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Applying new kinetic and deactivation models in simulation of a novel thermally coupled reactor in continuous catalytic regenerative naphtha process

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HIGHLIGHTS

- A novel thermally coupled reactor in CCR naphtha reforming process is modeled.
- A new kinetic model involving 32 pseudo-component and 84 reactions is proposed.
- Modeling is carried out in two dimensions considering a new deactivation model.
- Nitrobenzene hydrogenation is employed as the heat source.
- The aromatics and hydrogen increase 92 and 190 kmol/h, respectively.

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ABSTRACT

Naphtha reforming unit occupies a key position in refineries to obtain high octane gasoline and BTX (benzene, toluene, and xylene) components which are the basic substances of petrochemical industries. In this study, a novel thermally coupled reactor for continuous catalytic regenerative naphtha process has been proposed to boost the aromatics and hydrogen productions and to produce aniline as a valuable product. In this configuration, the naphtha reforming (endothermic reaction) and nitrobenzene hydrogenation (exothermic reaction) reactions are carried out simultaneously. According to complex kinetic of reforming process a new kinetic model including 32 pseudo components with 84 reactions is proposed. As well, a novel catalyst deactivation model considering acidic and metallic functions of catalyst is presented to predict the behavior of the reactions which subject to the catalyst deactivation. Mathematical modeling of coupled reactor is considered in two dimensions (radial and axial directions). In order to assess the performance of the new configuration, the modeling results of thermally coupled reactor (TCR) is compared with the obtained results of conventional reactor (CR). By employing coupled reactors, aromatics production rates is improved acceptably (about 92 kmol/h in comparison with conventional system), and the amount of produced hydrogen is increased greatly (190 kmol/h compared to CR).

1. Introduction

1.1. Naphtha reforming

In order to fulfill environmental legislations, octane number of the produced gasoline should be increased to an acceptable level. Catalytic naphtha reforming process is considered as a proper choice to reach this goal [1]. The significance of the catalytic naphtha reforming process in the petroleum refinery and petrochemical industry contributes to continuous evolution of this technology. This progress is observed in elucidating better kinetic and deactivation mechanisms with higher predictive ability, as well as presenting more efficient reactor setups for improving the production yield and operating conditions.

Naphtha feedstock is a complex mixture of different hydrocarbons which undergo various reactions. Considering all of these components and reactions in one kinetic model is a very complex task. In order to solve this problem, “lumped” models have been presented in which the large number of chemical components is classified to smaller set of kinetic lumps. The first significant

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Nomenclature

a_i	catalyst activity in endothermic reaction side
a_A	acidic function activity in endothermic reaction side
a_{C_A}	acidic function activity for coke formation in endothermic reaction side
a_{C_M}	metallic function activity for coke formation in endothermic reaction side
a_M	metallic function activity in endothermic reaction side
a'	catalyst activity in exothermic reaction side
A_r	cross section area of reactor in radial direction (m^2)
A_p	available side area for heat transfer (m^2)
A'	frequency factor
C	concentration in endothermic reaction side ($\mathrm{kmol\ m^{-3}}$)
C^{Exo}	concentration in exothermic reaction side ($\mathrm{kmol\ m^{-3}}$)
C_{ACP}	alkyl-cyclopentane concentration ($\mathrm{kmol\ m^{-3}}$)
C_{C_A}	coke weight fraction on acidic function of catalyst in endothermic reaction side ($\mathrm{kg\ kgcat^{-1}}$)
C_{C_M}	coke weight fraction on metallic function of catalyst in endothermic reaction side ($\mathrm{kg\ kgcat^{-1}}$)
C_{C-a}^{Exo}	coke weight fraction on active sites in exothermic reaction side ($\mathrm{kg\ kgcat^{-1}}$)
C_p	specific heat capacity at constant pressure in endothermic reaction side ($\mathrm{kJ\ kmol^{-1}\ K^{-1}}$)
C_P^{Exo}	specific heat capacity at constant pressure in exothermic reaction side ($\mathrm{kJ\ kmol^{-1}\ K^{-1}}$)
C_v	specific heat capacity at constant volume in endothermic reaction side ($\mathrm{kJ\ kmol^{-1}\ K^{-1}}$)
C_v^{Exo}	specific heat capacity at constant volume in exothermic reaction side ($\mathrm{kJ\ kmol^{-1}\ K^{-1}}$)
C_T	total concentration in endothermic reaction side ($\mathrm{kmol\ m^{-3}}$)
C_T^{Exo}	total concentration in exothermic reaction side ($\mathrm{kmol\ m^{-3}}$)
d_p	particle diameter (m)
dr	control volume thickness in radial direction (m)
dz	control volume length (m)
D_e	effective diffusivity ($\mathrm{m^2\ s^{-1}}$)
E_c	coke formation activation energy in endothermic reaction side ($\mathrm{J\ mol^{-1}}$)
E'	activation energy of the hydrogenation of nitrobenzene ($\mathrm{kJ\ mol^{-1}}$)
$E_{A,C-a}$	activation energy ($\mathrm{kJ\ mol^{-1}}$)
F_j	molar flow rate of component j in endothermic reaction side ($\mathrm{kmol\ h^{-1}}$)
F_j^{Exo}	molar flow rate of component j in exothermic reaction side ($\mathrm{kmol\ h^{-1}}$)
F_T	total molar flow rate in endothermic reaction side ($\mathrm{kmol\ h^{-1}}$)
F_T^{Exo}	total molar flow rate in exothermic reaction side ($\mathrm{kmol\ h^{-1}}$)
H_j	enthalpy of component j in endothermic reaction side ($\mathrm{J\ mol^{-1}}$)
H_j^{Exo}	enthalpy of component j in exothermic reaction side ($\mathrm{J\ mol^{-1}}$)
k	thermal conductivity ($\mathrm{W\ m^{-1}\ K^{-1}}$)
k_{C_A}	constant of deactivation equation for acidic function in endothermic reaction side $\left(\mathrm{kg\ kgcat^{-1}\ kPa_1^n\ m^{1.5}\ kmol^{-1.5}}\right)$
k_{C_M}	constant of deactivation equation for metallic function in endothermic reaction side $\left(\mathrm{kg\ kgcat^{-1}\ kPa_1^n\ m^{1.5}\ kmol^{-1.5}}\right)$
$k_{C-a,0}$	constant of deactivation equation in exothermic reaction side ($\mathrm{kPa^{(m_2-m_1)}\ s^{-1}}$)
$k_{dea1,H}$	constant of deactivation equation in exothermic reaction side

$k_{dea2,H}$	constant of deactivation equation in exothermic reaction side
$k_{dea3,H}$	constant of deactivation equation in exothermic reaction side
$k_{dea,C-a}$	constant of deactivation equation in exothermic reaction side
k_{eff}	effective thermal conductivity ($\mathrm{W\ m^{-1}\ k^{-1}}$)
k_{in}	reaction rate constant for endothermic reaction (in)
K_{in}	equilibrium constant for endothermic reaction (in)
k'	reaction rate constant for exothermic reaction ($\mathrm{mol\ kg^{-1}\ s^{-1}}$)
K_{NB}	adsorption constant of nitrobenzene ($\mathrm{Pa^{-1}}$)
K_{H_2}	adsorption constant of hydrogen ($\mathrm{Pa^{-0.5}}$)
L	length of reactor (m)
m	number of reactions in endothermic reaction side
M_j	molecular weight of component j ($\mathrm{kg\ kmol^{-1}}$)
M	mean molecular weight in the flow ($\mathrm{kg\ kmol^{-1}}$)
n	number of components in endothermic reaction side
n_1	constant of deactivation equation in endothermic reaction side
n_2	constant of deactivation equation in endothermic reaction side
n_A	acidic function activity power number in endothermic reactionside
n_{CA}	acidic function activity power number in endothermic reaction side
n_M	metallic function activity power number in endothermic reaction side
n_{C_M}	metallic function activity power number in endothermic reaction side
n'	number of components in exothermic reaction side
N_j	molar flux of component j ($\mathrm{kmol\ m^{-2}\ h^{-1}}$)
P	total pressure (kPa)
P_{A_n}	partial pressure of n carbon aromatic (kPa)
P_{ACH_n}	partial pressure of n carbon alkyl-cyclohexane (kPa)
P_{ACP_n}	partial pressure of n carbon alkyl-cyclopentane (kPa)
P_{H_2}	partial pressure of hydrogen in endothermic reaction side (kPa)
P_{H2}	partial pressure of hydrogen in exothermic reaction side (Pa)
P_{IP_n}	partial pressure of n carbon iso-paraffin (kPa)
P_{NB}	partial pressure of nitrobenzene (Pa)
P_{NP_n}	partial pressure of n carbon normal-paraffin (kPa)
r	radius (m)
r_i	rate of ith reaction ($\mathrm{kmol\ kgcat^{-1}\ h^{-1}}$)
r_{in}	rate of inth reaction ($\mathrm{kmol\ kgcat^{-1}\ h^{-1}}$)
r'	rate of hydrogenation of nitrobenzene reaction ($\mathrm{mol\ kgcat^{-1}\ s^{-1}}$)
r_C^o	rate of coke formation on fresh catalyst in endothermic reaction side ($\mathrm{kg\ kgcat^{-1}\ h^{-1}}$)
r_{C_A}	rate of coke formation on acidic function of catalyst in endothermic reaction side ($\mathrm{kg\ kgcat^{-1}\ h^{-1}}$)
r_{C_M}	rate of coke formation on metallic function of catalyst in endothermic reaction side ($\mathrm{kg\ kgcat^{-1}\ h^{-1}}$)
r'_{C-a}	rate of coke formation on active sites in exothermic reaction side ($\mathrm{kg\ kgcat^{-1}\ s^{-1}}$)
R	gas constant ($\mathrm{J\ mol^{-1}\ K^{-1}}$)
R_i	inner diameter (m)
R_o	outer diameter (m)
S_a	specific surface ($\mathrm{m^2\ g^{-1}}$)
T	temperature of endothermic reaction side (K)
T^{Exo}	temperature of exothermic reaction side (K)
U	overall heat transfer coefficient ($\mathrm{W\ m^{-2}\ K^{-1}}$)
U_j	internal energy of component j ($\mathrm{J\ mol^{-1}}$)
u_r	radial velocity in endothermic reaction side ($\mathrm{m\ s^{-1}}$)