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Thermodynamic characteristics of reactants and energy conversion in steam reforming of calcium carbide furnace off-gas to produce hydrogen

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ABSTRACT

In this study, to reveal the thermodynamic reaction mechanism and the conversion characteristics of material and energy for the steam reforming of multi-component materials, a chemical equilibrium model was constructed, and the reaction mechanism of the steam reforming of calcium carbide furnace off-gas (CCFG) was also identified. The conversion characteristics of material and energy were ascertained by assessing four independent reactions and their reverse reactions. And the effects of temperature, pressure and steam-to-gas ratio on the conversion ratios of CO and CH_4, the yield of H_2 and the reaction heat were investigated. In addition, a method for determining the process parameters of steam reforming based on the follow-up utilization scheme of CCFG was proposed; the method involves using a four-panel diagram that plots parameters of the steam reforming process. Thus, the range of H_2/CO mole ratio that could be obtained from the equilibrium system of steam reforming of CCFG was determined.

Introduction

Liu [1] proposed a new oxy-thermal method for producing calcium carbide. The research showed that the oxy-thermal method had lower energy consumption and carbon emission than the electro-thermal method from the viewpoint of multi-product process [2]. But the conclusion is based on the fact that the calcium carbide furnace gas (CCFG) is treated as the process product of calcium carbide production. Besides, one of the innovations of the oxy-thermal method is the variety of raw materials used. With the exception of coke, low- to mid-rank coal, such as sub-bituminous coal, can also be used as feedstock. This new method provides an efficient approach to utilizing low- to mid-rank coal, but a large amount of CCFG is also discharged by the furnace in the process [3]. Whether CCFG can be reasonably and economically utilized is thus the bottleneck of this new method. Kein [4] reported that H_2 might be needed in the utilization of CCFG and that the H_2/CO mole ratio varies with the utilization scheme employed. The different H_2/CO mole ratios can be obtained through the H_2 generation from CCFG and the parameter adjustment of steam reforming. The process to produce chemicals and clean fuels, such as ethylene glycol and dimethyl ether, from CCFG can be expanded further. The H_2/CO mole ratio in the reaction system determines the choice of CCFG utilization scheme

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directly. Thus, the steam reforming process to produce H_2 from CCFG is essential to the utilization of CCFG and the oxy-thermal method.

Recently, most research on steam reforming reported in the literature has focused on the kinetics of hydrogen production reactions [5] and catalysts [6]. The main materials used in steam reforming to produce H_2 include methane [7], bio-oil [8], coke oven gas [9], methanol [10] and ethanol [11], each of which requires a different catalyst in experimental or practical production. Many studies on the kinetics of the water–shift reaction in steam reforming have been performed [12]. Sá [13] studied kinetic models of the steam reforming of methane on different catalysts. Zhang [14] also experimentally investigated a kinetic model of the steam reforming of coke oven gas. Wang [15] compared different kinetic models of methane steam reforming over a Ni/YSZ anode and identified the most effective model. Han [11] produced hydrogen from the steam reforming of ethanol over a $Ni–Al_2O_3–ZrO_2$ aerogel catalyst. Other novel catalysts with better performance have also been explored for the water-gas shift reaction and steam reforming [10]. The reaction kinetics of these processes generally vary with reaction temperature and catalyst type.

Reactor design has also attracted attention in recent studies of steam reforming. Hong [16] discussed the effect of operating parameters on reactor design. The steam reforming reaction is a thermodynamically limited reaction. To break chemical equilibrium and obtain the maximum hydrogen production, different membrane reactors have been developed and reviewed [17]. In a previous study, the chemical reaction and hydrogen separation were combined in a membrane reactor, which could also be adapted to the steam reforming reaction. Bottino [18] studied the equilibrium of methane steam reforming in membrane reactors.

Although many studies concerning steam reforming have been performed, studies on the reaction mechanism of steam reforming with a complex gas have rarely been reported, especially gas with a special composition such as CCFG. The reaction rate is mainly taken into account during the reactor design process, and the chemical reaction employed in practical production does not proceed in an equilibrium state. Nevertheless, the chemical equilibrium always affects the operating parameters that can be selected [19]. In some cases, information about the chemical equilibrium can be used to predict the kinetic rate constants through linear free–energy relations. The laws of chemical equilibrium determine the direction toward which a chemical reaction proceeds as well as the quantities of reactants and products remaining in the equilibrium state. The equilibrium constant and Gibbs energy are generally used to describe chemical equilibrium. The equilibrium constant indicates the extent to which reactants are converted to products, and the Gibbs energy reaction determines the direction of the reaction.

Rossi [20] studied the thermodynamic characteristics of steam reforming for producing hydrogen, but only ethanol or glycerin and water were considered as the reactants. Phoenix [21] developed a non-ideal multiphase chemical equilibrium algorithm to calculate the reaction of complex components and phases. Bermúdez [22] studied the chemical equilibrium of the CO_2 reforming of coke oven gas and proposed a series of operating parameters suitable for producing methanol, but the reaction mechanism was not analyzed. Özkara [23] analyzed the thermodynamic equilibrium of the methane steam reforming and CO_2 reforming reaction. However, the mechanisms thereof were analyzed from the perspective of the reaction itself, in particular, the relationship between the reactants and catalysts. The proposed mechanisms were not adapted to describe the steam reforming reaction with complex components. Chen [9] also studied the steam reforming of coke oven gas, and some possible reactions were listed to describe the reaction mechanism. However, the listed reactions were not independent reactions and could not accurately represent the reaction mechanism. Chemical equilibrium characteristics have been repeatedly investigated to maximize the amount of hydrogen produced, but the requirement for breaking the chemical equilibrium of the steam reforming reaction has not been evaluated with respect to different applications of the gas mixture. In some schemes for the subsequent utilization of CCFG, the chemical equilibrium of the steam reforming process might not necessarily be broken. Moreover, the reaction mechanism of the steam reforming of the gas mixture has not been clearly elucidated, including the proper set of independent reactions for describing the reaction pathway. The reaction characteristics of steam reforming can determine the energy consumption of the reactor, but relevant studies have hardly been reported.

The aim of this study was to investigate the reactants and energy conversion characteristics of the steam reforming of CCFG, which is derived from the coal-based oxy-thermal method. A chemical equilibrium model of the steam reforming of CCFG was constructed, and the reaction mechanism of the process was analyzed according to the thermodynamic features of the independent reactions. Based on the chemical equilibrium model and the reaction mechanism, the effects of temperature, pressure and steam-to-gas ratio on the conversion ratios of CO and CH_4, the H_2 yield and the reaction heat of reactor were explored. Finally, the optimum operating conditions of the steam reforming of CCFG were determined.

Chemical equilibrium model and reaction mechanism of the steam reforming of CCFG

Chemical equilibrium model [19]

In mathematical optimization, to analyze the effect of multiple factors on a dependent variable, the method of Lagrange's undetermined multipliers is applied to the extremum solution for multivariate functions.

In a given material system, each element contributes to the mass balance of the system as follows:

$$\sum_i n_i a_{ij} = A_j \quad (j = 1, 2 \ldots M; i = 1, 2 \ldots N) \tag{1}$$

where A_j is the total atomic mass of the jth element in the system, a_{ij} is the atomic number of the jth element in component i and n_i is the molar flow of the component i. Lagrange multipliers λ_j are introduced into the equation, and the summation of all elements can be expressed as follows: