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Conversion enhancement of heavy reformates into xylenes by optimal design of a novel radial flow packed bed reactor, applying a detailed kinetic model

N. Hamedi[a], T. Tohidian[a], M.R. Rahimpour[a,*], D. Iranshahi[b], S. Raeissi[a]

[a] *Department of Chemical Engineering, School of Chemical and Petroleum Engineering, Shiraz University, Shiraz 71345, Iran*
[b] *Department of Chemical Engineering, Amirkabir University of Technology, No. 424, Hafez Avenue, Tehran 15914, Iran*

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ABSTRACT

Xylenes are aromatic hydrocarbons naturally present in petroleum and crude oil. Since market demand has shown a growing tendency toward xylenes consumption, investigators have been seeking for more efficient ways of their production by converting surplus toluene and less useful heavy aromatics to more valuable xylenes by means of disproportionation/transalkylation reactions.

In this study, a novel radial-flow packed bed reactor configuration has been proposed for transalkylation reactions owing to its remarkably lower pressure drop in comparison to axial flow packed bed reactors. According to the complex nature of the feedstock, an accomplished reaction network based on 18 pseudo-components and 39 reactions was applied to design the reactor more reliably. Afterwards, the differential evolution (DE) method was used in order to optimize the operating conditions of the proposed reactor design. Finally, the performance of the optimized reactor was compared with that of an optimized conventional axial flow packed bed reactor to ascertain the superiority of the proposed reactor configuration.

1. Introduction

Aromatic compounds are of great importance in petrochemical industries as intermediate materials. The final products derived from such fragrant compounds have a wide variety of applications from domestic and agricultural areas to pharmaceutical and industrial usages. Among different aromatics, benzene (B), toluene (TOL), and xylenes with the acronym of BTX are the most valuable ones (Tsai et al., 1999).

Catalytic reforming and naphtha pyrolysis are considered as the most commonly used processes that lead to the coproduction of benzene, TOL, xylenes, and their derivatives

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Abbreviations: A_{10}, aromatic with 10 carbons; A_9, aromatic with 9 carbons; A_8, aromatic with 8 carbons; B, benzene; BTX, benzene-TOL-xylenes; CAFR, conventional axial flow reactor; CC, crossover constant; CCR, continuous catalytic reforming; CR, conventional reactor; DE, differential evolution; EB, ethylbenzene; FFSR, feed flow scale up ratio; MEB, methylethylbenzene; MX, meta xylene; N_6, naphthene with 6 carbons; N_7, naphthene with 7 carbons; NP, number of populations; OAFR, optimized axial flow reactor; OF, objective function; ORFR, optimized radial flow reactor; OX, ortho xylene; P_1, paraffin with 1 carbon; P_2, paraffin with 2 carbons; P_3, paraffin with 3 carbons; P_4, paraffin with 4 carbons; P_5, paraffin with 5 carbons; PB, propylbenzene; PET, poly ethylene teraphthalate; PTA, purified terephthalic acid; PX, para xylene; RFR, radial flow reactor; SF, scaling factor; TeMB, tetramethylbenzene; TMB, trimethylbenzene; TOL, toluene; TOS, time on stream; Xs, xylenes.

* *Corresponding author*. Tel.: +98 711 2303071; fax: +98 711 6287294.
E-mail address: rahimpor@shirazu.ac.ir (M.R. Rahimpour).

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Nomenclature

A	catalyst activity
A_c	cross sectional area of reactor (m^2)
C_T	total concentration ($kmol\,m^{-3}$)
C_i	coefficients of the correlations for heat capacity and viscosity estimation
C_j	concentration of component j ($kmol\,m^{-3}$)
C_{j0}	inlet concentration of component j ($kmol\,m^{-3}$)
C_p	specific heat capacity ($kJ\,kmol^{-1}\,K^{-1}$)
D_{ej}	effective diffusivity of component j in the gas mixture ($m^2\,s^{-1}$)
d_p	particle diameter (m)
E_i	activation energy for ith reaction ($kJ\,kmol^{-1}$)
F_i	molar flow rate of ith component ($mol\,s^{-1}$)
K	thermal conductivity ($W\,m^{-1}\,s^{-1}$)
K_{0i}	frequency factor for reactions 1–20 and 32 ($mol\,Pa^{-2}\,s^{-1}\,kg\,cat^{-1}$) ($i = 1$–$20$ and $i = 32$)
K_{0i}	frequency factor for reactions 21 and 22 ($mol\,Pa^{-4}\,s^{-1}\,kg\,cat^{-1}$) ($i = 21$ and 22)
K_{0i}	frequency factor for reactions 23–31 and 33–39 ($mol\,Pa^{-1}\,s^{-1}\,kg\,cat^{-1}$) ($i = 23$–$31$ and $i = 33$–39)
K_{ei}	chemical equilibrium constant
k_{eff}	thermal conductivity of the gas-phase ($W\,m^{-1}\,K^{-1}$)
K_i	rate constant for reactions 1–20 and 32 ($mol\,Pa^{-2}\,s^{-1}\,kg\,cat^{-1}$) ($i = 1$–$20$ and $i = 32$)
K_i	rate constant for reactions 21 and 22 ($mol\,Pa^{-4}\,s^{-1}\,kg\,cat^{-1}$) ($i = 21$ and 22)
K_i	rate constant for reactions 23–31 and 33–39 ($mol\,Pa^{-1}\,s^{-1}\,kg\,cat^{-1}$) ($i = 23$–$31$ and $i = 33$–39)
L	length of the reactor (m)
LOD	length/diameter ratio of the reactor
m	number of reaction
N	number of components
P	total pressure (Pa)
P_i	partial pressure of ith component (Pa)
Q	volumetric flow rate ($m^3\,s^{-1}$)
R	radius of the reactor (m)
R	gas constant ($kJ\,kmol^{-1}\,K^{-1}$)
r_i	rate of reaction for ith reaction ($mol\,kg\,cat^{-1}\,s^{-1}$)
T	temperature of gas phase (K)
T_0	standard temperature (K)
T_i	inlet temperature (K)
U_z	axial velocity ($m\,s^{-1}$)
U_r	radial velocity ($m\,s^{-1}$)
X_{A9}	A_9 conversion
Y	yield

Greek letter

ε	void fraction of catalyst bed
μ	viscosity of gas phase ($kg\,m^{-1}\,s^{-1}$)
υ_{ij}	stoichiometric coefficient of component i in reaction j
ρ_B	reactor bulk density ($kg\,m^{-3}$)
ΔC_p	specific heat capacity change of the reactions ($kJ\,kmol^{-1}\,K^{-1}$)
ΔH_0	heat of reaction in standard condition ($kJ\,kmol^{-1}$)
ΔH	heat of reaction ($kJ\,kmol^{-1}$)
ΔG_0	standard Gibbs free energy change of the reactions ($kJ\,kmol^{-1}$)
ΔG_i	Gibbs free energy change of the reactions ($kJ\,kmol^{-1}$)
ΔZ	control volume length (m)
ϕ_s	sphericity

Superscripts and subscripts

C	center pipe
Calculated	calculated data
E	exit
I	numerator for reaction
Inlet	inlet condition
J	numerator for component
Outlet	outlet condition
Plant	plant data

(Tsai et al., 1999; Waziri et al., 2010). Products obtained from either of the processes have a greater portion of TOL in comparison to xylenes and benzene. Due to the increasing demand toward xylenes consumption, it is necessary to investigate more efficient ways of TOL conversion to more valuable xylenes (Tsai et al., 1999; Waziri et al., 2010). In this regard, xylenes production via disproportionation/transalkylation of TOL and heavy reformates is a promising technology that has better control on thermodynamic constraints of the system (Odedairo and Al-Khattaf, 2011).

Xylenes are mostly used as solvents in the manufacturing of adhesives, coatings, paints, and agricultural sprays. In addition, they are common solvents in printing, rubber, and leather industries (Kandyala et al., 2010). Xylene compounds, sometimes called xylols, exist in three isomer forms including meta-xylene (MX), ortho-xylene (OX), and para-xylene (PX). Among them, PX has the largest market demand (Yeong et al., 2010). It is the principal feedstock in the manufacturing of purified terephthalic acid (PTA) and dimethyl terephthalate, both of which are intermediate materials in the production process of polyester fibers, resins, films, and polyethylene terephthalate (PET) (Tukur and Al-Khattaf, 2011; Waziri et al., 2010; Yeong et al., 2010). Moreover, PX isomer is the raw material for the production of di-paraxylene, herbicides, and plasticizers (Tukur and Al-Khattaf, 2011; Xu et al., 2007).

Bawa et al. (1973) were the first group who investigated the disproportionation reaction of TOL in gas phase over a metal exchanged molecular sieve catalyst. They observed that the acidity and degree of ion exchange can remarkably affect the activity of such catalysts.

Dumitriua et al. (1996) conducted the transalkylation reaction of TOL with trimethylbenzenes (TMBs) over AlPO-5 catalyst. The results attributed the transalkylation reactions to stronger acid sites, and showed that the active sites with weaker acidity strength are responsible for isomerization of xylenes and TMBs. Cejka and Wichterlovab (2002) made an attempt to identify key parameters controlling the activity and selectivity of zeolites in the transalkylation of TOL with TMB. They indicated that both properties depend strongly on the concentration of active sites and zeolite structure.

Thereafter, Iliyas and Al-Khattaf (2004) did a research to investigate the effect of reaction conditions on the selectivity of xylenes transformation over USY zeolite in a riser simulator. Their study indicated that both isomerization and