XV International Scientific Conference "Chemistry and Chemical Engineering in XXI century" dedicated to Professor L.P. Kulyov

Reactor-regenerator system joint work optimization in benzene alkylation with higher olefins unit

Irena Dolganova [a] *, Igor Dolganov [a], Emiliya Ivanchina [a], Elena Ivashkina [a], Nataliya Belinskaya [a], Vyacheslav Platonov [a]

[a] Tomsk Polytechnic University, Lenin Avenue 30, Tomsk, 634050, Russia

Abstract

The work has been carried out to provide smooth operation of "reactor-regenerator" system as an important step in the problem of synthetic detergents production efficiency enhancing. Reasons which cause violation of HF-catalyst regeneration column regime have been identified. The ways of benzene alkylation rector and catalyst regenerator column joint work optimization have been proposed. Optimization consists of HF-catalyst optimal activity achievement with further system conversion in to the steady state, as well as probable failure date predicting with the possibility of column drainage in order to prevent it. The concept of the optimal activity has been introduced and positive effect achieved by its maintaining has been shown.

Keywords: Alkylation; reactor; catalyst regeneration; catalyst activity; optimization.

1. Introduction

Over the last years a great success in the aromatic compounds with olefins alkylation processes development as an environmentally friendly technology has been achieved[1]. One of the most demanded products of the petrochemical synthesis are synthetic detergents produced from LAB. Such detergents have good foamability and high biodegradability. These facts make LAB production efficiency enhancing problem urgent.

The process intensification, in general, involves modification of technological scheme in order to reduce energy consumption[2], reconstruction of equipment using available raw materials and catalysts[3] or using of

* Irena Dolganova. Tel.: +7-906-950-6975
 E-mail address: dolganovaio@sibmail.com

innovative technologies[4]. One of the ways of process efficiency enhancing without reconstruction of existing equipment is organization of technology-related blocks smooth operation. In this case, it is the joint work of benzene with olefins alkylation reactor and HF- catalyst regeneration column.

The analysis of "reactor-regenerator" system joint work can be carried out with maximum efficiency using mathematical models[5,6] and based on them computer modelling systems[7-9], which should take non-stationary of processes occurring in the reactor into account[10].

The aim of this research is to identify directions of "reactor-regenerator" system work optimization and to analyse their efficiency.

Nomenclature	
LAB	linear alkylbenzenes
HAR	heavy aromatics
HAR-F	heavy aromatics fluorides
HA	heavy alkylate
ΔG	change in Gibbs energy of reaction, kJ/mole
a	current catalyst activity, relative units
a_0	initial catalyst activity, relative units
C	current concentration of HAR in HF, mole/m^3
C_∞	maximum concentration of HAR in HF, mole/m^3
N_{HAR}	current amount of HAR in HF, mole
n^∞_{HAR}	maximum amount of HAR in HF, mole
γ	coefficient of catalyst deactivation
n^0_{HF}	initial amount of pure HF in reactor, mole
T_{cube}	temperature in the column cube, °C

2. Materials and methods

Thermodynamic analysis of HAR hydrofluorination reaction with HAR-F formation, accumulation of which in the column bottom prevents HF evaporation causing operation failure, occurrence probability has been performed using quantum chemical methods for thermodynamic functions calculating (Gaussian-98 software).

The "reactor-regenerator" joint work analysis has been carried out by means of chemical processes mathematical modeling methods and software implementation in Delphi-7 programming environment.

3. LAB manufacturing complex technological scheme

Complex for LAB production is a set of consistently processes of higher paraffins to olefins dehydrogenation, diolefins selective hydrogenation and benzene alkylation with higher olefines (see Fig. 1). In addition to the above, the technology involves a number of auxiliary stages, the importance of which, however, is comparable with the importance of basic ones, as they determine operating condition of the system. One of these stages is the regeneration of alkylation process HF-catalyst in the distillation column.
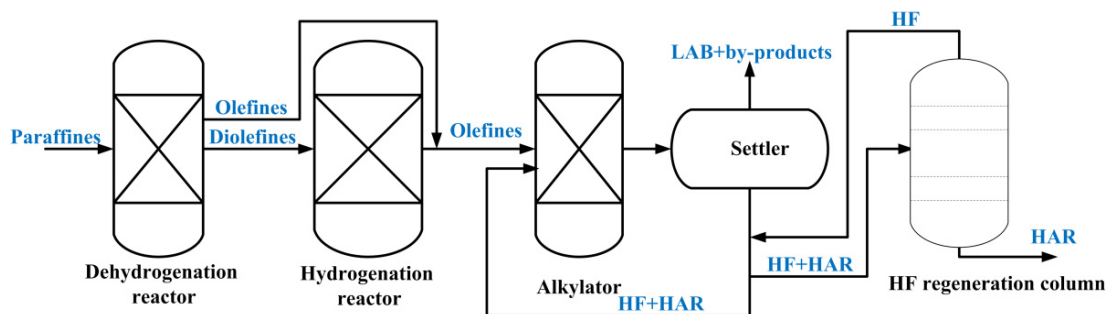
Fig. 1. LAB manufacturing complex technological scheme

Higher paraffins, which are raw materials, pass successively through dehydrogenation, hydrogenation and alkylation reactors. In the product decanter alkylation process products and acid contaminated with HAR are separated. The blend of HF and HAR goes to the regeneration column in order to remove high boiling unsaturated products (HAR) accumulating in HF because of their high solubility in acid[11,12]. This regeneration column is exposed to periodic malfunction. When catalyst regeneration is absent, there is accumulation of HAR in the alkylation reactor. This leads to desired product quality deterioration because of unsaturated components concentration increasing, as well as catalyst deactivation, that means decrease in the product yield. For these reasons periodic failures in the regenerator column operation negatively affect the entire technology.

4. Results and discussion

4.1. Failure causes identification

Failures in the regenerator column operation are as follows:

- Boiling of HF stops.
- There is uncontrolled growth of temperature in the column bottom reboiler but at the same time the bottom is cooled to about 60 °C.
- There is the HF/water azeotrope accumulation in the bottom of reboiler.

This situation is abnormal, requires unplanned column drainage and leads to loss of moisture in the system.

Below the possible reasons leading to HF-catalyst regeneration column operation failures analysis are described.

One of the reactions is HAR formation in alkylation reactor (See table 1).

Table 1. Thermodynamic analysis of HAR of different structure formation probability at 60 °C

Reaction	ΔG, kJ/mol
Benzene+Diolefine= HAR-1	-26.3
Benzene +2Diolefine =HAR-2	-23.2

Here HAR-1 and HAR-1 are HAR of 1 and 2 types, which correspond to the structure of unsaturated mono- and dialkylbenzenes.

One part of HAR formed in the alkylation reactor goes along the products stream, another one solves in HF and remains in the reactor, and other part goes to regeneration column into the mixture with acid.

HF evaporation termination can be explained by the film formation on the liquid surface in the column cube.

Substances which are able to form the film are HAR-F. One of the fundamental concepts is the film formation by the solvent evaporation (in this case HF). The film formation consists of three stages:

- Because of the solvent evaporation, the film-forming substances volume content in the liquid layer increases, the particles come closer up to the yet reversible contact and are stacked in a specific order
- Further solvent removal from the film, and the adsorption-hydrate shells destruction. As a result, initially spherical particles deform, take the polyhedrons form and gradually come into closer contact
- The film acquires characteristic structure and properties.

The temperature decrease at the cube bottom can be connected with the HF and azeotrope film boiling of, that is, the vapour layer formation with low thermal conductivity coefficient, which prevents heating of liquid under the steam layer. Additional cooling is associated with cold HF dripping from system to the column cube.

Reactions of HAR hydrofluorination are written as follows:

HAR-1+*HF*=*HAR* -*F*-1

HAR -2+*HF*=*HAR* -*F*-2
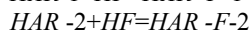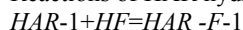
Here *HAR* -*F*-1 and *HAR* -*F*-1 are hydrofluorides of appropriate HAR.

Table 2 shows the thermodynamic analysis of HAR with different length of hydrocarbon chain hydroflyorination reactions occurrence probability.

Table 2. Thermodynamic analysis of HAR of different structure hydroflyorination at 150 °C

HAR-1		HAR-2	
Hydrocarbon chain	ΔG, kJ/mole	Hydrocarbon chain	ΔG, kJ/mole
C_{10}	-22.1	C_{10}	-28.6
C_{11}	-22.6	C_{11}	-28.9
C_{12}	-23.1	C_{12}	-29.5
C_{13}	-24.3	C_{13}	-30.2

The heat effect of the above types of HAR hydrofluorination reactions is insignificant (about 13 kJ/mol).

Calculated value of *HAR-F* ($C_{18}H_{30}F$) surface tension at temperature in the column bottom of 150 °C is 29.1 dyne/cm, which is 4 times higher than that of HF.

Thus, HAR-F formed in the column reboiler has all sufficient properties to form the film on the liquid surface in the column bottom and to prevent HF evaporation.

4.2. Catalyst deactivation accounting

HAR solubility in HF is limited because of complex compound formation, which has the following structure [13, 14]: $[HAR-H]^+[F-H-F]^-$. When reaching the HAR/HF molar ratio of 2/1, HAR stops being soluble in acid. That is, one mole of HAR is able to bind two moles of acid, taking them out of catalysis process. Thus, catalyst activity decreases. This complex is quite stable, but it is decomposed by hydrolysis, neutralization and in rectification process.

Mechanism of the HF-catalyst activity reducing caused by acid molecules by HAR in complex binding can be compared with homogeneous solid catalyst surface poisoning. Then

$$a=a_0-\gamma \cdot C/C_\infty = a_0-\gamma \cdot n_{HAR}/n^\infty_{HAR} \qquad (1)$$

Taking the fact that one molecule of HAR can bind 2 molecules of acid into account, the maximum content of HAR in HF saturated solution is 1440000 moles. The current content of HAR in reactor calculation with assumption of full reaction zone by acid filling gives value of 16704 moles.

The HF-catalyst relative activity represents the ratio of free acid not deactivated by HAR current amount to its initial amount when there is no HAR in the system.

As each HAR molecule can deactivate 2 moles of acid, catalyst relative activity dependence on HAR content in the reactor is linear and is written as follows:

$$a=(n^0_{HF}-2n_{TAP})/\ n^0_{HF} \tag{2}$$

Hence, if HAR content in the reactor is equal to 16704 moles, the current catalyst activity is 0.88.

The existing alkylation process computer modelling system [15, 16] has been supplemented with the HF-acid activity recalculation function depending on amount of generated HAR.

In accordance with the foregoing, the following reactor-regenerator system optimization variants have been proposed:

- The optimal HF activity determination with a temporary column load change and further system transfer to the steady state
- The catalyst current work activity maintaining and increasing the smooth column operation duration due to minimum required amount of acid contaminated with HAR to regeneration removal
- Possible failure forecasting and its prevention by early drainage of the column

4.3. Column mode failure forecasting

Fig. 2 presents the column mode failure forecasting algorithm.
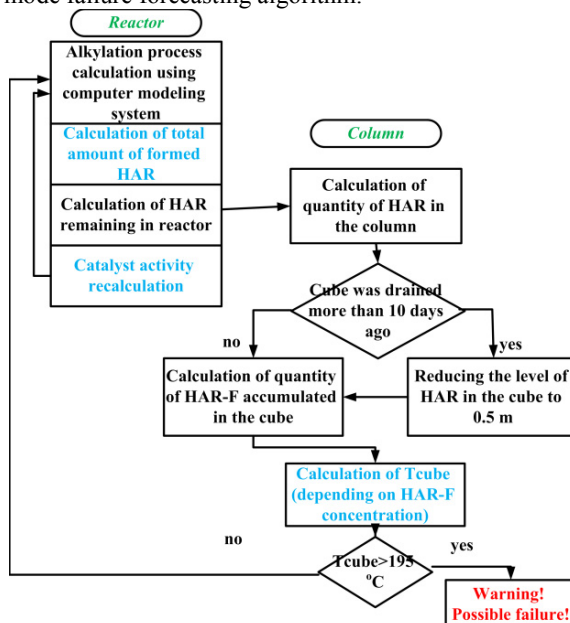

Fig. 2. Column mode failure forecasting algorithm

The algorithm essence is total amount of HAR formed in reactor calculation depending on the current catalyst activity; calculation of amount of HAR-F accumulated in the column bottom depending on the amount of HAR moved from the reactor to regeneration column with the HF flow; T_{cube} calculation as the HAR-F amount function.

The program ability to forecast has been tested using experimental data obtained in 2009-2012 years. The results are presented in Table 3.

Table 3. Date of possible column mode failure forecasting ability

Forecasted failure date	Real failure date
19.03.2009	08.03.2009
16.06.2009	25.06.2009
12.10.2009	01.10.2009
17.03.2010	22.03.2010
25.04.2010	12.04.2010
27.05.2010	04.06.2010
24.09.2010	29.09.2010
25.05.2012	18.05.2012
10.10.2012	10.10.2012

The forecasted failure date maximum deviation from the real one is 2 weeks (on average it is less than a week).

4.4. Optimal activity

The alkylation reactor and the HF regenerator column joint work investigation performed, using developed program, has allowed to find out a number of regularities:

- The LAB and HA output increases when catalyst activity increases up to 0.6 relative units. Its further increase does not lead to increase in product yield
- Fall in catalyst activity leads to LAB bromine index decrease, that is, improving product quality by reducing the unsaturated alkylbenzenes formation rate
- The process selectivity respected to LAB goes down rapidly to 0.96 with an increase in catalyst activity up to 0.5. Then the decrease in rate is not significant;
- The excess HAR accumulation in the reactor occurs only if catalyst activity is more than 0.6 relative units. At this activity rates of HAR accumulation value and its removal to regeneration in the HF flow are equal.

Reducing the load on regeneration column from 6 to 4 m^3/h leads to gradual decrease in HF activity. But even if maintaining this regime for at least 4 years, catalyst activity does not fall below 0.6 relative units, since in this case HAR accumulation in reactor rates and its removal to regeneration in the HF flow are equal (see Fig. 3).
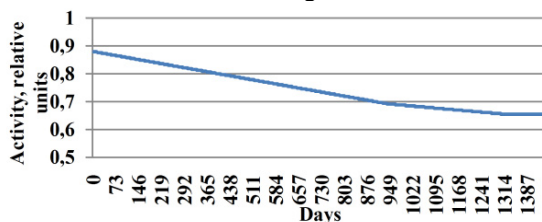

Fig. 3. The rate of HF activity change at its initial value of 0.88 relative units, unchanging composition of raw materials (for 02.04.2012) and acid consumption for regeneration of 4.069 m^3/h

There is a regime "self-regulation". Activity, at which there is the regime "self-regulation" and commercial products quality improvement without their output reducing, can be considered as optimal [17].

The optimal activity value depends on the raw materials composition and the volume of HF withdrawn from the reactor for regeneration. So, for example, for date 04.02.2012 the optimal activity value is 0.6 relative units.

Let us consider efficiency of the optimal catalyst activity maintaining in terms of column smooth operation period increasing (see Fig. 4).

Term of column smooth operation
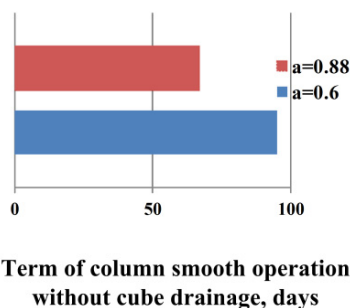**without cube drainage, days**
Fig. 4. Term of regeneration column smooth operation at current and optimal catalyst activity

The graph shows that when alkylation catalyst with activity of 0.88 is used, achievement of critical temperature in the column bottom and, therefore, the operation mode failure occurred on 23.05.2012. While catalyst optimal activity was 0.6 relative units maintaining, mode failure would happened a month later – on 20.06.2012.

Thus, the probable cause of HF regeneration column periodic failures is reaction of HAR hydrofluorination occurring in the column bottom. As a result of it HAR-F formation occurs. These substances are lighter than HF and have higher surface tension. They prevent evaporation of HF from the cube, which leads to failure and recorded uncontrolled temperature rise. Given the fact that one mole of HAR is able to bind two moles of acid in catalytically inactive complex, the mathematical model of alkylation process has been supplemented with catalyst deactivation linear function. Calculations carried out using the model have shown that there is some optimal HF activity for each feed composition, at which the HAR formation in the reactor rates and its removal to regeneration column are equal. Maintaining of catalyst activity at appropriate level significantly extends smooth operation of the column, and the mathematical model predicts the subsequent failure possible date. This allows to avoid the emergency situation by early column drainage.

5. Conclusions

1. The reasons which lead to HF-catalyst regeneration column mode violation have been identified. It has been shown that substances generated in the column bottom, while heavy aromatics hydrofluorination reaction occurs, form a layer with high surface tension and prevent HF evaporation from the cube. Thermodynamic analysis of HAR with different structure hydroflyorination reaction occurrence probability has been carried out.
2. The failures impact on benzene with higher olefins alkylation reactor has been described. Alkylation catalyst current activity and the rate of its change depending on HAR quantity have been calculated.
3. The ways of benzene alkylation rector and catalyst regenerator column joint work optimization have been proposed.
4. Positive effect of HF-catalyst optimal activity in alkylation reactor maintaining leads to increase in column smooth operation duration without alkylate quality compromising.

Acknowledgements