Journal of the Taiwan Institute of Chemical Engineers xxx (2013) xxx–xxx

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Chemical and Biomolecular Science and Technology

Experimental and modeling study of a catalytic reforming unit

Sorood Zahedi Abghari [a], Asghar Alizadehdakhel [b,*], Reza Seif Mohaddecy [a], Ammar Abdulaziz Alsairafi [c]

[a] Research Institute of Petroleum Industry (RIPI), Tehran, Iran
[b] Islamic Azad University, Rasht branch, Rasht, Iran
[c] Faculty of Mechanical Engineering, College of Engineering and Petroleum, Kuwait University, Kuwait

ARTICLE INFO

Article history:
Received 14 May 2013
Received in revised form 28 October 2013
Accepted 1 November 2013
Available online xxx

Keywords:
Catalytic reforming
CRU
Modeling
Kinetic
Reactor

ABSTRACT

An experimental and modeling investigation of catalytic reforming of naphtha in a pilot-scale packed bed reactor is described in the present work. The effects of operating conditions on the reactor products were studied utilizing statistical method. A kinetic model including three pseudo species and eight light components was proposed and the coefficients of reaction rate equations were obtained. Good agreement was achieved between the proposed model results and the experimental measurements. Different regions of the reactor with different growth rate of pseudo species and light components were detected by analyzing concentration profiles along the reactor. It was concluded that the precision of the developed kinetic model make it suitable for implementing in a reactor model to predict the analysis of products of an industrial catalytic reforming unit. This is crucial for optimum operation of the industrial unit and its downstream processes, including steam reforming and hydrocracking units which uses light component streams of catalytic reforming process as feed stock or part of their inputs streams. Also, the achieved results about the effects of different operating conditions on the reactor productivity, may offer several clues for improvement of control philosophy, startup and shutdown procedure of this process.

1. Introduction

Catalytic reforming process is used in many refineries in which high octane gasoline is produced from naphtha. Hydrogen and liquefied petroleum gas (LPG) are also produced in this process as by-products [1]. The temperature and pressure of the reactor, the flow rate and composition of the feed and molar ratio of the recycled hydrogen per injected feed are always considered as the main operating variables. An accurate model is an essential tool for studying such a process, particularly for cases where the effects of operating conditions on the reactor products are concerned [2]. Kinetics of chemical reactions has been considered a vital step in rigorous modeling and different kinetic models have been developed. Smith [3] as a pioneer developed a kinetic model containing five species as hydrogen, methane, ethane, propane and butanes and three lumped components. The three lumped species were aromatic, naphthenes and paraffins. Lumped species and other components were connected to each other by some reactions such as aromatization, dehydrocyclisation and hydrocracking through reaction network in the oldest catalytic reforming kinetic model. Krane et al. [4] developed a kinetic network containing 53 reactions and twenty lumped species. Aromatics, naphthenes and paraffins with six to ten carbons were considered as the lumped species and the reaction network included dehydrocyclisation, dehydrogenation, and hydroisomerisation of aromatics and naphthenes. Zhorov et al. [5] developed a six lumped kinetic model where the effects of carbon number were only considered in definition of naphthenic lumped species. Ramage et al. [6] were the pioneer researchers who used the Hougen–Watson type rate equations in the development of kinetic models. Aromatics, naphthenes and paraffins with six, seven and more than eight carbons were defined as nine discrete lumped components. Paraffins with less than five carbons were also defined as the products of hydrocracking reactions. Later, Marin and Froment [7] developed the kinetic model of Ramage et al. [6] and split heavier hydrocarbons to more lumped species.

Developing a reliable kinetic model that can accurately simulate reactions and predict product distributions of the hydrocracking process is very challenging both from a commercial and a research viewpoint. Vathi and Chaudhuri [8], Arani et al. [9] and Rodriguez and Ancheyta [10] were the researchers who worked on this process and developed different kinetic models

* Corresponding author at: Chemical Engineering Department, Islamic Azad University-Rasht branch, Iran. Tel.: +98 9117105287; fax: +98 131 7229629.
E-mail addresses: Alizadeh@iaurasht.ac.ir, Asghar.Alizadeh@gmail.com, A_Alizadehdakhel@yahoo.com (A. Alizadehdakhel).

1876-1070/$ – see front matter © 2013 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jtice.2013.11.001

Nomenclature

C_i	concentration, kmol m^{-3}
C_p	specific heat capacity, J/mol K
D	diffusivity coefficient, m^2 s^{-1}
d_b, d_p	diameter, cm
E_i	activation energy of species i, kJ $kmol^{-1}$
F_i	molar flow rate of Species i, mol h^{-1}
g	gravity acceleration, m s^{-2}
h_i	enthalpy of species i, kJ kg^{-1}
h_i^0	formation enthalpy of species i, kJ $kmol^{-1}$
H	total enthalpy, kJ kg^{-1}
$\vec{J}_i$	diffusion flux of species i, kg m^{-2} s^{-1}
K_{eq1}	equilibrium constant of the first reaction, kPa^3
K_{eq2}	equilibrium constant of the second reaction, kPa^{-1}
k_1	rate constant for the first forward reaction, mol/(kPa kgCatalyst h)
k_2	rate constant for the second forward reaction, mol/(kPa^2 kgCatalyst h)
k_{3i}, k_{4i}	the rate constants of hydrocrackings
k_{eff}, k_g, k_p	thermal conductivity, kJ m^{-1} K^{-1}
M_i	molecular weight of species i, kg $kmol^{-1}$
P	pressure, Pa
q	heat flux, kJ m^{-2} s^{-1}
R	universal gas constant, kJ $kmol^{-1}$ K^{-1}
R_i	rate of generation/consumption of species i, kmol m^{-3} s^{-1}
S	momentum source term, kg m^{-2} s^{-2}
S_R	energy source, kJ m^{-3} s^{-1}
T	temperature, K
x_i	mass fraction of species i
X	the operating variables

Greek Letters

ν	velocity, m s^{-1}
ρ	density, kg m^{-3}
μ	viscosity, kg m^{-1} s^{-1}
ε	porosity
α	constant of statistical model
β	the parameter of statistical model

Subscripts

eff	effective
g	gas
p	particle

with different number of pseudo component species. Recently, Wei et al. [11] developed an approach to model detailed kinetic reactions of the catalytic reforming unit including catalyst deactivation and by introducing a number of representative pseudo components by Monte Carlo simulation. Several kinetic researches on catalytic reforming unit (CRU) were carried out based on fundamental kinetic modeling theories [12]. The developed models have the capability of calculating the process variables without any dependence on the feed species. The complexity of this kind of kinetic models makes them difficult to use in more realistic complicated models in the computational fluid dynamics (CFD) simulations or in process optimization procedures. The optimization of the CRU is an example of the application of the kinetic models which was studied by some researchers to determine the best operating conditions for obtaining maximum possible profit [13–16]. In addition to rigorous models, statistical models are also used to declare the main and the interaction effects of different operating variables on the output of processes [17–19] or to optimize the processes [17,18]. They are also used as a part of some methods of design of experiments to analyze the obtained results, in pilot scales [19].

In most of the previous researches on the catalytic reforming process, the main and the interaction effects of operating variables on reactor outlet were not determined over a wide operating range. Also, different kinetic models with different aspects were developed which had different convergence rate and accuracy. Some of them had high accuracy and low convergence rate and the others were not precise but had enough convergence rate.

In the present work, a series of experiments were designed and carried out on a catalytic reforming pilot plant based on the experimental design methodology. The main and the interaction effects of operating conditions on the reactor performance were studied by analyzing the results. Moreover, a kinetic model was developed and the concentration profiles of the pseudo components and light hydrocarbons along the reactor were investigated.

2. Materials and methods

2.1. Experimental apparatus and procedure

The experiments were conducted in the pilot plant demonstrated in Fig. 1 that was designed and setup to perform catalytic reforming of naphtha. The reactor of this pilot plant was a 220 cm^3 vessel with 20 cm^3 catalyst that could operate at pressures below 50 bar and temperatures less than 600 °C. As shown in the figure, hydrocarbon feed and hydrogen are mixed in certain ratios before entering the reactor. The mixture then enters the reactor with definite pressure and reaches a predetermined temperature for performing the catalytic reforming reactions. Reactor products pass through a condenser and the light gases are separated from liquid products using two successive separators. Light gases are sent to an online gas chromatography (GC) and liquid products are gathered in a bottle and sent for analysis by an offline GC. The name and the characteristic of the gas and liquid GC analyzer are given in Table 1.

Nitrogen and air streams are used for regenerating the catalysts.

The typical compositions and characteristics of the used feed are given in Table 2. Fresh catalyst from the catalytic reforming unit of Tehran refinery was loaded into the reactor. The X-ray diffraction (XRD) and X-ray fluorescence (XRF) analysis showed that the chosen catalyst is a bifunctional catalyst consisting of Pt, Rhenium and has γ-Al_2O_3 structure.

2.2. Experimental design and statistical analysis

Thirty two experiments were conducted according to a full factorial design methodology to determine the effects of process variables, *i.e.*, temperature, pressure and feed flow rate, on the yield and composition of gasoline and light hydrocarbons. The coded and natural levels of design factors and the results of the experiments are respectively demonstrated in Tables 3 and 4. Thirty two main experiments and three replications were performed. The replicated tests are designed and carried out to check the replicability and catalyst stability of the pilot plant. Little errors between the main experiments and the replications proved the replicability of the pilot.

Please cite this article in press as: Abghari SZ, et al. Experimental and modeling study of a catalytic reforming unit. J Taiwan Inst Chem Eng (2013), http://dx.doi.org/10.1016/j.jtice.2013.11.001