Fuel 215 (2018) 66–79

Contents lists available at ScienceDirect

Fuel

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

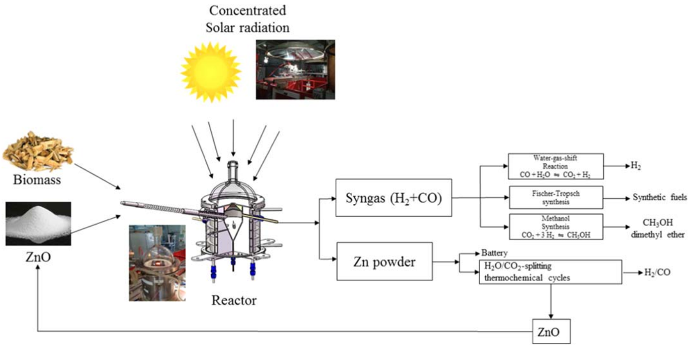
Full Length Article

Solar chemical looping gasification of biomass with the ZnO/Zn redox system for syngas and zinc production in a continuously-fed solar reactor

Srirat Chuayboon[a,b], Stéphane Abanades[a,*], Sylvain Rodat[c,d]

[a] Processes, Materials and Solar Energy Laboratory, PROMES-CNRS, 7 Rue du Four Solaire, 66120 Font-Romeu, France
[b] Department of Mechanical Engineering, King Mongkut's Institute of Technology Ladkrabang, Prince of Chumphon Campus, Chumphon 86160, Thailand
[c] Univ. Grenoble Alpes, INES, BP 332, 50 Avenue du Lac Léman, F-73375 Le-Bourget-du-lac, France
[d] CEA-LITEN Laboratoire des Systèmes Solaires Haute Température (LSHT), F-38054 Grenoble, France

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Gasification
Pyrolysis
Biomass
Solar fuel
Syngas
Redox cycle

ABSTRACT

The high-temperature solar-driven chemical looping gasification of lignocellulosic biomass with ZnO/Zn redox pair was investigated as a novel process producing both syngas and metallic zinc. A lab-scale solar reactor (1.5 kW) was operated for continuous combined biomass gasification and ZnO carbo-thermal reduction using solar energy as the source of high-temperature process heat. Experiments were performed at temperatures ranging from 1050 °C to 1300 °C with biomass/ZnO molar ratios from 0.5 to 1, using beech wood as a biomass feedstock. The objective of this study was to unveil the advantages and reliability of the combined process involving biomass pyro-gasification with solid ZnO as an oxidizing agent under continuous process operation for co-production of syngas and metallic Zn. The influence of temperature and reactant molar ratio on syngas production was highlighted and compared to the case of a pyrolysis process without any oxidant. Moreover, the chemical conversion of ZnO to Zn obtained by this endothermic step was also addressed, confirming pure Zn production with low recombination in the collected solid products. The evolved H_2 increased significantly, CO production also tended to increase slightly, while CO_2 and CH_4 decreased when increasing the temperature. The syngas yield of the combined gasification/carbo-thermal reduction (up to $\sim 8\ mol_{syngas}/mol_{biomass}$ for a biomass/ZnO molar ratio of 0.75 at 1250 °C) was much higher in comparison with pyrolysis. The calorific value of the feedstock was solar up-graded through syngas and Zn production in the case of the biomass gasification using ZnO, whereas pyrolysis was not energetically efficient because of the energy content still remaining in the

---

* Corresponding author.
E-mail address: stephane.abanades@promes.cnrs.fr (S. Abanades).

https://doi.org/10.1016/j.fuel.2017.11.021
Received 27 March 2017; Received in revised form 3 November 2017; Accepted 7 November 2017

produced char. The optimal biomass/ZnO molar ratio was evidenced at 0.75 yielding maximum syngas production. The energy upgrade factor of the feedstock by the solar power input and the solar-to-fuel energy conversion efficiency were 1.17 and 19.8% respectively for a molar ratio of 0.75 at 1250 °C.

1. Introduction

Currently, climate change owed to continuous consumption of fossil fuels and associated greenhouse gases emissions is of major concern. Therefore, renewable energy sources are the most favorable answer to replace fossil fuel supply and to reduce pollutant emissions. Biomass and solar energy are both widely available renewable sources that can be combined in a solar thermochemical process to produce carbon-–neutral solar fuels such as hydrogen, syngas and derived synthetic hydrocarbon fuels. The solar thermochemical processes consist in using solar energy as the heat source to drive high-temperature chemical reactions such as solar biomass pyro-gasification or carbo-thermal metal oxide reduction [1]. Consequently, in order to capture solar energy, concentrated solar technologies can be used to heat chemical reactors [2]. The carbo-thermal reduction is the reduction of metal oxides using carbon as a reducing agent in order to decrease the reaction temperature. Besides, both gaseous and solid carbonaceous feedstocks can be used as reducing agents for the reaction with metal oxides. Regarding metal oxides, ZnO/Zn redox pair is one of the most interesting candidates due to its suitable physical properties [3]. The ZnO decomposition temperature is about 2000 °C, which can be decreased to about 950 °C by using carbon as reducer [4]. This means the reaction produces Zn in gaseous form at the reaction temperature since Zn boiling point is 907 °C (Zn melting point is 419 °C). Zn vapor thus condenses as small particles during gas cooling, which are collected at the outlet of the reactor. Therefore, continuous process operation with particle feeding can be considered. In this study, ZnO was selected as the metal oxide, while lignocellulosic biomass (beech wood) was used as the reducing agent, in order to demonstrate the feasibility of co-production of Zn and syngas in a continuously-fed solar reactor. The overall endothermic chemical reaction consisting of combined ZnO carbo-thermal reduction and biomass gasification (with molecular formula assumed as $C_6H_9O_4$) can be written according to Eq. (1).

$$2ZnO(s) + C_6H_9O_4(s) \rightarrow 2Zn(g) + 6CO(g) + 4.5H_2(g) \quad \Delta H^\circ = 1.28\,\text{MJ/mol} \tag{1}$$

The stoichiometric molar ratio of biomass to ZnO is thus 0.5. For this highly endothermic step, the reaction releases not only syngas composed of H_2 and CO, but also lower-valence metal species (Zn).

Moreover, the reduction reactions of ZnO with the gas products of the biomass gasification must be taken into account.

$$ZnO(s) + CO(g) \rightarrow Zn(g) + CO_2 \quad \Delta H^\circ = 197.9\,\text{kJ/mol} \tag{2}$$

$$ZnO(s) + H_2(g) \rightarrow Zn(g) + H_2O(g) \quad \Delta H^\circ = 239.1\,\text{kJ/mol} \tag{3}$$

The produced syngas can be further processed to hydrogen (via water–gas shift) or liquid hydrocarbon fuels (via Fisher-Tropsch synthesis) for the power or transportation sectors, while Zn can be used in batteries or as a high value chemical commodity. In addition, the Zn particles produced from the first step can be further processed in a second step via exothermic reaction with H_2O and/or CO_2 as described in Eqs. (4) and (5). Zn(s) is thus re-oxidized to produce additional pure H_2 and/or CO and ZnO is then recycled to the first step (two-step H_2O/CO_2 splitting cycle).

$$Zn(s) + H_2O \rightarrow ZnO(s) + H_2 \quad \Delta H^\circ = -108.7\,\text{kJ/mol} \tag{4}$$

$$Zn(s) + CO_2 \rightarrow ZnO(s) + CO \quad \Delta H^\circ = -67.5\,\text{kJ/mol} \tag{5}$$

Concerning the conventional gasification reaction, the thermochemical process basically encompasses two steps. First, a pyrolysis step occurs via the decomposition of solid hydrocarbons at temperatures from 300 °C to 1000 °C. The biomass chiefly decomposes into char, tars and incondensable gases, as represented in Eq. (6) [5]. During this step, both high temperatures and heat transfer rates favor the production of gas products over char and tars.

$$Biomass \rightarrow char(carbon) + CO + CO_2 + H_2 + CH_4 + tars \tag{6}$$

Second, the char is gasified with an oxidizing agent (such as steam or CO_2) yielding different reactions.

$$C + H_2O \rightarrow CO + H_2 \quad \Delta H^\circ = 131.3\,\text{kJ/mol} \tag{7}$$

$$C + 2H_2 \rightarrow CH_4 \quad \Delta H^\circ = -74.6\,\text{kJ/mol} \tag{8}$$

$$C + CO_2 \rightarrow 2CO \quad \Delta H^\circ = 172.4\,\text{kJ/mol} \tag{9}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H^\circ = -42\,\text{kJ/mol} \tag{10}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H^\circ = 206\,\text{kJ/mol} \tag{11}$$

Equilibrium gas compositions of carbon-steam and carbon-CO_2 systems as a function of temperature show that H_2 and CO are the main gas produced when the temperature exceeds 1000 °C. In contrast, CH_4 decreases considerably when increasing the temperature both because CH_4 formation is thermodynamically favored at lower temperatures (CH_4 is unstable above ~1000 °C) and because the kinetics of methane formation is too slow [5].

Conventional gasification processes to produce synthesis gas involve a partial combustion of the feedstock with air or oxygen to supply energy [6], which discharges a large amount of CO_2 to the atmosphere [7]. Moreover, a purification of the produced syngas may be needed, thereby consuming additional energy in separation systems [8,9]. Another approach for achieving improved chemical performance is solar thermochemical gasification [10–15]. The main advantages of using solar radiation as the energy source are: the calorific value of the feedstock is upgraded by the solar power input, the gaseous products are not contaminated by combustion by-products, and the discharge of pollutants is avoided. The solar hybrid thermochemical process saves the feedstock and reduces CO_2 emissions. It further converts intermittent solar energy into a storable and transportable chemical fuel. Meanwhile, biomass is solar-upgraded to a clean synthetic fuel. In contrast to the gasification using process heat derived from internal combustion, the solar-driven gasification produces energy-rich and high-quality syngas that is not contaminated by the products of combustion [10–15].

When using solid ZnO as an oxidizing agent instead of H_2O/CO_2 in the reaction of biomass gasification, the reaction with the char (solid–solid reaction) corresponds to the ZnO carbo-thermal reduction:

$$ZnO(s) + C \rightarrow Zn(g) + CO \quad \Delta H^\circ = 370.4\,\text{kJ/mol} \tag{12}$$

Concerning carbo-thermal reduction, the use of a solid or gaseous carbonaceous feedstock as reducing agent aids in reducing the operating temperature [16–19], while the metallic compound can be processed in a thermochemical cycle [20,21]. In this case, either pure carbon or natural gas was used as a reducing agent. Carbo-thermal reduction of ZnO with solid carbon was tested in a 5 kW two-cavity beam down solar reactor [22] and further scaled-up to 300 kW [23]. The pilot was batch-operated in the temperature range 1000–1200 °C, yielding 50 kg/h of 95%-purity Zn. Besides, a vortex-flow solar chemical reactor for the combined ZnO-reduction and CH_4 reforming was investigated [24]. The reactor was operated at 950–1200 °C yielding 83–100% chemical conversion and 11–28% thermal efficiency. Koepf et al. [25] investigated the carbo-thermal reduction of ZnO with beech