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Modeling-based optimization of a fixed-bed industrial reactor for oxidative dehydrogenation of propane

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ABSTRACT

An industrial scale propylene production *via* oxidative dehydrogenation of propane (ODHP) in multi-tubular reactors was modeled. Multi-tubular fixed-bed reactor used for ODHP process, employing 10000 of small diameter tubes immersed in a shell through a proper coolant flows. Herein, a theory-based pseudo-homogeneous model to describe the operation of a fixed bed reactor for the ODHP to correspondence olefin over V_2O_5/γ-Al_2O_3 catalyst was presented. Steady state one dimensional model has been developed to identify the operation parameters and to describe the propane and oxygen conversions, gas process and coolant temperatures, as well as other parameters affecting the reactor performance such as pressure. Furthermore, the applied model showed that a double-bed multitubular reactor with intermediate air injection scheme was superior to a single-bed design due to the increasing of propylene selectivity while operating under lower oxygen partial pressures resulting in propane conversion of about 37.3%. The optimized length of the reactor needed to reach 100% conversion of the oxygen was theoretically determined. For the single-bed reactor the optimized length of 11.96 m including 0.5 m of inert section at the entrance region and for the double-bed reactor design the optimized lengths of 5.72 m for the first and 7.32 m for the second reactor were calculated. Ultimately, the use of a distributed oxygen feed with limited number of injection points indicated a significant improvement on the reactor performance in terms of propane conversion and propylene selectivity. Besides, this concept could overcome the reactor runaway temperature problem and enabled operations at the wider range of conditions to obtain enhanced propylene production in an industrial scale reactor.

1. Introduction

Light olefins are obtained by processes such as steam cracking, fluid catalytic cracking of light oil fractions [1] and catalytic dehydrogenation of light alkanes. These processes are endothermic and operate under very severe conditions (high temperature and low contact time) with subsequent high energy consumption. The demand for ethylene and propylene is growing at different rates where the demand of propylene is foreseen to overtake that of ethylene [2]. Catalytic dehydrogenation of paraffins is an alternative for thermal steam cracking, and has for a long time been a commercialized process [3]. Thermodynamic equilibrium restriction on conversion, irreversible catalyst deactivation and rapid coke formation are major limitations [4]. The severity of the reaction condition increases with decreasing carbon chain length, and therefore dehydrogenation of propane is by far the least thermodynamically favored reaction [5]. An alternative process for propylene production is the ODHP that has been recognized as a potentially attractive process [6]. Propane dehydrogenation process is an equilibrium-limited, endothermic process that requires external heat sources. The presence of oxygen in the exothermic oxidative dehydrogenation (ODH) process offers thermodynamic advantages and lowers the energy requirements. However, it increases the tendency of the produced propylene towards further oxidation to CO_x. The CO_x is produced *via* consecutive (propylene oxidation) and parallel (propane oxidation) reactions. Although the ODH of paraffins for the production of light olefins (ethylene, propylene or butenes) continues to be of interest at laboratory research level, industrial applications are still hindered by unsatisfactory yields (due to the formation of carbon oxides) and technical conditions (flammability of the reaction mixture and reactor choice) [5]. The catalysts employed are generally based on vanadium [7–9]. There are several investigations reported in the open literature that deal with the determination of the kinetic parameters of the reactions involved in the ODH process as well as reaction mechanism and pathways [10–20].

In spite of its significant economic potential as an alternate route to alkenes and in spite of extensive scientific studies, the ODH of alkanes to alkenes is not currently practiced because the secondary combustion of primary alkene products limits alkene yields to about 30% for propane and higher alkanes [21]. Alkene selectivities decrease markedly as conversion increases [21,22]. One important reason for these yield

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limitations is the typically higher energies of the C–H bonds in alkane reactants compared with those in the desired alkene products [23], which lead to rapid alkene combustion at the temperatures required for C–H bond activation in alkanes. A literature survey of product yields in oxidation reactions [23] suggested that low yields are obtained when the energy of the weakest bond in the products is 30–40 $\mathrm{kJ \cdot mol^{-1}}$ lower than that of the weakest bond in the reactants. Alkenes are primary ODH products while CO and CO_2 (CO_x) can form either from secondary combustion of alkenes or direct combustion of alkanes.

The reaction of propane with gaseous oxygen is favored to form carbon oxides, thus lowering the propylene selectivity at a given propane conversion. In order to increase the propylene selectivity at a given conversion, lattice oxygen can be used to replace gaseous oxygen for the ODHP to propylene. Dense oxygen-permeable membrane reactors can continuously supply lattice oxygen for ODHP to propylene and higher propylene selectivity could be obtained in such a membrane reactor. A recent investigation, the performance of a fixed-bed reactor and a dense tubular membrane reactor over $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) at 700 °C and 750 °C reported that the propylene selectivity in the membrane reactor (44.2%) was much higher than that in the fixed-bed reactor (15%) at similar propane conversions (23%–27%) [24]. Propane reacts directly from the gas phase with the adsorbed oxygen on the catalyst. Chen *et al.* [25] showed that propane is dehydrogenated to propylene, and the total oxidation of propane to carbon dioxide occurs in parallel. Carbon monoxide is exclusively formed by oxidation of propylene while CO_2 is generated by oxidation of both propane and propylene.

The systems of main and undesired reactions of combustion are represented by the equations below:

$$C_3H_8 + 0.5O_2 \rightarrow C_3H_6 + H_2O \tag{1}$$

$$C_3H_8 + 3.5O_2 \rightarrow 3CO + 4H_2O \tag{2}$$

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \tag{3}$$

$$C_3H_6 + 3O_2 \rightarrow 3CO + 3H_2O \tag{4}$$

$$C_3H_6 + 4.5O_2 \rightarrow 3CO_2 + 3H_2O \tag{5}$$

$$CO + 0.5O_2 \rightarrow CO_2 \tag{6}$$

$$C_3H_8 + 1.5O_2 \rightarrow C_2H_4 + CO + 2H_2O \tag{7}$$

$$C_3H_8 + 2O_2 \rightarrow C_2H_4 + CO_2 + 2H_2O \tag{8}$$

$$C_3H_6 + O_2 \rightarrow C_2H_4 + CO + H_2O \tag{9}$$

$$C_3H_6 + 1.5O_2 \rightarrow C_2H_4 + CO_2 + H_2O. \tag{10}$$

In the ODHP process, the yield of propane is limited by the total oxidation reactions, namely, the parallel propane combustion and the in-series propylene combustion, both forming CO_x. At present, intensive research is being carried out to develop both adequate reactor technologies for an effective and safe plant operation [26] as well as active and selective catalyst formulations. For exothermic processes, the control of the reaction temperature appears as a key factor to maintain a good selectivity level. The reactor choice and design therefore become outstandingly important. Industry makes extensive use of multi-tubular reactors to conduct these exothermic processes, with the aim of efficiently removing the generated heat from the catalyst bed. Thousands of tubes of small diameter are employed in order to minimize thermal radial gradients and enhance the ratio between heat exchange area and reaction volume. Lopez *et al.* [27] reported simulation studies of a multitubular ethane-to-ethylene ODH reactor. Results suggested that the reactor operation would be feasible, provided that high heat transfer area per unit volume and low oxygen concentrations along the tube are maintained. This last consideration proved to be a key factor to achieve adequate selectivity levels leading to high ethylene productions. An attractive alternative to fixed-bed reactors when a distributed feed is required is the use of a membrane reactor. The catalyst and reactor design must improve the yield and productivity of the desired intermediate products together with accomplishing an economical process that uses effectively all the active catalyst sites. Cavani and Trifirò [28] in a review on state-of-the-art selective oxidations, suggest paying particular attention to the inorganic membrane reactor. Different arrangements of the inorganic membrane reactor were studied theoretically and applied to partial oxidation processes with a valuable intermediate product [29–38]. The membrane can be used as a porous wall containing a catalytic packed bed and the resulting configuration is called inorganic membrane packed bed reactor (IMPBR). The advantages of the application of membrane reactors on ODH at lab scale have been reported for propane [39,40].

In this work, a theoretical study of a fixed-bed reactor for the ODHP to propylene over $V_2O_5/\gamma\text{-}Al_2O_3$ catalyst is presented. The performance of the ODHP reactor is analyzed by means of a mathematical model of the catalytic unit. The influence of several operational and design variables, such as pressure and temperature was discussed. The bed was considered with the 0.5 m inert zone in the entrance section. The conversion of propane and 100% oxygen conversion were taken as the performance criteria for the system. An alternative design with two and more catalytic beds in series with distributed oxygen injection and the optimum length was presented to investigate the effect of the oxygen feed schemes.

2. Mathematical Modeling

The following assumptions for modeling of multi-tubular fixed-bed reactor for ODHP were considered:

- One-dimensional,
- Pseudo-homogeneous model,
- Steady-state condition,
- The coolant was flowed in the shell co-currently with the gas process,
- Mass and energy dispersions were assumed to be negligible,
- Plug flow regime,
- Internal and external mass as well as energy transport limitations were not considered,
- The reactor shell assumed to be adiabatic,
- A first section of the tubes was considered filled with inert particles, with the rest of the tubes filled with the $V_2O_5/\gamma\text{-}Al_2O_3$ ODH catalyst.

The balances used to represent the steady-state reactor behavior, along with the corresponding initial conditions, are presented below:

Mass balance:

$$\frac{\mathrm{d}f_i}{\mathrm{d}x} = n\left(\frac{\pi}{4}d_t^2\right)\rho_b\sum_{j=1}^{3}\nu_{ji}R_j \quad i = O_2, N_2, C_3H_8, CO_2, H_2O, C_3H_6. \tag{11}$$

Energy balance of gas:

$$\frac{\mathrm{d}T}{\mathrm{d}x} = \frac{\left\{n\left(\frac{\pi}{4}d_t^2\right)\rho_b\right\}\sum_{j=1}^{3}R_j(-\Delta H_j) - n\pi d_t U(T-T_C)}{\sum_{i=1}^{6}f_iC_{Pi}}. \tag{12}$$

Energy balance of coolant:

$$\frac{\mathrm{d}T_C}{\mathrm{d}x} = \frac{n\pi d_t U(T-T_C)}{m_C C_{PC}}. \tag{13}$$

Initial conditions:

$$\text{at } x = 0 \quad f_i = f_{i,0}, \quad T = T_0, \quad T_C = T_{C,0}. \tag{14}$$

It should be reiterated that the pressure drop along the reactor length is very small due to the standard model of non-isothermal plug