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Assessment of Energy Flows in Integrated Catalytic Adsorption (ICA) Steam Gasification for Hydrogen Production

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Abstract

Biomass has a potential to produce sustainable and renewable hydrogen due to its low sulphur and nitrogen content (low NOx and SOx emissions) and contributes towards net CO_2 cycle. Biomass steam gasification is found to be most promising among thermal conservation processes for renewable hydrogen production. The energy required for gasification using steam is high compared to other gasification agents e.g. air or pure oxygen. The integrated catalytic adsorption (ICA) utilizes catalyst and CO_2 adsorbent together in the single fluidized bed gasifier. The present study investigates the energy flows to optimize the gasification energy requirement with respect to hydrogen concentration and yield in the ICA process at 600, 650 and 750 °C. The overall gasification energy required increased with increasing gasification temperature from 675 to 750 °C. However, a slight reduction in required energy was 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. This was further verified with zero CO_2 and highest hydrogen compositions (82 vol%) at 675 °C. However, ICA steam gasification is found to be a high energy consuming process and heat integration has to be considered for an economical hydrogen generation process.

Keywords: Mass and energy; hydrogen; fluidized bed, Integrated, steam gasification;

1. Introduction

New developments demonstrate the tremendous efforts that are being made to enhance the quality and quantity of renewable hydrogen from biomass gasification. The efforts are mainly focused on reducing the number of process units by introducing novel catalyst [1, 2], CO_2 sorption [3-5] or coupling both in the same reactors (after gasification) [6] and/or in separate reactors (after the pyrolysis step) [7]. However, utilizing methane reforming catalyst and CO_2 sorbent together in one bed may have an advantage of needing a single reactor. The CO_2 capturing through carbonation reaction shifts the equilibrium of water gas shift and steam methane reforming towards more hydrogen production [8]. The addition of catalyst will further enhance the activity of steam methane reforming towards hydrogen production [9]. Steam gasification is being identified as a potential process to produce clean hydrogen [10] and using steam as the sole gasification agent has numerous advantages over air or pure oxygen, which is considered

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costly for small scale operation [11]. However, utilizing steam has a high energy penalty; consequently, optimal experimental conditions need to be identified to allow efficient and economical gasification operation.

The present study addresses the energy flow of ICA steam gasification in a pilot scale bubbling fluidized bed. The study investigates the energy balances with respect to gasification temperature along with hydrogen production under the limitation of CO_2 adsorption temperature inside the gasifier.

Nomenclature

H	enthalpy
H_f	formation enthalpy
ΔH_i	change in enthalpy of individual component
n_i	moles flow rate of individual component
Q_{Steam}	energy associated with steam
Q_{Ext}	external energy (energy provide by external heater)
PKS	palm kernel shell

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2. Material and Methods

2.1. ICA steam gasification system

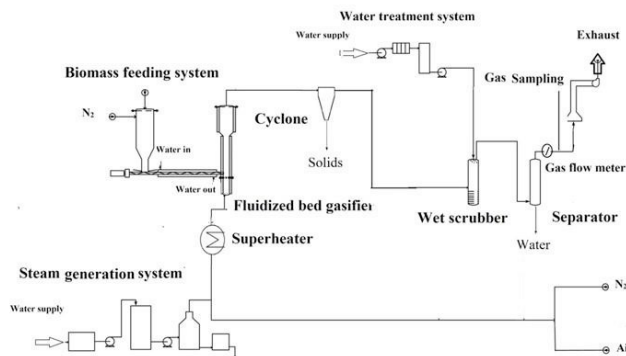Figure 1 shows a process diagram of pilot scale fluidized bed ICA steam gasification system.

Fig. 1. ICA steam gasification system

The gasification system mainly comprises a fluidized bed reactor with external electric heaters, biomass feeding system, steam generator and superheater, cyclone solid separator, wet scrubber, water separator, and gas analyzing system. After the gasifier, product gas passes through the cyclone to separate solid particles from the product gas. The product gas then passes through the scrubber and attains a temperature less than 40 °C and followed by a separator to remove any final traces of water in the product gas stream. The gas sampling point is located at the exit of water separator. The gas analyzing system consisted of Gas Chromatography (Teledyne 7500, Teledyne Analytical Instrument) with an Infrared (IR) type detector. Hydrogen and nitrogen were detected by Gas Chromatography utilizing a Molecular Sieve.

2.2. Energy balance

The energy balance over the fluidized bed gasifier is shown in Figure 2 and is carried out using Equation (1).

$$\sum_{i=1}^{N}(H_{PKS} + H_{H_2 0} + Q_{steam} + Q_{Ext}) = \sum_{e=1}^{M}(H_{H_2} + H_{CO} + H_{CO_2} + H_{CH_4} + H_{unreacted steam}) \tag{1}$$

Generally, H is calculated based on the heat of formation or formation enthalpy represented as H_f. The enthalpy of each component is calculated using Equation (2).

$$H_i = n_i \times (H_{f(i)} + \Delta H_i) \tag{2}$$

This can be further elaborated in terms of specific capacity, C_p, along with initial T_1 and T_2 final temperatures. ΔH_i is then calculated using Equation (3).

$$\Delta H_i = \int_{T_1}^{T_2} C_p \, dT \tag{3}$$

The values for H_f and C_p are given in Appendix A. The energy balance was carried out using eSankey 2.x software.
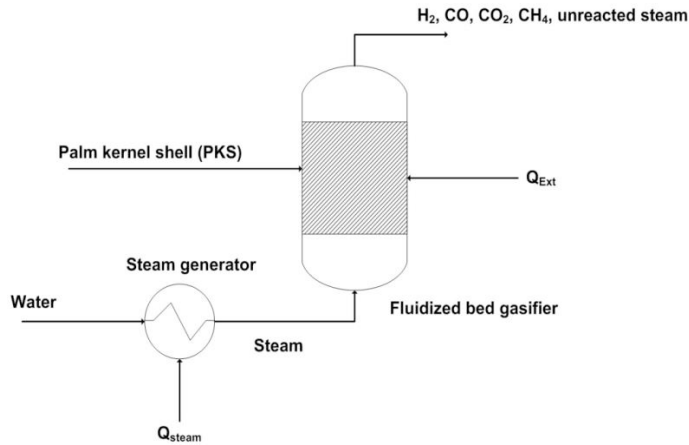

Fig. 2. Energy balance of integrated catalytic adsorption (ICA) steam gasification of palm kernel shell

3. Results and discussions

From the energy analysis of the energy inputs into the gasifier, it was found that the energy required for gasification increased from 3.64 to 4.74 kW with an increase gasifier temperature from 600°C to 750°C. The analysis clearly indicates that the required energy increases due to the endothermic nature of the process. Generally, the energy is utilized to heat up the injected steam to the desired reactor temperature, biomass decomposition and associated endothermic reactions i.e. char gasification and methane reforming. As the temperature of the gasifier increases, the energy requirements increase inside the reactor. This increasing energy consumption enhances the product gas yield via endothermic reactions which corresponds to higher energy released in the outlet stream, as shown in Figures 3 and 4. Similarly, high activity of endothermic reactions increase the steam consumption inside the reactor which reduces the energy associated with unreacted steam at the exit of the fluidized bed gasifier. A major part of the energy is released as unreacted steam in the process which can be optimized through heat integration. The increase of external energy requirements with increasing gasification temperature was also observed by Franco et al. [10] for biomass steam gasification in fluidized bed gasifier.
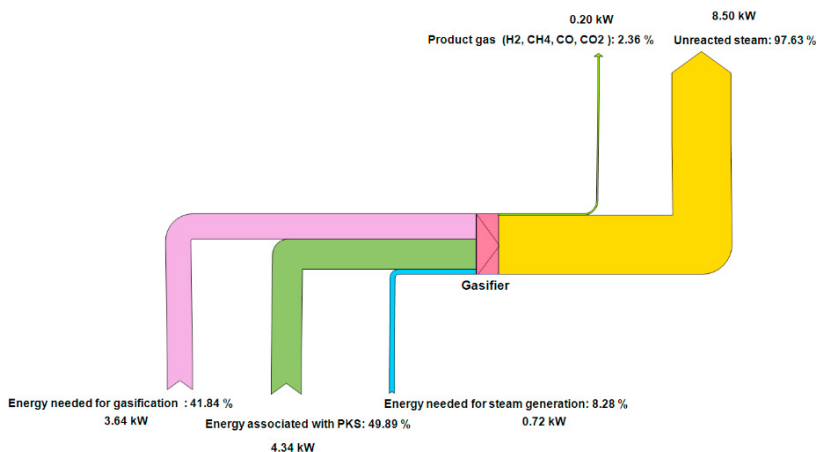

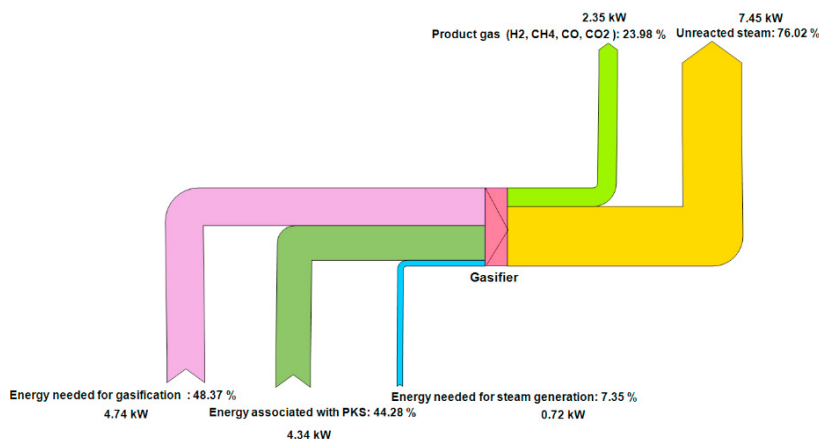Fig. 3. Energy balance over gasifier at 600°C

Fig. 4. Energy balance over gasifier at 750°C

Figure 5 shows the product gas composition with the gasification energy required at 600 °C, 675 C° and 750 °C. The energy required first decreased from 600 °C to 675 °C (3.64 kW to 3.41 kW) and then increased at 750 °C (4.74 kW). This may be due to the highly active CO_2 adsorption reaction at 675 °C which can also be verified by maximum H_2 with zero CO_2 concentration. The exothermic nature of the CO_2 adsorption reaction provides heat for endothermic gasification reactions and reduces the overall energy requirements for the process in the gasifier [12]. Besides, H_2 yield increases with increasing gasification energy and the maximum yield were observed at 750 °C. At high temperature, biomass to gaseous conversion is high and the individual gas component flow rates are higher compared to that at lower temperatures. High temperatures favour endothermic reactions i.e. methane reforming which forms three hydrogen molecules for each methane molecule consumed. This can also be justified by lower methane concentration at high temperature (750 °C). Tar cracking is also an endothermic reaction and may contribute to an increase in hydrogen content in the product gas [13].
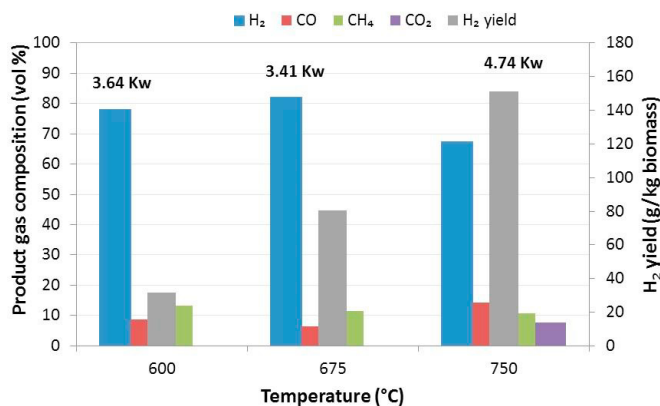

Fig. 5. Effect of temperature on product gas composition and required gasification energy at steam to biomass ratio of 1.5 (wt/wt), catalyst to biomass ratio of 0.1 (wt/wt) and fluidization velocity of 0.21 m/s

4. Conclusions

Steam is found to be the most promising gasification agent for hydrogen production as compared to air or pure oxygen. However, steam brings a high energy plenty to the process in terms of required energy for gasification. The present study showed that the process power requirements were overall increased with increasing temperature from 675 to 750 °C, whilst a slight drop was observed from 600 °C to 675 °C. This affect contributed to high CO_2 adsorption at 675 °C which helped to reduce the energy requirements. The unreacted steam carried away the major portion of the energy from the system, capturing and integrating this potential heat loss improves the viability, energy efficiency and economic case for hydrogen production via gasification.

Appendix A.

Table 1. Enthalpy and heat capacity of components at the reference state [14, 15]

Component	H_f ,(J.mol^{-1})	C_p(J.mol^{-1}$_K$)
Water	-241830	$72.43+(10.39\times10^{-3})T-(1.50\times10^{-6})T^2$
Hydrogen	0	$27.01+(3.51\times10^{-3})T-(0.69\times10^5)T^{-2}$
Carbon monoxide	-110530	$28.07+(4.63\times10^{-3})T-(0.26\times10^5)T^{-2}$
Carbon dioxide	-393520	$45.37+(8.69\times10^{-3})T-(9.62\times10^5)T^{-2}$
Methane	-74870	$14.15+(75.5\times10^{-3})T-(18\times0^{-6})T^2$
Calcium oxide	-635600	$41.84+(2.03\times10^{-2})T-(4.52\times10^5)T^{-2}$
Calcium carbonate	1206900	$82.34+(4.97\times10^{-2})T-(12.87\times10^5)T^{-2}$
PKS (Cellulose)	$LHV + H^f_{CO_2} + \dfrac{x}{2}(H^f_{H_2O})$	$176.67+(406.84\times10^{-3})T-(59.82\times10^5)T^{-2}-(151.54\times10^{-6}(T^2)$

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