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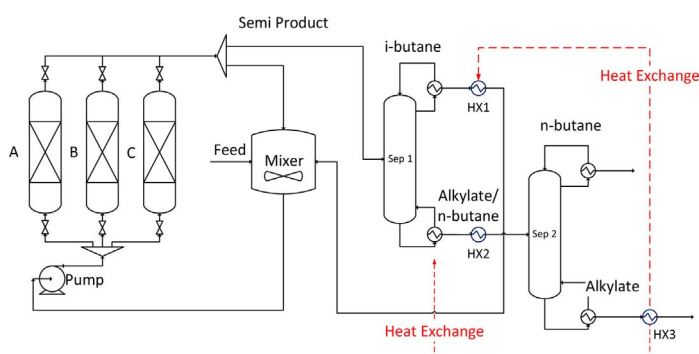
Simulation and optimization of fixed bed solid acid catalyzed isobutane/2-butene alkylation process



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GRAPHICAL ABSTRACT



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ABSTRACT

The isobutane/2-butene alkylation process using fixed bed arrays as reactors and β -zeolite as the catalyst is simulated and analyzed. By employing the Lagrange's method, numerical problems that originate from nonlinear reactions and Eulerian grids are neutralized. Sensitivity of operating parameters on process performance are discussed, such as paraffin/olefine ratio, alkylate reflux ratio and liquid velocity. It is found that larger paraffin/olefine is required for greater olefine to alkylate selectivity. And alkylate reflux is also necessary to save energy cost in the distillation operations. Alternative configurations such as multiple inlet points and radical bed are discussed. To determine the optimal operating parameters, a techno-economical model is established and optimized. In the final analysis, guidelines for the further design of solid acid catalyzed alkylation process are presented.

1. Introduction

The importance of isobutane/2-butene alkylation stems from gasoline manufacture for which it is essential in providing a high-octane, low density and volatility blending component (trimethylpentanes, TMPs) virtually without sulfur and nitrogen. For the time being, liquid-phase processes with concentrated sulfuric acid (H_2SO_4) or hydrogen

fluoride (HF) as catalysts are currently being used for the commercial manufacture of alkylation gasoline. Yet, acid catalyzed alkylation suffers from disadvantages for example, high acid consumption and toxicity. Though viewed as an alternative to H_2SO_4 and HF [1], however, ionic liquid catalyzed alkylation is still under development, mainly on improving selectivity [2,3]. Researchers have also been advocating solid catalyst alkylation (SCA) process that would eliminate the safety

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Nomenclature

<i>P</i>	concentration of paraffin, kmol/m ³
<i>S</i>	Concentration of acid site in catalyst, kmol/m ³
<i>O</i>	Concentration of olefin, kmol/m ³
<i>A</i>	Concentration of alkylate, kmol/m ³
<i>HO</i>	Concentration of higher olefin, kmol/m ³
<i>HA</i>	Concentration of heavy alkylate, kmol/m ³
<i>k_i</i>	Kinetic constant of reaction, i
<i>X</i>	Blocked acid site by HO
<i>Y</i>	Blocked acid site by HA
<i>V</i>	Liquid velocity, m/s

ρ	Molar density, kmol/m ³
<i>R_i</i>	Rate of reaction i, kmol/m ³ /s
ΔH	Enthalpy change of reaction G, J/kmol
<i>T</i>	Temperature, K
α	Ratio of active site in catalyst
<i>A_r</i>	Contacting area between liquid and catalyst, m ²
<i>C_j</i>	Concentration of component in cell j, kmol/m ³
<i>OS</i>	Olefine selectivity to C8
<i>PO</i>	P/O ratio in mole
<i>Re_{mf}</i>	Minimal fluidized Ranald number
<i>Ar_{mf}</i>	Archimedes number in minimal fluidized velocity calculation

and corrosion issues associated with liquid acid catalyst. Flego et al. studied Y-zeolite's application in alkylation [4] as well as the machinery in catalyst's deactivation [5]. Feller proposed the mechanism in alkylation [6]. And Josl et al. also investigated on regeneration properties [7]. Since the pioneering work of Weitkamp [8], faujasites exchanged with lanthanum have been extensively investigated. Sievers compared the LaX and LaY catalysts [9] and discussed on the stages of ageing and deactivation for the catalysts [10]. Guzman studied the influence of temperature on LaX zeolites's activity [11] and the formation of lanthanum acid sites [12].

With the growing demand for green energy, new plants for alkylation gasoline are in the plan. And more attention is paid to the plant-wide optimization of alkylation flowchart with the purpose of improving profit as well energy efficiency.

Flowsheet simulation and optimization of liquid acid catalyzed alkylation has been investigated extensively. In his monograph, Edgar [13] optimized a H₂SO₄ catalyzed process using sequential quadratic programming techniques. The unit operation as well as economic models are simplified as empirical equations which can be directly turned into expressions in MATLAB and then solved by the solver "NPSOL".

Luyben [14] studied the auto refrigerated alkylation process. H₂SO₄ catalyst is in a series of agitated reactors that require refrigeration to suppress undesirable side reactions that are favored by high temperatures. Employing simplified kinetics proposed by Mahajanam [15], Luyben's work throw light on the design trade-offs among design optimization variables such as reactor size, reactor temperature, compressor work and isobutane recycle.

Tripathi et al. [16] proposed a plant-wide control (PWC) structure for the auto refrigerated H₂SO₄ alkylation process by step-by-step application of the recently proposed integrated framework of simulation, heuristics, and optimization methodology [17]. The performance of the developed control structure has then been compared to that of Luyben [14] using various performance measures.

García [18] presents a hybrid simulation and multiobjective optimization that simultaneously finds the optimal in production cost and minimizes the associated environmental impacts of the H₂SO₄ catalyzed isobutane alkylation. A superstructure was systematically generated which includes alternatives not previously considered. The problem is formulated as a Generalized Disjunctive Programming problem and solved using state-of-the-art logic-based algorithms.

As with solid catalyzed alkylation, Ramaswamy [19] evaluated the performance of a solid acid contained slurry reactor using the multi-scale mathematical models. A pseudo-steady state catalyst pellet level model, incorporating the alkylation and deactivation kinetics, is coupled to the transient model of back mixed reactor configurations. Effect of catalyst shape, initial acid strength of the catalyst, paraffin-to-olefine feed ratio on the conversion of the olefine, on the yield of alkylates and on the time required for complete deactivation of the catalyst is investigated.

Based on literature review [19,20], researchers have preferred

continuous stirred tank reactor (CSTR). A typical CSTR model assumes perfect mixing in the reactor, which is ideal for alkylation because of the high Paraffin/Olefine ratio achieved. However, CSTRs encounter mixing problem when equipment scales up. Hence, for commercialized plants especially that undertake large production [21], packed bed or fixed bed are usually adopted due to the simplicity in design and the reliability in operation [22]. Apparently, the plug flow pattern in fixed bed is different from the ideal mixing model in CSTR. Hence it is important to predict the performance such as catalyst lifetime and the overall design of SCA plant.

Though a Liu's work simulated SCA fixed bed reactor, the equation discretization issue that may influence the prediction was not addressed [23]. Moreover, further literature investigation shows even few effort was made to analyze SCA on a process scale. In this work, trough process scale simulation, the influence of design parameters on the SCA is discussed and the optimal condition is proposed.

2. Kinetics and unit operation models

2.1. Chemistry of alkylation

The chemistry of isobutane alkylation with 2-butene has been discussed extensively in previous work [6,20,24–26]. Subtle differences are apparent depending on the catalyst involved. For solid acid catalyzed alkylation with zeolites, eight types of elementary steps was identified as the most likely transformations occurring within the reaction network [26]. The kinetics are complex for practical concerns. Therefore, in order to capture important features of the chemistry system, several simplified kinetics are proposed, as has been suggested by de Jong et al. [20] and Mahajanam et al. [15]. Compared with de Jong's work, Mahajanam et al. has neglected the oligomerisation reaction. For more accurate description, we employed the kinetics proposed by de Jong et al.

According to de Jong et al. [20], the main and desired reaction is the one between isobutane (P) and 2-butenes (O) producing trimethylpentanes (A). Whereas, the main side reactions include (i) to form heavy alkylate (HA) from secondary reactions of alkylate with an additional olefine and (ii) oligomerisation reactions to produce higher olefines (HO). Eqs. (1)–(3) illustrates the simplified chemistry for alkylation.



Deactivation is modeled by the blocking the acid sites (S) by HA or HO. Once formed, HA will block the acid site directly, while HO's coverage on the acid site is modeled with an adsorption mechanism. Desorption of HA or HO is not considered in this work, and the detailed analysis can be found in literature [27]. By including the active sites in the reactions, the chemistry in alkylation would become

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