the bottom stream contains the alkylate product. The inert components (mainly n-butane) are distributed between the top and bottom products. The operating pressure (6 bar) is selected such that water can be used as cooling medium for the overhead condenser. The recycle is routed to the reaction section for mixing with the fresh streams; the bottom stream goes to a third purification column (fig. 1) which operates at atmospheric pressure to strip the n-butane from the alkylate product in order to meet the quality requirements. Since the relative volatility between the alkylate and n-butane is high and the column is outside the reactor-separator-recycle loop, this separation step is cheap and does not influence significantly the optimal cost of the plant.

Problem statement

In a previous publication [9] we found out the reaction conditions (temperature, reactants feed policy) and the reactors size which led to a minimum recycle flow rate. In the present study, the objective is to reach the minimum cost of the plant (*TAC*). This will represent the objective function (*FO*) of the optimization problem. Besides the objective function, the optimization problem also includes equality and inequality constraints. The mass balance equations containing *NV* variables, together with the set of specified variables, provide the equality constraints (*EC*) of the problem. The difference between the total number of variables (specified and unknown, *NV*) and the number of equality constraints represent the degrees of freedom (*DF*), which in turn corresponds to the decision variables.

$$DF = NV - EC \qquad (1)$$

Minimum and maximum bounds are imposed on the decision variables (inequality constraints).

In the following chapters, the components of the optimization problem (objective function, constraints and variables) will be detailed.

Objective function

Typical objective functions in industrial engineering are the economic potential, the cost of investment and/or operation, or any other key variable that strongly influences the efficiency of the process [9]. Since the prices of the raw materials and products are usually correlated, the typical approach is to consider an economic optimization which relies on minimising the total annual cost of the plant (*TAC*); it consists of the investment cost (*CI*) divided by the payback time (return of investment), plus the operational cost (*CO*).

$$TAC = \frac{CI}{R_I} + CO \qquad (2)$$

The optimization algorithm will minimize the objective function by finding out the proper values of the decision variables while ensuring that the equality and inequality constrains (the mathematical model of the plant) are fulfilled.

The investment cost consists of the prices of the main equipment within the flowsheet: reactors, columns and heat exchangers. Although during the conceptual design the pumps are usually excluded from the economic analysis because of their low contribution on the total cost, this study considers the cost of the recycle pump; the pumping cost is directly determined by the recycle rate and therefore by the separation performances. Ignoring the recycle cost might favour a solution with high recycle flow rates, since on that route there is no constraint. Note that the cost of recycle is significant in systems with gaseous recycles, which are achieved by means of expensive compressors. The price of the equipment depends on their size (e.g. height, diameter, heat transfer area, number of trays, etc.) which in the end depends on the process and decision variables. The investment cost calculation of each item is presented in the following chapters.

The operational cost consists of the cost of utilities used to satisfy the process requirements: steam for reboilers, chilled water / refrigerant for condensers and reactors and electricity for the dynamic equipment. There is always a trade-off between the size of the equipment and the utility consumption: large equipment usually requires less utility consumption (e.g., large heat transfer area requires less heating / cooling agent). The calculation of the price of utilities is presented in the followings chapters.

Process model

The mathematical model of the process consists of material balance equations written for the units presented in Figure 1 (splitter, reactors and separation unit); it is a nonlinear system of equations. The calculated flows are used for sizing the equipment and calculating the capital and operational costs.

Butene splitter

The fresh butene stream, coming from storage and containing amounts of isobutane and impurities, is distributed to all three reactors. In some publications [3], the split ratios are specified, whereas here the split ratios represent decision variables to be optimized. The following equations are used to describe the splitter and to calculate the reactant flows towards each reactor:

$$F_{i,0a1} = s_1 \cdot F_{i,0a} \qquad (3)$$

$$F_{i,0a2} = s_2 \cdot F_{i,0a} \qquad (4)$$

$$F_{i,0a3} = s_3 \cdot F_{i,0a} \qquad (5)$$

where s is the flow fraction and $F_{i,k}$ is the molar flowrate of component i in stream k.

A fraction of the fresh butene, the fresh isobutane and the recycle coming from the second separation column (which separates the products from reactants) are mixed in the first reactor. The other fraction of butene, which is fed to the first reactor, is optimally distributed to the other two reactors.

Eighteen equations define the splitter unit: equations (3) ÷ (5) written for all 6 components (reactants, products and inerts).

Reactors

The reaction section consists of a series of three cooled (isothermal) CSTR reactors; good mixing is required to achieve: high (acid/hydrocarbons) interfacial areas, heat dissipation, uniform distribution of the hydrocarbons in the acid and reduced temperature gradients (which supress olefin polymerization reactions in favour of the alkylation reaction) [11].

The following equation, written for each component, describes the ideal CSTR reactor model:

$$F_{i,in} - F_{i,out} = -\left(\sum_{j=1}^{R} \nu_{ij} \cdot r_j \cdot V_n \right) \qquad (6)$$

The inlet flow ($F_{i,in}$) is different for each reactor. For reactor R1 the inlet flow consists of $F_{i\text{-},0a1}$, $F_{i,0b}$ and $F_{i,3}$; for reactor R2 - $F_{i,0a2}$ plus the outlet flow from reactor R1, $F_{i,20}$; for reactor R3 - $F_{i,0a3}$ and the outlet flow from reactor R2, $F_{i,21}$.

In order to be able to solve the system for the reaction section, the stoichiometry and kinetics of the chemical reactions should be known. The alkylation is a complex process consisting of more than thirty chemical, physical and transfer (in the liquid-liquid dispersions) steps [5]. Several side reactions occur, producing undesired by-products including light paraffins and isoparaffins, acid soluble oils, and pseudo-alkylates [5]. Nevertheless, the process can be reasonably / accurately modelled using the following two main reactions [8]:

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

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

In the first reaction, isobutane (B) reacts with butene (A) to produce the alkylate (P), whereas the second reaction is a side reaction that consumes the alkylate formed in the first reaction by reacting it with butene to produce heavy species (modelled here as dodecane, R). Besides the main 4 components involved in the reaction system, the inert components (impurities in the feed streams), propane (I) and n-butane (N), are also considered.

The reaction rates are second order and follow an Arrhenius type temperature dependence [12].

$$r_1 = k_1 \cdot C_A \cdot C_B \qquad (7)$$

$$r_2 = k_2 \cdot C_A \cdot C_P \qquad (8)$$

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

where:

$$k_1 = k_{01} \cdot \exp\left(-\frac{E_{a1}}{R \cdot T}\right) \tag{9}$$

and,

$$k_2 = k_{02} \cdot \exp\left(-\frac{E_{a2}}{R \cdot T}\right) \tag{10}$$

The pre-exponential factors, activation energies and heats of reaction are provided in table 1 [12].

Another two equations complete the reaction system. They represent the concentration of isobutane, butene and alkylate in the reactor, which are used in the reaction rate calculation, and the volumetric flowrate at the reactor outlet, respectively.

$$C_{i,2} = \frac{F_{i,out}}{D_v} \tag{11}$$

$$D_v = \sum_{i=1}^{NC} F_{i,out} \cdot V_{\mu i} \tag{12}$$

Equation assumes that the volumes are additive.

The reaction system consists of 36 equations, 12 for each reactor: 6 mass balance equations, 3 equations for the concentration of the reacting species (A, B, P), one equation for the volumetric flowrate and 2 equations for the reaction rates. The heat balance equation affects only the operational cost and not the material balance; therefore, it will be provided in the economical evaluation chapter.

Separators

The effluent from the reaction system, consisting of unconverted reactants, products and inert components, flows to the separation system. The separation is performed by distillation, in two steps: the first column (C1) removes the propane, while the second column (C2) separates the product, by-product and inert (alkylate, dodecane, n-butane) from unconverted reactants (butene and isobutane). The following two equations represent the mass balance for the separation block. For each species, the outlet flows from the column (distillate (D) and residue (B)) are linked to the inlet flows (F) through the recovery factor (β);

$$F_i = D_i + B_i \tag{13}$$

$$D_i = \beta_i \cdot F_i \tag{14}$$

Equations (13) and (14) are written for both columns; therefore:

$$F_{i,2} = F_{i,22} + F_{i,23} \tag{15}$$

$$F_{i,22} = \beta_i \cdot F_{i,2} \tag{16}$$

and

$$F_{i,23} = F_{i,3} + F_{i,4} \tag{17}$$

$$F_{i,3} = \beta_i \cdot F_{i,23} \tag{18}$$

The bottom stream of the first column represents the feed of the second column. Therefore, the separation section consists of 2 × 12 = 24 equations.

The model contains now 78 nonlinear equations: 18 for the splitter, 36 for the reactors and 24 for the separation unit.

Variables and Constraints

The 78 equations describing the model of the alkylation plant contain 111 variables: 3 splits, 3 volumes, 3 temperatures, 3 volumetric flowrates, 9 concentrations, 6 reaction rates, 12 component recoveries and 72 flowrates; therefore, the system cannot be solved. In order to get a square system, 111 – 78 = 33 variables should be specified.

The constraints are also part of the optimization problem. The material balance equations written in the previous section together with the specified variables provide the equality constraints (*EC*) of the optimization problem. 22 variables can be specified, namely 2 × 5 = 10 component recoveries and 2 × 6 = 12 fresh inlet component flows. Therefore, the 11 unspecified variables represent the degree of freedom of the problem that bring the optimization into discussion. The degrees of freedom are variables that completely define the model and must be adjusted to satisfy the constraints. These variables represent the decision variables that will be determined by the optimization algorithm while the problem is solved, in order to get the minimum of the objective function: 3 splits, 3 reactor volumes, 3 reaction temperatures and 2 component recoveries; they have associated inequality constraints which specify the minimum / maximum bounds within they can vary while solving the problem.

Having 100 equality constraints (78 model equations and 22 specified variables) and 11 new variables being automatically provided at each step of the optimization, the nonlinear system becomes square; it is solved in Matlab, using *fsolve* function.

Economic evaluation

The decision variables should be determined with the scope of reaching the minimum total annual cost (*TAC*) of the plant. Therefore, the link between the decision variables and equipment sizes and utilities consumption must be determined. The following sections present the sizing equations, the energy balance and the cost equations of the equipment. The capital expenses are based on a 2010 *M&S* (Marshall and Swift) index of 1400 [13].

Reactor

The capital investment of the reactors depends on the volume, operating conditions and material of construction. The operating pressure is chosen such that, at the reactor temperature, the reactants remain in the liquid phase, 5 bar being enough to satisfy this requirement. Usually, up to operating pressures of 10 bar, the design pressure is taken as the operating pressure plus one bar.

Since the catalyst is sulphuric acid, which is very corrosive, stainless steel is used as construction material. The following equations are used for sizing and estimating the cost of reactors:

- the height of the vessel is based on a H/D ratio of 2; therefore:

$$H = 2 \,.\, D \tag{19}$$

-Vessel diameter (for H = 2D):

Table 2
PRICES OF COOLING AGENTS

Cooling agent	*Refrigerant -50°C*	*Refrigerant -20°C*	*Chilled water 5-15°C*
Price (P_{CA}), \$/GJ	13.1	7.9	4.5

$$D=\sqrt[3]{\frac{4\cdot V}{\pi\cdot 2}} \tag{20}$$

The installed cost of the reactor is based on the following equation [8] (*D* and *H* in m):

$$IC_R/[\$]=(M\,\&\,S/280)\cdot\left(957.9\cdot D^{1.066}\cdot H^{0.82}\right)\cdot(2.18+F_c) \tag{21}$$

where:

$$F_c=F_m\cdot F_p \tag{22}$$

$$F_p=1+0.0074\cdot(P-3.48)+0.00023\cdot(P-3.48)^2 \tag{23}$$

The material factor F_m is 3.67 (for stainless steel) and *P* is the design pressure of the equipment (in bar).

The operational expenses consist of the cost of the cooling agent required to remove the heat of reaction (to cool down the reactors) generated by the exothermic reactions. To find out the cooling agent flowrate, the heat balance over the reactors, based on reaction heats (Table 1), is performed, assuming that the feed is already at the required temperature:

$$Q_R=r_1\cdot(-DH_{R1})\cdot V+r_2\cdot(-DH_{R2})\cdot V \tag{24}$$

The selection of the cooling agent (refrigerant -50°C, refrigerant -20°C, chilled water 5°C) is based on the optimum reaction temperature, determined by solving the optimization problem that provides the lowest cost. The prices of the cooling agents are given in the table below [3]:

The operational cost of the reactors (OC_R) is calculated multiplying the cost of the cooling agent by the overall reactor duty (the duty of all three reactors):

$$OC_R = Q_R\,.\,P_{CA} \tag{25}$$

Columns

The capital investment of the columns depends on: height, diameter, design parameters and material of construction. The cost of the trays is also included in the cost of the columns.

The height of the column depends on the number of separation trays required to achieve a certain separation. The Underwood-Fenske short-cut method is used for an estimation of the minimum number of theoretical trays and minimum reflux ratio. It consists of the following system of equations:

1.Fenske equation – for determining the minimum number of theoretical trays:

$$N_{TT}=\frac{\log\left[\frac{\beta_{L,D}}{1-\beta_{L,D}}\cdot\frac{\beta_{H,B}}{1-\beta_{H,B}}\right]}{\log(\alpha_{LH})}, \tag{26}$$

The equation determines the minimum number of theoretical trays (N_{TT}) based on the recoveries of the key components (β_L, β_H) in distillate (*D*) and residue (*B*) and the relative volatility ratio between the light and heavy key components (β_{LH}).

2.Underwood equations – for determining the minimum reflux ratio, $R_{\min}$:

$$\sum_{i=1}^{6}\frac{\alpha_{ij}\cdot x_{i,F}}{\alpha_{ij}-\vartheta}=1-q, \tag{27}$$

$$R_{\min}+1=\sum_{i=1}^{6}\frac{\alpha_{ij}\cdot x_{i,D}}{\alpha_{ij}-\vartheta}, \tag{28}$$

The equations assume that the relative volatility (α_{ij}) and molar overflow are constant through the column [14] (assumption valid when the molar latent heats of vaporization of the components are equal). The feed, to both columns, is liquid at boiling point (the feed condition *q* = 1). There are *NC* – 1 = 5 real positive values of θ; since there are no intermediate components between the key components, only the root θ between the relative volatilities of the key components is used to solve the second equation.

To calculate the minimum reflux ratio, the molar fraction of the components in the distillate ($x_{i,D}$) must be known. To make the calculation simpler and fulfilling the main scope of estimating the cost of the column, a reasonable assumption [14] can be done: that all components lighter than the light key component (LLK) go to the overhead and all components heavier than the heavy key component (HHK) go to the bottom; therefore, the recoveries of the LLK components in the top and of the HHK components in the bottom are assumed to be 1; the flows and molar fractions are then calculated from the material balance of the columns and equation below, respectively:

$$x_{i,D}=\frac{F_{i,D}}{D} \tag{29}$$

The second Underwood equation can be now used to find out the minimum reflux.

The actual reflux ratio and the real number of trays (for cost calculation purposes) are determined based on Gilliland correlation and the rules of thumb provided in [3, 8, 15]:

$$Y=0.2778-1.3154\cdot X+0.4114\cdot X^{0.2910}+ \\ +0.8268\cdot\ln X+0.902\cdot\ln\left(X+\frac{1}{X}\right), \tag{30}$$

where,

$$X=\frac{R-R_{\min}}{R+1}, \tag{31}$$

$$Y=\frac{N-N_{\min}}{N+1}, \tag{32}$$

Specifying an operating reflux (*R*) of 1.2 x R_{min}, the actual number of trays (N_{TR}) is determined.

The total height (h_c) of the column is calculated assuming a tray to tray height of 0.6 m plus the height of the two heads estimated as $d_c/2$.

$$h_c/[m]=0.6\cdot N_{TR}+2\cdot\left(\frac{d_c/[m]}{2}\right) \tag{33}$$

The diameter of the column (d_c) is determined by means of determining the flooding velocity (w_F), which is the velocity of the vapour rising through the column at which the liquid flow on each stage is suspended [16].

$$w_F/[m/s]=\frac{1.2}{\sqrt{\rho_V/[kg\cdot m^{-3}]}} \tag{34}$$

The velocity of the vapour in the column is recommended to be maximum 80% of the flooding velocity [17]. Therefore, the diameter of the column is:

$$d_c = \sqrt{\frac{4 \cdot D_V}{0.8 \cdot \pi \cdot w_F}} \qquad (35)$$

where D_v is the volumetric flowrate of the vapour in the column:

$$D_v = D \cdot (R+1) \cdot \frac{MW}{\rho_v} \qquad (36)$$

The installed cost (*IC*) of the column is estimated as:

$$IC/[\$] = (M\&S/280) \cdot \left(957.9 \cdot d_c^{1.066} \cdot h_c^{0.82}\right) \cdot \left(2.18 + F_c\right) \qquad (37)$$

The F_c factor that accounts for the design pressure of the column and the material of construction is calculated similar as for reactors. Both columns are made of stainless steel. The first column works at 10 bar in order to increase the dew point of the overhead vapour and to be able to use cooling water to condense it, whereas the second column requires only 6 bar. The cost of the trays depends on the column diameter and the type and material of the tray.

$$IC_T/[\$] = (M\&S/280) \cdot 97.2 \cdot d_c^{1.55} \cdot F_c \qquad (38)$$

where F_c is:

$$F_c = F_t + F_m; \qquad (39)$$

The type of trays used for the columns are sieve trays. The F_t factor for sieve trays is 0. For stainless steel trays, F_m is 1.7.

The operational expenses of the columns are given by the amounts of cooling / chilled water used to condense the overhead vapour and the steam used to boil-up the bottom mixture in the reboiler to provide the required heat in the column.

The molar overhead vapour flowrate is V_m:

$$V_m = (R+1) \cdot D \qquad (40)$$

and hence, the condenser duty (Q_c) is:

$$Q_c = (V_m \cdot MW) \cdot h_v \qquad (41)$$

where h_v represents the (mass) heat of vaporization.

Assuming constant vapour flow through the column, the duty of the reboiler (Q_r) is obtained in a similar way:

$$Q_r = (V_m \cdot MW) \cdot h_v \qquad (42)$$

Based on the heat duties calculated above, the water and steam prices are calculated (*Heat exchangers* section).

The design of the condensers and reboilers can now be performed.

Heat exchangers

The capital investment of the heat exchangers depends on the heat transfer area (A), design parameters, material of construction and the design type. The following equation can be used to estimate the capital investment of the heat exchangers:

$$IC_E/[\$] = (M\&S/280) \cdot \left(474.7 \cdot A^{0.65}\right)\left(2.29 + F_c\right) \qquad (43)$$

The heat transfer area (*A*) depends on the duty of the heat exchanger (*Q*) given by the process requirements, the overall heat transfer coefficient (*U*) and the temperature difference between the utility and process fluid (*LMTD*).

$$A = \frac{Q}{U \cdot LMTD} \qquad (44)$$

Table 3

OVERALL HEAT TRANSFER COEFFICIENTS

Service	*U, W/(m²K)*
Gas-gas	170
Gas-condensing vapor	280
Gas-vaporizing liquid	280
Liquid-liquid	570
Liquid-condensing vapor	850
Liquid-vaporizing liquid	850

In table 3, the overall (estimated) heat transfer coefficients are shown for different services [3].

The F_c factor in the installed cost equation, accounts for the material of construction of the heat exchanger, design type and design pressure.

$$F_c = F_m \cdot \left(F_d + F_p\right) \qquad (45)$$

Ten heat exchangers are used in the alkylation flowsheet. Three heat exchangers (E1, E2 and E3) are installed at the inlet of the reactors to bring the temperature of the feeds (plus recycle) up to the reaction temperature, designed as floating head; 2 inter-coolers / heaters (floating head, E4 and E5) are foreseen between the reactors to bring the temperature of the effluent from one reactor to the temperature of the following reactor; 1 heat exchanger (floating head, E6) at the inlet of the first column that aims to bring the temperature of the effluent from the last reactor up to the saturation conditions (*q* = 1 at first tower inlet) and 2 reboilers plus 2 condensers (designed as fixed tubesheet) for the 2 separation columns.

The design pressure of the reboilers and condensers exceeds 10 bar which involves an F_p factor of 0.1, whereas the design pressure of the other heat exchangers is up to 10 bar which involves an F_p factor of 0 [3].

Table 4

DESIGN TYPE OF HEAT EXCHANGERS

Design type	F_d
Kettle reboiler	1.35
Floating head	1
U-tube	0.85
Fixed tube sheet	0.8

The operational expenses of the heat exchangers are given by the heating / cooling medium flowrate and the utility price. Medium pressure steam (11 bar) is used for heating while refrigerant or chilled water are used as cooling agents. The price of the steam is P_S = 8.2 $/GJ [3].

The operational cost of the heaters is calculated multiplying the duty of the heat exchanger (Q_E) with the price of the steam:

$$OC_E/\left[\$ \cdot yr^{-1}\right] = Q_E \cdot P_S \qquad (46)$$

Similarly, the operational cost of the coolers is calculated as:

$$OC_E/\left[\$ \cdot yr^{-1}\right] = Q_E \cdot P_{CA} \qquad (47)$$

Pumps

Although the cost of the pumps is not easily calculated and is not considered during the conceptual stages (it is usually specified by the manufacturer at the end of the basic design), a rough estimation is still done to account for the recycle cost; the cost of recycle has the role of a constraint, allowing the increase of flow through that path up to a certain point, when the recycle becomes too expensive.

The estimation is based mainly on the pumped flow, construction material of the pump and design pressure [18]; the design pressure is assumed 10 bar. The following equation, derived by regression the data from reference [18], is used to estimate the installed cost of the pump:

$$IC_P/[\$] = 18.6 \cdot 10^3 \cdot \left(\frac{F_3 \cdot MW}{\rho_L} \right)^{0.3695} \qquad (48)$$

where F_3 is the molar recycle flowrate.

The operational expenses of the pump are provided by the cost of energy consumed to pump the liquid up to the desired point. The energy requirement depends on the pump flow, the pressure drop across the pump and the efficiency (åε) of the pump (assumed 70%).

$$E = \left(\frac{F_3 \cdot MW \cdot DP}{36 \cdot \rho_L \cdot \varepsilon} \right) \qquad (49)$$

The cost of energy ($/h) is calculated by multiplying the required energy with its price (0.13 $/kWh).

Optimization

The optimization is performed in Matlab, using *fmincon* function, which finds the minimum of a constrained nonlinear multivariable function; the function uses a sequential quadratic programming method (SQP) [19]. The system is solved providing at each step values for the decision variable in between the specified lower and upper bounds, solving the model and calculating the objective function; the cycle is repeated until the minimum of the total cost is found with the specified tolerance.

Results and discussions

Running the optimization program, the following values of the decision variables and objective function are found for different cooling agents (table 5):

In all cases, the production of alkylate is almost the same (this also means that the selectivity is the same). That is, fixing the plant inlet flowrates, the products flowrates and therefore the selectivity are fixed; moreover, the amount of inert components that is to be removed is also fixed.

At the optimum point, the value of the reaction temperature is always equal to the minimum allowable (this constraint is given by the temperature of the available cooling agent). The optimum reaction temperature is equal for all three reactors; therefore, this makes useless the inter-coolers / heaters (E4 and E5). Moreover, the fresh reactant must be all fed in the first reactor (similar to the case when the recycle was minimized).

Decreasing the reaction temperature, the volume of reactors increases (larger reactors are needed to perform the same chemical transformation). High temperature promotes the secondary reaction, because it has higher activation energy; therefore, larger recycle (mainly isobutane) is needed to satisfy the selectivity constraint (given by the ratio of reactants at plant inlet).

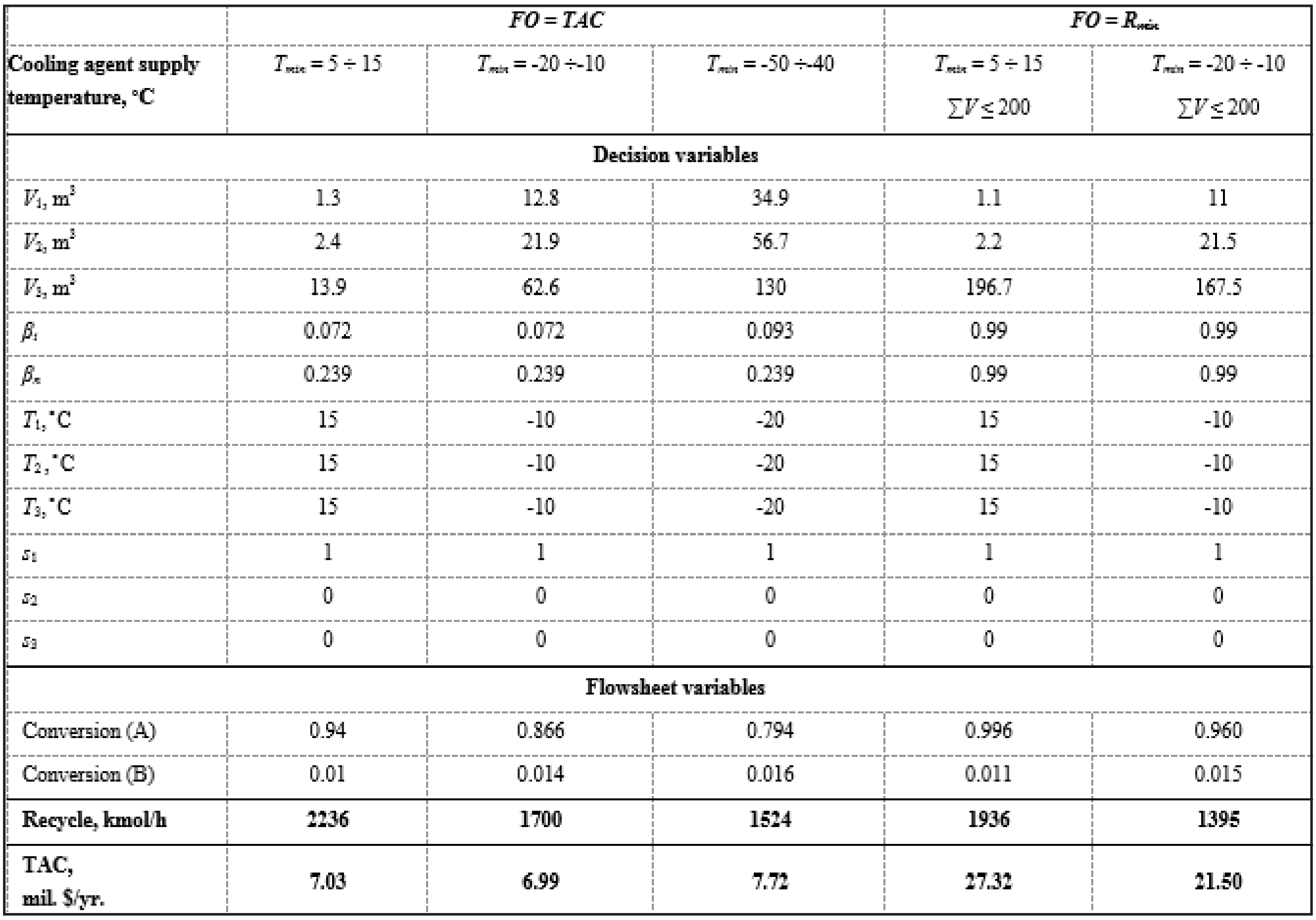
The minimum cost is reached for rather low recoveries of the inert components; it is cheaper letting them accumulate in the system and recirculating rather than performing the separation at high degree of recovery. High recoveries lead to more trays, higher columns and higher operational cost.

The difference between optimization using TAC and minimum recycle [9] as objective functions consists in the following:

- the recoveries of the inert components;
- the volume of reactors;

Table 5

OPTIMUM DECISION VARIABLES



	$FO = TAC$			$FO = R_{min}$	
Cooling agent supply temperature, °C	$T_{min} = 5 \div 15$	$T_{min} = -20 \div -10$	$T_{min} = -50 \div -40$	$T_{min} = 5 \div 15$ $\sum V \le 200$	$T_{min} = -20 \div -10$ $\sum V \le 200$
Decision variables					
V_1, m^3	1.3	12.8	34.9	1.1	11
V_2, m^3	2.4	21.9	56.7	2.2	21.5
V_3, m^3	13.9	62.6	130	196.7	167.5
β_i	0.072	0.072	0.093	0.99	0.99
β_n	0.239	0.239	0.239	0.99	0.99
T_1, °C	15	-10	-20	15	-10
T_2, °C	15	-10	-20	15	-10
T_3, °C	15	-10	-20	15	-10
s_1	1	1	1	1	1
s_2	0	0	0	0	0
s_3	0	0	0	0	0
Flowsheet variables					
Conversion (A)	0.94	0.866	0.794	0.996	0.960
Conversion (B)	0.01	0.014	0.016	0.011	0.015
Recycle, kmol/h	**2236**	**1700**	**1524**	**1936**	**1395**
TAC, mil. $/yr.	**7.03**	**6.99**	**7.72**	**27.32**	**21.50**

Column	*Reflux ratio*	*Tray no.*	*Diameter m*	*Height m*	*Condenser duty 10^6 kJ/h*	*Reboiler duty 10^6 kJ/h*	*Condenser area m^2*	*Reboiler area m^2*
C_1	25.8	21	1.0	13.3	3.46	3.70	78	5
C_2	0.036	38	3.9	24.8	43.15	43.30	346	62

Table 6
COLUMN DESIGN DETAILS FOR TAC MINIMIZATION AT 15°C (MATLAB)

Flow rate kmol/h	*0a*	*0b*	*0a1*	*0a2*	*0a3*	*20*	*21*	*2*	*22*	*23*	*3*	*4*
A	52.6	0	52.6	0	0	38.2	20.4	3.3	0	3.3	3.3	0.1
B	21	31.1	21	0	0	1986.3	1969.4	1953.5	0.2	1953.3	1951.4	2
P	0	0	0	0	0	16.7	32.7	47.4	0	47.3	0	47.3
R	0	0	0	0	0	0.5	1.4	2.6	0	2.6	0	2.6
I	5.4	3.1	5.4	0	0	116.5	116.5	116.6	8.4	108.2	108.1	0.1
N	27	27.9	26.9	0	0	229.4	229.4	229.4	0	229.4	174.5	54.9

Table 7
STREAM TABLE FOR TAC MINIMIZATION AT 15°C (MATLAB)

Equipment	*CAPEX mil. \$/yr.*	*OPEX mil. \$/yr.*	*TC mil. \$/yr.*	*TAC mil. \$/yr.*
Column C_1	0.094	0.366	0.459	**7.029**
Column C_2	0.463	4.377	4.840	
Reactors	0.157	0.168	0.325	
Recycle	0.045	0.073	0.118	
Heat exchangers	0.282	1.004	1.286	

Table 8
COST DATA FOR TAC MINIMIZATION AT 15°C (MATLAB)

Equipment	*CAPEX mil. \$/yr.*	*OPEX mil. \$/yr.*	*TC mil. \$/yr.*	*TAC mil. \$/yr.*
Column C_1	0.403	3.169	3.571	**26.605**
Column C_2	1.981	19.004	20.985	
Reactors	0.645	0.168	0.813	
Recycle	0.043	0.063	0.106	
Heat exchangers	0.161	0.969	1.130	

Table 9
COST DATA FOR RECYCLE MINIMIZATION AT 15°C (MATLAB)

The method presented in this article is better because it provides a practical and realistic way of designing an economical plant.

In minimum recycle case, the reactors tended to reach enormous volumes whereas for TAC minimization, the total volume is considerably lower. The degrees of recoveries were also very high; the separation was done at high degrees of recovery and did not allow inert accumulation, while now they tend towards low values. The similitude between the TAC and minimum recycle is the butene split and the reaction temperature, which are equal for both cases. In the tables below are presented the design details of the equipment within the alkylation plant and the material balance for the reaction temperature of 15°C.

At 15°C the difference of the recycle flow between the TAC case and *minimum recycle* is only 15%, but the cost is almost 4 times higher for the minimum recycle case; this high difference of the costs makes inappropriate the use of minimum recycle as design basis for the alkylation plant consisting of the reactions and kinetics described in the previous chapters and containing impure reactants.

It can be observed that for both cases the reactants/products separation column (C2) has the highest contribution to the total cost of the plant (≈ 70% for TAC vs. 80% for R_{min}). Moreover, increasing the recovery of the heavy key component (n-butane in bottom (β_N), say from 0.3 to 0.6) in C2, doubles the total cost (from 8 mil. \$ to almost 16 mil. \$, for β_I=0.07). TAC is less sensitive to the recovery of propane in the first column (β_I).

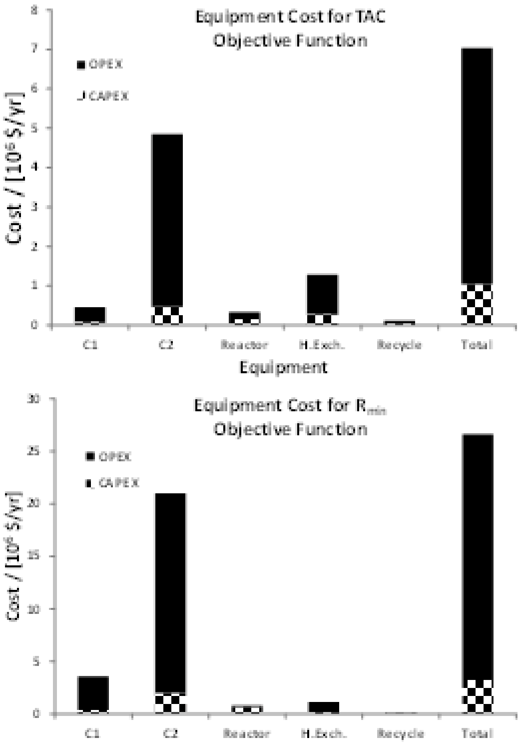


Fig. 2. Contribution of capital and operational costs to total cost of equipment for: a) TAC optimization case b) Rmin optimization case

Simulation

The results presented in the tables above are verified performing the simulation of the plant and rigorously sizing the equipment.

The simulation flowsheet is developed in Aspen HYSYS; for estimating the vapour-liquid equilibrium, Peng-Robinson property package is used. Figure 1 and the values in Table 5 and Table 6 (at 15°C) are used as basis for building the model. As compared to the Matlab model, the simulation considers the dependence of physical properties on temperature, pressure and composition; rigorous models are used for simulation of the distillation column.

To calculate the cost of the equipment in the flowsheet, the same equations as those written in the previous chapters are used. The third column (that purifies the alkylate) is also included in the simulation, but is excluded from the calculation of the total cost (for the same reasons that were previously mentioned). Running the simulation model, the following heat and material balance and parameters of the equipment are calculated:

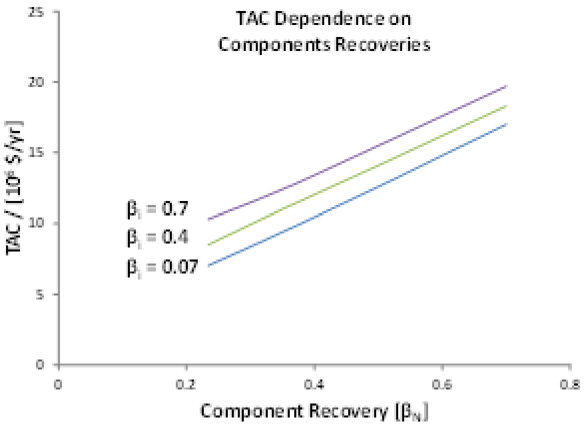


Fig. 3. The Influence of Recovery Degree on TAC

Table 10
STREAM RESULTS FOR
TAC MINIMIZATION AT 15°C
(HYSYS)

Flow rate kmol/h	*0a*	*0b*	*0a1*	*0a2*	*0a3*	*20*	*21*	*2*	*22*	*23*	*3*	*4*
A	52.6	0.0	52.5	0.0	0.1	37.5	19.6	3.1	0.0	3.1	3.0	0.1
B	21.0	31.1	21.0	0.0	0.0	1691.5	1674.7	1659.5	0.0	1659.4	1657	2.3
P	0.0	0.0	0.0	0.0	0.0	16.9	32.7	46.5	0.0	46.5	0.0	46.5
R	0.0	0.0	0.0	0.0	0.0	0.6	1.6	3.0	0.0	3.0	0.0	3.0
I	5.4	3.1	5.4	0.0	0.0	121.4	121.4	121.5	8.5	112.9	112.9	0.0
N	27.0	27.9	27.0	0.0	0.0	219.9	219.9	220.0	0.0	220.0	165.0	55.0

Table 11
COLUMN DESIGN
DETAILS FOR TAC
MINIMIZATION AT
15°C (HYSYS)

Column	*Reflux ratio*	*Tray no.*	*Diameter m*	*Height m*	*Condenser duty 10^6 kJ/h*	*Reboiler duty 10^6 kJ/h*	*Condenser area m^2*	*Reboiler area m^2*
C_1	25.8	21	1/1.9	13.8	3.34	3.38	95	9
C_2	0.32	38	4	25	45.6	42.7	530	143

Table 12
COST DATA FOR TAC
MINIMIZATION AT
15°C (HYSYS)

Equipment	*CAPEX mil. $/yr.*	*OPEX mil. $/yr.*	*TC mil. $/yr.*	*TAC mil. $/yr.*
Column C_1	0.078	0.340	0.418	**7.812**
Column C_2	1.109	4.244	5.353	
Reactors	0.158	0.274	0.432	
Recycle	0.449	0.071	0.116	
Heat exchangers	0.232	1.261	1.493	

The main difference between the Matlab model and the simulation is due to the columns: for the former the columns are designed using a short-cut method; for the latter, the design is rigorously performed. This explains the different diameter of the bottom section of the first column (last 5 trays out of 21 have 1.9 m instead of 1 m, mainly because of the vapour velocity in the column) and the higher reflux ratio of the second column (0.32 instead of 0.036). Anyhow, the cost difference between the model and the simulation, brought in by the above mentioned estimations, is around 10%.

The simulation flowsheet is similar with the one presented in figure 1.

The Matlab model provided results which were in line with the results provided by the simulator.

Conclusions

The optimum reactor consists of a series of well-mixed zones, with the reactants fed to the first one;

The minimum cost was obtained for a reaction temperature of -10°C. However, the optimum is not sensitive to this value, operation at 15°C incurring only 0.5% cost penalty;

It is better to let the inert components accumulate in recycle, rather than completely remove them. Recycling is cheaper compared to the investment and operating cost of the distillation columns;

The approach of designing the plant considering recycle minimization as design basis proved to be inappropriate for alkylation reactions with the given kinetics [12]. Economics should be considered from an early stage of the design.

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