Optimal design of catalytic distillation for alkylation of isobutane with 2-butene on a solid catalyst

KEYWORDS: Reactive distillation, alkylation, isobutane, butane, zeolites.

Abstract

Alkylation of isobutane with butenes is one of the most important processes making high octane number gasoline. Highly exothermicity requires efficient heat removal. Low temperature implies application of strong (sulphuric and hydrofluoric) acids as catalysts albeit inherent corrosion, pollution and safety problems. The difficulty in applying alternative solid alkylation catalysts is related to deactivation by coking. In order to minimize deactivation an excess of olefin is required. Catalytic distillation, combining reaction and separation, could be proposed to considerably reduce the isobutane recycle and simultaneously to ensure high butenes conversion. Detailed simulations for reactive distillation in a zeolite catalysed alkylation of isobutane with butane were conducted. Various options regarding placement of the reaction section were considered and optimal conditions determined.

INTRODUCTION

Alkylation of isobutane with butenes can be considered as one of the most important processing for obtaining high octane number gasoline. Alkylate, which is the desired product of this process, has a lower vapour pressure and is free from presence of sulphur, nitrogen and aromatic compounds. At the moment the share of alkylates in high octane number gasoline in developed countries approaches 13% (1, 2).

The modern processes for industrial alkylation are based on utilization of sulphuric and hydrofluoric acids. An excess of isoparaffin is beneficial from the view of selectivity suppressing side reactions and improving the octane number. Otherwise polymerization of olefins gives undesirable low-octane, high boiling point components. The heavier polymerization products (with more than 10 carbon atoms) known as acid soluble oils tend to deactivate the catalyst. At the same time if the excess is too high it would lead to unnecessary high costs for recycling. In industrial conditions typically the mole excess of isoparaffin is varied from 6 to 20 depending on the process. The usual I/O ratio ranges from 5 to 8 in sulphuric acid plants and from 10 to 15 in HF plants.

Alkylation reactions are highly exothermic (on average 75-96 kJ/mol), therefore heat removal is essential. Low temperature such as 0-10°C with sulphuric acid and ca. 30°C for HF is preferred being also beneficial by minimizing formation of polymerization and cracking by-products. Too low temperature in case of sulphuric acid would result in unwanted increase of viscosity, while an increase of temperature would lead to formation of tars and sulphur dioxide. Since HF is not an oxidant somewhat higher temperature can be used simplifying obviously the cooling arrangements, while for the process with sulphuric acid cryogenic cooling is needed.

Influence of pressure on the reaction equilibrium is less straightforward. From the viewpoint of thermodynamics high pressure should be applied influencing in a negative way side reactions, thus in practice mildly elevated pressures (0.2-2 MPa) are used.

A requirement of a low temperature implies that such strong acids as sulphuric and hydrofluoric acids are used as catalyst even if such processes have inherent corrosion, pollution and safety problems. The traditional alkylation reaction takes place in a medium in which the hydrocarbon drops are dispersed in a continuous acid phase. Thus alkylation is often treated as a homogeneous process where the reaction rate is proportional to the interfacial area.

Application of HF results in a higher octane number due to the hydrogen transfer reactions having lower catalyst consumption and higher isobutane consumption. Total acidity is decreased during operation by contamination with water and organics. Contamination with organics more pronounced in HF process due to higher (order of magnitude compared to sulphuric acid) solubility of isobutane.

The catalyst activity decreases with time due to dilution,
formation of red oil and impurities. Although HF can be purified by fractionation to remove water and red oil at the plant site some losses are inevitable as HF forms an azeotrope with water. Contrary to HF complete removal of H$_2$SO$_4$ is needed requiring regeneration by complete decomposition of the acid which is done outside of refineries leading to high overall H$_2$SO$_4$ consumption (100 kg/t of product) compared to HF losses.

Due to these clear shortcomings there is an apparent interest to apply solid catalysts (1-4). The difficulty in applying solid catalysts in alkylation is related with catalyst deactivation, which is related to coking and subsequent pore blocking preventing access to the active sites. In order to minimize deactivation an excess (I/O ratio above 7) is required obviously elevating manufacturing costs for solid-catalyzed alkylation. Based on available information two technologies are close to implementation, namely UOP Alkylene based on AlCl$_3$ (1, 4, 5) and AlkyClean which relies on a zeolitic catalyst (4). UOP Alkylene process uses a riser reactor concept and a complex catalyst containing AlCl$_3$ supported on Al$_2$O$_3$ with promoters, while the AlkyClean process employs several reactors (6). A demonstration unit of the process had 3 reactors, where one was used for alkylation, another one was in mild regeneration (mild liquid-phase regeneration using isobutane and hydrogen) and the third one underwent high temperature regeneration.

As an alternative to these technologies a scheme with a catalytic distillation unit could be proposed to considerably reduce the isobutane recycle and simultaneously to ensure high butenes conversion. Such technology (Evofuel) was developed by Lurgi in co-operation with Südchemie (7) making use of a moving bed reactive distillation, when isobutene and the catalyst enter at the top of the tower, while alkene with premixed isobutene is introduced in stages. The catalyst is faujasite based zeolite with a hydrogenation function. Such arrangements are beneficial from the viewpoint of reaction heat utilization as well as diminishing capital costs.

No details on the energy consumption are available, thus the present work is aimed at filling this gap by defining an optimal structure of the reactive distillation system and determining an influence of the main parameters on the operational costs.

**PROCESS SIMULATION**

**Reaction model**

A large number of chemical reactions are happening during alkylation, the main being hydride-transfer, olefin addition, isomerisation, b-scission and self-alkylation (3, 8-10).

Since the current work is devoted to a detailed analysis of product separation it was necessary to describe formation of individual components $i$-C$_5$, C$_6$, C$_7$ and C$_8$. As in other alkylation processes the reaction starts with generation of a carbocation by protonation of the olefin. After than it can abstract a hydride from isobutane forming a tert-butyl carbenium ion

This is followed by an exothermal step of electrophilic addition to another olefin giving a larger carbenium ion

Subsequent hydride transfer sustains the catalytic cycle resulting primarily in 2,2,3 trimethylpentane

Generation of hydrocarbons with a carbon number not proportional to four, occurs according to the b-scission mechanism. Figure 1 displays several potential routes of b-scission and olefin addition, which are the most probable for formation of C$_5$-C$_8$ components. For instance, carbocations formed because of b-scission in the olefin addition step will react predominantly with butenes, which concentration is higher compared to other olefins. As a result of b-scission of C$_9$ at 60-90°C C$_4^+$ hydrocarbons are formed (11,12) while C$_1$-C$_3$ compounds were not detected in butene alkylation (9).

In the current work it was assumed that generation of components C$_5$-C$_9$ occurs according to the overall reactions illustrated in Table 1. In addition to these reactions which reflect possible reaction pathways from Figure 1, self-alkylation with formation of n-butane was also considered.

**Table 1. Overall equations for production of C$_4$-C$_9$ components.**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Selectivity(%) mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: C$_2$H$_6$ + C$_4$H$_8$ → 4 C$_3$H$_8$</td>
<td>1.81</td>
</tr>
<tr>
<td>2: C$_3$H$_6$ + C$_4$H$_8$ → 2 C$<em>5$H$</em>{12}$</td>
<td>4.59</td>
</tr>
<tr>
<td>3: C$_4$H$_8$ + 6 C$_2$H$_6$ → 8 C$_3$H$_8$</td>
<td>4.25</td>
</tr>
<tr>
<td>4: C$_4$H$_8$ + 5 C$_3$H$_8$ → 6 C$<em>5$H$</em>{12}$</td>
<td>79.25</td>
</tr>
<tr>
<td>5: C$_4$H$_8$ + 50 C$_3$H$_8$ → C$<em>5$H$</em>{12}$</td>
<td>8.20</td>
</tr>
<tr>
<td>6: C$_4$H$_8$ + 10 C$_3$H$_8$ → C$<em>5$H$</em>{12}$</td>
<td>1.70</td>
</tr>
</tbody>
</table>

Selectivity was calculated in a way that the product composition corresponds to experimental data in laboratory scale experiments for a zeolitic catalyst (4, 9-10,13). The distribution of isomers C$_5$-C$_9$ provided information about isomerization reactions. Comparison between the calculated and experimental data is given in Table 2.
**Modelling of catalytic distillation**

For modelling purposes the systems of equations for the reactor and distillation column were solved separately. Calculations for the complete reactive distillation system were done interactively. The distillation column was described using the MESH approach (material balance, phase-equilibrium, mole balance and energy balance equations).

The phase equilibrium constants have a complicated dependence on temperature, pressure and composition (15).

The separate approach to modelling allowed to use standard calculation methods for the distillation column. Namely the bubble-point method was applied for calculating each tray (16).

The model for the reaction section correspond to a reactor with separation of products:

\[ \begin{align*}
L_{j-1} \cdot x_{i,j-1} + V_{j+1} \cdot y_{i,j+1} &= L_j \cdot x_{i,j} + V_j \cdot y_{i,j} \\
y_{i,j} &= K_{i,j} \cdot x_{i,j} \\
\sum_{i=1}^{n} y_{i,j} &= 1 \\
\sum_{i=1}^{n} x_{i,j} &= 1 \\
L_j \cdot h_{j-1} + V_{j+1} \cdot h_{j+1} &= L_j \cdot h_j + V_j \cdot h_j
\end{align*} \]

where:
- \( L_j \) - liquid flow from the tray \( j \) (kg mol/h)
- \( V_j \) - vapor flow from the tray \( j \) (kg mol/h)
- \( x_{i,j} \) - liquid molar fraction of component \( i \) on the tray \( j \)
- \( y_{i,j} \) - vapor molar fraction of component \( i \) on the tray \( j \)
- \( h_j \) - specific molar enthalpy of liquid on the tray \( j \) (kJ/kg mol)
- \( \theta_{i,j} \) - phase-equilibrium coefficient

The values of selectivity to various compounds \( C_8-C_{12} \) and stoichiometric coefficients are displayed in Table 3.

**Table 3. Parameters of the model for the reaction section.**
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A drawback of the model is that the influence of reaction mixture evaporation on chemical transformations was not considered (17, 18). Two versions with internal and external (side) placement of the reactor section were considered (Figure 2).

RESULTS AND DISCUSSION

Process conditions and design
In the reactive distillation system the process parameters (temperature and pressure) are determined by the chemical reactions, and therefore could be non-optimal for the separation. Optimal pressure at the top of the distillation column is selected in way that the vapours condense at 30-50°C when water or air are used as coolants. Theoretical regions of temperature and pressure in alkylation are presented in Figure 3.

Based on reported data the optimal conditions for alkylation with zeolitic catalysts are 60-80°C and pressure above 10 bar (4, 9). The most energy demanding process, separation of isobutane/n-butane, can be optimally done at 4-7 bar. Therefore, in the combined process of catalytic distillation the conditions of separation are close to the optimal. The temperature at the top of column would be close to 65°C at a pressure level 10 bar. Influence of pressure on of the reflux ratio in debutanizing column (separation C<sub>4</sub>/C<sub>5</sub>+) and deisobutanizer (separation iC<sub>4</sub>/nC<sub>4</sub>) is presented in Figure 4. A substantial increase of energy consumption is seen above 15 bar.

A particular values of parameters depend on the separation system structure, reactor section design and properties of the catalysts. Figure 5 displays different options of the process design.

When the reaction section is located above the butane separation (option A), the reaction heat is not efficiently utilized and can be used only to separate the isobutane/propane mixture with the subsequent recycle of isobutane in the reactor (not shown). An alternative design with the reaction section below the butane separation section requires isobutane recycle from the top of the column (options B, C, D).

Reaction heat in variants C and D is used for separation of butanes, while n-butane is taken as a side stream. However, according to (19) these options are economically non-attractive, as alkylation is conducted in the significant excess of isobutane, meaning that it is not feasible to have such side fraction with high n-butane content. As a consequence we have considered only options A and B taking as a feedstock a narrow C<sub>4</sub> fraction from FCC (2) and butane–isobutane mixture (Table 4).

<table>
<thead>
<tr>
<th>Component</th>
<th>Olefin feed</th>
<th>n-Butane feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-butene-2</td>
<td>42.8</td>
<td>0.0</td>
</tr>
<tr>
<td>isobutane</td>
<td>39.1</td>
<td>25.0</td>
</tr>
<tr>
<td>n-butane</td>
<td>10.5</td>
<td>73.0</td>
</tr>
<tr>
<td>isopentane</td>
<td>7.6</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Table 4. Feeds composition
In this variant the reactor vapour product is send beneath tray 6, while the liquid is routed on tray 7. According to the calculation the amount of C5+ in the reactor feed diminished to 1.9% mass. The main advantage of such product distribution along the column is a decrease of a deisobutanizer reboiler duty to 18.4GJ/h. This is explained by a more complete utilization of the reaction heat for isobutane recovery. The calculated value of the generated heat was 6.2GJ/h.

Another advantage with a side reactor arrangement is a possibility to decrease a pressure in the distillation column, which requires installation of pumps and throttles in the reaction product recycle line back to the column. The calculation results for deisobutanizer pressure of 5.4 bar shown in Figure 9 indicate that the temperature at the column bottom decreases to 82°C.

Calculation results for an option with reaction products recycling to the debutanizer column, also presented in Figure 9, indicate 10.1GJ/h higher energy consumption, compared to an alternative recycle of the product to deisobutanizer. The drawback of the scheme shown in Figure 7 is that the reaction products are send directly to the tray located below the point of reactor feed withdrawal. Therefore, alkylate components enter the upper part of the column and concentration of C5+ (predominantly isopentane) reaches 2.4%.

This drawback of reaction section location can be mitigated by arranging a by-pass for the product stream of the column upper trays. This option can be implemented by introducing the reactor externally to the column as illustrated in Figure 2.

The calculations results for reactive distillation with a side reactor section are presented in Figure 8. The properties of alkylate and its flow rate are the same as the scheme considered previously.

For the calculations 50 and 20 theoretical plates were respectively considered for deisobutanizing and debutanizing. These parameters were determined taking into account an influence of the tray number on the reflux ratio of the columns (Figure 6). The optimal number of the reflux ratio (thus the corresponding number of trays) was defined as the minimal reflux ratio multiplied by 1.2 (20).

Results of catalytic distillation simulation
The calculations for reactive distillation were made for an alkylate production capacity of 10t/h (80 metric ton per year) and the paraffin to olefin ratio of 10. The parameters were selected in a way to assure that isobutane concentration in the recycle is 90 mass. % and the n-butane content in alkylate is 2% mass. The results are illustrated in Figure 7. The overall energy consumption was 2.44 per tonne of alkylate giving a product with the octane number (RON) equal to 91.5 and the vapour pressure 45kPa.

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Analysis of process parameters influence
Such analysis was performed for the reactive distillation scheme with a side reactor and product recycling to deisobutanizer. The most important parameters are paraffin to olefin (isobutene/butane) ratio and isobutane content in the recycle. Additionally an impact of selectivity in isopentane and self-alkylation was analysed. The results are given in Table 5.

For the calculations 50 and 20 theoretical plates were respectively considered for deisobutanizing and debutanizing. These parameters were determined taking into account an influence of the tray number on the reflux ratio of the columns (Figure 6). The optimal number of the reflux ratio (thus the corresponding number of trays) was defined as the minimal reflux ratio multiplied by 1.2 (20).
Simulation results clearly show that the main influence on the energy consumption for separation is the paraffin to olefin ratio. Thus by increasing this ratio from 10 to 15 the energy consumption increase 1.3 fold. At the same time an increase of the paraffin excess is beneficial from the viewpoint of catalyst stability, thus a compromise should be found for the paraffin to olefin ratio by balancing between the energy consumption and mitigation of deactivation.

An increase of isobutane concentration in the recycle above 90% leads to a substantial increase in the energy consumption in the deisobutanizer column. Influence of selectivity on energy consumption seems to be marginal in the studied range of 1.7 – 10 mol %.

Another important parameter with a profound impact of energy consumption is isobutane content in the feed (Table 6).

**Catalyst regeneration**

At the current stage of solid catalyst alkylation technology, the process efficiency is mainly determined by catalyst deactivation and subsequent regeneration. In the case of severe deactivation the technological scheme should allow for continuous restoration of catalyst activity. The most promising for alkylation process is a two-step regeneration with a mild regeneration by hydrogen dissolved in liquid isobutane and subsequent regeneration with hydrogen at elevated temperature (21, 22).

High activity of modern solid alkylation catalysts in subcritical conditions can be maintained only up to 40h, which leads to fast changes of reaction/regeneration in the reactor section. Therefore, for reactive distillation the most feasible option is to have side (external) reactor sections, which number depends on reaction and regeneration time. A potential scheme of such arrangement is visualized in Figure 10.

**CONCLUSIONS**

Simulations for reactive distillation in solid catalysed alkylation of isobutane with butane were conducted leading to the following conclusions.

The optimal conditions for separation and chemical reaction per se are close to each other being 70°C and 10 bar. Reaction section is located above butane separation, which does not allow efficient utilization of the alkylation reaction heat for separation of isobutane /n-butane. This drawback can be partially compensated by returning the products to the trays located below the withdrawing point of the reactor feed.

In order to arrange catalytic distillation the most optimal scheme is to utilize external reactors, working in reaction or regeneration modes.

The energy consumption data are in the range 1.5-3.5GJ per tonne of alkylate depending on the paraffin to olefin ratio and isobutane concentration in the feed.

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