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Simultaneous synthesis gas and styrene production in the optimized thermally coupled reactor

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ABSTRACT

Styrene (ST) is one of the most important monomers widely used in the production of polystyrene, resins, and elastomers. In this study, a thermally coupled reactor (TCR) has been suggested for styrene production in which styrene production reaction takes place in the endothermic side and a new process concept called methane tri-reforming for synthesis gas production (H_2 and CO) is considered in the exothermic side of the reactor. The heat generated in the exothermic side is transferred to the endothermic section. A one dimensional steady state model has been developed for thermally coupled reactor. Furthermore the optimization of TCR has been carried out in order to maximize the conversion of ethylbenzene (EB) and methane by Differential evolution (DE) method. Results of the optimization prove that in addition to saving energy, the production of styrene exceeds in the optimized thermally coupled reactor (OTCR) with respect to the conventional reactor (CR) about 5%. Additionally, high values of CO and H_2 yield, 2% and 3% respectively, could be achieved in the exothermic side.

1. Introduction

Due to importance of saving energy and reducing expenses, significant researches and techniques are developed to make exothermic and endothermic reactions proceeding simultaneously in one reactor and to utilize the thermal energy of the exothermic reaction as the heat source of the endothermic reaction (Fukuhara and Igarashi, 2005). It has been pointed out that coupling of exothermic and endothermic reactions in a single reactor, reduces the heat losses and capital and operational costs (Dautzenberg and Mukherjee, 2001). On the other hand, global demand for styrene (ST) and synthesis gas production is increasing annually because of their variety applications in industrial precious chemicals. Therefore, in this study an optimized thermally coupled reactor model is used to investigate benefits associated with coupling of ST production reaction and tri-reforming. Since tri-reforming of methane is a highly exothermic reaction, it can supply the heat needed for the endothermic styrene production reaction.

1.1. Dehydrogenation of ethylbenzene to styrene

Today, the catalytic dehydrogenation of ethylbenzene (EB) to styrene, have attracted worldwide attention because styrene can be polymerized and copolymerized easily to manufacture valuable products. The reversible endothermic reaction can produce more than 90% of total styrene and has a maximum ethylbenzene conversion of less than 50% (M.E.E. Abashar, 2004). Pure dehydrogenations are endothermic (15,000–35,000 kcal/kmol), and hence have large heat requirements. Considering to the importance of styrene and its high energy-demanding reaction, many efforts have been made to improve its production procedure and reduce costs. Elnashaie et al. (2000) developed a membrane catalytic reactor in which the dehydrogenation of ethylbenzene to styrene and hydrogenation of benzene to cyclohexane were coupled. They detected an increase of almost 51% in ethylbenzene conversion and also 45% increase in styrene yield compared with an industrial catalytic reactor. Abashar (2004) investigated a similar configuration and obtained a great increase in the conversion of ethylbenzene to nearly 100%. Nabeel et al. (2008), studied a coupled hydrogen-perm selective membrane reactor to integrate the catalytic dehydrogenation of ethylbenzene to styrene with the catalytic hydrogenation of nitrobenzene to aniline. They predicted that the conversion of EB was increased by 54.6% and 61.7% in the co-current and counter-current membrane reactor. Since styrene

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production depends on both reactor structure and type of the catalyst, effects of some parameters such as catalyst stabilization and minimizing coke formation on the performance of the reaction have been investigated in the literature. Liu et al. (2002), applied monolithic catalysts in styrene production and reported that monolithic catalysts can lead to novel reactor designs and considerable improvement in the performance of radial flow reactors commonly used for styrene production today. Their investigations finally showed a significant increase in the styrene yield. In the present work, the reaction is performed on the iron oxide catalysts (Fe_2O_3) promoted with potassium carbonate (K_2CO_3) and chromium oxide (Cr_2O_3).

1.2. Tri-reforming of methane

Recently, due to an increasing demand for hydrogen and/or synthesis gas (syn gas) used in many processes to fabricate wide variety of chemicals, there is a strong incentive for researchers to develop novel technologies in order to minimize finance problems and promote productions. Methane reforming has been the most important industrial process which is a precursor to hydrogen and/or synthesis gas yield in the manufacture of ammonia, methanol, dimethyl ether and other chemicals. It is recently a well-established technology which has been studied (Dybkjaer, 1995; Bharadwaj and Schmidt, 1995; Mleczko and Baerns, 1995; Ma and Trimm, 1996; Pena et al., 1996; Heinzel et al., 2002; Aasberg-Petersen et al., 2003). The premier reforming processes include steam methane reforming (SMR), partial oxidation reforming (POX), catalytic partial oxidation (CPO), auto-thermal reforming (ATR) and tri-reforming of methane (TRM). Rh, Ru, Ir, Ni, Pt and Pd catalyst contents supported on alumina, silica or zirconia, have the highest activity for the reforming reactions (Rodrigues et al., 2012).Recently, a new process, called tri-reforming of methane (TRM), has been proposed for production of synthesis gas by Song and Pan (2004).This process is an integration of CO_2 reforming, steam reforming and partial oxidation of methane in a single reactor. In this process, reduction in carbon deposition on the catalyst is demonstrated owing to presence of O_2 and H_2O and the H_2/CO ratio in tri-reforming of methane can be better adjusted to values close to 2. Furthermore, some of the reactions are exothermic and the others are endothermic in TRM; however this new process is exothermic overall Walker et al. (2012); Song and Pan (2004). Izquierdo et al. (2013), studied the production of synthesis gas and hydrogen through biogas tri-reforming and dry reforming processes on several catalysts. They proposed a conventional fixed bed reactor and an advanced micro reactor system in their research. Cho et al. (2009), developed a new di-methyl-ether (DME) plant using natural gas tri-reforming. In 2011 Arab Aboosadi et al. used differential evolution method to model an optimized tri-reforming reactor to produce synthesis gas. They reported that methane conversion has increased by 3.8%compared with industrial reformers in a single reactor. Rahimpoura et al. (2012), suggested and modeled a hydrogen and oxygen perm-selective membrane tri-reformer. Results showed that saving in providing oxygen from external, a reduction in costs of oxygen separation unit and high methane conversion were the positive points of this membrane reactor.

1.3. Coupled reactors

Coupling of the exothermic and endothermic reactions in a single reactor is a recently proposed method with the aim of improving the energy efficiency at minimum cost and reducing harmful emissions. In the coupled reactors, endothermic side adsorbs the heat released by the exothermic reactions without any reactants mixing between these two sides (Kolios et al., 2002). The idea of coupling of endothermic and exothermic reactions without direct heat transfer was first explained by Hunter and McGuire (1980). This opinion was then followed by Itoh and Wu (1997).They modeled an integrated adiabatic palladium membrane reactor to couple endothermic and exothermic reactions. Elnashaie et al. (2000), developed a heterogeneous model for ethylbenzene dehydrogenation process in a membrane catalytic reactor. In their study, the endothermic dehydrogenation of ethylbenzene has been coupled with an exothermic hydrogenation reaction. In 2006, Chen et al. investigated an integrated process for hydrogen production by coupling of gasoline performing with ATR in a fixed-bed reactor. Altimari and Bildea (2009) also studied the design and control of plant systems including coupling of exothermic and endothermic reactions. Patel and Sunol (2007) investigated a thermally coupled membrane reactor containing three channels for methane-steam reforming. Bhat and Sadhukhan (2009) developed a thermally coupled membrane separation technology for methane steam reforming. Arab Aboosadi et al. (2011) worked on the modeling of a novel integrated thermally coupled configuration for methane-steam reforming and hydrogenation of nitrobenzene to aniline.

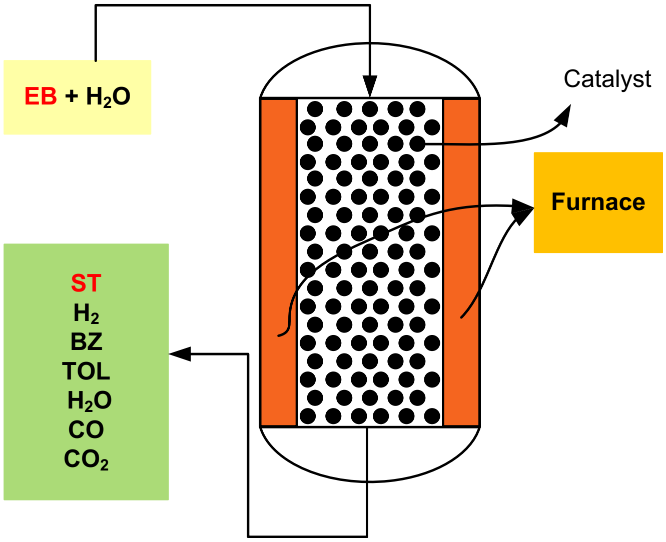

Fig. 1. Schematic of dehydrogenation of ethylbenzene to styrene adiabatic in an adiabatic packed bed reactor.

1.4. Objectives

The purpose of this work is to model a novel thermally coupled reactor for integration of the endothermic styrene production reaction and methane tri-reforming (selected as exothermic reaction), which is named TCR. The operating conditions of TCR configuration are optimized via the differential evolution (DE) method to maximize ethylbenzene and methane conversions. The optimization results show that ethylbenzene and methane conversions have been increased considerably in the TCR configuration under the optimized operating conditions. Finally the results of TCR are compared with the ones in conventional reactors (CR) of styrene production and tri-reformer.

2. Process description

2.1. Conventional ethylbenzene dehydrogenation reactor (CR)

Fig. 1 shows the schematic drawing of dehydrogenation of ethylbenzene to styrene which consists of an adiabatic packed bed reactor as well as a vertical shell and tube heat exchanger.