Journal of Natural Gas Science and Engineering 19 (2014) 295–302

Contents lists available at ScienceDirect

Journal of Natural Gas Science and Engineering

journal homepage: www.elsevier.com/locate/jngse

Optimal condition of radial flow moving bed reactors to enhance isobutene production through heat coupling of isobutane dehydrogenation and nitrobenzene hydrogenation

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ARTICLE INFO

Article history:
Received 27 April 2014
Received in revised form
4 May 2014
Accepted 12 May 2014
Available online 14 June 2014

Keywords:
Oleflex technology
Thermally coupled reactor
Heterogeneous model
Optimization
Genetic algorithm

ABSTRACT

This paper has focused on optimization of thermally coupled radial flow moving bed reactors to produce isobutene and aniline. A heterogeneous two-dimensional model is developed to predict the performance of the heat-integrated configuration at steady state condition. The catalytic nitrobenzene hydrogenation takes place in the exothermic side and supplies a part of necessary heat for isobutane dehydrogenation in the exothermic side. To prove the accuracy of the considered model, simulation results of the conventional process are compared with the plant data at the same process condition. Then, the Genetic algorithm as an effective method in the global optimization is applied to optimize the operating condition of the integrated system to enhance isobutene productivity and selectivity. The feed temperature of exothermic and endothermic sides and exothermic feed flow rate are considered as decision variables. Isobutene production is enhanced about 12.7% and 7.4% in the optimized thermally coupled process compared to the conventional Oleflex and thermally coupled processes. The results suggest that operating of the propose system at optimal condition is feasible and beneficial.

1. Introduction

Isobutene, also known as isobutylene, is a colourless, extremely flammable gas that presents an explosion danger. It reacts with methanol and ethanol to produce MTBE and ETBE as gasoline additive to enhance fuel octane number, respectively. It is used as a monomer or copolymer to produce synthetic rubber and various plastics. Although, isobutene can be isolated from refinery streams, the common industrial method to produce isobutene is catalytic dehydrogenation of isobutane. Catofin, Oleflex, Star, and FBD are common industrial technologies that are used to produce isobutane. The Catofin technology uses fixed-bed reactors in which there is an alternation between reaction and regeneration cycles (Arora, 2004). Oleflex technology utilizes mobile adiabatic reactors in series. The catalyst flows slowly along the axial direction by gravity, while the feed stream flows in radial direction of reactors. The catalyst is collected at the bottom of the last reactor and is transported to the regenerator (Bhasin et al., 2001). In the Star technology, catalyst is contained in tubes placed inside a fired furnace to supply the heat of reaction. In this case, too, the need for periodic regeneration of the catalyst imposes the use of several parallel reactors. FBD technology uses a fluidized-bed reactor that catalyst circulates continuously from the bottom of the reactor to the top of the regenerator plant and vice versa (Sanfilippo and Miracca, 2006).

There are few articles in the literature, which discuss about modelling of isobutane dehydrogenation process. Buzari et al. (2006) studied the kinetic of isobutane dehydrogenation over the commercial Pt–Sn catalyst at a temperature range of 698–848 K. The results indicated that the obtained rate equation based on the Langmuir–Hinshelwood mechanism, considering isobutene adsorption as a rate-limiting step, has very good agreement with the experimental data. Farsi et al. (2012) modelled isobutane dehydrogenation in moving bed radial flow reactors considering reaction network. The isobutane conversion and isobutene selectivity were about 38.53% and 90.76%, respectively, which had good agreement with the plant data. Farsi et al. (2011) proposed an axial flow membrane reactor for isobutane dehydrogenation and optimized the process condition to enhance isobutene production and selectivity.

The energy management is a main key in process design, particularly in the reactors. Thermally coupling of exothermic and

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http://dx.doi.org/10.1016/j.jngse.2014.05.011
1875-5100/

endothermic reactions is prime case of process intensification for heat management. This concept that is so-called multifunctional reactor, integrates more than one unit operation in a single unit. This integration results in more compact and efficient units with lower operational and capital costs (Agar, 1999). In addition, thermally coupling of exothermic and endothermic reactions eliminates cooling and heating mediums in conventional reactors. Farsi et al. (2010a,b) developed a mathematical model for a thermally coupled reactor that is composed of two sides for methanol dehydration and benzene synthesis. This novel configuration decreased temperature of methanol dehydration reaction in the second half of the reactor and shifted the thermodynamic equilibrium to enhance methanol conversion. Farsi et al. (2010a,b) optimized the operating condition of a thermally coupled membrane reactor to enhance hydrogen, DME and benzene. The optimization enhanced the methanol conversion about 2.76%. Farsi (2014) modelled thermally coupled radial flow moving bed reactors to produce isobutene and aniline at steady state condition. The isobutene production in the proposed process was improved about 5% compared to the conventional Oleflex process.

In this paper, the operating condition of the thermally coupled configuration for isobutane dehydrogenation and nitrobenzene hydrogenation is optimized to enhance isobutene production and selectivity. In this configuration, the radial flow moving bed reactors in Oleflex process is modified, so nitrobenzene hydrogenation and isobutane dehydrogenation reactions take place in the exothermic and endothermic sides, respectively. Thermally coupling of isobutane dehydrogenation with an exothermic reaction in a reactor is an effective method to increase heat content in the isobutane dehydrogenation side. Although the high temperature increases rate of isobutane dehydrogenation and shifts the equilibrium towards the higher isobutene production, it enhances the rate of side reaction and decreases process selectivity. Thus, operating the thermally coupled reactors at optimal condition can improve isobutene production and selectivity. To prove the accuracy of the considered model, the simulation results of the commercial Oleflex process are compared with the plant data.

2. Isobutane, isobutene and NGL

Some liquids are found in the produced natural gas from reservoirs, which include propane, butane, and ethane among others. In the gas refinery plants, the liquids are separated from the natural gas and send into NGL (Natural Gas Liquids) plants to fractionation. The NGL plant consists of a series fractionators whose purpose is to separate a mixture of hydrocarbons into various pure products. Normal butane is a valuable hydrocarbon obtained from natural gas in the NGL process. It is used as a refining blend stock for gasoline and is used as a petrochemical feedstock to produce isobutane. Commercial butane isomerisation units convert extracted normal butane form LNG or refinery streams into mixed normal and isobutane, which is fractionated into high purity isobutane and residual normal butane. The produced isobutane from isomerisation is converted to isobutene as intermediate product in MTBE plants to produce MTBE as a gasoline octane number enhancer.

3. Kinetic model

3.1. Isobutane dehydrogenation

In the Oleflex technology isobutane dehydrogenation, isobutane cracking and coke formation reactions occur as the main side reactions (Poli, 2007). The kinetic of isobutane dehydrogenation and side reactions over $Pt{-}Sn/Al_2O_3$ catalyst is as follows:

$$\text{i-}C_4H_{10} \leftrightarrow \text{i-}C_4H_8 + H_2 \tag{1}$$

$$\text{i-}C_4H_{10} + H_2 \leftrightarrow C_3H_8 + CH_4 \tag{2}$$

$$C_3H_8 \leftrightarrow H_2 + C_3H_6 \tag{3}$$

$$\text{i-}C_4H_8 \rightarrow 4C + 4H_2 \tag{4}$$

In this work, the kinetic models and reaction rate parameters have been selected from literature (Abdi and Kiamanesh, 2008; Moghimpour Bijani and Sahebdelfar, 2008).

3.2. Nitrobenzene hydrogenation

Aniline as an important organic substance is used to produce variety of products such as dyes, pigments, rubber additives, pesticides, and pharmaceuticals. The reduction of nitrobenzene with iron turnings and water in the presence of small amounts of hydrochloric acid is the oldest form of industrial aniline production method. Recently, the catalytic gas phase hydrogenation of nitrobenzene in fixed-bed or fluidized-bed reactors has been developed to produce aniline. In this process, benzene reacts with nitric acid to produce nitrobenzene in presence of sulphuric acid. In the second step, the produced nitrobenzene is converted to aniline in presence of hydrogenation catalysts. The kinetic models and reaction rate parameters are selected from literature (Amon et al., 1999). The hydrogenation reaction of nitrobenzene to aniline is as follows:

$$C_6H_5NO + 3H_2 \leftrightarrow C_6H_5NH_2 + 2H_2O \tag{5}$$

4. Process modelling

4.1. Conventional Oleflex process

The conventional Oleflex process consists of three moving bed radial flow reactors in series. In this system, the feed stream is heated in the inter-stage furnaces and is entered to the reactors. The reactors are two perforated concentric tubes that feed is entered from inner tube and flows along the radial direction. The outlet product from the first reactor is fed to the second reactor. Due to coke formation on the catalyst surface, catalyst flows along the axial direction of reactors by gravity force towards regeneration system. In the regeneration reactor, formed coke is burnt and the regenerated catalyst is recycled to the first reactor and flows along the axial direction of reactors. Fig. 1(a) shows the schematic diagram of the Oleflex process. The detail mathematical model of the conventional Oleflex reactors can be seen in our previous work (Farsi, 2014). Table 1 shows Feed specifications, reactor, and catalyst characteristics of the Oleflex dehydrogenation reactors (Operating condition, 2002).

4.2. Heat integrated process

In the considered thermally coupled reactor, the plates have been inserted in the reactors vertically along the radial direction and reactors are divided to some zones. The exothermic and endothermic reactions have been placed in the zones, decussately. Thermally coupling of isobutane dehydrogenation with nitrobenzene hydrogenation reaction is an effective method to increase heat content and conversion in the isobutane dehydrogenation as an endothermic reaction. In addition, since the nitrobenzene hydrogenation reaction supplies a part of required heat in the isobutane dehydrogenation side, the smaller furnaces can be used in the