Energy 147 (2018) 187–196

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Entropy generation minimization for CO_2 hydrogenation to light olefins

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ARTICLE INFO

Article history:

Keywords:
Carbon dioxide hydrogenation to light olefins
Tubular reactor
Finite-time thermodynamics
Entropy generation minimization

ABSTRACT

An optimization model is established for the reaction process of CO_2 hydrogenation to light olefins in a fixed-bed tubular reactor based on finite time thermodynamics or entropy generation minimization theory. In the present study, the specific generation rate (entropy generation rate averaged by the production rate of the target product) is proposed as an optimization objective function and the optimal design parameters which minimize the objective function have been investigated. The model is developed based on the reversible kenetic models and their cooresponding kinetic parameters, which are obtained by fitting the experimental data. The irreversibilities due to heat transfer, chemical reactions and viscous flow are considered and the local entropy generation rate of each term is calculated according to the irreversible thermodynamics. The analyses of the performance characteristics are conducted as well. The results show that the CO_2 hydrogenation to light olefins accords with a two-step reaction mechanism, and Fischer-Tropsch reaction is the rate-controlling step. The irreversibility mainly located in the front of the reactor, which most contributions are caused by chemical reactions. The reductions of the specific entropy generation up to 24.78% and 10.04% can be achieved for optimal reactor inner diameter and optimal catalyst bed density, respectively.

1. Introduction

A series of energy and environment issues, such as sharp consumption of fossil fuels and global climate warming, have been the main obstacles to the developments of human society. Many countries, including China, are committed to developing new technologies and policies for energy saving, emission reduction and renewable energy [1–3]. The new method of fuel synthesis by CO_2 and H_2 extracted from seawater has great significance for the security of offshore military energy and the development of alternative energy. The technique of utilizing CO_2 with H_2, which is derived from renewable energy sources, to produce light olefins through chemical catalytic process is popular in scientific teams around the world [4–8]. Much literature about chemical kinetics [9–12], thermodynamics [13,14] and catalysts of the hydrogenation reaction [15–19] have been published. However, CO_2 hydrogenation to light olefins is still confronted with the problems of high energy consumption, low selectivity and high production cost [1,20]. Therefore, analyzing and optimizing the thermodynamic performances of the industrial CO_2 hydrogenation to light olefins reactors is essential.

Finite-time thermodynamics (FTT) or entropy generation minimization (EGM) theory [21–59] is a multidisciplinary discipline, where different basic sciences including thermodynamics, heat transfer, fluid mechanics and chemical kinetics are combined to obtain the optimal performances and optimal configurations of various energy conversion devices and systems. With the development of the theory, the research fields and connotations of FTT have been enriched and expanded, all the objective functions which are valuable or meaningful can be used in the optimization work to obtain the optimal performance of real systems and devices. Especially in recent years, the studies about multi-objective FTT optimization are growing [38–46]. In chemical engineering, optimization efforts using production rates, conversion rates, profit rates and entropy generation rate as objective functions are reasonable and useful. Månson and Andresen [60] firstly applied FTT to obtain the optimal configuration of the reaction

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https://doi.org/10.1016/j.energy.2018.01.050
0360-5442/

temperature with maximum ammonia production rate as objective function. Szwast and Sieniutycz [61] investigated the optimal path of an unsteady-state reactor with parallel-consecutive reactions with maximum profit rate as objective function. Bak et al. [62] obtained optimal configuration of a generalized consecutive chemical reaction $A \leftrightharpoons B \leftrightharpoons C$ with maximum target product yield as objective function. Chen et al. [63] studied more generalized consecutive chemical reaction $xA \leftrightharpoons yB \leftrightharpoons zC$, considering orders of the chemical reactions, and obtained optimal path with maximum yield of target product B as objective function. Wang et al. [64] obtained the optimal configuration of the sulphuric acid decomposition reactor with maximum production rate as objective function, which is different from that derived from minimizing the entropy generation rate.

EGM uses the models that feature rate processes (heat transfer, mass transfer, fluid flow and chemical reactions) in which irreversibilities are due to the irreversible operation of the real-world systems and devices. The core mission of EGM is the reduction or minimization of the irreversibilities that are responsible for various irreversible transport phenomenon. The Gouy-Stodola theorem makes it clear that the minimization of the entropy generation rate is the equivalence of the optimization of the second law efficiency from the viewpoint of reduction in thermodynamic irreversibility. The entropy generation rate is independent of the reference environment and socio-political situation, and measures the irreversibilities of the energy systems as a pure thermodynamic objective function which reflects the long-term objective for energy saving of the system. Many scholars [65–71] analyzed and optimized various chemical and mass transfer processes with minimum entropy generation rate as objective function. Kjelstrup et al. [65] obtained the optimal temperature profiles of a methanol reactor using minimum entropy generation rate as objective function. Johannessen and Kjelstrup [66] used optimal control theory to obtain the optimal temperature configurations of SO_2 oxidation reactor based on EGM. van der Ham et al. [67] studied optimal configuration of the heating utility and optimal reactor length design of the sulphuric acid decomposition reactor when total entropy generation rate is minimum. Nummedal et al. [68], Wilhelmsen et al. [69,70] and Ao et al. [71] obtained different optimal temperature profiles of the tubular steam reformer using minimum entropy generation rate as objective function, in which heat transfer laws were different. Xia et al. [72,73] studied entransy dissipation minimization (EDM) of one-way isothermal mass transfer processes [72] and isothermal throttling process [73], and the results obtained were compared with other mass transfer strategies, such as that based on EGM. Zheng et al. [74] firstly investigated EDM of a thermochemical energy storage-reactor with tubular steam reformer, which optimal configuration is different with those based on EGM. Wang et al. [75] obtained the optimal control strategy of a consecutive chemical reaction $A \leftrightharpoons B \leftrightharpoons C$ with minimum entropy generation rate as objective function and concentration A as control variable. Wang et al. [76] and Chen et al. [77] analyzed the entropy generation rate of the removal process of carbon dioxide from seawater by using hollow fiber membrane contactor [76] and obtained the optimal concentration configuration of carbon dioxide with minimum entropy generation rate as objective function [77].

In summary, EGM, a method of modelling and optimizing the real-world systems and devices that owe their thermodynamic imperfection to the irreversibilities due to various transport phenomenon, has been widely employed to minimize the energy quality losses of chemical devices subjected to a specified set of constraints. The most important task of the chemical reactors is to produce the desired chemicals as many as possible. Therefore, it is essential to establish a link between the entropy generation rate and the production rate. The specific entropy generation (entropy generation rate averaged by the production rate of the target product) will be the first application in evaluating and analyzing the thermodynamic performance of the CO_2 hydrogenation to light olefins in tubular reactor based on the theory of EGM to explore better configurations with minimum thermodynamic irreversibilities. The mathematical model of an industrial reactor will be established and the total entropy generation rate originating in irreversibilities of fluid flow, heat and mass transport phenomena will be calculated using irreversible thermodynamic theory.

2. Model of chemical reaction system

2.1. Reference reactor

Consider the CO_2 hydrogenation to light olefins process in fixed-bed reactor based on the experimental results of iron-based catalyst (K/Mn/Fe) exploited by Willauer et al. [11,12]. According to the two-step mechanism, the three central chemical reactions taking place on iron-based catalyst surfaces are:

$$CO_2 + H_2 \leftrightharpoons CO + H_2O \quad \Delta_r H_{I} > 0 \tag{I}$$

$$CO + 2H_2 \leftrightharpoons \frac{1}{3}C_3H_6 + H_2O \quad \Delta_r H_{II} < 0 \tag{II}$$

$$CO + 3H_2 \leftrightharpoons CH_4 + H_2O \quad \Delta_r H_{III} < 0 \tag{III}$$

In this tandem process, the intermediate product CO is produced through the reverse water gas shift (RWGS) reaction which is endothermic. The CO can further react with H_2 in an exothermic Fischer-Tropsch (FT) reaction, forming light olefins. Propane (C_3H_6), which is the major unsaturated hydrocarbons in the complex product composition, is served as typical species for FT reaction. A thermodynamic favorable side reaction, methanation reaction, is also taken into account. This side reaction (FTs) is also an exothermic reaction. The product distribution of high temperature FT (HTFT) reaction on iron-based catalysts is different from that in low temperature FT (LTFT) reaction on Co-based catalysts, the liquid product is absent. Therefore, all substances are in gaseous state and can be taken as ideal gases under the operating conditions used herein.

A simple reactor model is established. As shown in Fig. 1, heat is transferred perpendicular to the reactor wall by heat convection, some assumptions must be made in this simple reactor model. It is assumed that no radial temperature and concentration profiles occur. Further assumptions are that there is not dispersion or back-mixing in axial direction and the chemical reactions are kinetically controlled, so all heterogeneous effects due to internal

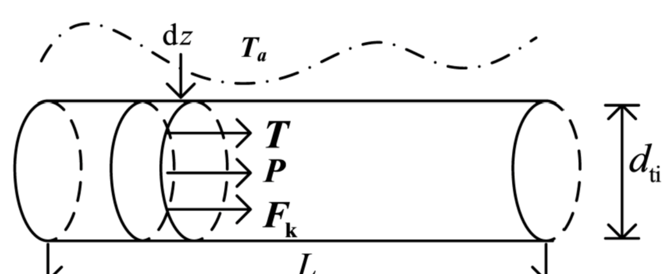

Fig. 1. Schematic diagram of the one-dimensional plug-flow reactor model.