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 Institute of Information Technology, Lahore, 54000, Pakistan
[b]Centre for Biofuel and Biochemical, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, Tronoh, 31750, Perak, Malaysia
[c]Systems Power and Energy, School of Engineering, University of Glasgow, Glasgow, G12 8LL, UK
[d]Future Energy Center, School of Business, Society and Engineering, Mälardalens University, Västerås, Sweden

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.

Keywords

Energy flow, energy efficiency, hydrogen, fluidized bed, Integrated, steam gasification

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 (Equations 1-4). The capturing of CO_2 takes place via the 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 but also provides more CO (even at low temperature) to allow the water shift reaction to move in the forward direction.

Char gasification reaction (CGR),

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

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

$CO_2 + CaO \rightarrow CaCO_3 \quad \Delta H = -170.5$ kJ/mol (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 the biomass steam gasification utilizing sorption enhanced reforming (SER) process model to evaluate the fuel-to-hydrogen and 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 integrated catalytic adsorption (ICA) biomass steam gasification for hydrogen production in a pilot scale bubbling fluidized bed system. Energy balance over gasifier with variable temperature, S/B, A/B, fluidization velocity and biomass particle 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.

Table 1. Proximate and ultimate analysis of PKS [13]

Moisture (wt %)	9.61
Proximate analysis (wt. % dry basis)	
Volatile matter	81.03
Fixed carbon	14.87
Ash content	4.10
Ultimate analysis (wt. % dry-ash free basis)	
C	44.61
H	5.58
N	0.46
S	0.11
O (by difference)	49.24
Higher heating value (MJ/kg)	17.32

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 0.150-0.250 mm. The physical properties of the bed material are given in Table 2. Pure Ni powder was used as the catalyst and was purchased from Merck Chemicals.

Table 2. Physical properties and chemical composition of CaO (bed material) [27]

Particle density (kg/m^3)	3053
Bulk density (kg/m^3)	1047
Chemical composition (wt. %)	
CaO	93.32
MgO	4.24
SiO_2	0.95
Fe_2O_3	0.23
Other metal oxides	1.0
(MnO, CuO, SrO, ZnO)	

2.1 Experimental setup

Figure 1 shows the process diagram of the pilot scale fluidized bed 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. The diameter and height of the fluidized bed reactor were 0.15 m and 2.5 m, respectively. A perforated type distributor plate was used. The gasifier operated with the superficial velocity of 0.15-0.26 m/s (3-5 times the minimum fluidization velocity). The fluidized bed gasifier was continuously fed with biomass at 1.0-1.8 kg/h from the biomass feeding system at the side of the plant. The cooling water jacket was provided to avoid biomass decomposition prior to injection into the gasifier. N2 was used to transfer the biomass into the gasifier and to avoid any back flow. Saturated steam was provided by the steam generator which was further heated to 250-300 °C in a superheater prior to

injection into the gasifier. To avoid tar condensation at the exit of the fluidized bed reactor, a heating tape was wrapped and insulated all the way to the cyclone exit. The temperature range of the heating tape was 300-400 °C. Before the start of each experiment, N_2 gas was purged into the system to remove any entrapped gases. After the gasifier, product gas was passed through the cyclone to separate solid particles from the product gas. The product gas was then passed through the scrubber to attain a temperature less than 40 °C and then followed by a separator to remove any final traces of water in the product gas stream. The gas sampling point was located at the exit of the water separator. At the same point, the volumetric flow rate was measured by the flow meter. All experimental runs lasted for 60 min. At the end of the experiment, the biomass supply was stopped and the air was purged into the system. The amount of char was determined by the amount of CO_2 formed when combusting residual solid sample in the fluidized bed gasifier and downstream pipelines. The product gases i.e. CO_2, CO, and CH_4 were analyzed by Gas Chromatography (Teledyne 7500, Teledyne Analytical Instrument) with an Infrared (IR) type detector. Hydrogen and nitrogen were detected by Gas Chromatography utilizing Molecular Sieve 5A column (Teledyne 4060, Teledyne Analytical Instrument) with Thermal Conductive Detector (TCD). The product gas was measured every 6 minutes at the sampling point located after the water separator.

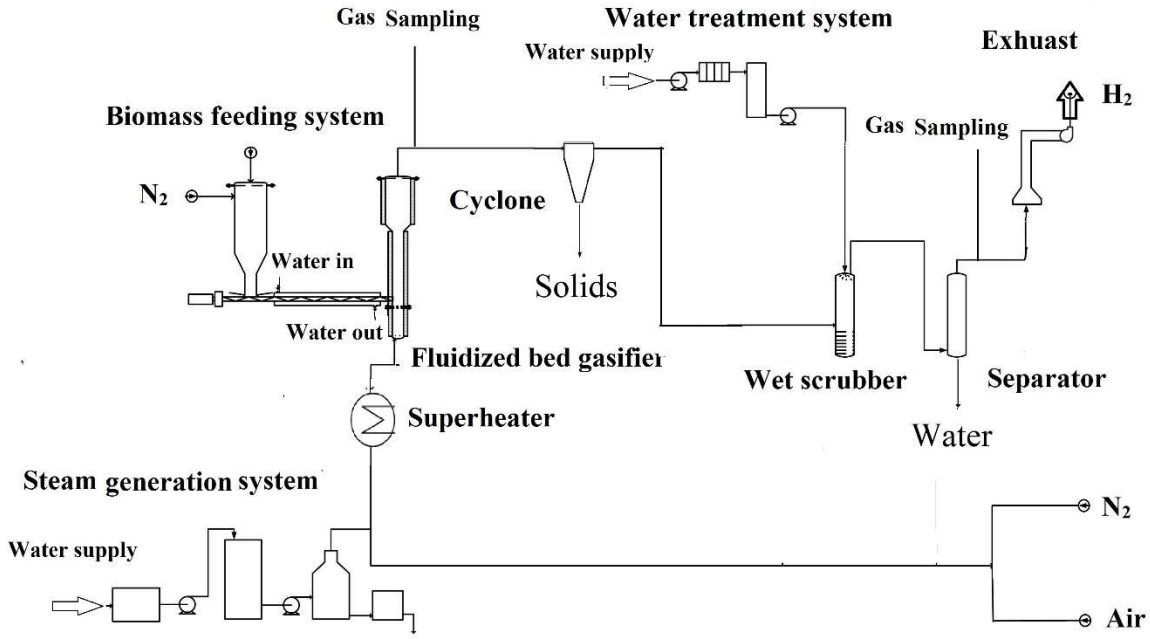


Fig. 1. ICA steam gasification system

2.2 Energy balance

The energy balance over the fluidized bed gasifier is shown in Figure 2 and is carried out using Equation (5).

$$\sum_{i=1}^{N}(H_{PKS}+Q_{steam}+Q_{Ext})=\sum_{e=1}^{M}(H_{H_2}+H_{CO}+H_{CO_2}+H_{CH_4}+H_{unreacted\ steam}) \quad (5)$$

H_{PKS}, Q_{steam}, Q_{Ext} are input enthalpies associated with PKS, steam and external energy provided by external heater while H_{H_2}, H_{CO}, H_{CO_2}, H_{CH_4} *and* $H_{unreacted\ steam}$ are output enthalpies associated with H_2, CO, CO_2, CH_4 and unreacted steam.

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 (6).

$$H_i = n_i \times (H_{f(i)} + \Delta H_i) \quad (6)$$

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 (7).

$$\Delta H_i = \int_{T_1}^{T_2} C_p dT \tag{7}$$

The values for H_f and C_p are given in Table 3. The energy balance was carried out using eSankey 2.x software.

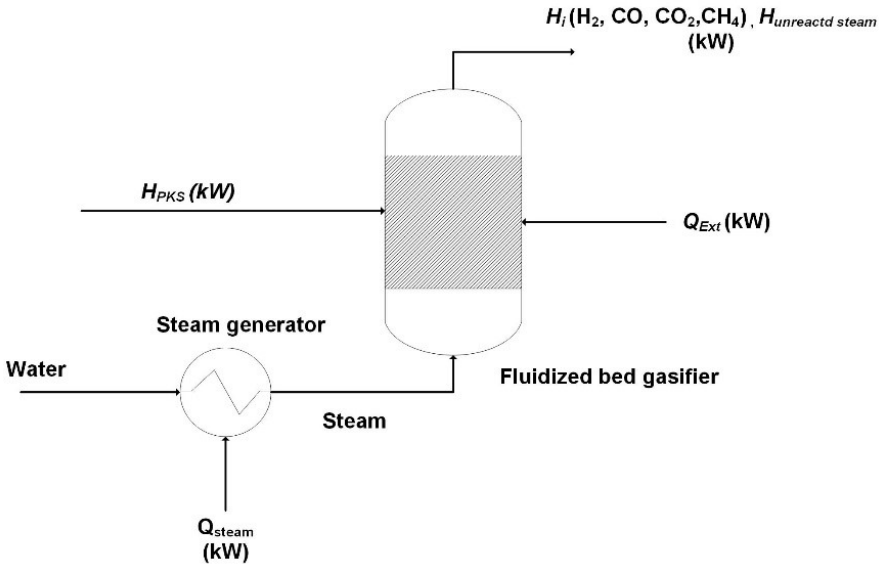


Fig. 2. Energy balance of ICA steam gasification of palm kernel shell

Table 3. Enthalpy and heat capacity of components at the reference state [28, 29]

Component	H_f ,(J.mol^{-1})	C_p(J.mol^{-1}K^{-1})
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)	$LHV+H^f_{CO_2}+\frac{x}{2}(H^f_{H_2O})$	$176.67+(406.84\times10^{-3})T-(59.82\times10^{5})T^{-2}-(151.54\times10^{-6}\ (T^2)$

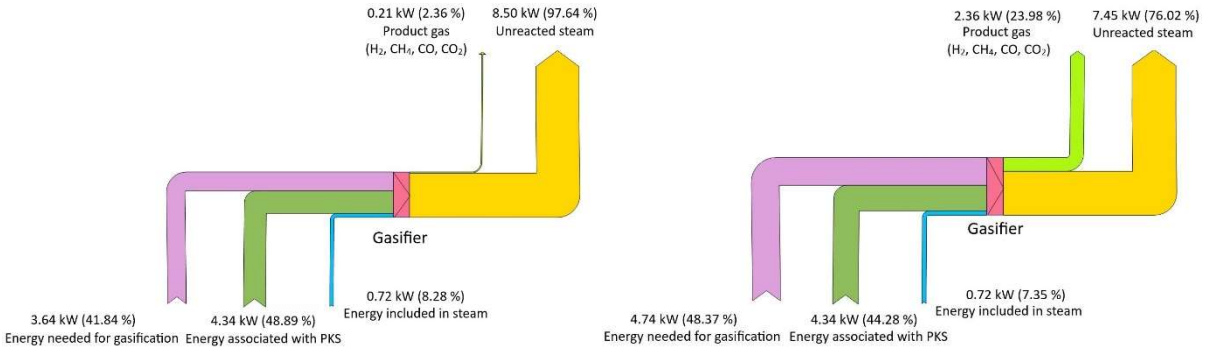
2.3 Energy efficiencies

The present study considers the energy efficiencies based on the output energy associated with hydrogen and total gas generated in the ICA gasification system. The input energy to the gasifier is associated with biomass, steam and the energy required for gasification. The energy efficiency based on hydrogen, η_1, is the energy associated with hydrogen in the product gas to the sum of input energies associated with PKS (E_{PKS}), steam (Q_{steam}) and gasification process as an external energy (Q_{ext}). Similarly, the energy efficiency based on product gas (H_2, CO, CO_2 and CH_4), η_2, is the energy associated with the product gas to the sum of E_{PKS}, Q_{steam} and Q_{ext}.

3. Results and discussions

3.1 Effect of temperature

Figure 3 shows 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 the higher energy released in the outlet stream, as shown in Figures 3 (b). Similarly, higher activity of the endothermic reactions increases 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 a fluidized bed gasifier.



(a) **(b)**

Fig. 3. Energy balance over gasifier at (a) 600 °C and (b) 750 °C (steam to biomass ratio = 2.0, adsorbent to biomass ratio = 1.0, catalyst to biomass ratio = 0.1, fluidization velocity = 0.21 m/s)

Figure 4 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 the 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 [30]. Besides, the H_2 yield increases with increasing gasification energy and the maximum yield was 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. Higher temperatures favour endothermic reactions i.e. methane reforming which forms three hydrogen molecules for each methane molecule consumed.

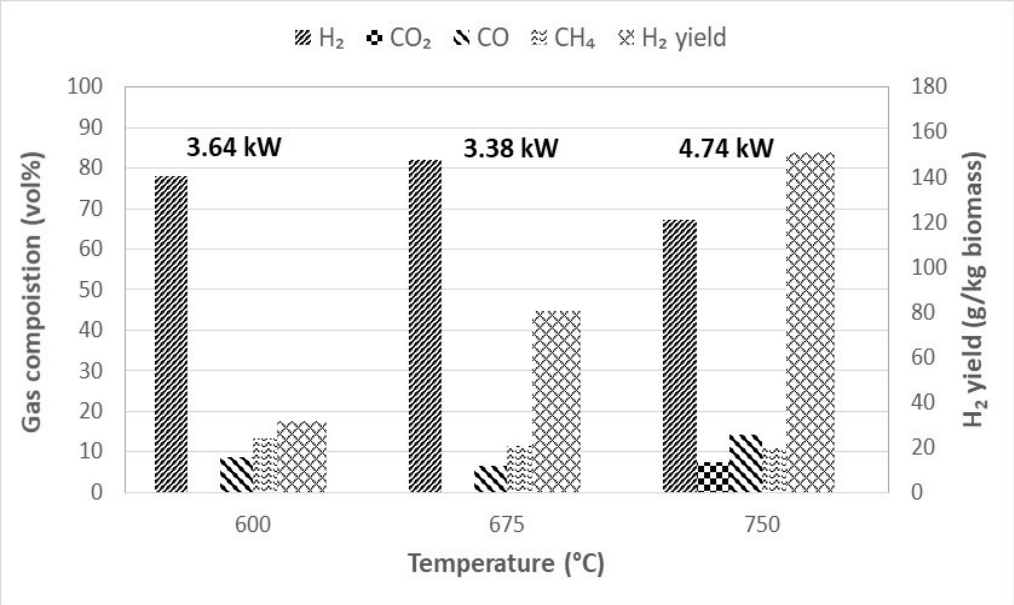


Fig. 4. Influence of temperature on gas composition and gasification energy required (steam to biomass ratio = 2.0, adsorbent to biomass ratio = 1.0, catalyst to biomass ratio = 0.1, fluidization velocity = 0.21 m/s)

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 [31]. The energy efficiencies associated with hydrogen (η_1) increases with increasing gasification temperature as shown in Figure 5. However, the efficiency associated with product gas first decreases and then increases to 12 % at 750°C. This might be due to a strong adsorption reaction which not only adsorbs all CO_2 gas in the mixture but also contributes to the add-in energy and reduces the overall gasification energy requirements. The maximum η_1 and η_2 values observed in the present study are 4 % and 11.8 % (at 750 ℃ and S/B ratio of 2.0) which can be comparable to 5 % and 12% (750 ℃ and S/B ratio of 0.43) [20]. For the subject study, slightly higher energy efficiencies at low S/B ratio may be due to the consideration of energy associated with char and tar in the modelling and simulation of gasifier (type unknown) for biomass steam gasification. Moreover, the part of external energy (provide by an electric source) in the present experimental study is not considered in the subject study due to the assumption of isothermal reactor with waste heat stream. This study is considered for comparison purpose due to unavailability of energy efficiencies (associated with hydrogen and product gas) reported from experimental gasification system.

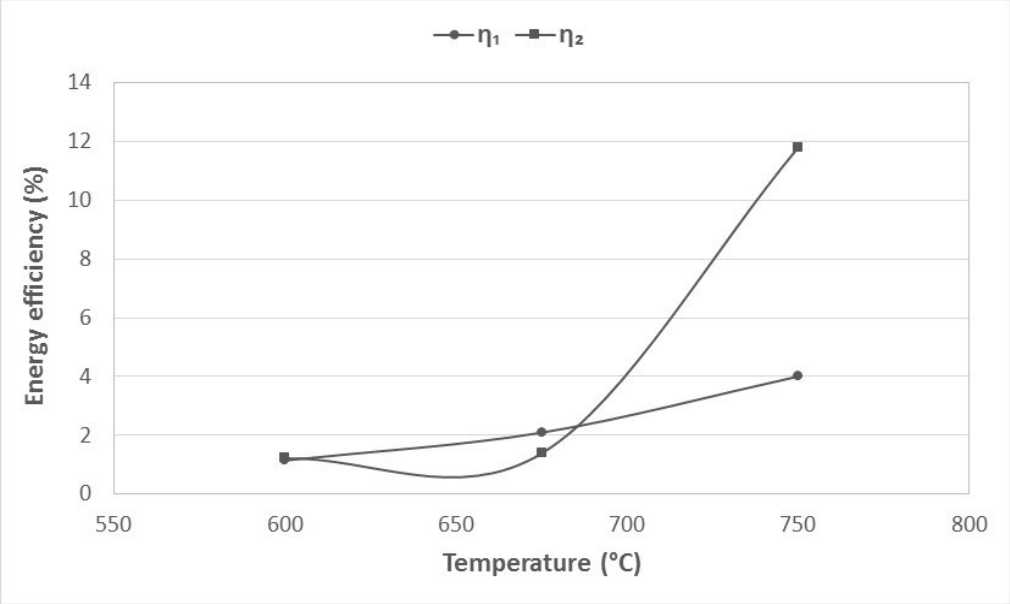


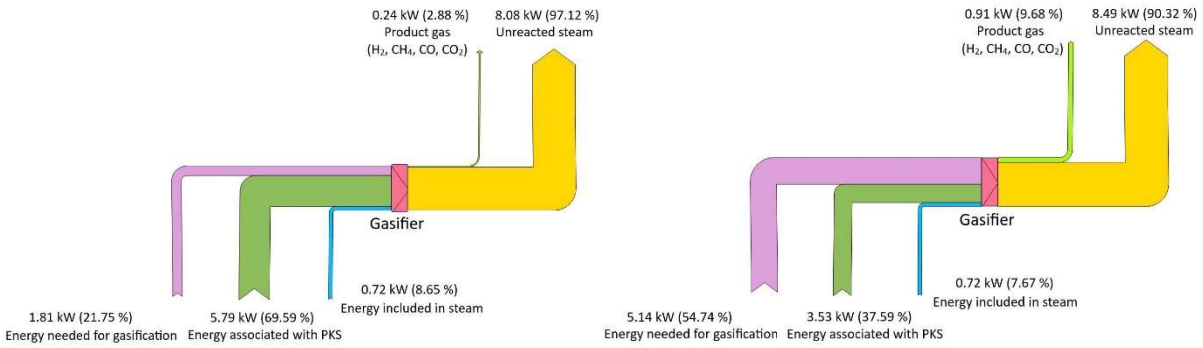
Fig. 5. Effect of temperature on energy efficiency associated with hydrogen (η_1) and product gas (η_2) generation (steam to biomass ratio = 2.0, adsorbent to biomass ratio = 1.0, catalyst to biomass ratio = 0.1, fluidization velocity = 0.21 m/s)

3.2 Effect of steam to biomass ratio

The energy balance was performed over the gasifier by varying the steam to biomass (S/B) ratio of 1.5 and 2.5, as shown in Figure 6. In the present study, the biomass flow rate was varied from 1100 to 1800 g/h with a constant flow rate of steam at 2700 g/h. Keeping constant steam flow rate, the fluidization velocity is constant even though the S/B ratio is changed from 1.5 to 2.5.

As shown in Figure 6 (a), the energy required for gasification process is 1.81 kW while the energy associated with PKS (based on the 1800 g/h of biomass) contributes about 5.79 kW at S/B ratio of 1.5. On the other hand, the energy associated with steam generation contributes to 0.72 kW. At the exit of the gasifier, a major part of the energy is released as unreacted steam and contributes about 8.08 kW of energy. The energy balance at the inlet and outlet streams at S/B ratio of 2.5 is shown in Figure 6 (b). The results showed that the energy required for

gasification reactions is increased to 5.14 kW. The greater portion of energy required for gasification is used to raise the temperature of excess steam to the bed temperature which surely increases the total energy requirement. However, this excess steam helps to provide better energy output (0.91 kW) associated with the product gas via gasification/reforming reactions with the CO_2 adsorbent. The steam flowrates are kept constant while varying the biomass flow rates unable to keep the fluidization velocity constant. This provides a decrease of energy associated with PKS by varying S/B from 1.5 to 2.5.



(a) **(b)**

Fig. 6. Energy balance over gasifier at (a) steam to biomass ratio of 1.5 and (b) steam to biomass ratio of 2.5 (gasification temperature = 675 °C, adsorbent to biomass ratio = 1.0, catalyst to biomass ratio = 0.1, fluidization velocity = 0.21 m/s)

Figure 7 shows the gasification energy required along with the gas composition and hydrogen yield with respect to the S/B ratio. Overall, high S/B ratio provides better hydrogen composition and yield at the expense of more gasification energy required. However, the increase from 2.0 and 2.5 (of S/B) is not significant and better results can be obtained at S/B ratio of 2.0. This energy overhead for the higher S/B can be justified with the higher output energy associated with the product gas. These findings are similar to that reported by other researchers [32, 33].

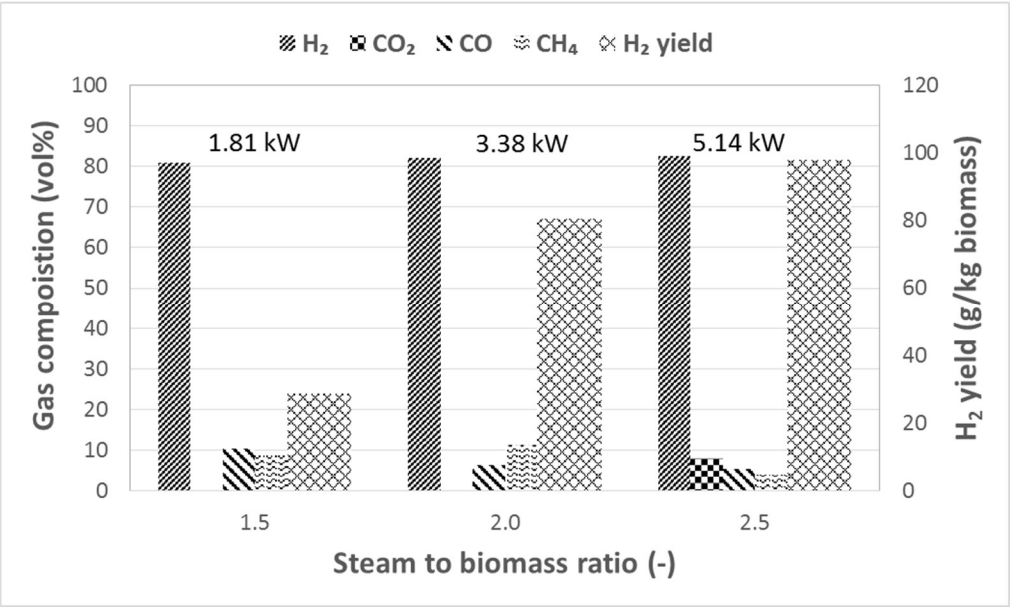


Fig. 7. Influence of steam to biomass ratio on gas composition and gasification energy required (gasification temperature = 675 ℃, adsorbent to biomass ratio = 1.0, catalyst to biomass ratio = 0.1, fluidization velocity = 0.21 m/s)

Apparently, higher energy efficiencies for the product gas are observed at high S/B (2.5) which shows high gas yield in the process as shown in Figure 8. However, a high steam to biomass ratio results in high unreacted steam at the gasifier exit, corresponding to a major portion of the energy leaving the gasifier unutilized. For similar ICA gasification system, Yusup *et al*. [13] reported the optimum value of S/B was 2.0 at 675 °C, through the response surface methodology (RSM). The maximum energy efficiency for hydrogen production is observed at 2.0 whereas efficiency is slightly decreased at 2.5. A large amount of steam available did not show much increase in hydrogen content (Figure 7) but obviously increased the external energy usage to its highest value (5.14 kW), decreasing overall energy efficiency. The η_1 and η_2 values observed in the present study are 1.6 % and 3.7 % (at 675 ℃ and S/B ratio of 1.5) which are lower than the 5 % and 7 % (677 ℃ and S/B ratio of 0.43) reported by [20]. As discussed earlier, the study [20] is modelling and simulation of a theoretical gasifier with the number of

assumptions especially with the exclusion of external heat source which contribute to 21.75 % of input energy in the present study as shown in Figure 6 (a).

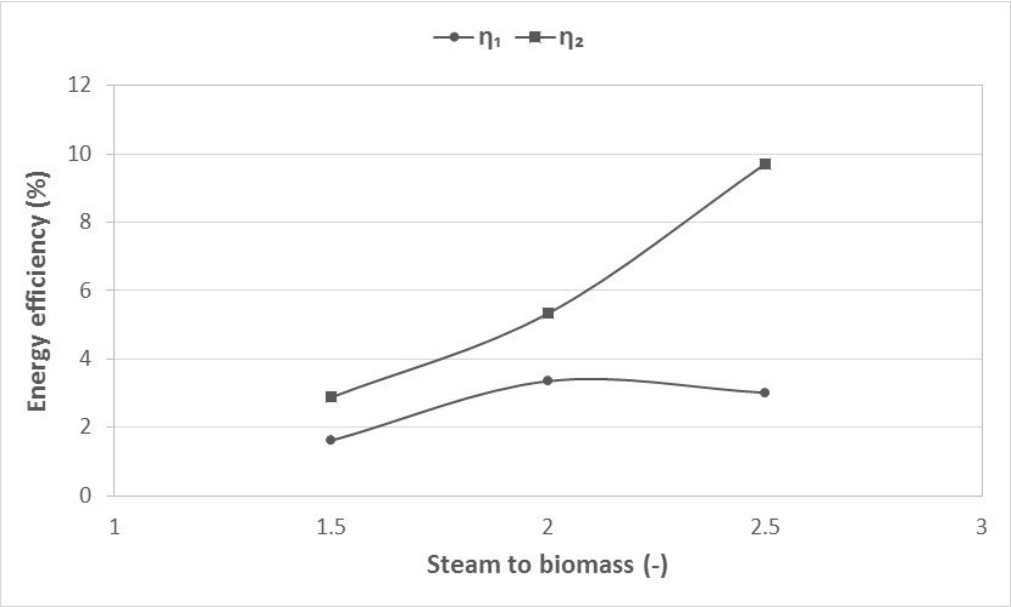
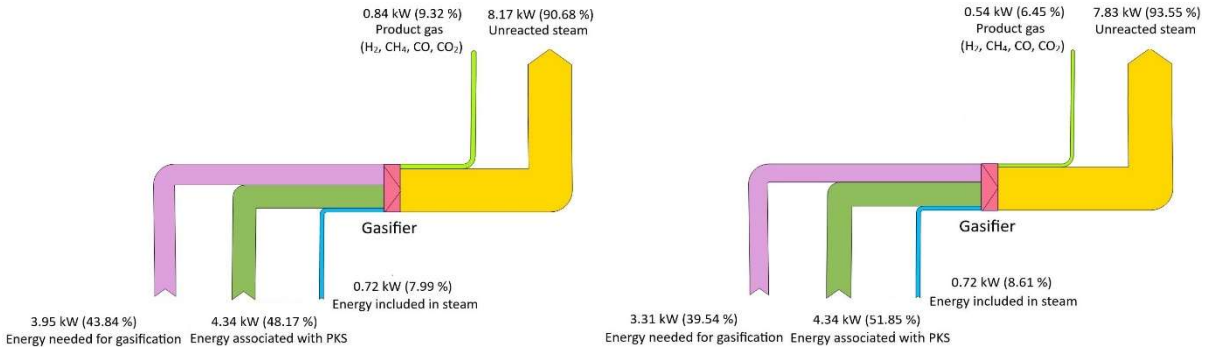


Fig. 8. Effect of steam to biomass ratio on energy efficiency associated with hydrogen (η_1) and product gas (η_2) generation (gasification temperature = 675 °C, adsorbent to biomass ratio = 1.0, catalyst to biomass ratio = 0.1, fluidization velocity = 0.21 m/s)

3.3 Effect of adsorbent to biomass ratio

The energy balance is conducted for the gasifier system by varying A/B from 0.5 to 1.5 as shown in Figure 9. The biomass flow rate is constant at 1350 g/h with constant steam flow rate of 2700 g/h. At an A/B ratio of 0.5, the power needed for gasification process is found to be 3.95 kW. The energy input associated with PKS at the inlet stream contributes about 4.34 kW which makes the maximum proportion at the input. Additionally, energy consumed by generating steam is 0.72 kW. At the exit of the gasifier, the major part of the energy is released as an unreacted steam in the process and contributes about 8.17 kW. The mixture of the product gas i.e. H_2, CO, CO_2 and CH_4 provide 0.84 kW of energy. The results showed that the energy required for gasification reactions decreased from 3.31 kW to 3.95 kW while decreasing A/B

from 0.5 to 1.5. This indicates that the amount of CO_2 adsorbent in the bed not only reduces the CO_2 to a minimal concentration (Figure 10) but also reduces the overall energy required for gasification. Meanwhile, the energy input associated with PKS and steam generation is the same as in the first case (A/B=1). It appears that the energy released from the product gas decreased from 0.84 to 0.54 kW by increasing the A/B ratio. However, there is a minimal decrease of overall gasification energy when A/B ratio varies from 1.0 to 1.5 which infers that the optimum A/B ratio is 1.0.



(a) **(b)**

Fig. 9. Energy balance over gasifier at (a) adsorbent to biomass ratio of 0.5 and (b) adsorbent to biomass ratio of 1.5 (gasification temperature = 675 °C, steam to biomass ratio = 2.0, catalyst to biomass ratio = 0.1, fluidization velocity = 0.21 m/s)

Figure 10 depicts the gasification energy required with respect to the A/B biomass ratio. The gasification energy required is decreased by varying the A/B ratio from 0.5 to 1.5. This decrease is due to the high activity of the CO_2 adsorption reaction in the presence of excess amount of adsorbent. The CO_2 adsorption reaction is an exothermic reaction and hence reduces the overall energy requirement in the process. This conclusion is well supported by the results presented by the previous study [34]. The subject study found that the energy requirement of the absorption enhanced reforming (AER) steam gasification is lower than the conventional dual fluidized bed steam gasification process. It can be concluded that the CO_2 adsorption reaction

not only enhanced the H_2 content but also reduced the external energy requirements of the catalytic steam gasification.

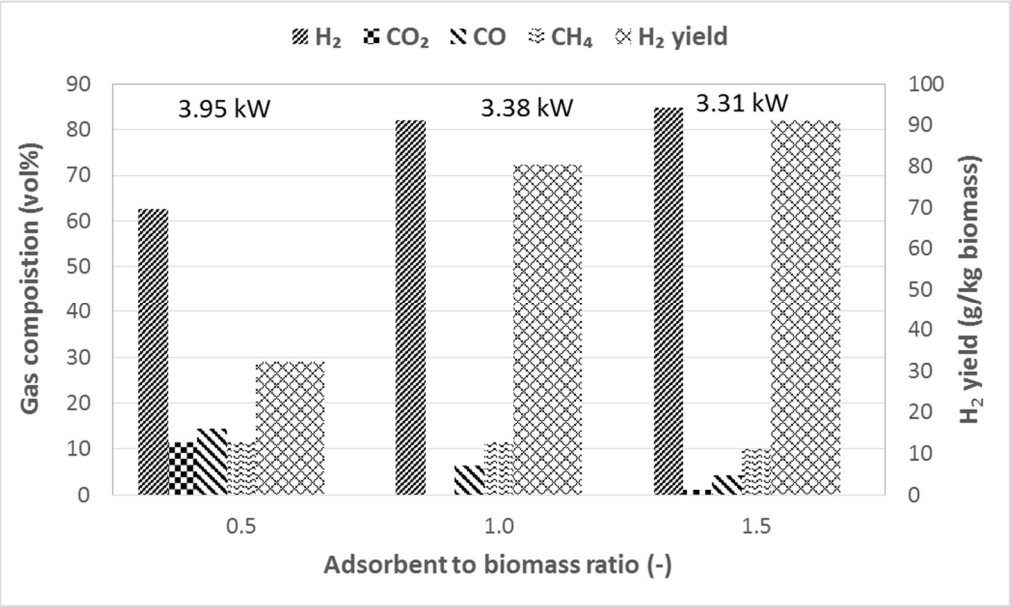


Fig. 10. Influence of adsorbent to biomass ratio on gas composition and gasification energy required (gasification temperature = 675 °C, steam to biomass ratio = 2.0, catalyst to biomass ratio = 0.1, fluidization velocity = 0.21 m/s)

The energy efficiencies associated with hydrogen and product gas show opposite trends as shown in Figure 11. The total energy needed for gasification is continuously decreasing as A/B varies from 0.50-1.5 whereas η_1 first increases at 1.0 and then shows no change while η_2 decreases and becomes constant afterwards. These two opposite trends are mainly due to a vital change in gas composition as explained earlier when A/B varies from 0.5-1.0. The current scenario suggests two different A/B ratios for η_1 and η_2 which can be 0.5 and 1.0, respectively.

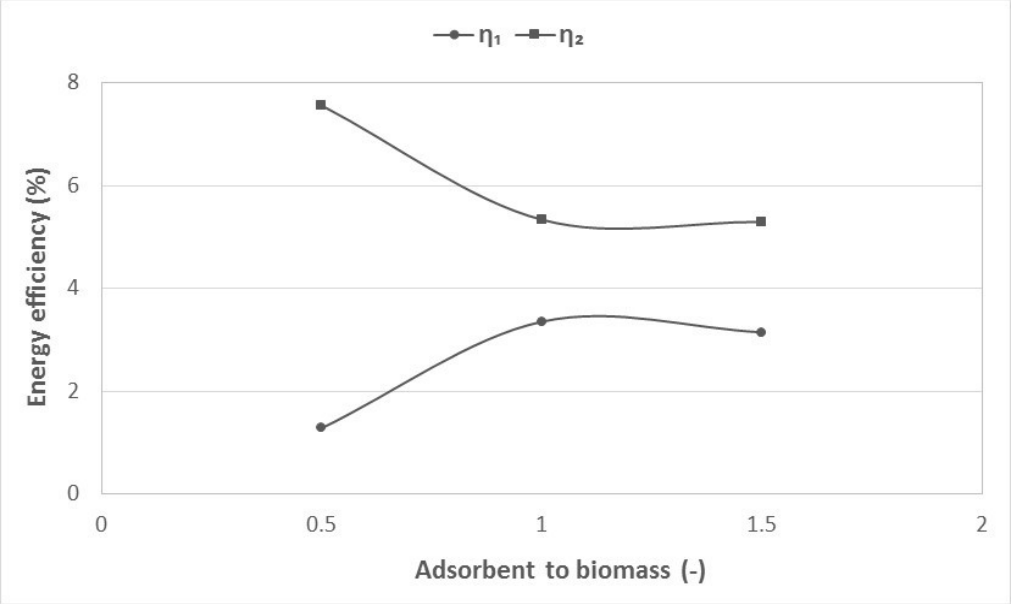


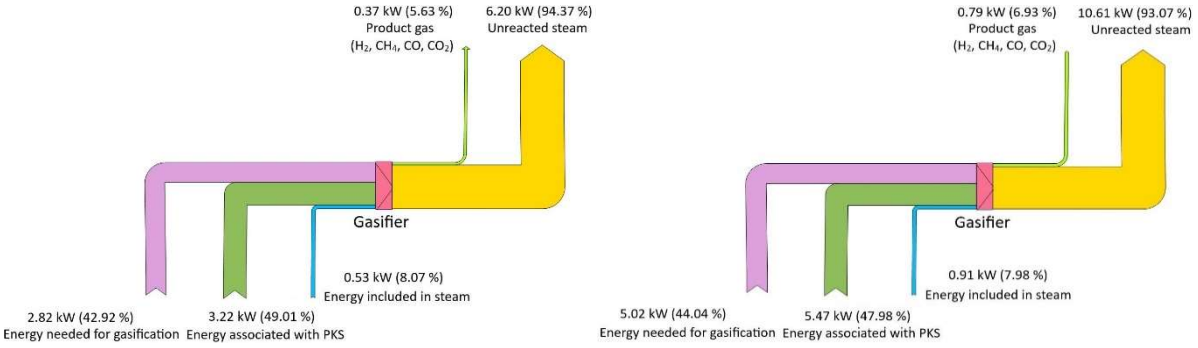
Fig . 11. Effect of adsorbent to biomass ratio on energy efficiency associated with hydrogen (η_1) and product gas (η_2) generation (gasification temperature = 675 °C, steam to biomass ratio = 2.0, catalyst to biomass ratio = 0.1, fluidization velocity = 0.21 m/s)

3.4 Effect of fluidization velocity

The energy balance was carried out over the gasifier by varying the fluidization velocity from 0.15 m/s to 0.26 m/s (3 and 5 times the minimum fluidization velocity, respectively) as shown in Figure 12. The biomass flow rate was varied from 1000 g/h to 1700 g/h while varying the steam from 2000 g/h to 3400 g/h. These variable flow rates are provided to keep the steam to biomass ratio constant while varying the fluidization velocity.

As shown in Figure 12 (a), the energy needed for the gasification process is found to be 2.82 kW while energy associated with PKS is about 3.22 kW and utilized by generating steam is 0.53 kW. At the outlet stream, the major part of the energy is released as unreacted steam in the process and contributes to 6.23 kW of energy. The product gas carries 0.37 kW at the exit of the gasifier. Figure 12 (b) illustrates the energy balance at high fluidization velocity of 0.26 m/s. The energy associated with steam generation increased from 0.53 kW to 0.91 kW by

changing the fluidization velocity from 0.15 m/s to 0.26 m/s. This is due to the high amount of steam injected into the system which also increases the required gasification power from 2.82 to 5.02 kW. Furthermore, energy entered with PKS is increased to 5.47 kW which is due to the higher biomass flow rates (1700 g/h). At the exit of the gasifier, the energy of the unreacted steam reached its highest value of 10.61 kW. Meanwhile, the product gas contained 0.79 kW which is higher than with lower fluidization velocity.



(a) **(b)**

Fig. 12. Energy balance over gasifier at (a) fluidization velocity of 0.15 m/s and (b) fluidization velocity of 0.26 m/s (gasification temperature = 675 °C, steam to biomass ratio = 2.0, adsorbent to biomass ratio = 1.0, catalyst to biomass ratio = 0.1)

Figure 13 shows the effect of the fluidization velocity on gasification energy requirements. The results indicate that the gasification energy required is increased from 2.82 kW to 5.02 kW by varying the velocity from 0.15 to 0.26 m/s. This increase is due to higher steam flow rates injected into the gasifier. Furthermore, higher fluidization velocities increase the product gas flow rates which can be justified from the energy associated with product gas at the exit. However, high steam flow rates cause more unreacted steam to exit the gasifier, which needs to be justified when the economics of the process are considered.

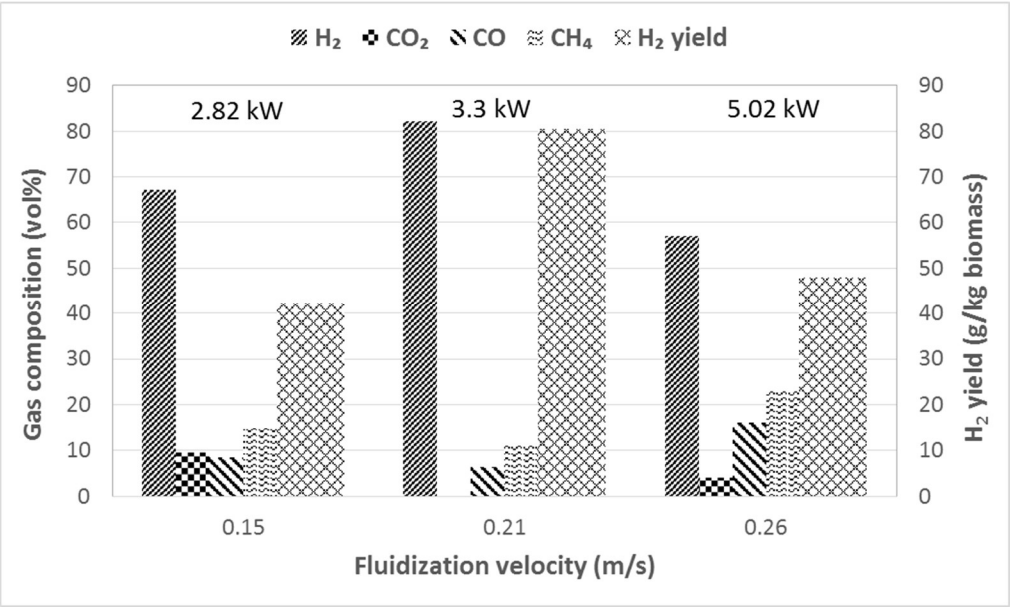


Fig. 13. Influence of fluidization velocity on gas composition and gasification energy required (gasification temperature = 675 °C, steam to biomass ratio = 2.0, adsorbent to biomass ratio = 1.0, catalyst to biomass ratio = 0.1)

Figure 14 shows η_1 and η_2 with respect to different fluidization velocities. The trends clearly show the medium velocity (0.21 m/s which is four times of the minimum fluidization) provide better efficiencies.

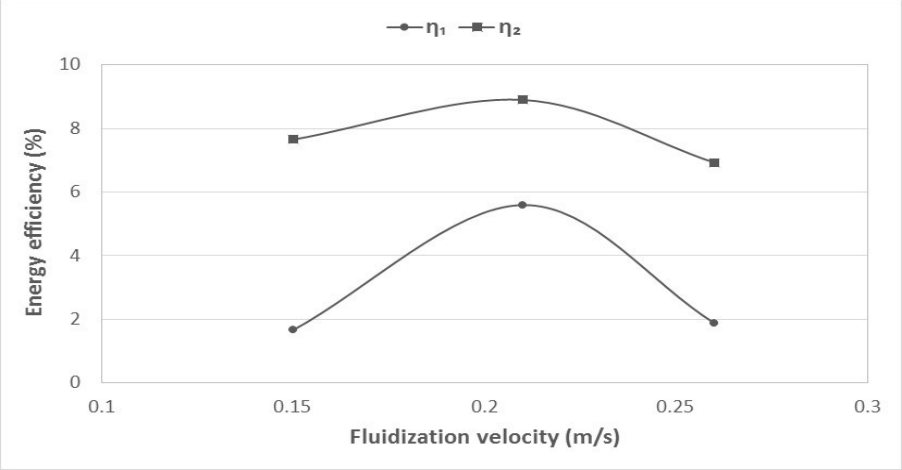


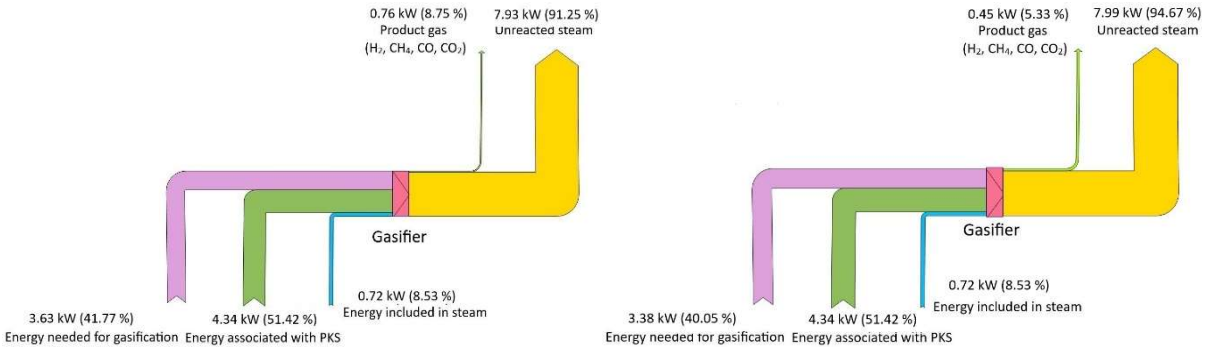
Fig . 14. Effect of fluidization velocity on energy efficiency associated with hydrogen (η_1) and product gas (η_2) generation (gasification temperature = 675 °C, steam to biomass ratio = 2.0, adsorbent to biomass ratio = 1.0, catalyst to biomass ratio = 0.1)

3.5 Effect of particle size

The energy balance was carried out over the gasifier by varying the biomass particle size from 0.355-0.500 mm to 1.0-2.0 mm at a temperature of 675 °C, S/B ratio of 2.0, adsorbent to biomass ratio of 1.0 and catalyst to biomass ratio of 0.1 as shown in Figure 15. The biomass flow rate was constant at 1350 g/h with a steam flow rate of 2700 g/h.

Figure 15 (a) shows the input and output energy stream over the gasifier for biomass particle size of 0.355-0.500 mm. The power required for the gasification process was found to be 3.38 kW. At the outlet stream, the major part of the energy is released as an unreacted steam in the process and contributes 7.93 kW. The product gas contributes 0.77 kW. Figure 15 (b) shows the energy balance over the gasifier by considering the larger biomass particle size (1.0-2.0 mm). The results showed that no significant variation was observed in the required gasification energy. Furthermore, the input energy with steam and PKS were the same as with the smaller particle size. This is due to the similar flow rates (1350 g/h) for the two cases. The energy associated with unreacted steam is almost similar in both cases i.e. ~ 8 kW. However,

the energy contained within the product gas was slightly higher in the case of small particle. This effect may be due to the high heat transfer rates in smaller particles compared to the larger one. Due to this, high product gas flow rates are expected with smaller particles which increases the energy output at the exit of the gasifier.



(a) **(b)**

Fig. 15. Energy balance over gasifier at (a) biomass particle size of 0.355-0.500 mm and (b) biomass particle size of 1.0-2.0 mm (gasification temperature = 675 °C, steam to biomass ratio = 2.0, adsorbent to biomass ratio = 1.0, catalyst to biomass ratio = 0.1, fluidization velocity = 0.21 m/s)

Figure 16 shows the effect of biomass particle size on the required gasification energy. The results show no significant variations in terms of energy required for gasification. However, the product gas generated in small particle size is higher than larger particles. The larger particle size may exhibit high temperature gradient between the core and its surface which result in low gas yield and high char yield. This is further verified by other researchers [35] that observed more gas yield in small biomass particle size (0.3 mm) as compared to the large particle size (1.0 mm) at a temperature range of 600-750°C in fluidized bed gasifier. However, they further found no significant effect of biomass particle size at high temperature (800°C) due to high heating rates which reduced overall heat transfer resistance in large particles. Secondly, small particles (<1.0 mm [36]) may exhibits reaction kinetics as the controlling step for biomass

decomposition whereas the decomposition step in large particles may control by the reaction kinetics and heat transfer thus produces lower conversion rate. It can be concluded that high gas yield is observed in small biomass particle (0.355-0.500) as compared to bigger particles size (1.0-2.0 mm) whereas no significant effect on the energy required for biomass particle size in ICA biomass steam gasification is observed. However, it should be noted that there is a higher energy required to produce the smaller particulate size which may impact the overall process economics.

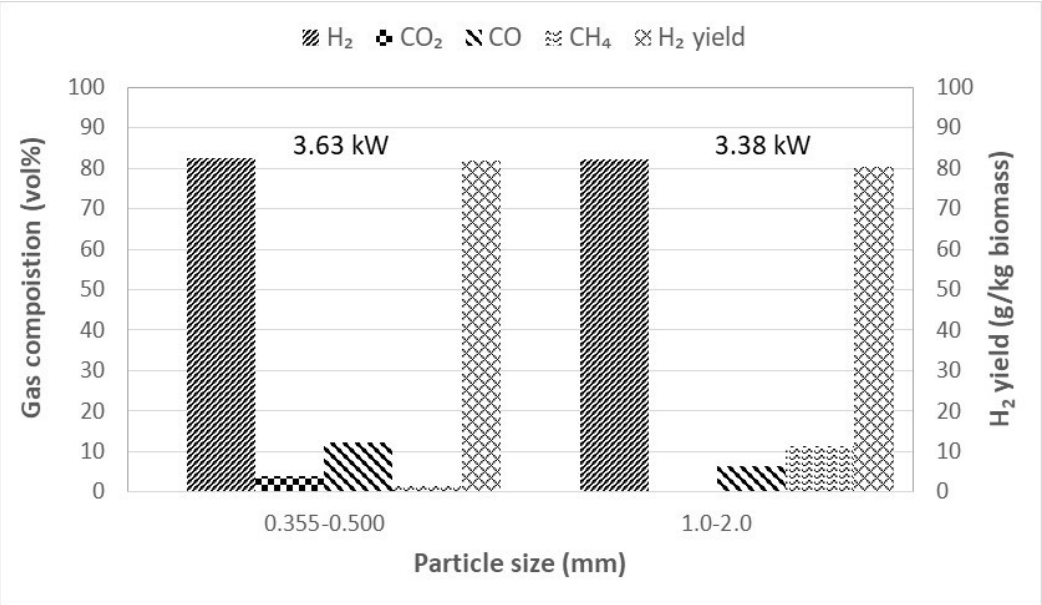


Fig.16. Influence of biomass particle size on gas composition and gasification energy required (gasification temperature = 675 °C, steam to biomass ratio = 2.0, adsorbent to biomass ratio = 1.0, catalyst to biomass ratio = 0.1, fluidization velocity = 0.21 m/s)

Figure 17, shows no variations for η_1 while varying the particle size whereas η_2 show higher values for smaller particles. This might be due to a better contribution of CO and CO_2 (at small particle size) accompanied by the lower gasification energy required at the same inlet energies associated with biomass and steam.

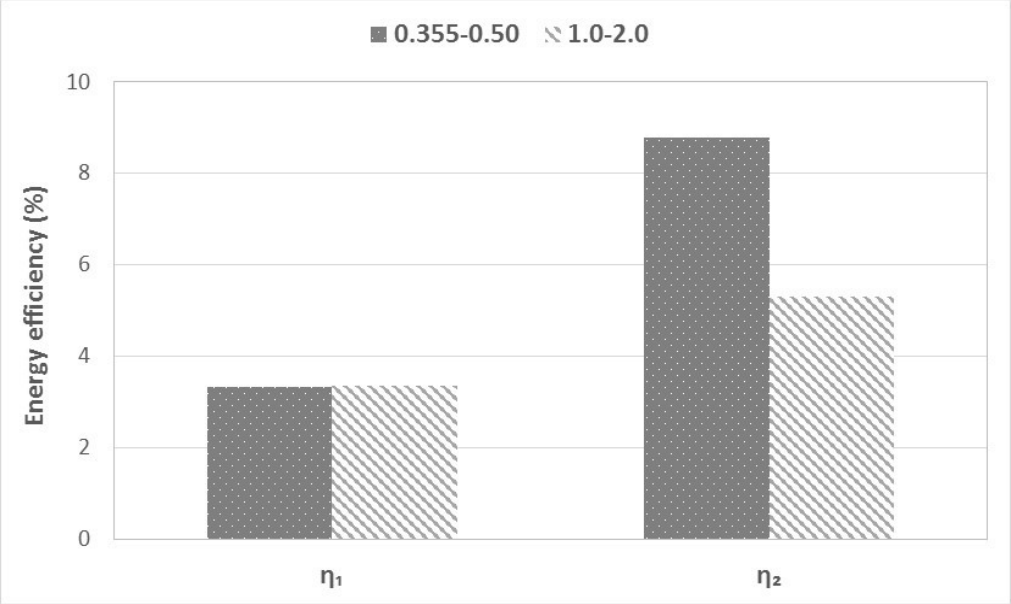


Fig. 17. Effect of particle size on energy efficiency associated with hydrogen (η_1) and product gas (η_2) generation (gasification temperature = 675 °C, steam to biomass ratio = 2.0, adsorbent to biomass ratio = 1.0, catalyst to biomass ratio = 0.1, fluidization velocity = 0.21 m/s)

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 penalty to the process in terms of required energy for gasification. The present study showed that the energy requirements in integrated catalytic adsorption gasification system for hydrogen production were overall increased with increasing temperature, steam to biomass ratio and fluidization velocity whilst decreased with the adsorbent to biomass ratio and with no significant change observed with biomass particle size between 0.355-2.000 mm. However, a slight drop was observed from 600 °C to 675 °C. This might be due to high CO_2 adsorption at 675 °C which helped to reduce the energy requirements. The optimum operating conditions for hydrogen production in terms of energy requirements were found to be 675 °C, 2.0 steam to biomass

ratio, 1.0 adsorbent to biomass ratio and medium fluidization velocity of 0.21 m/s. Similar optimum conditions were also found to be valid for hydrogen based energy efficiencies whereas the optimum conditions for product gas energy efficiencies were high temperature, steam to biomass ratio (2.5) and smaller biomass particle size (0.355-0.500 mm). The unreacted steam carried away the major portion of the energy from the system, capturing, recycling and integrating this potential heat loss improves the viability, energy efficiency and economic case for hydrogen production via gasification.

Acknowledgements

The authors gratefully acknowledge financial and technical support by Universiti Teknologi PETRONAS.

References

[1] Kalinci Y, Hepbasli A, Dincer I. Biomass-based hydrogen production: A review and analysis. International Journal of Hydrogen Energy. 2009;34:8799-817.
[2] Li J, Yin Y, Zhang X, Liu J, Yan R. Hydrogen-rich gas production by steam gasification of palm oil wastes over supported tri-metallic catalyst. International Journal of Hydrogen Energy. 2009;34:9108-15.
[3] Kumagai S, Alvarez J, Blanco PH, Wu C, Yoshioka T, Olazar M, et al. Novel Ni–Mg–Al–Ca catalyst for enhanced hydrogen production for the pyrolysis–gasification of a biomass/plastic mixture. J Anal Appl Pyrolysis. 2015;113:15-21.
[4] Huang B-S, Chen H-Y, Chuang K-H, Yang R-X, Wey M-Y. Hydrogen production by biomass gasification in a fluidized-bed reactor promoted by an Fe/CaO catalyst. Int J Hydrogen Energy. 2012;37:6511-8.
[5] Yan L, He B, Pei X, Wang C, Duan Z, Song J, et al. Design and comparisons of three biomass based hydrogen generation systems with chemical looping process. International Journal of Hydrogen Energy. 2014;39:17540-53.
[6] Cormos CC. Biomass direct chemical looping for hydrogen and power co-production: Process configuration, simulation, thermal integration and techno-economic assessment. Fuel Processing Technology. 2015;137:16-23.
[7] Hafizi A, Rahimpour MR, Hassanajili S. High purity hydrogen production via sorption enhanced chemical looping reforming: Application of 22Fe2O3/$MgAl_2O_4$ and 22Fe_2O_3/Al_2O_3 as oxygen carriers and cerium promoted CaO as CO_2 sorbent. Applied Energy. 2016;169:629-41.
[8] Dou B, Wang K, Jiang B, Song Y, Zhang C, Chen H, et al. Fluidized-bed gasification combined continuous sorption-enhanced steam reforming system to continuous hydrogen production from waste plastic. International Journal of Hydrogen Energy. 2016;41:3803-10.
[9] Udomchoke T, Wongsakulphasatch S, Kiatkittipong W, Arpornwichanop A, Khaodee W, Powell J, et al. Performance evaluation of sorption enhanced chemical-looping reforming for hydrogen production from biomass with modification of catalyst and sorbent regeneration. Chem Eng J. 2016;303:338-47.

[10] Koppatz S, Pfeifer C, Rauch R, Hofbauer H, Marquard-Moellenstedt T, Specht M. H2 rich product gas by steam gasification of biomass with in situ CO2 absorption in a dual fluidized bed system of 8 MW fuel input. Fuel Process Technol.90:914-21.
[11] Li C, Hirabayashi D, Suzuki K. Development of new nickel based catalyst for biomass tar steam reforming producing H_2-rich syngas. Fuel Process Technol. 2009;90:790-6.
[12] Khan Z, Yusup S, Ahmad MM, Chin BLF. Hydrogen production from palm kernel shell via integrated catalytic adsorption (ICA) steam gasification. Energy Conversion and Management. 2014;87:1224-30.
[13] Yusup S, Khan Z, Ahmad MM, Rashidi NA. Optimization of hydrogen production in in-situ catalytic adsorption (ICA) steam gasification based on Response Surface Methodology. Biomass and Bioenergy. 2014;60:98-107.
[14] Xu G, Murakami T, Suda T, Kusama S, Fujimori T. Distinctive effects of CaO additive on atmospheric gasification of biomass at different temperatures. Ind Eng Chem Res. 2005;44:5864-8.
[15] Pfeifer C, B. Puchner, Hofbauer H. In-Situ CO_2-Absorption in a Dual Fluidized Bed Biomass Steam Gasifier to Produce a Hydrogen Rich Syngas. International Journal of Chemical Reactor Engineering. 2008;5, A9:1-13.
[16] Zamboni I, Debal M, Matt M, Girods P, Kiennemann A, Rogaume Y, et al. Catalytic gasification of biomass (Miscanthus) enhanced by CO_2 sorption. Environmental Science and Pollution Research. 2016:1-14.
[17] Aarlien R, Røkke NA, Svendsen HF, Schweitzer D, Beirow M, Gredinger A, et al. Pilot-scale emonstration of Oxy-SER steam gasification: production of syngas with pre-combustion CO_2 apture. Energy Procedia. 2016;86:56-68.
[18] Florin NH, Harris AT. Enhanced hydrogen production from biomass with in situ carbon dioxide capture using calcium oxide sorbents. Chem Eng Sci. 2008;63:287-316.
[19] Pfeifer C, Hofbauer H. Development of catalytic tar decomposition downstream from a dual fluidized bed biomass steam gasifier. Powder Technol. 2008;180:9-16.
[20] Abuadala A, Dincer I. Efficiency evaluation of dry hydrogen production from biomass gasification. Thermochimica Acta. 2010;507-508:127-34.
[21] Taheri MH, Mosaffa AH, Farshi LG. Energy, exergy and economic assessments of a novel integrated biomass based multigeneration energy system with hydrogen production and LNG regasification cycle. Energy. 2017;125:162-77.
[22] Yao J, Kraussler M, Benedikt F, Hofbauer H. Techno-economic assessment of hydrogen production based on dual fluidized bed biomass steam gasification, biogas steam reforming, and alkaline water electrolysis processes. Energy Conversion and Management. 2017;145:278-92.
[23] Galanti L, Franzoni A, Traverso A, Massardo AF. Existing large steam power plant upgraded for hydrogen production. Applied Energy. 2011;88:1510-8.
[24] Liszka M, Malik T, Manfrida G. Energy and exergy analysis of hydrogen-oriented coal gasification with CO2 capture. Energy. 2012;45:142-50.
[25] Schweitzer D, Albrecht FG, Schmid M, Beirow M, Spörl R, Dietrich R-U, et al. Process simulation and techno-economic assessment of SER steam gasification for hydrogen production. International Journal of Hydrogen Energy. 2018;43:569-79.
[26] Perejón A, Romeo LM, Lara Y, Lisbona P, Martínez A, Valverde JM. The Calcium-Looping technology for CO2 capture: On the important roles of energy integration and sorbent behavior. Applied Energy. 2016;162:787-807.
[27] Khan Z, Yusup S, Ahmad MM, Chin BLF. Performance Study of Ni Catalyst with Quicklime (CaO) as CO2 Adsorbent in Palm Kernel Shell Steam Gasification for Hydrogen Production. Advanced Materials Research. 2014;917:292-300.
[28] Himmelblau DM, Riggs JB. Basic principles and calculations in chemical engineering2003.
[29] Kelly-Yong TL, Lee KT, Mohamed AR, Bhatia S. Potential of hydrogen from oil palm biomass as a source of renewable energy worldwide. Energy Policy. 2007;35:5692-701.

[30] Mahishi MR, Sadrameli MS, Vijayaraghavan S, Goswami DY. A novel approach to enhance the hydrogen yield of biomass gasification using CO_2 sorbent. Journal of Engineering for Gas Turbines and Power. 2008;130:1-8.
[31] Xiao X, Meng X, Le DD, Takarada T. Two-stage steam gasification of waste biomass in fluidized bed at low temperature: Parametric investigations and performance optimization. Bioresour Technol. 2011;102:1975-81.
[32] Franco C, Pinto F, Gulyurtlu I, Cabrita I. The study of reactions influencing the biomass steam gasification process. Fuel. 2003;82:835-42.
[33] Mountouris A, Voutsas E, Tassios D. Solid waste plasma gasification: Equilibrium model development and exergy analysis. Energy Conversion and Management. 2006;47:1723-37.
[34] Pfeifer C, Puchner B, Hofbauer H. Comparison of dual fluidized bed steam gasification of biomass with and without selective transport of CO2. Chemical Engineering Science. 2009;64:5073-83.
[35] Rapagnà S, Latif A. Steam gasification of almond shells in a fluidised bed reactor: the influence of temperature and particle size on product yield and distribution. Biomass and Bioenergy. 1997;12:281-8.
[36] Guo J, Lua A. Kinetic Study on Pyrolysis of Extracted Oil Palm Fiber. Isothermal and non-isothermal conditions. Journal of Thermal Analysis and Calorimetry. 2000;59:763-74.