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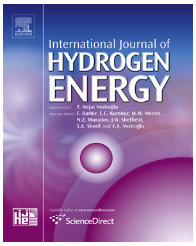

Combining continuous catalytic regenerative naphtha reformer with thermally coupled concept for improving the process yield

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ABSTRACT

Advancements in the catalytic naphtha reforming process, as one of the main processes in petrochemical industry, contributed to development of continuous catalytic regenerative naphtha reformer units. Increasing the yield of aromatic and hydrogen as well as saving the energy in this process through the application of thermal coupling technique is a potentially interesting idea. This novel idea has been assessed in this paper. In the proposed configuration, continuous catalyst regeneration naphtha reforming process is coupled with hydrogenation of nitrobenzene in a two co-axial reactor separated by a solid wall, where the generated heat in nitrobenzene hydrogenation reaction transfers to naphtha reforming reaction medium through the surface of the tube. A steady-state, homogeneous, two-dimensional model is used to describe the performance of this configuration and a kinetic model including 32 pseudo-components with 84 reactions is considered for naphtha reforming reaction. After validating the model with the commercial data of a domestic plant, the obtained results of coupled reactor are compared by the conventional one. The obtained results show the superiority of CCR coupled reactor against the conventional one.

1. Introduction

1.1. Catalytic naphtha reforming process

Catalytic naphtha reforming is considered as a critical process for generating high-octane reformate products for gasoline blending and producing benzene, toluene, and xylene (BTX) aromatics. In this process, naphtha, typically having low-octane hydrocarbons, converts to reformates, which are components of high-octane gasoline (also known as high-octane petrol).

Due to the importance of catalytic naphtha reforming process in petrochemical industry, various studies have been accomplished on different aspects of this process. These

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studies are mainly focused on three important issues, which are as follow:

1.1.1. *Modeling and reactor configurations*

Because of the industrial importance of naphtha reforming process, researchers have studied the design aspect widely to find appropriate configurations to enhance the production of the aromatics and hydrogen. In this regard, various types of reactor with different mode of operation have been suggested. Liang et al. [1] modeled four radial-flow tubular reactors in series in semi-regenerative (SR) mode of operation. Iranshahi et al. [2] assessed the effect of membrane addition to a radial-flow tubular reactor. They divided the cross-sectional area of the tubular reactor into some subsections in which walls of the gaps between subsections were coated with the Pd–Ag membrane layer. Rahimpour [3] suggested axial-flow fluidized-bed membrane tubular reactor in SR system. In this configuration, the reactants are flowing through the tube side which is a fluidized-bed membrane reactor while hydrogen is flowing through the shell side which contains carrier gas. Hydrogen penetrates from fluidized-bed side into the carrier gas due to the hydrogen partial pressure driving force. In addition, Rahimpour et al. [4–7] evaluated radial- and axial-flow spherical reactors as well as combination of tubular and spherical reactors in SR mode of operation. Mahdavian et al. [8] and Stijepovic et al. [9] studied axial- and radial-flow tubular moving bed reactor, respectively, in which catalysts moved continuously through reactors.

1.1.2. *Kinetics of catalytic naphtha reforming process*

Large numbers of the accomplished studies on catalytic naphtha reforming are focused on presenting a suitable kinetic network. Presenting an accurate kinetic model consisting all of the components and reactions is a very complex and nearly infeasible task due to the large number of components (approximately 300) and their relevant reactions [10,11]. Thus, “lumped” models have been presented in which the large numbers of chemical components are classified to smaller set of kinetic lumps. The first significant attempt to model a reforming system by this approach has been made by Smith [12] in 1959. More comprehensive lumped modes involving larger number of components and lumps are also presented. For instance, Jenkins and Stephens [13] presented a kinetic model involving 31 lumped components and 78 reactions. The suggested model by Froment [14] involves 28 lumps and 81 reactions, and the revealed model by Ancheyta-Juarez and Villafuerte-Macias [15] contains 24 lumps and 71 reactions. Stijepovic et al. [16] recommended a semi-empirical kinetic model for catalytic reforming and considered the most important reactions of the catalytic reforming process in their kinetic model in 2009.

1.1.3. *Catalysts of naphtha reforming process*

Naphtha reforming catalyst is a bifunctional catalyst consists of a metal function, mainly platinum, and an acid function, usually chloride alumina. The metal function catalyzes the hydrogenation and dehydrogenation reactions and the acid function promotes the isomerization and cyclization reactions [17–19]. The first formulation of the naphtha reforming catalyst, which was introduced in 1949 by UOP, consisted of monometallic platinum supported over chloride alumina (Pt/Al_2O_3–Cl) [20,21]. Improving the stability and selectivity of the catalyst as well as reducing catalyst deactivation is a vital issue for enhancing the efficiency and yield of the process. In this regard, bimetallic catalysts were developed by adding a secondary metal such as Re [22], Sn [23], Ge [24], Ir [25] and In [26] to Pt/Al_2O_3 catalyst. The third metal has also been added to the bimetallic catalysts to improve the function of catalysts, therefore, $Pt–Re–Ge/Al_2O_3$ [27], $Pt–Re–Ir/Al_2O_3$ [28], $Pt–Ir–Sn/Al_2O_3$ [29], and $Pt–Sn–In/Al_2O_3$ [30] are presented.

1.2. **Mode of operation of catalytic reforming units**

Catalysts are used extensively in chemical and petrochemical industry to increase the rate of reactions. Although catalysts are not consumed by the reaction itself, they may be inhibited, deactivated, or destroyed by secondary processes. Thus, replacing and regenerating of the catalyst seem unavoidable in catalytic units.

According to the catalyst regeneration procedure, catalytic reaction processes are mainly categorized in three modes of operation, including: semi-regenerative reformer (SR), cyclic regenerative reformer (CR), and continuous catalyst regenerative reformer (CCR).

In semi-regenerative reformer, fixed bed reactors operate continuously and the catalyst activity decreases due to the coke deposition. When the reactors reach end-of-cycle levels (once each 6–24 months) the reformers are shut down to regenerate the catalyst in situ. In the cyclic catalytic reformer unit, an extra spare or swing reactor exists, which, as well as other reactors, can be individually isolated. Thus, each reactor can be undergoing in situ regeneration while the other reactors are in operation. However, the cyclic catalytic reformer units are not very common, and rarely are used for naphtha reforming process.

Continuous catalyst regenerative reformer (CCR) is the most modern type of the catalytic reformers. In this unit, the catalysts move along the moving bed reactors and regenerate continuously in a special regenerator, then add to the operating reactors. This unit has advantages against traditional methods such as production of higher octane reformate even working with a low feed quality, long time working of the process for hydrogen demand, using catalyst with less stability but higher selectivity and yield, lower required recycle ratio and the lower operational pressure with high yield of hydrogen [32–34]. The design reformate octane number in this process is in the range of 95–108 [31].

1.3. **Thermally coupled reactor**

In recent years, thermally coupled reactors have been regarded to an important topic of so many articles in the literature. In this type of reactors, an exothermic reaction is considered as the heat source to drive an endothermic one. It should be considered that using the presented configuration leads to combination of two separate plants which indeed reduces the capital costs. It also contributes to energy saving which is extremely needed due to the environmental issues and climate problems.

Hunter and McGuire [35] were among the first ones who investigated the experimental coupling of endothermic and