Assessment of energy flows and energy efficiencies in integrated catalytic adsorption steam gasification for hydrogen production

Zakir Khan[a,*], Suzana Yusup[b], Prashant Kamble[c], Muhammad Naqvi[d], Ian Watson[c]

[a] Department of Chemical Engineering, COMSATS University, Lahore 54000, Pakistan
[b] Chemical Engineering Department, Biomass Cluster Centre of Biofuel and Biochemical Research, Institute of Sustainable Living, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak Darul Ridzuan, Malaysia
[c] Systems Power and Energy, School of Engineering, University of Glasgow, Glasgow G12 8QQ, UK
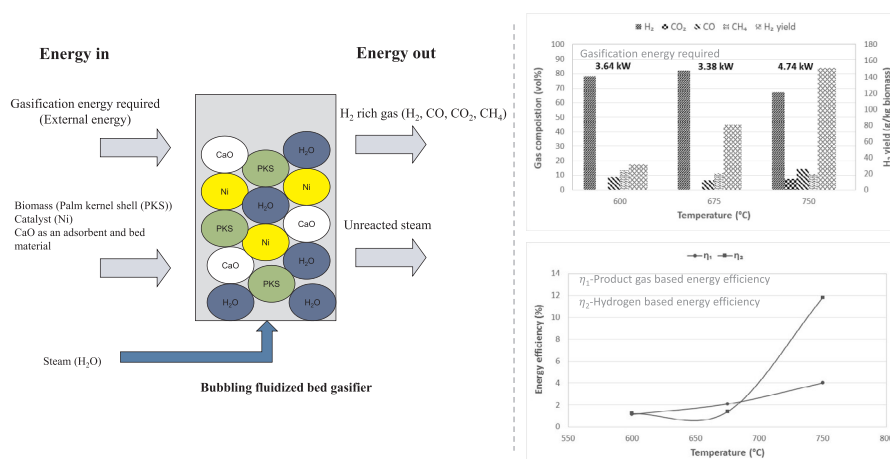[d] Department of Engineering and Chemical Sciences, Karlstad University, Sweden

HIGHLIGHTS

- Energy flows and efficiencies for H_2 in Integrated catalytic adsorbent gasification.
- In-situ CO_2 adsorption reaction minimized overall gasification energy usage.
- Energy usage increases with temperature, steam to biomass and fluidization velocity.
- H_2 based energy efficiencies increases with temperature.
- Product gas energy efficiencies increases with temperature and steam to biomass.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

This study addresses the energy flows and energy efficiency of integrated catalytic adsorption biomass steam gasification for hydrogen production in a pilot scale bubbling fluidized bed system utilizing palm kernel shell as feedstock. The integrated catalytic adsorption utilizes catalyst and CO_2 adsorbent together in the single fluidized bed gasifier. Various variables such as effect of temperature (600–750 °C), steam to biomass ratio (1.5–2.5 w/w), adsorbent to biomass ratio (0.5–1.5 w/w), fluidization velocity (0.15–0.26 m/s) and biomass particle size (0.355–0.500 to 1.0–2.0 mm) are investigated. The results imply that the overall requirement of gasification energy increases with increasing gasification temperature, steam to biomass ratio, fluidization velocity, and decreases with adsorbent to biomass ratio whilst no significant increase is observed by varying the biomass particle size. However, a slight reduction in required energy is observed from 600 °C to 675 °C which might be due to strong CO_2 adsorption, an exothermic reaction, and contributes to the energy requirements of the process. Besides, hydrogen-based energy efficiencies increase with increasing temperature while first increases to a medium value of steam to biomass ratio (2.0), adsorbent to biomass ratio (1.0) and fluidization velocity (0.21 m/s) followed by a slight decrease (or remains unchanged). The integrated catalytic adsorption steam gasification is
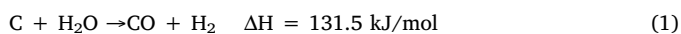
found to be a high energy consuming process and thus, waste heat integration needs to be implemented for feasible hydrogen production.
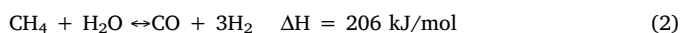
1. Introduction

There is growing interest in hydrogen as an energy carrier due to serious environmental issues and greenhouse gas emissions caused by conventional fossil fuels. Presently, almost 98% hydrogen comes from fossil fuels [1]; however, their fast depletion rate and other competing use of fossil fuels have serious concerns, and search for renewable sources has been intensified. Biomass is one of the most promising sources among renewable resources to produce abundant, clean and renewable hydrogen and is the only real alternative to fossil fuel derived hydrogen, with likely emerging competition from water electrolysis which is electrically intensive. Among thermal conversion processes, biomass gasification is the one process which shows great potential for renewable hydrogen production [2]. Biomass gasification produces gaseous mixtures that mainly contains: H_2, CH_4, CO and CO_2 (by using air, oxygen and steam or in combination as the gasifying agent).

Recent application of catalyst and *in-situ* CO_2 adsorption to enhance hydrogen from biomass gasification makes the process more viable for commercial scale. Efforts are mainly focused on reducing the number of process units by introducing novel catalyst [3,4], CO_2 sorption [5–7] or coupling both in the same reactors (after gasification) [8] and/or in separate reactors (after the pyrolysis step) [9]. However, utilizing methane reforming catalyst and CO_2 sorbent together in one bed may have an advantage of needing a single reactor. CO_2 capturing through carbonation reaction shifts the equilibrium of water gas shift and steam methane reforming towards more hydrogen production [10]. The addition of catalyst will further enhance the activity of steam methane reforming towards hydrogen production [11]. Based on our previous research work, there are advantages of the process to operate in a single unit in order to minimize the capital cost by avoiding additional downstream units [12,13]. Secondly, the benefits of utilizing methane reforming catalyst and CO_2 sorbent together in one bed and a single reactor can be understood by considering the main biomass steam gasification reactions with *in-situ* CO_2 adsorbent (Eqs. (1)–(4)). The capturing of CO_2 takes place via carbonation reaction (Eq. (4)) which accelerates the water gas shift reaction towards enhanced hydrogen production under Le Chatelier's principle. The amounts of CO react in water gas shift (Eq. (3)) comes from steam methane reforming (Eq. (2)) and char gasification (Eq. (1)), and provides an opportunity to accelerate the former reaction through the enhanced activity of later reactions. Steam methane reforming and char gasification are both endothermic reactions and the activities are heavily dependent on maintaining a high temperature. However, with temperatures > 725 °C for biomass gasification, with *in-situ* CO_2 adsorbent in the bed, is a matter of concern due to reverse carbonation, especially when CaO is used as an adsorbent [14–17]. Therefore, using steam methane reforming catalyst in the bed not only enhances hydrogen production (even at low temperature) but also provides more CO to allow the water shift reaction to move in the forward direction.
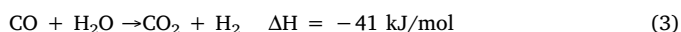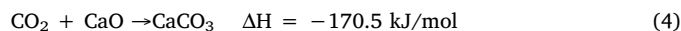
Char gasification reaction (CGR)

$$C + H_2O \rightarrow CO + H_2 \quad \Delta H = 131.5 \text{ kJ/mol} \tag{1}$$

Steam methane reforming (SMR)

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H = 206 \text{ kJ/mol} \tag{2}$$

Water gas shift reaction (WGSR)

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H = -41 \text{ kJ/mol} \tag{3}$$

Carbonation reaction

$$CO_2 + CaO \rightarrow CaCO_3 \quad \Delta H = -170.5 \text{ kJ/mol} \tag{4}$$

Steam gasification is being identified as a potential process to produce clean hydrogen [18] and using steam as the sole gasification agent has numerous advantages over using air or pure oxygen, which is considered costly for small scale operation [19]. However, utilizing steam has a high energy penalty; consequently, optimal experimental conditions need to be identified to allow efficient and economical gasification operation. Few papers in the literature have been found to address the energy flows and efficiency of biomass steam gasification for hydrogen production [20–22]. Galanti et al. [23] reported the equivalence efficiency (sum of net electrical and thermal energy to the thermal power input) related to syngas and hydrogen production along with electric and thermal energy using coal and coal-biomass mixture in Web-based Thermo Economic Modular Program (WTEMP) software. The main objective of the study was to analyze the co-production of hydrogen and electricity via pyrolysis and gasification in an existing steam power plant. For energy applications, Wang et al. [23] reported the energy and exergy analysis of a combined cooling, heat and power (CCHP) system based on air gasification. Some researchers, however, have reported the assessment of coal-based hydrogen production with CO_2 capture [24] and biomass direct chemical looping for hydrogen production [6]. Recently, Schweitzer et al. [25] carried out biomass steam gasification utilizing sorption enhanced reforming (SER) process model to evaluate the fuel-to-hydrogen and electricity efficiencies. The concept of the model was to use *in-situ* CO_2 capture limestone as a bed material using a gasifier and regenerator in biomass steam gasification whereas additional energy was required to decompose $CaCO_3$ to produce CaO in the regenerator. Based on the literature cited, it can be concluded that most of the previous studies are limited to the theoretical approach to evaluate hydrogen based energy efficiencies in the biomass steam gasification system. Secondly, the assessment of biomass steam gasification with integrated catalytic-adsorption (ICA) for hydrogen production is not reported yet and will be worthwhile to investigate. The CO_2 adsorption reaction is an exothermic reaction and a few studies [18,26] discuss the benefits of its add-in energy in overall energy requirement in the heat intensive processes such as biomass steam gasification.

The present study addresses the energy flows and energy efficiency of ICA biomass steam gasification for hydrogen production in a pilot scale bubbling fluidized bed system. Energy balance over gasifier with variable temperature, steam to biomass (S/B), adsorbent to biomass (A/B), fluidization velocity and biomass particle size are investigated. The total energy requirements and energy efficiency based on hydrogen and overall gas production are also reported and discussed in detail.

2. Material and methods

2.1. Materials

Palm kernel shell (PKS) as oil palm waste was used as the feedstock for hydrogen production via integrated catalytic adsorption (ICA) steam gasification. The ground palm kernel shell was supplied by My 4-Seasons International Sdn. Bhd, Malaysia, which was sieved to a particle size of 0.355–0.500 mm and 1.0–2.0 mm. The proximate and ultimate analysis of palm kernel shell is shown in Table 1.

Quicklime, commonly known as calcium oxide was used as a bed material as well as the source of CaO to adsorb CO_2 in the product gas. The quicklime was obtained from Universal Lime Sdn. Bhd., Malaysia. The sample was ground and sieved to a particle size of