J. of Supercritical Fluids xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

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

A mathematical model and numerical investigation for glycerol gasification in supercritical water with a tubular reactor

Hui Jin[a,*], Simao Guo[a], Liejin Guo[a,b], Changqing Cao[a]

[a] State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an 710049, China
[b] The College of Engineering, Department of Mechanical Thermal Engineering and Chemical & Material Engineering, King Abdulaziz University, Jeddah 21589, Saudi Arabia

ARTICLE INFO

Article history:
Received 25 January 2015
Received in revised form 27 June 2015
Accepted 27 June 2015
Available online xxx

Keywords:
Supercritical water gasification
Tubular reactor
Numerical study
Glycerol
Hydrogen production

ABSTRACT

This paper developed a three-dimensional computational fluid dynamics model of the supercritical water gasification (SCWG) process of glycerol. The detailed flow field, temperature field and chemical species distributions inside the reactor were revealed, and the effects of the operating parameters on the results in the SCWG of glycerol were investigated. The reasons for incomplete gasification were discussed, and relevant possible improvements were proposed. (1) The residence time is not long enough for the complete gasification; therefore, the optimal length of the tubular reactor was obtained under different operating conditions. (2) A side-reaction region was formed near the feeding inlet and methods to reduce the volume of the side-reaction region were investigated. A high preheated water temperature and a 135° feeding angle were proved to obviously avoid side-reaction. A multi-injection feeding method can also suppress the side-reaction, but the carbon gasification efficiency decreased.

1. Introduction

Supercritical water (SCW) is defined as water with temperature and pressure beyond the critical point (374 °C, 22.1 MPa), and it has many unique properties, such as low viscosity, high diffusivity and low dielectric constant. These properties make supercritical water a good solvent for both organic matters and gas to provide a homogenous reaction medium for efficient gasification within a short residence time. Supercritical water gasification (SCWG) is a promising technology to convert glycerol and other organic wastes to hydrogen-rich gas products [1–4]. Much research on SCWG has been carried out by various authors in the last two decades. These works have mainly focused on the development of SCWG reactors [5–7], investigation of different feedstocks (such as glucose [8,9], cellulose [10,11], lignin [12–14], real biomass [15–17], coal [18–21] and waste organics [22–24]), investigation of effects of different gasification parameters (such as temperature, pressure and residence time) [25], evaluation of catalysts [26,27] and thermodynamic analysis [28,29]. The research work mentioned above has proven the feasibility of glycerol gasification in SCW and helped uncover more information about the characteristics of SCWG to obtain a method to improve the carbon gasification efficiency.

Most published reactors for SCWG are bench-scale reactors or even micro-reactors. It is essential to gain a better understanding of the complex physical process (including flow and heat transfer) and chemical reactions in continuous SCWG reactors from the point of view of chemical reaction engineering for the reactor scale-up and industrial applications. Unfortunately, little information about internal fluid flow, heat transfer, mass transfer and reactions in SCWG reactors has been revealed by experimental measurement methods thus far due to the extreme operating conditions. As a result, computational fluid dynamics (CFD) modeling may be applied to obtain valuable information about the gasification process in an SCWG reactor. It is a good way to understand the detailed gasification process inside the reactor and provide guidance for upgrading reactors. However, little work has been done in modeling the SCWG process, especially taking gasification kinetics into account. The difficulty in modeling the SCWG process may lie in the following aspects: (1) thermodynamic and transport properties of the reaction mixture in the reactor [30], (2) an appropriate turbulent heat-transfer model of supercritical water and (3) reliable gasification kinetics in SCW. Yoshida [31] conducted CFD simulations to investigate the reactant flow and particle participation in his reactor for structural design improvement, but the chemical reactions were not considered. Goodwin [32] proposed a CFD model to simulate xylose gasification in the microchannel reactor and studied the effect of residence time on gasification. Moreover, the kinetics model for xylose in SCW was incorporated in the CFD

* Corresponding author. Tel.: +86 29 8266 0876; fax: +86 29 8266 9033.
E-mail address: jinhui@mail.xjtu.edu.cn (H. Jin).

http://dx.doi.org/10.1016/j.supflu.2015.06.028
0896-8446/

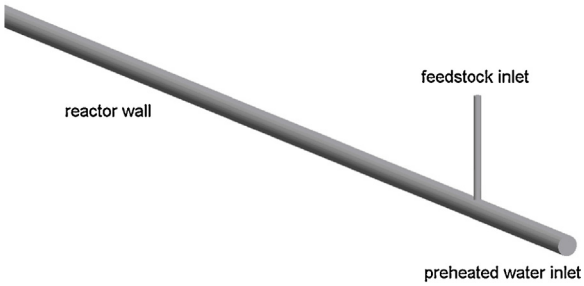

Fig. 1. Geometric construction for tubular reactor of hydrogen production by glycerol gasification in supercritical water.

model, which could predict gas yields. Adaze [33] studied effects of various operating parameters on heating time and heating length of supercritical water reactors with a CFD model and proposed a semi-theoretical model for calculating the heating time constant of a SCW reactor.

The objective of this study is to develop a model of the SCWG process, considering flow, heat transfer and gasification reaction. A three-dimensional computational fluid dynamics (CFD) model was established with a kinetics model for supercritical water gasification of glycerol. The combined model was validated by our experimental results regarding the SCWG of glycerol in a tubular reactor. The detailed distributions of velocity, temperature and species in the reactor were revealed by the CFD model. The effects of operating parameters on the SCWG of glycerol were also investigated. Moreover, the CFD model was also used for the optimal design for SCWG tubular reactor including the feeding method.

2. Experimental setup

2.1. Apparatus and procedure

The experiments were performed in a continuous SCWG system developed in State Key Laboratory of Multiphase Flow in Power Engineering (SKLMFPE) [18,22]. The feedstock (glycerol solution) was first mixed with high-temperature preheated water for fast heating to suppress side reactions. The mixing flow entered the reactor located in the center of three ovens equipped along the reactor length. The reactor was fabricated from Hastelloy C276 tubing and had dimensions of 17.15 mm o.d. × 10.85 mm i.d. × 1.26-m length (Fig. 1). The design temperature and pressure were 800 °C and 30 MPa, respectively. Two type-K thermocouples were inserted into the central line of the inlet and outlet of the reactor, respectively, to measure the fluid temperature.

2.2. Data interpretation

The GE, CE and gas yield were selected to evaluate the gasification characteristics and are defined as follows [20]:

$$\mathrm{CE} = \frac{(\text{total carbon in the gaseous products})}{(\text{total carbon in the feedstock})} \times 100\,(\%)$$

$$\mathrm{GE} = \frac{(\text{mass of the gaseous products})}{(\text{mass of the feedstock})} \times 100\,(\%)$$

$$\text{Gas yield} = \frac{(\text{molar amount of a certain component of the gaseous products})}{(\text{molar amount of glycerol})}\ (\text{mol/mol})$$

3. Mathematical model

3.1. Governing equations

Mass conservation:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \left(\rho \vec{\upsilon}\right) = 0 \tag{1}$$

where ρ is the fluid density and $\vec{\upsilon}$ is the velocity vector.

Momentum conservation:

$$\frac{\partial}{\partial t}\left(\rho \vec{\upsilon}\right) + \nabla \cdot \left(\rho \vec{\upsilon}\vec{\upsilon}\right) = -\nabla p + \nabla \cdot \vec{\tau} + \rho \vec{f} \tag{2}$$

where $\vec{\tau}$ is the viscous stress tensor and $\vec{f}$ is the mass force vector.

Energy conservation:

$$\frac{\partial (\rho h)}{\partial t} + \nabla \cdot \left(\rho \vec{\upsilon} h\right) = \nabla \cdot \left(\lambda \nabla T - \sum_i h_i J_i\right) + \frac{Dp}{Dt} + \vec{\tau} : \nabla \vec{\upsilon} \tag{3}$$

where $h = \sum_j Y_j h_j$, $h_i = h_i^0\left(T_{ref,i}\right) + \int_{T_{ref,j}}^{T} c_{p,i}\mathrm{d}T$, λ is the thermal conductivity, and $h_i^0\left(T_{\mathrm{ref},i}\right)$ is the standard mole enthalpy of the formation of species *i*.

Species conservation:

$$\frac{\partial}{\partial t}\left(\rho Y_i\right) + \nabla \cdot \left(\rho \vec{\upsilon} Y_i\right) = -\nabla \cdot \vec{J}_i + R_i \tag{4}$$

where Y_i is the mass fraction of i, $\vec{J}_i$ is the diffusion flux of specie i, R_i is the total chemical reaction rate, and

$$R_i = M_{w,i} \sum_{r=1}^{N} \nu_i Q_r \tag{5}$$

where Q_r is the reaction rate of reaction r, ν_i is the stoichiometric coefficient of species i in reaction r, and $M_{w,i}$ is the molar weight of species i.

3.2. Reaction kinetics

A kinetic model used for calculating gas yields by glycerol gasification in supercritical water was developed in our previous work [34]. The reactions and rates were as follows:

Glycerol pyrolysis I.

$$C_3H_8O_3 \xrightarrow{K_1} Int + CO_2 + 2H_2$$

$$Q_1 = 10^{2.60} \exp\left(\frac{-53.3 \times 10^3}{(\mathrm{RT})}\right) C_{C_3H_8O_3} \tag{R1}$$

Glycerol pyrolysis II.

$$C_3H_8O_3 \xrightarrow{K_2} \mathrm{Int} + \mathrm{CO} + \mathrm{H_2} + \mathrm{H_2O}$$

$$Q_2 = 10^{2.76} \exp\left(\frac{-59.8 \times 10^3}{(\mathrm{RT})}\right) C_{C_3H_8O_3} \tag{R2}$$

Intermediate steam reforming I.

$$\mathrm{Int} + \mathrm{H_2O} \xrightarrow{K_3} 2\mathrm{CO} + 3\mathrm{H_2}$$

$$Q_3 = 10^{6.63} \exp\left(\frac{-114.1 \times 10^3}{(\mathrm{RT})}\right) C_{\mathrm{Int}} C_{\mathrm{H_2O}} \tag{R3}$$

Please cite this article in press as: H. Jin, et al., A mathematical model and numerical investigation for glycerol gasification in supercritical water with a tubular reactor, J. Supercrit. Fluids (2015), http://dx.doi.org/10.1016/j.supflu.2015.06.028