



Modeling, numerical analysis and simulation

Modeling and sensitivity analysis of styrene monomer production process and investigation of catalyst behavior

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ABSTRACT

In this work, a fundamental kinetic model based upon the Hougen–Watson non-porosity formalism was derived and used to simulate dehydrogenation and oxidation axial flow reactors. In addition, partial pressure profiles of components during styrene production process inside porous catalyst were obtained using Dusty-Gas model. The preservation equations are adopted to calculate temperature and flow profiles in the reactors filled with iron–potassium promoted catalyst pellets. The presented mathematical model for ethylbenzene dehydrogenation consists of nonlinear simultaneous differential equations with multiple dependent variables. Simulation results such as selectivity and operating temperature for different conventional catalysts have been presented and compared with those of a new introduced catalyst based on Fe_2O_3 . Comparison of simulation results with experimentally observed ones shows that the model can precisely predict behavior of the industrial unit. Furthermore, the obtained results show that application of the new introduced catalyst increase ethylbenzene conversion and decrease necessary inlet temperature.

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1. Introduction

Styrene (ST) is the second most important monomers in the chemical industries. In 2002, more than 2.5×10^7 MT/year of styrene monomer was produced worldwide (Product Focus: Styrene, 2002). The styrene production process was originally developed in the 1930s by BASF (Germany) and Dow Chemical (USA). The major commercial process for the production of styrene is the dehydrogenation of ethylbenzene (EB), which accounts for 85% of the commercial production (James & Castor, 1994). The dehydrogenation process mostly consists of the catalytic reaction of ethylbenzene. This process involves a highly endothermic reaction carried out in the vapor phase over solid catalyst particles. Steam, supplies the necessary reaction heat, prevents excessive coking or carbon formation, shifts the equilibrium of the reversible reaction toward the products, and cleans the catalyst from any existing carbon. The potassium-promoted iron oxide catalyst has been extensively used for styrene production (Coulter, Goodman, & Moore, 1995).

There are several common dehydrogenation methods for the production of styrene monomer from ethylbenzene including adiabatic dehydrogenation of the ethylbenzene, isothermal dehydrogenation of the ethylbenzene, simultaneously producing styrene and oxidation of propylene, membranous process for

dehydrogenation of ethylbenzene and dehydrogenation and oxidation of ethylbenzene using carbon dioxide. However, adiabatic dehydrogenation of the ethylbenzene is the most widely used method (Chon, 2003; Mcketa, 1996; Sun, Qin, Chen, & Wang, 2004; Tabriz Petrochemical Complex Operating Manual, 1993). Thanks to the recent enhancements in technology, nowadays further developments in the efficiency of the above-mentioned processes have occurred.

In a recent study, Gonzalez and Moronta (2004) reported the dehydrogenation of ethylbenzene over natural clay and its pillared aluminum form impregnated with either cobalt nitrate or cobalt acetate. Although the total conversion was less than 20% for these catalysts in their unreduced forms, the co-impregnated natural clay showed a higher conversion than natural Al-pillared and co-impregnated aluminum-pillared clays. Moreover, those catalysts derived from the cobalt nitrate salt were more active than those obtained using the cobalt acetate salt. Gonzalez and Moronta has demonstrated that incorporation of cobalt has been significantly influenced by the nature of the starting clay, being the Co content in T_1 natural clay higher than Al-PILCT1 clay and this strongly effect governed the catalytic process via Lewis–Bronsted acidity more than gallery access. The most active catalysts were those prepared using cobalt nitrate, but due to coke formation those prepared from cobalt acetate were less active than the others. However, all catalysts presented good styrene selectivity.

Preparation of SnO_2 – ZrO_2 nanocomposite catalysts by simplified and environmentally acceptable conditions has been achieved by Burri and his co-workers. Whereat, the formation of mixed

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Nomenclature

A_r	surface area of reactor
$D_{e,j}$	effective diffusivity of component j , $\text{mf}^3/\text{m}_r \text{ s}$
E	activation energy, kJ/kmol
F_i	molar flows of components i
K_{EB}	equilibrium constant
k_j	rate constant of reaction j
P_i	partial pressure of component i , bar
$P_{s,j}$	the partial pressure of component j inside the catalyst
P_t	total pressure, bar
R	gas constant ($8.314 \text{ kJ}/\text{kmol K}$)
R_j	total rate of reaction of the component j , $\text{kmol}/(\text{kg-cat h})$
r	radial coordinate of reactor, m
r_{ci}	rate of catalytic reaction i , $\text{kmol}/(\text{kg-cat h})$
r_j	rate of reaction j , $\text{kmol}/\text{kg h}$
r_{ti}	rate of thermal reaction i , $\text{kmol}/(\text{mf}^3 \text{ h})$
r_7	oxidation rate, $\text{kmol}/\text{m}^3 \text{ h}$
T	temperature, K
ν_{ij}	stoichiometric coefficient of components i in reaction j
ρ_c	bulk density of catalyst
ρ_s	catalyst pellet density, $\text{kg-cat}/\text{mf}^3$
η_i	effectiveness factors
ε_s	catalyst internal void fraction, mf^3/mf^3

oxide nanocomposite catalysts, consequent enhancement in the acid–base functional behavior and the augmentation of catalytic performance for the oxidative dehydrogenation of ethylbenzene to styrene, has been accomplished (Burri, Choi, Han, & Jiang, 2008).

Preparation of highly active $\text{Cr}_2\text{O}_3\text{-SiO}_2$ catalyst by sol–gel method for ethylbenzene dehydrogenation in the presence of CO_2 was investigated by Huiyun to illustrate influence of catalyst particles characteristics upon dehydrogenation process yield (Huiyun et al., 2006).

Abo-Ghander et al. (2010) determined optimal design for an auto thermal membrane reactor coupling the dehydrogenation of ethylbenzene to styrene with the hydrogenation of nitrobenzene to aniline. In their work, the Pareto optimal design frontier of a catalytic membrane reactor coupling dehydrogenation of ethylbenzene to styrene with hydrogenation of nitrobenzene to aniline has been obtained. To achieve this goal, a bi-objective optimization problem with linear and nonlinear constraints has been formulated. Their objective function has been on simultaneous maximizing styrene production and nitrobenzene hydrogenations yields. Bounds and constraints with real industrial values have been imposed on both operational and design variables (Abo-Ghander et al., 2010).

The kinetics of EB dehydrogenation have been widely investigated (Bird, 2007; Pars Petrochemical Complex Operating Manual, 2010) but seldom in a fundamental way, developed empirical polynomial correlations for the optimization of the commercial unit (Ellis, 1999; Sulzer Chemtech Ltd., 2010). Obviously, a small improvement in the plant operation has led to a substantial increase of economical returns. In other words, most styrene producers and researchers have not pursued the research toward the fundamental kinetic model such as using Hougen–Watson modeling approach. Furthermore, the reaction rates published in the most of papers are not really intrinsic but rather are effective. Recently, Bennet (2000) derived a mechanistic model using a single-crystal unpromoted iron oxide film. His model included EB dehydrogenation into ST,

but does not consider benzene (BZ) and toluene (Tol) formation and effects of reaction heating on conversion and catalyst activity.

In this work, with a new approach, the thermal and mass differential equations, which are applied in dehydration–oxidation reactors, will be solved by Hougen–Watson method as a non-porosity model. In addition, the mass transfer equation inside the catalyst particles will be solved using Dusty-Gas method for evaluating partial pressure of components in porous catalyst. For evaluation of modeling approach, the simulation results will be compared to actual data of an industrial plant.

2. Production process description

Nowadays, adiabatic dehydrogenation of EB is a highly advanced technology to produce styrene monomer in the commercial scale. Most commercial units that use adiabatic dehydrogenation have two catalytic beds. The conversion percent of EB for these two stages reactors is about 60–75%. Thus, selectivity of EB is 87–96%. Three stages reactors have also been used to gain higher conversion percent and production value. Although regarding to both kinetics and thermodynamic views, higher temperature is ideal for dehydrogenation of EB in accordance with EB conversion but high temperature can result in the production of more by-products. Thus there is a limit for the reactor's inlet temperature with regard to the by-products and the mechanical design (Chon, 2003; Mcketa, 1996; Sun et al., 2004; Tabriz Petrochemical Complex Operating Manual, 1993).

Since the dehydrogenation of styrene production reaction is endothermic reaction, during the dehydrogenation bed, the reaction rate decreases as the temperature decreases. Even with the highest molar ratio of vapor to hydrocarbon (HC), in case no heat is added during the reactor, the conversion percent is about 40%. Thus, the conversion percent increases and the ratio vapor to hydrocarbon decreases using multiple catalyst beds and heating among beds. Both these changes result to reduce the energy consumption and equipment expenses. Conversion percent of EB and selectivity of styrene depend on operating parameters such as temperature, pressure, vapor/hydrocarbon, flow rate and the kind of catalyst used (Mcketa, 1996; Sun et al., 2004).

Fig. 1 shows reaction and fraction units in styrene production process that the reactors are filled with iron–potassium promoted catalysts.

The first reactor only has dehydrogenation bed. The second and third reactors, however, have the additional oxidation bed set into the dehydrogenation bed and the examined reactors are radial.

During the process, ethylbenzene flow and major part of steam are entered to the first reactor and the dehydrogenation reaction is occurred. The outlet flow is mixed with oxygen–steam mixture and ethylbenzene in the feed and the mentioned flows are injected to the second reactor. In this reactor, at first, an oxidation reaction is occurred and, after all, the dehydrogenation reaction is considered. The reactive process in the third reactor is similar to the second reactor. Finally, after decreasing temperature of the final production flow in suitable heat exchangers, the flow is transferred to fraction unit.

Cerium/molybdenum promoted chrome-free iron/potassium Girdler (G-84C) catalyst is used in dehydrogenation reactors and OC/4.2 catalyst is applied in oxidation reactors to produce styrene monomer. To address (at least part of) this problem, a ceramic bed is used in the first and second reactors at around of the dehydrogenation bed. However, this bed occupies a space in the catalyst and hence the reactor is filled by less catalyst particles.

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