Integrated catalytic adsorption steam gasification in a bubbling fluidized bed for enhanced H_2 production: Perspective of design and pilot plant experiences

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ABSTRACT

It is important to build knowledge on the design of an integrated catalytic adsorption (ICA) steam gasification process in a bubbling fluidized bed to reduce CO_2 content with enhanced hydrogen production. The news value of this study is presentation of detailed design considerations for performance evaluation of ICA system utilizing palm oil wastes as feedstock. The main advantage of utilizing ICA gasification system is the CO_2 adsorption through carbonation reaction (using CaO) that help water gas shift reaction to move forward. Whereas the catalyst activity improves steam methane reforming in parallel which not only produces additional hydrogen but also releases CO to enhance the activity of water gas shift reaction. The performance of the developed system has shown least temperature variation (< 1%) inside reactor which inferred the positive role of exothermic reactions between reactive bed material (CaO) and CO_2 in the product gas. The low-pressure drop in the gasifier (100-130 mbar) further strengthens the presented design strategy for ICA gasification system for hydrogen production. Further, the challenges encountered during the pilot plant operations and their potential solutions have been discussed to improve and optimize the operation, especially for downstream equipment and auxiliaries.

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1. Introduction

Concerted efforts have been made to develop advance biomass gasification technologies in the last couple of decades. Present biomass gasification technologies are based on coal gasification processes but with slight modification due to the high volatile matter and low temperature of operation. These technologies mainly comprised of a fixed bed, fluidized bed entrained flow reactors, plasma reactors and rotary kiln reactors [1]. However, fixed bed, fluidized bed and entrained flow gasifiers are mostly utilized for hydrogen production from biomass gasification [2]. Fluidized bed (FB) gasifiers have proven to be the efficient for combustion and gasification processes due to their high mass and heat transfer capability. The FB gasifiers are considered to be an effective choice for biomass gasification as they accept a wide variety of biomass, produce high carbon conversion rates and provide uniform temperature distribution in the gasifier [3]. These types of gasifiers accept small feed size compared to the fixed bed gasifiers, and they are capable of handling higher and lower quality fuels [4].

Recent application of catalyst and *in situ* CO_2 adsorption to enhance hydrogen from biomass gasification makes the process more viable for commercial scale. Udomsirichakorn and Salam [5] review biomass steam gasification technologies utilizing *in situ* CO_2 adsorption techniques to produce hydrogen. Most of these studies [5] comprise fixed and fluidized beds including a dual fluidized bed reactor. Many researchers [6-8] have developed the concept of gasification via chemical looping for hydrogen production utilizing CaO as an adsorbent which implied regeneration of the adsorbent in a different reactor. More recently, the development of fluidized bed gasifier and sorption-enhanced reforming process (SERP) has been proposed for biomass steam gasification to enhance hydrogen production [9]. This system has worked on gasification

followed by SERP contains a mixture of Ni-based catalyst and CaO sorbent. 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 [10, 11], CO_2 sorption [6-8] or coupling of both in the same reactors (after gasification step) [9] and/or in separate reactors (after the pyrolysis step) [12]. Therefore, development of a single gasifier utilizing catalyst and CO_2 adsorbent in the same bed will be worthwhile to investigate.

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 [13, 14]. 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 carbonation reaction (Eq. 4) 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 depending on the high temperature. However, temperature > 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 [15-18]. Therefore, using steam methane reforming catalyst in the bed not only enhance hydrogen production but also provide more CO (even at low temperature) to allow the water shift reaction to move in a forward direction.

Char gasification reaction (CGR),

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

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

$$CO_2 + H_2O \rightarrow CaCO_3 \quad \Delta H = -170.5 \text{ kJ/mol} \tag{4}$$

The present study is a continuation of our research work to develop integrated catalytic adsorbent (ICA) steam gasification using the bubbling fluidized bed. A part of ICA steam gasification process evaluates the optimum process conditions for hydrogen production, has been published [13, 14, 19] whereas detail process and design development, and operational challenges of this pilot scale study are not reported yet. The news value of this study is the design considerations and pilot plant experiences of a bubbling fluidized bed gasification system for enhanced H_2 production that utilizes a catalyst (Ni-based) and adsorbent (CaO) in a single bed inside the reactor. The design strategy is carried out by combining the reactor hydrodynamics and reaction based steam required for the gasification reactions. A number of parameters e.g. minimum fluidization velocity, transport disengaging height, maximum bubble diameter, bed to distributor plate pressure drop ratio are investigated to evaluate reactor dimensions and distributor plate design. The performance of the developed pilot scale ICA gasification system is carried out through temperature pressure profiles and velocity-pressure diagrams to ensure sufficient fluidization conditions in the bed. The issues encountered during the system operation and the potential solutions have been discussed to improve and optimize the operation, especially for downstream equipment and auxiliaries. The impact of vital performance parameters, such as product gas composition, hydrogen yield and gas heating

values are further discussed. The study is intended to assist the scientific community, companies, governmental energy agencies and relevant stakeholders to further develop efficient ICA steam gasification process for enhanced H_2 production.

2. Methodology and key design parameters

2.1 ICA steam gasification system

Fig. 1 shows a process diagram of pilot scale fluidized bed ICA steam gasification system. The gasification system mainly comprises of fluidized bed reactor with external electric heaters, biomass feeding system, steam generator and superheater, cyclone solid separator, wet scrubber, water separator, and gas analyzing the 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 then 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 the water separator. The gas analysing system consists of Gas Chromatography (Teledyne 7500, Teledyne Analytical Instrument) with Infrared (IR) type detector. Hydrogen and nitrogen are detected by Gas Chromatography utilizing Molecular Sieve 5A column (Teledyne 4060, Teledyne Analytical Instrument) with Thermal Conductive Detector (TCD). The product gas is measured every 6 minutes at the sampling point located after the water separator.

ICA gasification system is developed to operate at a temperature range of 600-750 °C, under atmospheric pressure. This temperature range provides an active carbonation region when CaO is used as a bed material to adsorb CO_2 [20].

2.2 Materials and gasification agent

Palm kernel shell (PKS) is selected as the feedstock for hydrogen production via ICA steam gasification. It is estimated that a total of 12.8 Mt of PKS are generated in 2015 by Malaysia and Indonesia [21, 22] which are the largest oil palm producers in the world [23] . Based on its abundance and physical properties i.e. high proportion of fixed carbon, volatile matter, and low ash and moisture content, PKS has the potential to enhance hydrogen production via gasification [24]. The ultimate analysis of PKS has performed in LECO CHNS 932 elemental analyser. A standard sample of approximately 2 mg was put in the silver capsule and analysed. The furnace temperature was maintained at 1000°C. The proximate analysis (volatile matter, ash content, and fixed carbon) was determined based on a dry basis. For ash content, ASTM D-3175-01 procedure was used to evaluate the ash content in the biomass. The sample was then cooled and weighed. The volatile matter was determined by following ASTM E-872 procedure. Fixed carbon was determined by subtracting the sum of volatiles matter and ash content in the biomass based on the dry basis. The calorific value of PKS was determined in IKA C5000 oxygen bomb calorimeter. The ASTM E711-87 procedure was considered to determine the calorific value. The physical properties of PKS are listed in Table 1.

The present work proposes *in situ* CO_2 adsorption and emphasis on the reactive bed particle which can provide smooth fluidization as well as effective CO_2 absorption in the bed. Naturally occurring metal oxides (MO), abundant in natural rocks, are proved to be low-cost CO_2 adsorbent material [25] through the following reaction.

$$MO + CO_2 \leftrightarrow MCO_3 \quad (5)$$

However, decomposition temperature (calcination temperature) of these metal carbonates (MCO_3) i.e. $MgCO_3$ (385˚C), $ZnCO_3$ (340˚C) and $MnCO_3$ (440˚C) is low which makes them unsuitable for *in situ* CO_2 capture in biomass gasification [26]. Among these metal oxides, the decomposition temperature for $CaCO_3$ is 800˚C which makes CaO more suitable as a sorbent [27]. Besides, CaO can also be extracted from different sources i.e. eggshell [28] and cockle shell

[29] in the form of $CaCO_3$ which is further calcined and used as a CaO for CO_2 adsorption. In the present study, Quicklime (CaO) is used as the bed particle to adsorb CO_2 at the gasification temperature. The quicklime was purchased from Universal Lime Sdn. Bhd., Malaysia. The main source of the quicklime is natural occurring limestone which is abundant in the local area of Perak, Malaysia. The physical properties and chemical composition [30] is shown in Table 2. Based on their properties, these materials are well represented by the Geldart particle B (sand like) which represents good fluidization characteristics to achieve better heat and mass transfer rates to keep homogeneous temperature all over the bed.

Steam as an oxidizing agent has gained a high reputation due to the resulting hydrogen-rich gas production [26]. The properties of steam for the case are given in Table 2. Steam gasification produces 5 times more hydrogen content than air gasification in fluidized bed gasifier [31] and thus considered as the gasification medium in the present study.

Nickel (Ni) is the most widely used catalyst in steam and dry reforming processes. There is a significant body of work reported on the application of Ni catalysts in biomass gasification [32, 33]. In the present study, purified Ni powder with 99.5 % purity and average particle size of 10 μm is used. The Ni catalyst is purchased from Merck KGaA, Germany. Throughout the ICA gasification runs, Ni catalyst is mixed with palm kernel shell (PKS) at a fixed ratio of 0.1 (wt./wt.) and introduce to the gasifier via the biomass feeding system.

2.3 Reactor diameter evaluation

Fluidized bed gasifier design initially considers the evaluation of the gasifier diameter. Steam as a gasification agent also has an additional role of fluidizing the bed. This dual role needs to be balanced. Fig. 2 shows the diameter estimation process through the combination of minimum fluidization velocity (U_{mf}) as a hydrodynamics parameter and total steam requirement as a reactant for the gasification reactions. The present study considers that the

bubbling fluidized bed is characterized by a superficial gas velocity (U) of the order of a U_{mf} [34]. Similarly, the total steam required for U_{mf} is a few orders of steam required for gasification reaction. The evaluation of U_{mf} is based on the physical properties of the bed particles and steam. These properties include average particle diameter, particle density, bulk density, and steam density and viscosity. The density and viscosity of steam are considered at the fluidization conditions of 750 °C and 1 atm [35, 36] (Table 2).

The minimum fluidization velocity (U_{mf}) is a basic design parameter to define fluidization conditions in the bed. The modified form of Ergun's equation in the form of Archimedes number (Ar) for the pressure drop across a fixed bed at minimum fluidization conditions is used to estimate U_{mf} [37] and given by Equation (6):

$$Ar = 150\left(\frac{1-\varepsilon_{mf}}{\varphi_b^2(\varepsilon_{mf}^3)}\right)\mathrm{Re}_{mf} + \left(\frac{1.75}{\varphi_b^2(\varepsilon_{mf}^3)}\right)\mathrm{Re}^2{}_{mf} \tag{6}$$

Where Ar can be calculated as:

$$Ar = d_b^3\rho_f\left(\frac{\rho_p - \rho_f}{\mu^2}\right)g \tag{7}$$

The Reynolds number at the minimum fluidization condition is:

$$\mathrm{Re}_{mf} = \frac{d_p\rho_f U_{mf}}{\mu} \tag{8}$$

Where d_b and ρ_b are the bed particle diameter (m) and density (kg/m^3), respectively, ρ_f and μ are the viscosity (Pa. s) and density (kg/m^3) of steam, g is the acceleration due to gravity (m/s^2), ε_{mf} is the bed voidage at the minimum fluidization velocity and φ_b is the bed particle sphericity.

Bed voidage and sphericity must be known at minimum fluidization to estimate U_{mf} using

Equations (6), (7) and (8). These basic equations give more reliable predictions of U_{mf} as compared to empirical expressions [37] and thus they are used herein. ε_{mf} is calculated from the following expression [38]:

$$\varepsilon_{mf} = \frac{\rho_b}{\rho_p} - 1 \tag{9}$$

The sphericity for CaO is calculated from previously published work [39] using Equations (6)-(8) for known minimum fluidization velocity. The sphericity determined value is 0.43 which is in a good agreement with the value reported by Basu [40].

The steam, needed for the gasification reactions as the reactant is evaluated. These main reactions are char gasification, methane steam reforming and the water gas shift as represented by Equations (1- 4):

The total amount of steam required (S_{total}) for gasification is given by:

$$S_{Total} = S_{CGR} + S_{SMR} + S_{WGSR} \tag{10}$$

The following scheme is considered to calculate the amount of steam required for each of the reactions involved:

- CGR: Char is produced according to the fixed carbon content of biomass from the proximate analysis [41]. This char is expected to participate in the CGR and thus can be estimated directly from the given biomass feed rate.
- SMR: The biomass devolatilization produces gases such as H_2, CO, CO_2, CH_4 and H_2O [42]. The amount of CH_4, released from biomass, is estimated based on the proximate and ultimate analysis. The total elemental carbon content in biomass is 49.74 wt% which consists of fixed carbon (C) and volatile matter (assumed to be CH_4 only). The remaining carbon portion in the volatile matter is estimated by subtracting the fixed carbon from the total elemental carbon.

- WGSR: The amount of steam available for the water gas shift reaction is estimated from CO produced by char gasification and steam methane reforming reactions. The amount of CO in the water gas shift reaction is considered as the sum of the CO generated from char gasification and steam methane reforming reactions.

2.4 Gasifier Height

The height of the fluidized bed reactor is calculated based on the transport disengaging height (TDH) [24], the height over which only fine particles are carried over, and the bed height (Fig. 3) [37]. The equation of reactor height can be written as:

$$\text{Reactor height} = \text{TDH} + \text{Bed height} \tag{11}$$

Above the TDH, the rate of carryover of fine particles is constant. Moreover, the height of which gas exits from the fluidized bed reactor should be higher than TDH to minimize the entrainment of solid particles.

Several empirical expressions are used to determine the TDH based on the maximum bubble diameter. Among these, Horio's empirical equation and Zenz's graphical presentation are more reliable [38]. However, the graphical presentations are only available for fine particles corresponding to Geldart particles A [37]; whereas the present study considered Geldart particles B. The equation presented by Horio [38] for TDH is considered in the present case which can be used for Geldart particles B:

$$\text{TDH} = 4.47\left(D_{bm}\right)^{0.5} \tag{12}$$

Where D_{bm} is the maximum bubble diameter on the surface of the bed.

The maximum bubble diameter (D_{bm}) is an important parameter to avoid slugging in bubbling fluidized bed reactors. The mass transfer rate between the bubble and emulsion phases is an important parameter that influences the overall reaction rate.

In the present study, Mori and Wen's correlation, [43] is used to determine the D_{bm}. This correlation is valid for both Geldart types B and D particle classification:

$$D_{bm} = 0.652\left[A\left(U - U_{mf}\right)\right]^{2/5} \tag{13}$$

Where U is the superficial gas (steam) velocity (m/s) and A is the bed cross-sectional area (m^2). Maximum bubble diameter increases with increasing superficial velocity and bed height [40, 44]. For better fluidization conditions in the bed, it is generally recommended that the ratio of bed height (Z) to bed diameter (D) needs to be $\leq$ 2.0 to avoid slugging [45]. Slugging occurs when the bubble reaches the size of the bed diameter. At this stage, the bubble passes through the bed as a slug and fluidization conditions are not sustained in the reactor [38]. In the present study, a ratio of 1.0 is considered to facilitate a good fluidization region and also to keep the bubble size sufficiently small to avoid slugging.

2.5 Distributor plate design

The distributor plate plays a vital role in generating homogeneous fluidization conditions all over the bed. It is important that the fluidized bed distributor is properly designed to ensure uniform distribution of gas flow. Better design approaches of distributor plates for good fluidization depends on a certain ratio between the pressure drop across the distributor plate and bed. A perforated plate type distributor is used due to its fabrication simplicity, hole size modification and ability to be cleaned easily

Zuiderweg et al. [37] used a rule of thumb to obtain the pressure drop across the distributor plate. They considered 0.2-0.4 ratio for the distributor pressure to the bed pressure drop. However, this approach gives a high-pressure drop inside the reactor [37] and is not considered in the present study. Qureshi et al. [46] developed an empirical relationship for the ratio of distributor pressure to bed pressure drop (R_c), and showed stable and unstable operational regions of the distributor using the following expression:

$$R_c = 0.01 + 0.02\left(1 - \exp\left(\frac{-0.5D}{Z}\right)\right) \tag{14}$$

Where D is the bed diameter (m) and Z is the bed height (m). The aspect ratio of the bed (D/Z) is assumed as 1.0 to ensure a stable operating region for the distributor [46]. The pressure drop across the bed at superficial velocity (5 times of U_{mf} in the present study) is then calculated from Equation (14) [37].

$$\Delta P_b = Z(1-\varepsilon)(\rho_p - \rho_f) \tag{15}$$

Where ε refers to bed voidage and Z is the bed height at the superficial gas velocity. Bed voidage at superficial velocity can be considered equal to the bed voidage at minimum fluidization ($\varepsilon=\varepsilon_{mf}$) because no change in pressure drop can be seen for Geldart B type particles, if the gas velocity rises over the minimum fluidization velocity [38]. The distributor pressure drop is determined using Equation (13) which is further used to determine the total number of orifices needed in the perforated distributor plate (Table 3).

A general design procedure for estimating the total number of orifices on a triangular pitch [37] is followed:

- Number of orifice (N_{or}) in the distribution plate is determined using the following expression:

$$N_{or} = A_{or}\left(\frac{U_{or}}{Q_{mf}}\right) \tag{16}$$

Q_{mf}, A_{or}, U_{or} are the minimum fluidization volumetric flow rate (m^3/h), area of each orifice (m^2) and gas velocity (m/s) through the orifice in the distributor plate respectively. All of these quantities are dependent on the properties of the fluidizing agent (density and viscosity of steam).

- The gas velocity through the orifices is calculated using:

$$U_{or} = C_{d\,or}\left(\frac{2\Delta P_d}{\rho_f}\right) \tag{17}$$

Where ΔP_d is the pressure drop (bar) across the distributor plate. This is calculated based on the pressure in the bed as $\Delta P_d = 0.089\ \Delta P_b$, where 0.089 represents R_c (Equation 14). Constant, C_{dor}, is the drag coefficient.

- The drag coefficient, C_{dor} (dimensionless), and Vessel Reynolds number ($R_{e(v)}$) based on the diameter of the vessel (reactor) are related as follows:

$$R_{e(v)} = \rho_f\left(\frac{U_{or}D}{\mu}\right) \tag{18}$$

The total number of orifices in the distributor plate is then evaluated.

3. Results and Discussions

3.1 Fluidized bed gasifier configuration

A schematic of the fluidized bed gasifier is shown in Fig. 4. Inconel 625 is a nickel-chromium alloy preferred over stainless steel 316 as the material of construction as it has excellent corrosion and heat resistance properties.

The outputs from the reactor design process are the gasifier diameter, height of the fluidized bed reactor and the distributor plate configuration. The reactor dimensions evaluated in the

design process are listed in Table 4. As shown in Fig. 4, the freeboard is kept b than the bed area size to reduce solid entrainment from the gasifier and to provide a longer residence time of the product gas to enhance tar cracking [47]. The freeboard of the reactor is expanded up to a diameter of 0.19 m with a height of 0.3 m.

The location of feeding the biomass into the gasifier is an important criterion. It is beneficial for large systems to feed the biomass at the bottom, nearer to the distributor plate. This type of design is recommended to reduce tar and char content [48]. In the present study, the feed-in point is 0.20 m above the distributor plate. The fluidized bed mainly comprises of three parts: i) region below the distributor plate, called the plenum, ii) the main bed region above the distributor plate and iii) the top expanded zone is known i.e. freeboard. The main bed section is the section where the bed material is fluidized and the entire gasification reactions take place. This region also contains the biomass feed-in point. The main gasifier is equipped with three internal temperature indicators (TI) to monitor temperature at 1) just below the distributor plate and 0.1 m from the bottom of the gasifier, 2) located in the bed and 0.85 m from the bottom of the gasifier, and 3) situated in the freeboard and 1.85 m from the bottom section. The pressure differential indicator is provided between the point below the distributor plate and in the freeboard section to monitor the total pressure drop across the reactor. The additional air inlet is provided to ensure post-experiment combustion to remove any unwanted carbon in the gasifier and downstream. Similarly, N_2 is used to purge the gasification system to remove entrapped gases before the start of each experiment.

3.2 Gasifier operation

3.2.1 Temperature and pressure profiles

The fluidized bed gasifier as designed, built and described in this paper, is equipped with three internal TIs at different locations as shown in Fig. 4. Temperature variation at these points

needs to be monitored to avoid large variation of temperature within the reactor. Temperature variation in the bed is studied at three different temperature levels i.e. 600, 675 and 750°C. Temperature profiles are plotted with respect to time for 60 min, the total time of gasification considered for all of the experiments in the present study. Each temperature reading is taken at 6 min intervals.

Fig. 5 shows the temperature profiles in the bed (TI (2)) for the temperature of 600, 675 and 750°C over 60 minutes. The analysis shows no significant temperature variation in the bed for the ICA steam gasification system. Standard variations of the temperature readings are $\pm$5.0°C, $\pm$5.8°C and $\pm$6.0°C for 600°C, 675°C and 750°C, respectively. Thus, the variation is small, (<1%) and this is due to the carbonation reaction, an exothermic reaction, which produces heat for the endothermic gasification reactions. Similar observations are reported by other researchers [49] as well.

The temperature profiles at the three different locations in the fluidized bed gasifier can be seen in Fig. 6. The data shows the average value over 60 min. Attempts are made to keep the temperature constant throughout the fluidized bed reactor by using an external heating system. Amongst the three locations, significant variation is observed just below the distributor plate particularly at high temperature (675°C and 750°C) due to the steam injection at a lower temperature (250-300°C). The results show no significant variation in the freeboard temperature over the considered range for each experiment.

Initially, the pressure drop variation is measured with respect to time for each velocity i.e. 0.15 ($3U_{mf}$), 0.21 ($4U_{mf}$) and 0.26 m/s ($5U_{mf}$). A velocity to pressure drop diagram is then generated at a given fluidization velocity. The average pressure drop during 60 min gasification operation is then plotted with respect to fluidization velocity. The pressure drop is measured through the

pressure differential indicator (PDI) between the points located below the distributor plate and the freeboard region, as shown in Fig. 4.

Fig. 7 shows the pressure drop fluctuation with respect to time for different fluidization velocities i.e. 0.15, 0.21 and 0.26 m/s which represent 3, 4 and 5 times the fluidization velocity in the fluidized bed gasifier. The pressure drop evaluated using Equation (14) is shown for comparison (dotted line) which is based on the diameter to height ratio of 1.0. The analysis shows that total pressure drop increases as the fluidization velocities increases. The maximum pressure drop is observed at high fluidization velocity. However, low fluidization velocity produces a lower pressure drop and shows less fluctuation as compared to high fluidization velocities i.e. 0.21 m/s and 0.26 m/s.

Fig. 8 shows the relationship of pressure drop to fluidization velocity in the fluidized bed gasifier. The pressure drop represents an average value over 60 min of operational time. The analysis shows that the average pressure drop observed is in the range of 100-130 mbar by varying fluidization velocity in the range of 0.15-0.26 m/s. It shows that the pressure drop variation in the present study is not significant by varying the fluidization velocity between 0.15-0.26 m/s for the ICA steam gasification system. The bed starts to expand at the onset of minimum fluidization velocity, and a further increase in fluidization velocity does not show any significant increase in the pressure drop.

3.3 Gasifier operational challenges and solution

The following section elaborates operational problems observed in ICA steam gasification utilizing PKS as the feedstock. It also highlights the appropriate remedy for the associated problems related to the gasification system.

3.3.1 Downstream Clogging

The product gas carries tar (high hydrocarbon), excess steam, fine char and solid particles separated from the bed material due to attrition. The drastic decrease in temperature results in steam saturation and tar condensation in the mixture. In this situation, fine particles are started to agglomerate and produce a paste-like mixture which clogged the downstream pipe and equipment as shown in Fig. 9. Heating tape is used to provide a maximum temperature of 300-400°C to eliminate this effect. But due to the excess amount of steam in the product gas, the heating tape is not able to maintain sufficient heat at further distances along the pipe.

3.3.2 *Presence of moisture in gas analyzing system*

In the gas analyzing system, the product gas passes through the small condenser which separate~~s~~ the remaining moisture from the product gas stream. The efficiency of the condenser depends on the moisture present in the product gas. At high steam to biomass ratios, a high amount of unreacted steam exits from the gasifier and contributes a major part of the product gas stream. The product gas still carries a significant amount of moisture after passing through the cleaning system. Such high moisture level reduces–the separation efficiency of the condenser. The moisture enters into the tubing system of the analyzers, as shown in Fig. 10 (a) and then passes through the sample flow meter as shown in Fig. 10 (b) associated with the gas analyzing system. This situation results in the accumulation of moisture in the gas analyzing system which causes inaccurate measurements and serious damage to the gas analysing system.

3.3.3 Solutions to address operational problems

To avoid clogging in downstream, nitrogen is injected into the system just before the biomass feeding into the system. Nitrogen flows consume heat from the reactor at high temperature i.e. 600-750°C and then pass~~ed~~ through, and heat~~ed~~ up the pipe and equipment downstream. This enhanced the efficiency of the heating tape which is able to maintain high temperature operation between 300-400°C. This procedure is followed for all of the experiments to avoid

blockage within the system. The second problem is associated with moisture content ~~is~~ and its presence in the gas analyzing system which can cause false readings of the product gas composition measured by the GC. This effect is eliminated by nitrogen purging before the start of each experiment. N_2 carried away any residual moisture and entrapped gases (H_2, CO, CO_2 and CH_4) present in the gas analyzing the system. N_2 purging is also used for a couple of minutes during the experiments for removal of the moisture. During this operation, the connection to the main analyzer is opened and the moisture is drained before entering the gas analyzer.

3.4 Performance of ICA gasification system

A few parameters are selected to identify the performance of the ICA gasification system in the context of the present work. However, the detailed experimental results and their optimization can be found elsewhere [13, 14, 19].

Table 5 shows the product gas composition, hydrogen yield and gas heating values at 600, 675 and 750°C. The results infer that the H_2 composition (82.10 vol%) is maximum at 675°C while the CO_2 composition is zero at 600 and 675°C. However, at 750°C, the H_2 composition is drastically decreased to its minimum value (67.40 vol%) whereas CO_2 increases to its maximum value (7.57 vol%). This increase clearly shows the existence of reverse carbonation (calcination reaction) in the system which has been reported by Xu et al. [15] and Pfeifer et al. [16] at temperatures higher than 727°C and 675°C, respectively. Moreover, Zamboni et al. [17] and Aarlien et al. [18] reported maximum CO_2 sorption temperature at 660°C and 700°C for enhanced H_2 production, respectively. This infers the optimum temperature of 675°C is suitable for high H_2 composition with minimal CO_2 in ICA steam gasification and also provides evidence of a good fluidized bed operation in the present study. The lowest CH_4 concentration at 750 °C is due to high reactive steam methane reforming in the presence of the Ni catalyst which is further

verified by the highest CO concentration observed at 750 °C. The high activity of Ni catalyst in steam methane reforming at a temperature >740°C is also reported by other researchers [50]. It is concluded from the product gas profile of the ICA gasification system that the carbonation reaction remains effective at a lower temperature (600-675 °C, below the calcination temperature of $CaCO_3$) with high H_2 and negligible CO_2 content; while with higher temperature (750 °C) the process is dominated by Ni-based catalysed steam methane reforming, and generated high CO and low CH_4 concentrations. For this reason, the product gas profiles generated in ICA steam gasification might be different from biomass steam gasification with in-situ CO_2 adsorbent [20] and biomass steam gasification using Ni catalyst [50, 51]. Besides, H_2 yield increases with increasing temperature and maximum yield (150.99 g H_2/kg biomass) is achieved at 750°C which is 5 times the yield at 600°C. The maximum H_2 yield at higher temperature is mainly due to the endothermic reactions of catalytic steam methane reforming and tar cracking [52] in the process. A comparative study of the ICA gasification system ((150.99 g H_2/kg biomass at 750 °C) with catalytic sorption enhanced steam gasification (133 g H_2/kg biomass at 700 °C in 0.5 g sample fixed bed reactor) [53] shows the prospects of the present work. The lower heating values of the product show a continuous decrease as the temperature increases. This trend can be explained by decreasing trend of CH_4 with increasing temperature. Overall, the ICA steam gasification produces a gaseous mixture with medium heating values (12-18 MJ/Nm^3). Besides, carbon conversion and gasification efficiency show an increasing trend as temperature increases. Low efficiencies at low temperature (600-675 °C) might be a case of negligible CO_2 and low activity of endothermic reactions.

The important aspect of the ICA steam gasification process is to maximize hydrogen generation in the product gas at lower gasification temperature. However, lower temperature in steam gasification might need to be observed closely due to high tar content nature of the process (as

shown in the Fig. 9). The proper heating of the downstream pipes and equipment needs to be maintained above tar condensation temperature up to the point of separation/collection.

4. Conclusions

The design considerations and pilot plant experiences of a bubbling fluidized bed gasification with integrated Ni catalyst and CO_2 adsorbent for enhanced are presented. The gasifier operation showed minimal temperature variation (< 1%) below distributor plate, in the bed, and freeboard regions. Similarly, minimal pressure drop (<150 mbar) is observed which is found proportional to fluidization velocities in the bed. The negligible CO_2 and high H_2 concentration (82 vol. %) in the product gas verify the active nature of the carbonation reaction even at a lower gasification temperature (600-675 °C, below the calcination temperature of $CaCO_3$). Moreover, high H_2 yield (31-150 g/kg biomass) and gas heating values (12.88-14.27 MJ/Nm^3) at a temperature range of 600-750°C shows the good operation of the system. In order to address the issue of clogginer, nitrogen is injected into the system just before the biomass feeding system since N_2 flow may consume heat from the reactor at high temperature and could heat up the pipe and equipment downstream while passing through. For the solution of moisture accumulation, N_2 is purged before the start of each experiment since N_2 carried away any residual moisture and entrapped gases (H_2, CO, CO_2 and CH_4) present in the gas analyzing the system.

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Tables

Table 1. Proximate and ultimate analysis of PKS[24]

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 basis)	
C		49.65
H		6.13
N		0.41
S		0.48
O (by difference)		43.33
Higher heating value	(MJ/kg)	20.40

Table 2. Physical properties and chemical composition of CaO (bed material)[30] and steam[35 36]

Bed Material (CaO)		
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)		
Steam (At 750 °C, 1 atm)		
Density (kg/m^3)		0.22
Viscosity (Pas)		4×10^{-5}

Table 3. Input design parameter for distributor plate design

Orifice diameter	(m)	0.002
Minimum fluidization velocity	[m/s]	0.051
Gas (steam) superficial velocity	[m/s]	0.26
Bed voidage	-	0.66
D/Z	-	1.0
R_c	-	0.089

Table 4**.** Fluidized bed gasifier system configuration

Internal diameter (ID)	[m]	0.15
Total height	[m]	2.00
Freeboard height	[m]	0.30
Freeboard ID	[m]	0.19
Plenum height	[m]	0.30
Distributor plate hole ID	[m]	0.002
Feeding point location from the distributor	-	0.20
Number of orifices in the distribution plate	-	158
Operating temperature	[°C]	600-750
Preheat temperature of the steam	[°C]	250-300

Table 5. Effect of temperature on performance parameters

Temperature	[°C]	600	675	750
Biomass feed rate	[kg/h]	1.35	1.35	1.35
Steam/biomass	[wt/wt]	2.0	2.0	2.0
Adsorbent to biomass	[wt/wt]	1.0	1.0	1.0
Catalyst to biomass ratio	[wt/wt]	0.1	0.1	0.1
Gas composition (dry-N_2 free)	[vol%]			
H_2		78.00	82.10	67.40
CO		8.78	6.45	14.33
CO_2		0.00	0.00	7.57
CH_4		13.22	11.43	10.70
Hydrogen yield	[g/kg biomass]	31.80	80.39	150.99
Lower heating value	[MJ/Nm^3]	14.27	13.78	12.88
Carbon conversion efficiency	[%]	11.06	20.06	87.01