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Optimal operating condition of membrane reactors to enhance isobutene production, selectivity and hydrogen production

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ABSTRACT

In the isobutene synthesis process, coupling reaction and separation improves isobutene production and selectivity, reduces operation cost and lets to produce hydrogen. This study focuses on the steady state optimization of the isobutane dehydrogenation in hydrogen-permselective Pd/Ag based membrane reactors. The membrane reactors have been modeled heterogeneously based on the mass and energy conservation laws at steady state condition. The Genetic algorithm has been considered to optimize the operating condition of membrane reactors. Optimization results of membrane reactors are compared with conventional adiabatic reactors at the same catalyst loading. This optimal configuration has enhanced isobutene mole fraction about 16.4%.

1. Introduction

Isobutene as one of the main unsaturated hydrocarbons is used as a feedstock to produce a variety of chemical components such as polybutene, methyl tert-butyle ether and ethyl tertiary butyl ether. The most common industrial method to produce isobutene is catalytic dehydrogenation of isobutane. Some of commercial technologies have been developed for dehydrogenation of light alkanes such as isobutane. The Catofin isobutane dehydrogenation technology is a continuous cyclic process to produce isobutene over chromia–alumina catalyst in the fixed-bed reactor [1,2]. The reactors operate adiabatically and to regenerate the catalyst, multiple reactors operate at a controlled sequence of reaction and regeneration. In the UOP process, dehydrogenation reaction occurs in the several adiabatic moving-bed reactors over modified Pt-alumina catalyst considering continuous catalyst regeneration [3].

Although a large number of researches have been presented on the n-butane and n-butene dehydrogenation, few articles in the literature discuss about isobutane dehydrogenation and process modeling [4]. Korhonen et al. investigated the performances of zirconia, alumina, and zirconia/alumina supported chromia catalysts in the dehydrogenation of isobutane in order to elucidate the role of the support material in the dehydrogenation reaction [5]. They showed that activity of chromia catalysts, acidity of the support and the phase of zirconia are important in the dehydrogenation rate. Cortright et al. presented a rate equation for isobutane dehydrogenation over Pt–Sn catalyst over a wide range of temperatures [6]. Bakhshi et al. modeled a bench scale fixed bed reactor for selective dehydrogenation of isobutane at steady state condition, homogeneously [7]. Sahebdelfar et al. modeled the dehydrogenation of isobutane to isobutene in adiabatic radial-flow moving bed reactors without considering catalyst regeneration section [8]. They neglected from side reactions while the isobutene selectivity in the considered commercial process was about 90%.

The integration of membrane separation and reaction in a vessel has attracted much attention in the recent years [9]. Simultaneous occurrence of reaction and separation in a membrane reactor leads to shift thermodynamic equilibrium limitations and reduces separation cost compared to conventional processes. Casanave et al. studied isobutane dehydrogenation over Pt–In catalyst in a packed-bed zeolite membrane reactor [10]. Higher dehydrogenation yield was observed due to the hydrogen removal from the reaction zone. Ciavarella et al. investigated isobutane dehydrogenation in a MFI membrane reactor [11]. The performance of membrane reactor was studied as a function of the feed and sweep gas flow rates. Liang and Hughes studied isobutene synthesis from isobutane in a membrane reactor over Pt/Al_2O_3 catalyst, experimentally [12]. Also, they modeled the considered Pd/Ag membrane reactor under similar operating conditions.

In this work, the radial flow reactors in the UOP process have been substituted by membrane fixed bed reactor at the same catalyst loading. The object of this study is modeling and optimization of Pd/Ag hydrogen permselective membrane reactors to enhance isobutene selectivity, isobutane conversion and hydrogen production from isobutane dehydrogenation. The sum

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Nomenclature

a_v	specific surface area of catalyst pellet ($m^2\ m^{-3}$)
A_c	cross section area of each tube (m^2)
C_p	specific heat of the gas at constant pressure ($J\ mol^{-1}$)
C_i	molar concentration of component i ($mol\ m^{-3}$)
D	tube diameter (m)
E_p	activation energy of permeability ($kJ\ mol^{-1}$)
F	total molar flow rate ($mol\ s^{-1}$)
h_f	gas–solid heat transfer coefficient ($W\ m^{-2}\ K^{-1}$)
k	reaction rate constant ($mol\ kg^{-1}\ s^{-1}\ bar^{-1/2}$)
K_{eq}	equilibrium constant I ($m^3\ mol^{-1}$)
L	reactor length (m)
P	total pressure (bar)
P_i	partial pressure of component i (bar)
P_0	pre-exponential factor of hydrogen permeability ($mol\ m^{-2}\ s^{-1}\ Pa^{-1/2}$)
Q	volumetric flow rate ($m^3\ s^{-1}$)
Q_H	hydrogen permeation rate ($mol\ m^{-1}\ s^{-1}$)
r	rate of reaction for dehydrogenation ($mol\ kg^{-1}\ s^{-1}$)
Re	Reynolds number
T	temperature (K)
u	superficial velocity of fluid phase ($m\ s^{-1}$)
U	overall heat transfer coefficient ($W\ m^{-2}\ K^{-1}$)
y_i	mole fraction of component i ($mol\ mol^{-1}$)
z	axial reactor coordinate (m)

Greek letters

α_H	hydrogen permeation rate constant ($mol\ m^{-1}\ s^{-1} Pa^{-1/2}$)
η	catalyst effectiveness factor
ρ	density of fluid phase ($kg\ m^{-3}$)
ε	bed void fraction
ΔP	pressure difference (Pa)

Superscripts

g	in bulk gas phase
m	in the sweep gas side
p	particle
s	at surface catalyst

of isobutane conversion and isobutene selectivity has been considered as the objective function that should be maximized using genetic algorithm. The performance of the optimized membrane reactors is compared with conventional reactors at the same catalyst loading. The clear advantages of this membrane reactor are: hydrogen production, improving isobutene productivity and selectivity and lower purification cost in the next stage.

2. Kinetics model

The traditional method of isobutene synthesis is isobutane dehydrogenation over $Pt–Sn/Al_2O_3$ catalyst, which is an endothermic and equilibrium reaction.

$$\text{i-}C_4H_{10} \leftrightarrow \text{i-}C_4H_8 + H_2 \quad \Delta H_{298} = 120\ kJ\ kmol^{-1} \tag{1}$$

Use of high contact times or high temperatures causes isobutane cracking to methane and propane as the main side reaction:

$$\text{i-}C_4H_{10} + H_2 \leftrightarrow \text{i-}C_3H_8 + CH_4 \quad \Delta H_{298} = 80\ kJ\ kmol^{-1} \tag{2}$$

In this work, the rate expressions have been selected from the literature [13,14]. The rate equations for isobutane dehydrogenation and isobutane dissociation combined with the equilibrium constant provides enough information about kinetics of isobutene synthesis.

3. Process modeling

3.1. Reaction side

The conventional dehydrogenation process consists of three series reactors. The inter heaters are take placed between reactors to increase the temperature of inlet streams. In this work, the conventional reactors have been substituted by Pd/Ag based hydrogen permselective membrane reactors at the same catalyst loading. Fig. 1 shows the schematic diagram of the considered process.

A one-dimensional steady state heterogeneous model, based on mass and energy conservation laws, has been developed to simulate the hydrogen permselective membrane reactors. In this model the following assumptions are considered:

- The gas mixture is ideal.
- Radial diffusion of mass and energy is negligible.
- Axial diffusion of mass and heat are negligible duo to high gas velocity.
- The system is well isolated.

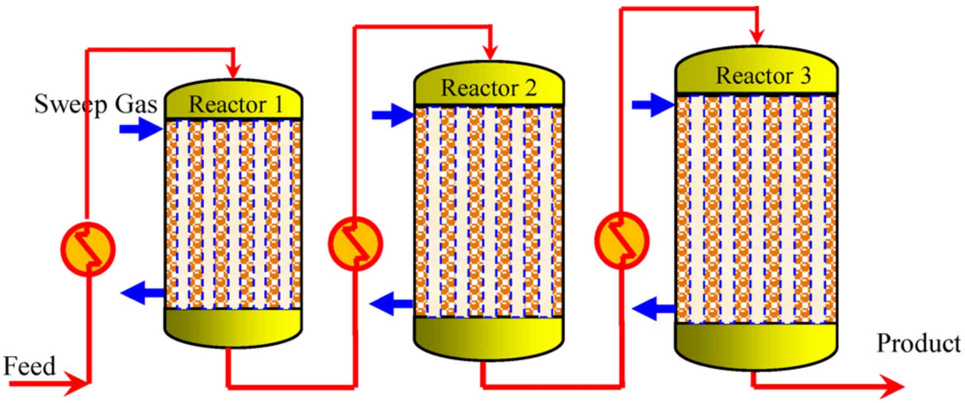

Fig. 1. The schematic diagram of the considered process.