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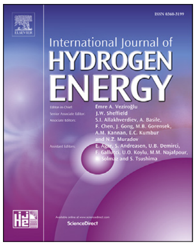

Thermodynamic equilibrium analysis of combined dry and steam reforming of propane for thermochemical waste-heat recuperation

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ABSTRACT

The thermochemical waste-heat recuperation is one for perspective way of increasing the energy efficiency of the fuel-consuming equipment. In this paper, the thermochemical waste-heat recuperation (TCR) by combined steam-dry propane reforming is described. To understand the influence of technological parameter such as temperature and composition of inlet gas mixture on TCR efficiency, thermodynamic equilibrium analysis of combined steam-dry propane reforming was investigated by Gibbs free energy minimization method upon a wide range of temperature (600–1200 K) and different feed compositions at atmospheric pressure. The carbon and methane formation was also calculated and shown. From a thermodynamic perspective, the TCR can be used for increasing energy efficiency at temperatures above 950 K because in this range the maximum conversion rate is reached (from 1.22 to 1.30 for the different feed composition). Approximately 10 mol of synthesis gas can be generated per mole of propane at the temperatures greater than 1000 K. Furthermore, the propane conversion rate and yield of hydrogen are increased with the addition of extra steam to the feed stock. Also, undesirable carbon formation can be eliminated by adding steam to the feed. The thermodynamic equilibrium analysis was accomplished by IVTANTHERMO which is a process simulator for thermodynamic modeling of complex chemically reacting systems and several results were checked by Aspen-HYSYS.

Introduction

The experts of the International Energy Agency showed that fossil fuel such as, oil and natural gas, will be the primary fuel for the World Economy during the future 100–150 years [1]. Nearly 80% of energy demand in the world by 2040 will be supplied by fossil fuels and the share of natural gas will reach 26% of the global demand for energy from the current 21% in 2015. Gas fuel such as propane is very important commodities because it is the main feeds of different industrial sectors [2]: transport [3–7], gas turbine [8–10], agriculture [11–13], e.a. Propane has replaced many older other traditional fuel sources. Propane is clean burning and effectively competes with other fossil and renewable fuels on efficiency and greenhouse gas emissions in many applications. Its simple chemical make-up allows it to burn cleaner than coal, light and heavy petroleum fuels, ethanol, and even natural gas in some cases. It is expected that the usage of propane in the future will increase continuously. Therefore, problems of improving energy

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efficiency get more relevant for the many propane-consuming equipment.

A common way to improve the energy efficiency of such equipment is heating of air for combustion by means of cooling flue gases [14–18]. This leads to significant increase of energy efficiency [19], but that way of recovery has some disadvantages. The heat exchangers for the preheat air have a large size, because heat-transfer coefficient in such exchangers is very low [20,21]. Preheat of propane in the heat exchangers by means of flue gases is not widely used, because it leads to high temperature propane cracking [22,23] which results in a reduction of heat-transfer coefficient in the exchangers. These disadvantages can eliminated using thermochemical heat recuperation of waste flue gases [24–27]. Thermochemical recuperation (TCR) is a perspective way to increase energy efficiency of the much propane-consuming equipment, for example, industrial propane-consumed gas furnaces, gas turbines and others.

Thermochemical recuperation of waste flue gases occurs when chemical endothermic reactions are used, for example, steam methane reforming [26], combined steam-dry methane reforming [28], steam ethanol reforming [25], propane reforming, etc. The idea of improving the efficiency of an energy plant by using the chemical recuperation of waste heat was discussed as early as in 1972 [24]. In recent years, the questions of chemical recuperation have been discussed in many papers [25,27–30].

Generally, for the thermochemical heat recovery can be used different chemical endothermic reaction, but the most obvious its advantages and feasibility of using a reforming of hydrocarbon gas, such as methane and propane [26]. To understand the effects of process variables such as temperature and composition of inlet gas mixture on TCR efficiency, thermodynamic equilibrium analysis of combined steam-dry propane reforming was investigated by Gibbs free energy minimization method upon a wide range of temperature (600–1200 K) and different feed compositions at atmospheric pressure.

Investigate studies of steam and dry propane reforming [31–35] were generally concentrated on research of catalyst performance and the results of these researches cant be matched because its the big difference of the operation conditions (temperature and inlet reactant composition). Nevertheless, the influence of the feed composition and temperature on equilibrium conversion rate and outlet composition can be determined by thermodynamic analysis. Different catalysts have been studied in propane reforming, including nickel-based [36–39] and noble metal-based catalysts (Pt, Rh, Pd, etc.) [40–43]. Concerning dry reforming of propane, Raaberg et al. [36,37] showed an exceptionally stable Ni/Mg(Al)O hydrotalcite derived catalyst. The intrinsic activity of catalysts depended strongly on Ni particle size. Further mechanistic studies showed C–C bond rupture is the rate determining step. Solymosi et al. [42,44] analyzed the characteristic of catalysts based on noble metal such as platinum (Pt), rhodium (Rh) and ruthenium (Ru) and reported the highest specific rates for hydrogen and carbon monoxide yield were on catalysts based on rhodium and ruthenium. Researching of catalyst based on bimetallic composition Co–Ni/Al_2O_3 in both CO_2 and H_2O propane reforming, it was concluded that coke deposition is the major reason of catalyst deactivation and poisoning [39,45–47]. Wang et al. [48] reported the results of thermodynamic equilibrium calculations steam and dry propane reforming which were obtained by equilibrium software Outokumpu HSC Chemistry 4.0, using the extensive thermochemical database delivered in the software package. Zheng et al. [49] reported a thermodynamic analysis of propane OSR in fuel cell for hydrogen and carbon monoxide production. However, there are no articles or reports which are contained results of thermodynamic equilibrium analysis of combined steam-dry propane reforming in terms of further influence of inlet feed ration and temperature by means of total Gibbs free energy minimization of the process (according to the author).

In this paper, author report the thermodynamic analysis of combined steam-dry reforming of propane, where total Gibbs free energy minimization method was employed to calculate equilibrium compositions for thermochemical waste-heat recuperation and transformation rate which is used to describe the relation of low heat value (LHV) of new synthesis fuel to LHV of initial propane. The carbon and methane formation was also calculated and illustrated. The effect of pressure on combined steam-dry propane reforming is not considered due to schematic diagram that is shown bottom on Fig. 1.

Thermochemical recuperation concept

Schematic diagram

The main concept of thermochemical waste-heat recuperation is transformation of flue gases heat into chemical energy of a new synthetic fuel that has higher calorimetric properties such as low heating value [50]. If in the conventional fuel-consuming equipment, for example the industrial furnaces, conversion of chemical energy of fuel into heat energy occurs by fuel combustion, then in the industrial furnaces with TCR the conversion of chemical energy of fuel is divided into two stages. The first stage is the increasing of the low heat value of initial propane by transformation of enthalpy waste-heat into chemical energy of the new synthetic fuel. The second stage is combustion of the new synthetic fuel that has low heat value greater than the low heat value of propane.

Fig. 1 shows the schematic diagram of the propane-consuming equipment with thermochemical heat recuperation of waste flue gases by propane reforming with flue gases.

In this diagram, the flue gases after the combustion chamber of the propane-consuming equipment are divided into two streams. First stream is fed to a reaction volume of the reformer. Also, propane is fed to the reformer. The reaction space of the reformer is activated by nickel catalysts [37–39,51–53]. In the reactor volume of the reformer occur reactions of the steam and dry reforming of propane and other chemical reactions which produce synthesis gas [54]. The produced gas (new synthetic fuel) is fed to the combustion chamber for combustion [55–59]. Second stream from the combustion chamber sequentially is passed through a heat-exchange space of the reformer and the air heater. The cool flue gases after the air heater are ejected into atmosphere. Second stream is passed through the heat-exchange space of

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