Energy 80 (2015) 642–653

Contents lists available at ScienceDirect

Energy

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

Thermoelectric generation coupling methanol steam reforming characteristic in microreactor

Feng Wang [a,*], Yiding Cao [b], Guoqiang Wang [c]

[a] Key Laboratory of Low-grade Energy Utilization Technologies and Systems (Chongqing University), Ministry of Education, Chongqing 400030, PR China
[b] Department of Mechanical and Materials Engineering, Florida International University, Miami, FL 33174, United States
[c] College of Power Engineering, Chongqing University, Chongqing 400030, PR China

ARTICLE INFO

Article history:
Received 23 July 2014
Received in revised form
17 October 2014
Accepted 5 December 2014
Available online 27 December 2014

Keywords:
Thermoelectric
Endothermic steam reforming
Hydrogen production
Cold spot
Microreactor

ABSTRACT

Thermoelectric (TE) generator converts heat to electric energy by thermoelectric material. However, heat removal on the cold side of the generator represents a serious challenge. To address this problem and for improved energy conversion, a thermoelectric generation process coupled with methanol steam reforming (SR) for hydrogen production is designed and analyzed in this paper. Experimental study on the cold spot character in a micro-reactor with monolayer catalyst bed is first carried out to understand the endothermic nature of the reforming as the thermoelectric cold side. A novel methanol steam reforming micro-reactor heated by waste heat or methanol catalytic combustion for hydrogen production coupled with a thermoelectric generation module is then simulated. Results show that the cold spot effect exists in the catalyst bed under all conditions, and the associated temperature difference first increases and then decreases with the inlet temperature. In the micro-reactor, the temperature difference between the reforming and heating channel outlets decreases rapidly with an increase in thermoelectric material's conductivity coefficient. However, methanol conversion at the reforming outlet is mainly affected by the reactor inlet temperature; while at the combustion outlet, it is mainly affected by the reactor inlet velocity. Due to the strong endothermic effect of the methanol steam reforming, heat supply of both kinds cannot balance the heat needed at reactor local areas, resulting in the cold spot at the reactor inlet. When the temperature difference between the thermoelectric module's hot and cold sides is 22 K, the generator can achieve an output voltage of 55 mV. The corresponding molar fraction of hydrogen can reach about 62.6%, which corresponds to methanol conversion rate of 72.6%.

1. Introduction

Thermoelectric (TE) generation is a static electricity generation method which converts heat energy to electric energy by a thermoelectric material. Heat sources of this method are very broad, including waste heat from industries, automobiles, fuel cells, marine engines and solar energy. Thermoelectric module creates voltage when there is a temperature difference between its cold and hot sides. Therefore, output power is in direct proportion to the temperature difference across the generator [1–5]. According to many studies on the thermoelectric generation, the key measures to improve efficiency of the power generation lie in the removal of the heat on the cold side of the module. Cooling methods of natural convection, air cooling, or water cooling has been adopted by researchers to remove the heat. However, these methods are either passive heat dissipation or active cooling with low cooling efficiency [6–10]. In this paper, an innovative cooling method is used by adopting the strong endothermic reaction of methanol steam reforming as the heat sink on the cold side of the thermoelectric module.

Fuel (such as methanol) steam reforming for hydrogen production is a strong endothermic process, in which a temperature difference between the reforming channel and heating channel always exists due to the heat transfer resistance when an external heat source is supplied [11–15]. This temperature difference between the two channels can be harnessed to generate electricity by coupling a thermoelectric generator in the process of heat transferring from the heating channel with the reforming channel [16,17]. Furthermore, low grade exhausted or waste heat with a temperature usually higher than 200 °C is widely available in

* Corresponding author. Tel.: +86013618203569.
E-mail address: wangfeng@cqu.edu.cn (F. Wang).

http://dx.doi.org/10.1016/j.energy.2014.12.019
0360-5442/

industrial furnaces, engine exhaust, and metallurgy. The heat capacity of the exhausted or waste heat resource in various industries may represent about 17% ~ 67% of the total fuel consumption [18,19]. Therefore recycling the waste heat energy may contribute to energy saving and emission reduction strategy of the global society [20,21]. Different temperatures and temperature difference distributions and their characters in reforming channel and heating channel under different intensity of the heat sources have been examined [22–24]. However, the studies focus mainly on catalyst preparation and optimization [25–28], and the study of the reaction heat effect especially cold spot character on the reactor catalyst bed is limited [29–34]. Additionally, there is no study on thermoelectric power generation coupling endothermic steam reforming as heat sink for hydrogen production in micro-reactors.

Therefore, in this paper a coupling process of thermoelectric generation and methanol steam reforming for hydrogen production is designed and analyzed. Firstly, a monolayer catalyst bed of $CuO/ZnO/Al_2O_3$ is packed in a micro-reactor to study its endothermic nature and cold spot phenomena in methanol steam reforming process. Effects of inlet reactant temperatures on the reforming products composition and methanol conversion are investigated. Variation of the cold spot with inlet temperature is also inspected. Then simulated waste heat and catalytic combustion are used as heat supply sources for the strong endothermic methanol steam reforming reaction coupling thermoelectric generation. Through this design, the grade of methanol is improved, and simultaneously CO_2 in the reaction system is removed, achieving the goal of improving fuel efficiency and reducing emissions in one system [35–37]. Characteristic of this coupling process is also studied by numerical simulation.

2. Cold spot characteristic of methanol steam reforming in micro-reactor

2.1. Micro-reactor design and experimental system

Experiments of methanol steam reforming for hydrogen production are carried out in a self-designed micro-reactor that is integrated with reactant preheating, gasification, overheating and reaction in one unit, as shown in Fig. 1. The reactor is heated by electric heaters. The dimensions of the reaction volume are 50 mm × 60 mm × 3.5 mm, which has a designed area slightly larger than that of the thermoelectric module. A monolayer catalyst bed is designed and packed in it. The catalyst particles used are of the shape of cylinder with a diameter of 5 mm and a height of 3.5 mm, which is prepared specifically to exactly match the reaction dimension. The type of the catalyst is commercial $CuO/ZnO/Al_2O_3$ catalyst with a total mass of 4.7 g. Inlet temperature T_{in} before reaction and reaction temperature T in catalyst bed are measured separately. T_{in} is regarded as the temperature of the reactant gas before it enters the reaction section, which is calculated as the

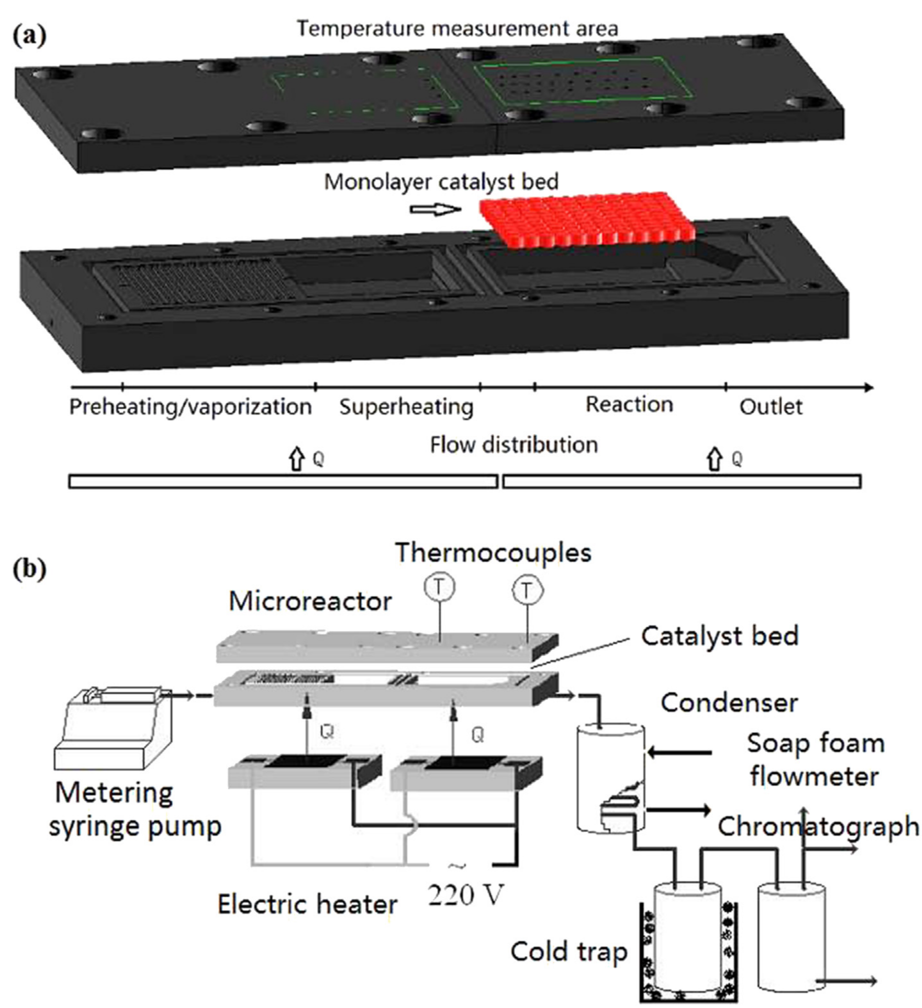

Fig. 1. Micro-reactor and experimental system for methanol steam reforming.