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Simulation of three-phase spouted bed reactor for solid catalyst alkylation

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Abstract

A process simulator was developed to afford better understanding of the performance of the isobutane–butene alkylation plant that uses a three-phase spouted bed-reactor hydrocyclon and a super acid solid catalyst. The system was simulated by using correlations developed in the cold model and apparent kinetic constants measured in a batch reactor for 1-butene–isobutene alkylation. A new type of catalyst, $PtSO_4Zr/TiO_2$, was used in the presence of recycled alkylate and hydrogen. The computer simulator numerically solved the mass and energy balance equations for the riser and downcomer. It was determined that a gas–liquid–solid with similar properties to the system under study do not shown a charm regime of flow and that the new design of the gas disengaging zone at the end of the riser prevent the undesired recirculation of large bubble and provide stability. New gas hold-up, linear velocity of the liquid, recycle ratio, and mass transfer correlations obtained reproduce the result within a ±10% error. The result of the alkylation plant simulation indicated a large influence of linear velocity and temperature on activity, selectivity, and stability of catalytic system. The other important operating parameters are alkylate/olefin and isobutane/olefin ratios. The optimal operating conditions were determined for a particular catalyst and set of cost.

Keywords: Alkylation; Spouted bed reactor; Solid super acid catalyst; Mass transfer

1. Introduction

The development of an alkylation process that uses a solid catalyst is one of the most challenging activities in efforts to improve the production process of a "green" gasoline component. Currently commercial alkylation of olefins is done using strong acids (HF and H_2SO_4) with good selectivity and activity but generating or a toxic sludge (H_2SO_4) or having strong safety limitations (HF). The development of an active and stable solid super acid alkylation catalyst will introduce interesting technical and economical possibilities and represent a big challenge. Weitkamp and Traa [1] has reviewed the state of the art in solid alkylation; since then there have been many contributions in this area. In this research, we used different catalyst formulations base on a wide porous Si-based mesoporous material in which Pt and $ZrSO_x$ species were present on the surface. In previous work [2], a kinetics model was developed using this type of catalyst for olefin–isobutane alkylation in the presence of hydrogen. We studied the application of this catalyst in a slurry-type reactor hydrocyclon coupled with a fluidized-bed regenerator. The simulation of a slurry reactor was recently summarized by De Jong et al. [3] and by Ramswamy et al. [4]. Our present research focuses on the use of three-phase spouted bed hydrocyclon instead of slurry reactor [5] technology.

1.1. Process description

In this alkylation process (Fig. 1), the feeds comprise a liquid phase composed of olefins, isobutene and alkylate, and a hydrogen-rich gas stream that comes into the bottom of the reactor (see callout 1, Fig. 1). Gas and liquid phase are internally contacted with a solid super acid catalyst coming from the regenerator (7, Fig. 1). At the inlet (1), fresh feeds are combined with those internally recycled through the downcomer (5). All components enter into the riser were they move upward. The gas is stripped from the reacting mixture at the top of the reactor where it is cooled and separated at high pressure. From the top of this separator the gas (mainly H_2) is recycled to the inlet of the

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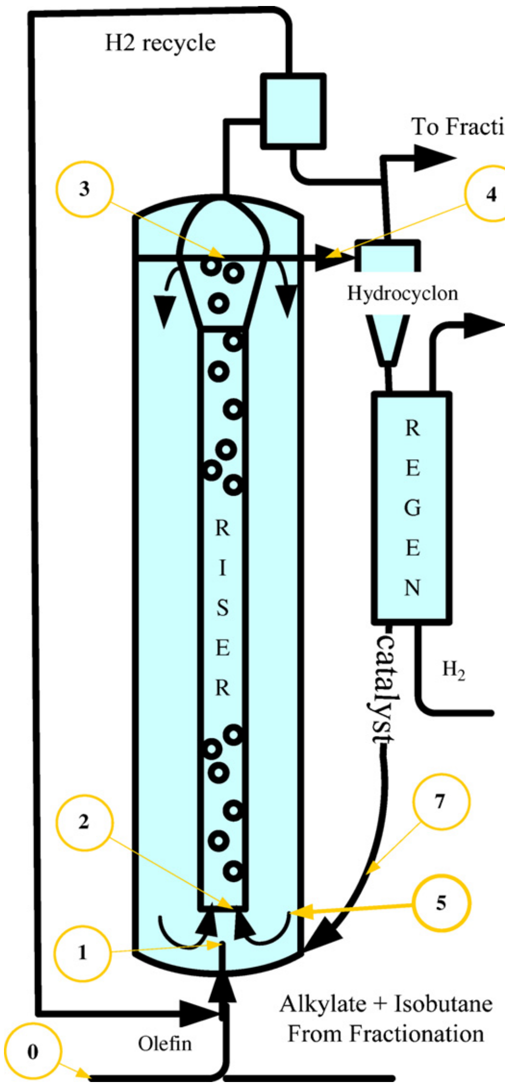

Fig. 1. Spouted bed-hydrocyclon system.

reactor, and from the bottom, the condensed liquid is sent to the fractionation section. Part of the solid and liquid phase leaving at riser outlet is sent to the hydrocyclon (4). There, liquid and gas are recovered from the top and fractionated, while wet solid is collected at the bottom of the hydrocyclon and regenerated by hot hydrogen. The recirculation of the alkylate guarantees the presence of a convenient liquid phase used here to control the rate of olefin transfer from the gas to the solid surface where reactions take place. The fractionation system consists in three columns dedicated to separate propane (C_3), butane (C_4), isobutane (iC_4) and alkylate components. The on-specification alkylate is obtained at the bottom, and one portion is recycled to the reactor. Within the reactor occur other secondary reactions such as the hydrogenation of olefins into paraffins and their polymerization into a larger molecule (C_{10}^+: soft coke). The soft coke remains adsorbed at the acid sites of the catalyst, generating an important catalyst deactivation. The spent catalyst coming from the leg of the hydrocyclon needs to be regenerated before being sent again to the reactor. It was experimentally demonstrated that between 90 and 100% of the original activity can be recuperated by hydrogen treatment at 100 °C [2]. The simulation of the regeneration was not included in the present results.

1.2. The three-phase spouted bed reactor

The three-phase spouted bed-hydrocyclon (hydrogen lift) system is characterized by its particular backmixing, extent of bubble size, catalytic efficiency of solids in suspension, and distribution of gas and solids in riser and downcomer. It is important to know the effect of residence time temperature and mass transfer on activity, as well as on selectivity and stability of the catalyst, to design a proper distribution of volume between the riser and downcomer. In practice, the magnitude of the driving force for liquid circulation, backmixing, and mass transfer is affected by the riser gas hold-up, and, in particular by the intensity of big-bubble penetration into the downcomer section. These phenomena cannot be totally understood from the results obtained in previous work using the water–air system for three-phase spouted bed reactors without special design at the inlet and outlet of the riser. Most of the information about bubble size and mass transfers in air–organic compounds (not polar hydrocarbon) was developed for slurry reactors [7,8], but there are some results for spouted bed reactors [9,10]. The importance of the ratio downcomer/riser diameter was recognized by several authors [11,12], and the design of the disengaging zone was reported by Klein et al. [13]. Basically, the head of the separator zone is usually designed with the purpose of controlling the extent of bubble penetration into the downcomer. This is usually achieved by changing the size of the reactor head zone (i.e. shape, diameter and height).

In the present study, two kinds of experiments were carried out in parallel: (1) determine the effect of (air + CH_4)/isooctane + benzene liquid feed ratio, solid content, and particle diameter on the performance of a constant geometry model of a cold three-phase spouted bed-hydrocyclon; (2) develop an apparent kinetics model to simulate the conversion of 1-butene and isobutane in presence of alkylate, hydrogen, and a $PtSO_4Zr/TiO_2$ catalyst using a batch type reactor and operating at different conditions. Fluid dynamic and kinetics, both together were employed to simulate this particular solid catalyst alkylation processes.

2. Experiments and model equations

2.1. Cold model apparatus

The cold model consists in a 0.4 m diameter and 3.5 m tall metallic reactor, with a 0.16 m internal riser and 0.04 m inlet liquid nozzle diameter, connected to a 0.18 m diameter hydrocyclon. The riser ends up in an enlarged degassing zone (cone of 0.35 m height and 60° angle). The basic configuration can be seen in Fig. 2. The octane is continuously fed to the reactor into a conical bottom, and the gas (air + 10% of CH_4) is distributed inside the riser inlet zone. The gas is injected at 0.1 m above the bottom of the draft tube by means of a parallel set of five tubes of 0.002 m internal diameter and 0.05 m length. The liquid-containing solid is withdrawn from the upper part and