Thermodynamic analysis of steam reforming and oxidative steam reforming of propane and butane for hydrogen production

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ARTICLE INFO

ABSTRACT

Thermodynamic analyses of cracking, partial oxidation (POX), steam reforming (SR) and oxidative steam reforming (OSR) of butane and propane (for comparison) were performed using the Gibbs free energy minimization method under the reaction conditions of $T = 250-1000$ °C, steam-to-carbon ratio (S/C) of 0.5−5 and O_2/HC (hydrocarbon) ratio of 0−2.4. The simulations for the cracking and POX processes showed that olefins and acetylene can be easily generated through the cracking reactions and can be removed by adding an appropriate amount of oxygen. For SR and OSR of propane and butane, predicted carbon formation only occurred at low S/C ratios (<2) with the maximum level of carbon formation at 550−650 °C. For the thermal-neutral conditions, the TN temperatures decrease with the increase of the S/C ratio (except for O/C = 0.6) and the decrease of the O/C ratio. The simulated results for SR or OSR of propane and butane are very close under the investigated conditions.

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Introduction

Hydrogen or hydrogen-rich gas can be produced by reforming (e.g., steam reforming, oxidative steam forming and dry reforming) and partial oxidation of hydrocarbons or alcohols, e.g., methane, methanol, ethanol, liquefied petroleum gas (LPG), gasoline and diesel [1]. For the distributed production of hydrogen (e.g., on-site steam reformers for refueling stations, portable or domestic uses), LPG is a practical candidate because it takes advantage of a wide distribution network as well as convenient transportation and storage [2]. Propane (C_3H_8) and butane (C_4H_{10}) are the main components in LPG. The volume percentages of propane and butane in LPG vary depending on various standards and climates in different countries, e.g., 92.5%−100% propane for LPG produced in Canada and 65%−90% butane for LPG produced in Korea [3].

Experimental studies of the catalytic steam reforming (SR) and partial oxidation (POX) of propane, butane and LPG are available in the literature (propane [4−8], butane [9−11] and LPG [12−17]), focusing on the development of novel catalysts with high stability and activity. Since the steam reforming is an endothermic reaction whereas the partial oxidation is an exothermic reaction, the combination of the two processes known as autothermal reforming (ATR) or oxidative steam reforming (OSR) is usually applied to achieve different goals such as thermal neutrality, control of product composition and suppression of coke formation. Under the SR conditions,

coke formation is the main issue both for the nickel and noble metal-based catalysts and can result in the deactivation of the catalysts. Furthermore, steam reforming of the heavier propane and butane is more prone to carbon formation than steam methane reforming (SMR) [18]. Under the OSR conditions, the oxygen in the system can depress coke formation by enhancing the gasification of carbon residues relative to the results obtained in SR conditions [7].

The operating conditions used in the experimental studies are T = 270−1000 °C, S/C = 0.06−7, O$_2$/HC (hydrocarbon) = 0−2.3 and conducted at around the atmospheric pressure. The operating conditions such as the pressure, temperature, steam-to-carbon ratio (S/C), oxygen-to-hydrocarbon ratio (O$_2$/HC) play important roles in the performance of the catalyst, product composition and energy efficiency of system [19–21]. Thermodynamic analysis can provide useful and rapid guidance of the proper or optimal zone for these operating conditions, e.g., operating in coke-free zone. Many studies of the thermodynamic analysis of the reforming process of hydrocarbons and alcohols can be found, e.g., methane [22–24], natural gas [25], propane [20–21], LPG [26], methanol [27] and butanol [28]. Zeng et al. [20] conducted the thermodynamics analysis on the reaction conditions of OSR of propane using the Gibbs free energy minimization method. The temperature of 700 °C, H$_2$O/C$_3$H$_8$ ratio above 7 and O$_2$/C$_3$H$_8$ ratio above 1.3 were proposed in order to obtain a high hydrogen yield, low carbon monoxide yield and avoid coke formation. Wang et al. [21] investigated the reaction conditions of dry reforming (DR) and SR of propane. The temperature range of 925−975 K and H$_2$O/C$_3$H$_8$ ratios of 12−18 were suggested to be favorable conditions for propane steam reforming. Silva et al. [26] compared the thermodynamic analysis results with the experimental data for SR and OSR of LPG with the propane to butane ratio of 1:1. The temperature of 973 K and the H$_2$O/C$_3$H$_8$ ratio of 7 were found to be the most suitable reaction conditions for both SR and OSR of LPG. However, there is still a lack of relevant thermodynamic analysis regarding the SR and OSR of the heavier component butane, which is the main component of LPG in some countries.

In the present study, the thermodynamic analyses of SR and OSR of butane were performed using the Gibbs free energy minimization method. The influences of the reaction conditions such as the temperature, S/C ratio and O$_2$/HC ratio were investigated and can provide guidance for the operation and design of an LPG steam reformer as well as reformers for heavier fuels (e.g., gasoline and diesel) the decomposition of which could result in the formation of the propane and butane intermediates. SR and OSR of propane were also considered in some results for comparison.

Methodology

The method of Gibbs free energy minimization is commonly used for the prediction of the thermodynamic equilibrium composition for a complex reactive system with an initial feed composition, certain phases and temperature and pressure conditions [29]. The process of (oxidative) steam reforming of hydrocarbons includes both the gas phase and the probable solid phase from coke formation. By assuming that the solid phase is a pure solid carbon (graphite) and using the Lagrange multiplier method, the Gibbs free energy minimization for the system can be expressed by the equations considering each species in the gas phase and the total system [22]:

$$\Delta G_{fi}^{\circ g} + RTln\frac{y_i \widehat{\varphi}_i P}{p^\circ} + \sum_k a_{ik}\lambda_k = 0 \tag{1}$$

$$\sum_{i=1}^{N} n_i \left(\Delta G_{fi}^{\circ g} + RTln\frac{y_i \widehat{\varphi}_i P}{p^\circ} + \sum_k a_{ik}\lambda_k \right) + n_c \Delta G_{fc(s)}^{\circ} = 0 \tag{2}$$

with the following constraint:

$$\sum_i n_i a_{ik} = A_k \tag{3}$$

where $\Delta G_{fi}^{\circ g}$ is the standard Gibbs free energy of formation of gaseous species i, y_i is the mole fraction of species i, $\widehat{\varphi}_i$ is the fugacity coefficient of species i, P and P$^\circ$ are the system pressure and standard state pressure (1 atm), respectively, a_{ik} is the number of the atoms of the kth element present in each molecule of gaseous species i, λ_k is the Lagrange multiplier, and A_k is the total atomic mass of the kth element in the feed. n_i and n_c are the mole number of species i and the solid carbon in the system, respectively, while $\Delta G_{fc(s)}^{\circ}$ is the standard Gibbs free energy of formation of the solid carbon which is assumed to be zero.

The thermodynamic analysis using the Gibbs free energy minimization method was performed using the Aspen Plus V9 (RGibbs reactor) software. The Peng-Robinson model was used as the equation of state. A flow rate of 1 mol/s was set for propane or butane (hereafter referred to as n-butane) in the feed. It should be noted that the branched isomer iso-butane was not considered in the feed due to the close Gibbs free energy values of n-butane and iso-butane. The conditions for SR and OSR of butane and propane were considered to be as follows: T = 250−1000 °C, S/C = 0.5−5 and O$_2$/HC = 0−2.4. The main products for SR of butane are H$_2$, H$_2$O, CH$_4$, CO, CO$_2$ and graphite carbon (O$_2$ was included in the products for OSR); other possible products such as C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_6$, C$_4$H$_6$, and C$_4$H$_8$ were also considered. It should be taken into account that other types of solid carbon can also be generated in the SR or OSR processes. Diaz Alvarado and Gracia [30] analyzed three different carbon representations (graphite, nanotubes and amorphous carbon) for SR of ethanol, and indicated that carbon nanotubes were more favorable at above 400 °C. Giehr et al. [24] also presented three carbon products (fullerene C$_{60}$, graphite and amorphous carbon) for the thermodynamic analysis of dry and steam reforming of methane, and mentioned that graphite was the most stable product among the three investigated carbon types. The present study is limited to the graphite carbon due to its properties are available in the database of Aspen Plus.

The conversion of reactant, selectivity and yield of the product are expressed by the following [6]:

$$C_i = \frac{n_{i,0} - n_{i,e}}{n_{i,0}} \tag{4}$$