Available online at www.sciencedirect.com

ScienceDirect

Procedia Engineering 152 (2016) 25 – 33

Procedia Engineering

www.elsevier.com/locate/procedia

International Conference on Oil and Gas Engineering, OGE-2016

Increasing the efficiency of liquid phase alkylation of benzene with propylene using the method of mathematical modeling

ChudinovaA.A.[a,b*], Buchatskaya N.I.[a], Ivashkina E.N.[b], Salischeva A.A.[b], Gavrikov A.A.[b], Nurmakanova A.E.[b], Khlebnikova E.S.[b]

[a] *P JSC «Omsky Kautchuk», prospekt Gubkina, 30, Omsk, 644035, Russia*

[b] *National Research Tomsk Polytechnic University, Lenina str. 30, Tomsk, 634050, Russia*

Abstract

In this study the existing problems of liquid-phase alkylation of benzene with propylene problems are indicated. The paper describes the stages alkylation of benzene with propylene mathematical model development. The model allows to define the composition of the product stream under changing of plant process parameters: temperature, benzene/propylene molar ratio and feed space velocity. The error of the model does not exceed 7.5%. «Alkylation» computer modeling system is developed in Borland Delphi 7 and the optimization module of the process parameters is called «Optimization». In Aspen HYSYS the technological scheme of rectification products alkylation of benzene with propylene using aluminum chloride catalyst was developed. Integration of computer models allowed to determine the technological modes of production, providing isopropylbenzene outlet with higher quality.

Peer-review under responsibility of the Omsk State Technical University

Keywords: alkylation; benzene; propylene; isopropylbenzene; mathematical modeling.

1. Introduction

The most important petrochemical products are alkylates [1-3]. In the Russian Federation, liquid catalytic systems are usually used. The use of such catalysts leads to equipment corrosion and formation of significant quantities of environmentally hazardous and difficulty recyclable drains. However, the change of existing

* Corresponding author. Tel.: +7(913) 619-54-19
E-mail address: chudinova_aa@ok.titan-chem.ru

Peer-review under responsibility of the Omsk State Technical University
doi:10.1016/j.proeng.2016.07.613

production on the modern solid catalysts [4-5] requires the radical plants reconstruction, which is characterized by long production downtime.

Today there is an acute problem for alkylate production as an efficiency increasing of existing facilities corresponded to strict standards of ecological safety. The problem of chemical-technological systems optimization in general is successfully solved using the mathematical modeling method.

One of the productions for which the solution of multi-factor problem is desirable is the production of isopropylbenzene (cumene). Currently, existing mathematical models of isopropylbenzene production cannot solve the problem of efficiency increasing for the operating plant. Presently, the evidence-based approach for the optimization of alkylation production that uses toxic and corrosive catalyst was proposed. Thus, the purpose of this study is to improve the efficiency of liquid-phase alkylation of benzene with propylene by the process optimum conditions ensuring with the use of mathematical modeling.

To achieve this goal the following tasks were solved:

1. The development, software implementation and verification of mathematical model adequacy of liquid phase alkylation of benzene with propylene.
2. Determination of reactor optimum technological modes that depend on the feedstock composition for the isopropylbenzene production corresponded to premium quality requirements.
3. Development of optimal scheme of process streams direction for the fractionation products block in liquid phase alkylation of benzene with propylene to create the conditions for a clearer alkylation products separation.

2. Object of research

Technological installation scheme of isopropylbenzene (cumene) production consists of six process units: the preparation of catalytic complex; catalytic column reactor; catalyst decomposition and catalytic complex washer; benzene trapping from absorption gases and their neutralization; benzene azeotropic drying units and rectification of product separation.

Process conditions are characterized by the top and bottom reactor temperature, pressure, raw and catalyst flows: T = 100 - 130°C; P = 0.11 - 0.19 atm.; benzene/propylene molar ratio: 2.5/1 ÷ 4/1; feed space velocity: 5.1 h^{-1}.

The input raw flow in the alkylator has the following composition, % wt.: propane-propylene fraction (PPF) (propane 2.03 – 11; propylene 89.00 – 97.97); dried benzene containing fraction (DBF) (60.29 benzene – 87.41; IPB 1.11 – 9.43; hexene 1.67 – 3.98; toluene 0.02 – 2.13; ethylbenzene (EB) 0.1 – 1.56; xylene 0.01 – 1.13; n-propylbenzene (NPB) 0.01 – 0.13; 3-butylbenzene (3-BB) 0.05 – 0.65; 2-butylbenzene (2-BB) 0.13 – 1.06; cymene 0.08 – 1.36; n-butylbenzene (NBB) 0.08 – 0.47; polyalkylbenzene (PAB) 6.54 – of 24.19). The reaction mass of alkylation reactor (RMA) has the following composition, % wt.: hexane 0.84 – 3.15; benzene 40.94 – 57.81; IPB 26.27 – 39; toluene 0.38 – 3.8; EB 0.08 - 1.32; xylene 0.01 – 1.13; NPB 0.05 – 0.15; 3-BB 0.05 – 0.44; 2-BB 0.1 - 0.65; cymene 0.15 – 0.75; n-BB 0.08 – 0.32; PAB 6.84 –18.07; xylene 0.01 – 0.05; the rest - 2.0.

The mechanism of the target alkylation reaction includes four stages [6]. The first stage is the reaction of propylene with hydrogen chloride resulting propyl formation and easily dissociates into ions. The second stage is the formation of carbocation. And the third stage is the electrophilic benzene attack by carbocation and intermediate or σ-complex with a high energy value formation. This stage is limited. The last stage involves hydrogen elimination from the intermediate, catalyst recovery and product formation.

3. Research methods

To evaluate the thermodynamic possibility of reactions quantum chemistry methods [7-9] were used.

Numerical studies were carried out with the use of density method of functional theory (DFT) at the B3LYP level. 6-31 ++ G (d, p) parameters were chosen in such a way to keep the controllability of calculations and do not reduce the accuracy of physical description. As a result, the basis set has been selected. The above reactions proceed in a liquid phase, so it is necessary to include the effect of solvation. For this model the limiting Thomas polarization (polarized continuum model (C-PCM)) has been used. It defines a cavity (space) as a combination of blocked atomic spheres series. The benzene solvent was chosen because benzene to propylene ratio in industry is at 3 - 10:1.

The first stage was carried out by optimization of molecular electronic structures of products and reactants at each stage for each of considered reactions, and vibrational frequencies are calculated, as well as enthalpy, entropy and Gibbs energy of benzene with propylene alkylation reactions in industry conditions.