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Effect of normal paraffins separation from naphtha on reaction kinetics for olefins and aromatics production

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ABSTRACT

The objective of this study is to investigate the effect of the normal paraffins (*n*-paraffins) separation by the simulated moving-bed (SMB) on reaction kinetics of the naphtha thermal cracking (NTC) and catalytic reforming (NCR) for the olefins and aromatics production, respectively. First a process simulation of the SMB unit integrated to the petrochemical complex (PCC) was performed. Chemical reaction kinetics of NTC and NCR were proposed and validated. And a retrofit PCC with the SMB unit (rPCC) was compared to a conventional PCC (cPCC) in terms of products composition, flow rate, and energy consumption. It was found that olefins and aromatics yields of NTC and NCR can increase by 14 wt% (41 kt/yr) and 11 wt% (127 kt/yr) for the naphtha capacity of 2475 kt/yr, respectively. However, the total energy consumption of rPCC increased by about 67.8 MW (or 25%) because of the desorbent recovery in the SMB unit.

1. Introduction

The paradigm of separations is changing. Factors like energy consumption, process performance or process environmental cleanness have become more and more of a major issue (Sá Gomes et al., 2009). The simulated moving-bed (SMB) process has been successfully applied to petrochemical separations such as *p*-xylene separation from its C_8 isomers, normal paraffins (*n*-paraffins) from branched and cyclic hydrocarbons, and olefins separation from paraffins (Sá Gomes et al., 2009). The MaxEne process, which is used to separate *n*-paraffins from naphtha, was developed by UOP to integrate refining and petrochemical facilities (UOP). MaxEne allows an increase of ethylene productivity with existing naphtha cracking units without making major changes to the existing equipment. *n*-Paraffins are preferred to be fed into the naphtha cracker to raise the yield of light olefins (ethylene and propylene). The catalytic reforming yield increases significantly when *n*-paraffins are removed from the feed. Therefore, the separated *n*- and non *n*-paraffins can be effectively applied to raw materials for olefins and aromatics production, respectively (Chang et al., 2005; Liu et al., 2009). *n*-Butane was used as a desorbent in the simulated moving-bed (SMB) unit for the separation of *n*-paraffins from C_5–C_{10} hydrocarbons (Liu et al., 2009). It may be of interest to evaluate technical feasibility as well as economical profitability for the integration of the SMB unit into an existing petrochemical plant.

Naphtha is a fraction of petroleum which typically constitutes 15–30 wt% of crude oil and boils between 30 °C and 200 °C. This complex mixture consists of hydrocarbon molecules with 5–12 carbon atoms, and it mainly includes paraffins, olefins, naphthenes, and aromatics (Rahimpour et al., 2013). Naphtha can be subdivided into 30–90 °C light naphtha (C_5 and C_6), 90–150 °C medium naphtha (C_7–C_9), and 150–200 °C heavy naphtha (C_9–C_{12}). In commercial practice, the medium naphtha is the most-preferred feed for catalytic reforming (Rodríguez and Ancheyta, 2011), while the light naphtha is suitable for thermal cracking (Belohlav et al., 2003). Basic petrochemicals such as ethylene, propylene, butadiene and aromatics like benzene, toluene, and xylene (BTX) are the main products of the petrochemical industry (Ren et al., 2009). Currently, most of them are produced via conventional routes such as the

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Abbreviations: ATC, annualized total cost; BTX, benzene, toluene, and xylene; CCR, continuous catalyst regenerative; cPCC, conventional petrochemical complex; CR, cyclic regenerative; H-HC, heavy hydrocarbons; L-HC, light hydrocarbons; NCR, naphtha catalytic reforming; NHT, naphtha hydro-treating; NTC, naphtha thermal cracking; *n*-paraffins, normal-paraffins; non *n*-paraffins, iso-paraffins, naphthenes, and aromatics; *i*-paraffins, iso-paraffins; PCC, petrochemical complex; PFD, process flow diagram; rPCC, retrofit petrochemical complex with SMB unit; SMB, simulated moving-bed; SR, semi-regenerative.

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Nomenclature

c_p	heat capacity (kJ/(kmol K))
d	reactor diameter (m)
D	distillate flow rate (t/h)
E_a	activation energy (kJ/mol)
F	molar flow rate (kmol/s)
$-\Delta H$	heat of reaction (kJ/mol)
i	component index
j	reaction index
k_0	pre-exponential factor ($\mathrm{kmol/m^3\,s\,Pa}^{\sum \alpha_i}$)
N	number of reactants
N_s	theoretical number of stages
p	partial pressure (Pa)
P_{butane}	*n*-butane purity (%)
Q	heat flow rate (kJ/s)
R	gas constant, J/(mol K) or molar reflux ratio
r	reaction rate (kmol/(m^3 s))
s	stoichiometric factor
T	temperature (K)
z	reactor length (m)

Greek letters

α_i	exponent of *i*th reactant
η	tray efficiency

reforming and cracking of naphtha, which are vital processes in petrochemical refineries (Ren et al., 2009). The significance of these industrial processes has induced researchers to investigate different aspects of both naphtha cracking and reforming, intensively (Rahimpour et al., 2013).

Naphtha thermal cracking (NTC) of hydrocarbons is the most important source for the production of olefins which are the main feedstock of the polymers industries (Niaei et al., 2004). Steam has been traditionally used to partially remove coke which causes several problems along the reactor such as low heat transfer and high pressure drop. Naphtha is usually the mixture of manifold hydrocarbons, and each hydrocarbon has complex reactions in the cracking process. The cracking performance and products yield depend on the composition and the carbon number of *n*-paraffins, *iso*-paraffins (*i*-paraffins), naphthenes and aromatics (Liu et al., 2009). In the typical reaction condition, *n*-paraffins in naphtha contribute most to the ethylene in the products. *i*-Paraffins are the main sources of propylene. Naphthenes mainly produce butadiene, and aromatics can hardly produce olefins (Liu et al., 2009).

The naphtha catalytic reforming (NCR) unit occupies a key position in refineries to obtain high octane gasoline and BTX components which are the basic substances of petrochemical industries (Gyngazova et al., 2011; Iranshahi et al., 2013; Rahimpour et al., 2013; Rodríguez and Ancheyta, 2011). Hydrogen is a valuable by-product of the naphtha catalytic reforming process, which in most refineries is used for the hydrocracking, hydrotreating, and other hydrogen-consuming processes. The NCR is accomplished mainly by converting of *n*-paraffins and naphthenes in naphtha to *i*-paraffins and aromatics over bifunctional catalysts. A large number of reactions take place during the catalytic reforming process such as alkylcyclohexane, dehydrogenation, dehydrocyclization to alkylcyclopentane, aromatization, isomerization, transalkylation, hydrodealkylation, hydrocracking, and coke formation (Rodríguez and Ancheyta, 2011). Industrial catalysts used in catalytic reforming units consist of γ-Al_2O_3 support. Some metals such as Pt, Re, Ge, Ir, and Sn promote dehydrogenation reactions, and acid function such as chlorine increases isomerization and dehydrocyclization reactions (Rahimpour et al., 2013). All reactions are desirable except the hydrocracking because it converts valuable compounds to light gases.

Reaction kinetics modeling of NTC and NCR for olefins and aromatics productions, respectively, is an attractive tool for feedstock selecting and mixing, production planning, optimal reactor controlling, reactor designing and revamping, and process modification (Belohlav et al., 2003). The large number of reactions and hundreds of components taking part in the actual reaction system make this a rather complex problem. An effective reaction kinetics model must properly represent all major types of reactions and at least account for the most important classes of chemical species present in the reaction mixture. Recently, various kinetics models for NTC (Belohlav et al., 2003; Jia et al., 2009; Keyvanloo et al., 2012; Niaei et al., 2004; Sadrameli and Green, 2005; Seifzadeh Haghighi et al., 2013) and NCR (Gyngazova et al., 2011; Hou et al., 2006; Iranshahi et al., 2013; Meidanshahi et al., 2011; Rahimpour et al., 2013; Rodríguez and Ancheyta, 2011; Zagoruiko et al., 2014) have been developed.

There are several approaches for reaction kinetics modeling of the NTC process: empirical (Jia et al., 2009), semi-empirical (Sadrameli and Green, 2005), free radical (Keyvanloo et al., 2012; Niaei et al., 2004), and molecular mechanism (Belohlav et al., 2003; Seifzadeh Haghighi et al., 2013). Jia et al. (2009) evaluated the desirability of the Wiehe's model (Wiehe, 1993) in describing the compositional changes of various oils in in situ processes. Sadrameli and Green (2005) applied an analytical semi-empirical model of pyrolysis to NTC. Niaei et al. (2004) used a rigorous kinetics model based on free-radical chain reactions for the decomposition of the naphtha feed. Keyvanloo et al. (2012) developed a semi-mechanistic kinetics model based on free radical chain reactions containing 4 pseudo components and 96 reactions. Belohlav et al. (2003) involved free radical reactions and a set of pure and formal molecular reactions as a kinetics model of NTC. Seifzadeh Haghighi et al. (2013) proposed a set of 20 molecular reactions for naphtha pyrolysis, which contained one primary decomposition and 19 secondary reactions.

Taskar and Riggs (1997) modeled and optimized a semi-regenerative catalytic naphtha reformer using a detailed kinetics scheme involving 35 pseudo components connected by a network of 36 reactions in the C_5–C_{10} range. Weifeng et al. (2007) applied an 18-lump reaction kinetics model for the naphtha continuous catalytic reforming. Gyngazova et al. (2011) developed an NCR kinetics model based on components aggregation into pseudo components according to their activity. Meidanshahi et al. (2011) used four dominant idealized reactions, which were dehydrogenation, dehydrocyclization, hydrocrackings of naphthenes and paraffins, and hydrodealkylation of toluene. Rodríguez and Ancheyta (2011) combined the simplicity of the lumped model with the complexity of the most advanced model to predict a detailed composition of the reformate. Iranshahi et al. (2013) applied a new kinetics model including 32 pseudo components with 84 reactions in a novel thermally coupled reactor in a continuous catalytic regenerative naphtha reforming process.

It should be noticed that a compromise between the simplified and the rigorous reaction models is necessary to effectively represent real complex reactions within a reasonable calculation time. In this study, two chemical reaction models of NTC and NCR are proposed, which consist of 83 and 86 reactions, respectively. The kinetics models are solved conveniently in the Aspen Plus platform (AspenTech, USA, 2013) that contains the thermodynamic database of hydrocarbon components. The SMB unit is directly connected to these NTC and NCR reactors.

The objective of this study is to investigate the effects of naphtha separation into *n*- and non *n*-paraffins on the NTC and NCR reaction kinetics in the retrofit petrochemical complex (rPCC) with the SMB unit. To achieve this objective, first a process model of the SMB unit