



# Oxy–steam gasification of biomass for hydrogen rich syngas production using downdraft reactor configuration

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## SUMMARY

The paper focuses on the use of oxygen and steam as the gasification agents in the thermochemical conversion of biomass to produce hydrogen rich syngas, using a downdraft reactor configuration.

Performance of the reactor is evaluated for different equivalence ratios (ER), steam to biomass ratios (SBR) and moisture content in the fuel. The results are compared and evaluated with chemical equilibrium analysis and reaction kinetics along with the results available in the literature. Parametric study suggests that, with increase in SBR, hydrogen fraction in the syngas increases but necessitates an increase in the ER to maintain reactor temperature toward stable operating conditions. SBR is varied from 0.75 to 2.7 and ER from 0.18 to 0.3. The peak hydrogen yield is found to be 104 g/kg of biomass at SBR of 2.7. Further, significant enhancement in H<sub>2</sub> yield and H<sub>2</sub> to CO ratio is observed at higher SBR (SBR = 1.5–2.7) compared with lower range SBR (SBR = 0.75–1.5).

Experiments were conducted using wet wood chips to induce moisture into the reacting system and compare the performance with dry wood with steam. The results clearly indicate the both hydrogen generation and the gasification efficiency ( $\eta_g$ ) are better in the latter case. With the increase in SBR, gasification efficiency ( $\eta_g$ ) and lower heating value (LHV) tend to reduce. Gasification efficiency of 85.8% is reported with LHV of 8.9 MJNm<sup>-3</sup> at SBR of 0.75 compared with 69.5% efficiency at SBR of 2.5 and lower LHV of 7.4 at MJNm<sup>-3</sup> at SBR of 2.7. These are argued on the basis of the energy required for steam generation and the extent of steam consumption during the reaction, which translates subsequently in the LHV of syngas. From the analysis of the results, it is evident that reaction kinetics plays a crucial role in the conversion process.

The study also presents the importance of reaction kinetics, which controls the overall performance related to efficiency, H<sub>2</sub> yield, H<sub>2</sub> to CO fraction and LHV of syngas, and their dependence on the process parameters SBR and ER. Copyright © 2013 John Wiley & Sons, Ltd.

## KEY WORDS

downdraft gasifier; hydrogen; syngas; oxy–steam gasification

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## 1. INTRODUCTION

Hydrogen is a clean energy source, and the future widespread use of hydrogen as a fuel is likely to be in the transport sector, and possibly in the distributed power generation sector. Currently, with 49% of hydrogen usage, agricultural sector is the single largest user of hydrogen, for ammonia production [1]. There are various methods for generating hydrogen from renewable and non-renewable resources. Some of the processes used are as follows: steam methane reformation, partial oxidation/autothermal reforming, electrolysis of water, coal gasification, biomass pyrolysis/gasification, thermochemical process with sulfur–iodine (SI cycle), photosynthesis/biological process and photocatalytic water splitting [2]. Hydrogen generated using these processes (except electrolysis) require separation and purification from the mixture of gasses

to different levels of purity depending on the need. Dincer [3] and Turner *et al.* [4] have critically analyzed and compared different green technologies for the hydrogen production. Dincer presents various renewables using renewable sources of energy as an input toward generating hydrogen, either directly or indirectly, by using the thermal, electrical or a combination of energy generated. Turner *et al.* [4] identify the biomass gasification as a better technology among the renewable and categorizes it as a promising technology for the future renewable hydrogen need.

Thermochemical conversion process of biomass to generate producer gas for use in thermal application to replace fossil fuel and power generation using internal combustion engine have been recognized as commercial technology package for energy production. Use of thermochemical conversion of biomass as a process for hydrogen generation is limited.

Pyrolysis and gasification are two thermochemical conversion processes of biomass to generate gaseous fuel used in syngas generation. Pyrolysis is the thermal decomposition of biomass in the presence or absence of a reactive environment. Secondary reactions of pyrolysis products further yield fraction of H<sub>2</sub>, CO, higher hydrocarbon (HHC) and tar with residual char, on the basis of the reacting environment. Biomass gasification is sub-stoichiometric combustion process in which pyrolysis, oxidation and reduction take place. Oxidation of pyrolysis products (volatile matter) further reacts with char and reduces to H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> and HHC.

Ayse *et al.* [5] did pyrolysis studies on the pistachio shells at different temperatures, varying from 673 K to 973 K. Keeping the temperature constant, they performed experiments by varying heating rate from 5 to 500 K min<sup>-1</sup> and nitrogen flow rates from 50 to 400 cm<sup>3</sup> min<sup>-1</sup>. Ayse *et al.* [5] reported maximum gas yield of 47% w/w at 973 K and heating rate of 300 K min<sup>-1</sup> with nitrogen flow rates 100 cm<sup>3</sup> min<sup>-1</sup>. The reported gas yield through pyrolysis is low compared with the gasification where gasifying agents (air/oxygen/steam) aid in conversion of solid char to gaseous fuel and conversion of liquid tar to gas through partial oxidation and thermal cracking, yielding higher percentage of combustible gas. Ahmed and Gupta [6] and Nimit *et al.* [7] have performed studies on pyrolysis and steam gasification of rubber, poplar wood, yellow pine-wood, paper trash and residual branches of oil palm tree as fuel. The research focused on pyrolysis and gasification in a thermally controlled environment using steam as a

reactant. Table I summarizes the results from Ahmed and Gupta [6] and Nimit *et al.* [7].

From Table I, it is evident that the hydrogen yield per kilogram of biomass is higher with steam gasification as compared with pyrolysis. Ahmed and Gupta [6] reported over 160% higher energy yield using gasification process compared with pyrolysis at 1173 K. This suggests the contribution and importance of the char–steam reaction in the overall process. On the basis of the energy in the gas and the solid residue left during the process (extent of carbon conversion), it is concluded that gasification is an efficient process compared with pyrolysis for syngas generation.

Nimit *et al.* [7] and Ahmed and Gupta [6] also performed experiments at varying reactor bed temperature and observed better hydrogen yield at higher temperature (Table I). Nimit *et al.* [7] reported the complete conversion of biomass in 29 min at 1273 K compared with 200 min at 873 K. Extremely slow rate of the char–steam reaction is cited as the reason for the slow rate of gasification at lower temperatures, whereas high temperature and increased residence time have been identified as the key parameters that favor higher H<sub>2</sub> yields. Similar results have been reported by Turn *et al.* [8] and Pengmei *et al.* [9]. Table II summarizes the results from their respective work on oxy–steam gasification. It is clear that high temperature and higher steam to biomass ratio (SBR) lead to better hydrogen yield. Turn *et al.* [8] reported over 114% higher hydrogen yield at 1223 K than working at 1073 K at a SBR of 1.8 and ER of 0.18. Pengmei *et al.* [9] had maintained the desired bed temperature by varying the ER. They observed 22% increase in hydrogen yield at an

**Table I.** Influence of temperature in pyrolysis and steam gasification process over hydrogen yield, syngas yield and solid residue [6,7].

		Ahmed and Gupta [6]		Nimit <i>et al.</i> [7]	
		1073 K	1173 K	1073 K	1173 K
Fuel		Paper trash (35 g)		Palm tree branches (35 g)	
Steam flow rate (g min <sup>-1</sup> )		8		3.1	
H <sub>2</sub> yield (g/kg biomass)	Pyrolysis	5.7	11.2	10	13
	Gasification	43	40	85	86
Syngas yield (g/kg biomass)	Pyrolysis	NA	NA	0.53	0.71
	Gasification	NA	NA	1.4	1.4
Solid residue (% of input biomass)	Pyrolysis	21	18	26 (at 873 K)	18
	Gasification	7.5	8	8.5 (at 873 K)	5.7

**Table II.** Effects of variation in steam to biomass ratio (SBR), equivalence ratios (ER) and temperature on hydrogen yield [8,9].

Author	Reactor configuration	Fuel	SBR	ER	Operating	H <sub>2</sub> yield
					Temperature (K)	(g/kg of biomass)
Turn <i>et al.</i> [8]	Fluidized bed, thermally controlled	Sawdust	1.8	0.18	1023	28
					1223	61
			4.7	0	1073	46
					1073	83
						23
1.7	0	1073	60			
		0.22	1073	36		
			0.25	1159	44	
Pengmei <i>et al.</i> [9]	Downdraft fixed bed	Pinewood with 8% moisture	0.8	0.22	1073	36
				0.25	1159	44

ER of 0.25 compared with 0.22. The reason for such a behavior is related to the increase in bed temperature by over 86 K with ER. Increasing the SBR from 1.1 to 4.7 without using oxygen, Turn *et al.* reported over 80% higher hydrogen yield at 1073 K. Franco *et al.* [10] had performed steam gasification using eucalyptus wood in a fluidized bed reactor and reported an increase in H<sub>2</sub> mole fraction from 22% to 45% when the temperature was increased from 1023 K to 1153 K at the SBR of 0.8 w/w.

One of the major problems identified in the literature is the high tar content in the syngas generated [8,9,11–15]. Turn *et al.* [8], using a fluidized bed reactor, reported tar level in the range of 6 g/kg of dry fuel, amounting to about 2500 ppm of tar and can have serious implications on the downstream elements for hydrogen separation. It is well known that the tar level in a fluidized bed gasification system is very high and is attributed to the non-existence of structured oxidizing and reduction process inside the reactor. In the work reported by Pengmei *et al.* [9], using a downdraft reactor configuration, reported tar of 3–20 g/kg of biomass, amounting to about 1200–3600 ppm of tar in the syngas. It has been reported that gasification at elevated temperature helped in reducing the tar level. Lucas *et al.* [11], using hot air and superheated steam mixture, reported a reduction in the tar level and subsequent increase in the lower heating value (LHV) when the temperature of hot air was increased from 623 K to 1103 K. Wei *et al.* [12] also reported significant tar reduction from 62.8 gNm<sup>-3</sup> at 1023 K to 3.7 gNm<sup>-3</sup> at 1123 K with SBR of 0.6. Umeki *et al.* [16] had used steam gasification in an updraft reactor configuration and reported high tar content in the range of 50–100 gNm<sup>-3</sup> of gas. Updraft and fluidized bed gasifiers suffer from the high tar content in the product gas [14,15]. Because of the inherent design of the updraft gasifier, the hot gasses pass through the fresh biomass bed, allowing little residence time and oxidizer for volatiles to crack and undergo combustion. On the other hand, downdraft gasifier design allows the volatiles to oxidize and provides higher residence time for the left over volatiles to crackdown to lower molecular weight, non-condensable hydrocarbon compounds, leading to lower tar content in the product gas. On the basis of the experience, Umeki *et al.* [16] and Takashi *et al.* [15] suggest using downdraft gasifier to reduce the tar level.

In a review article, Abdussalam and Dincer [14] have compared biomass-based conversion processes toward generating hydrogen. A comprehensive study has been carried out toward addressing the effect of different parameters on hydrogen production from biomass steam gasification using models, including kinetic, equilibrium and neural networks. The effect of temperature, SBR and equivalence ratio (ER) along with other parameters has been presented.

In summary, it is evident that very limited work has been carried out on the oxy–steam gasification using a fixed bed downdraft reactor configuration. The literature has indeed provided details on the various thermochemical conversion processes, behavior of different reactor configuration and

influence of various process parameters such as SBR, ER and temperature on hydrogen yield and overall performance. The hydrogen yield was found to be quite low compared with its potential (as per equilibrium studies discussed in Section 4.1). It must be emphasized that the thermochemical conversion of biomass for syngas generation, rich in hydrogen, is one of the efficient processes. Results from the previous work suggest the choice of gasification over pyrolysis for higher hydrogen yield and efficiency. Steam gasification of biomass has been studied in a batch reactor under controlled conditions but limitedly exploited in a fixed bed reactor for continuous hydrogen production. Further, the results from the literature report low hydrogen yield and issues arising from the gas contaminated with higher molecular weight compounds, that is, the ‘tar’, inducing difficulty in separating hydrogen from the syngas mixture.

The work carried out at the Indian Institute of Science, on the thermochemical conversion process, has resulted in establishing open-top air gasification process toward the generation of excellent gas quality with raw gas tar concentration less than 100 mg m<sup>-3</sup> and cold gas tar concentration less than 2 mg m<sup>-3</sup> [17,18]. With air as a gasifying medium, typical producer gas composition reported is H<sub>2</sub> – 20 ± 2%, CO – 20 ± 2%, CO<sub>2</sub> – 12 ± 1%, CH<sub>4</sub> – 1.5 ± 0.5% and balance N<sub>2</sub>, with small amounts of HHCs with hydrogen content amounting to about 35–40 g/kg of biomass [18].

The focus of the present work is to establish an oxygen–steam gasification system using a fixed bed reactor with open-top downdraft configuration for syngas generation using oxygen and steam as gasifying medium. Parametric studies on the hydrogen production at various SBR and the ER are carried out, and the results are analyzed. The results are compared with those available in the literature and the limiting conditions of equilibrium. The impact of change in SBR and ER on temperature and reaction kinetics; hence on H<sub>2</sub> yield, system performance and conversion efficiency are evaluated.

Section 2 describes the experimental setup and work methodology adopted for the study. Observations and results from experiments with varying process parameters are highlighted in Section 3. Section 4 provides an in-depth analysis of the experimental results and the influence of various process parameters using equilibrium analysis and reaction kinetics study. Section 4.3.2 presents the conclusion.

## 2. MATERIALS AND METHODS

### 2.1. Experimental setup and materials

Experiments were conducted using a scaled down version of an open-top downdraft gasifier (Figure 1) developed at the Indian Institute of Science [18]. Details regarding the principle of design of the open-top reactor configuration are presented in [18]. In brief, the principle used in the

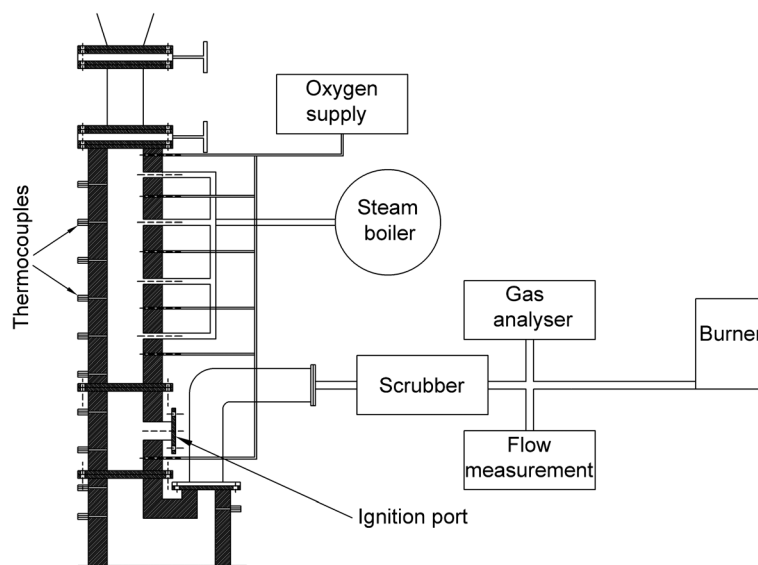


Figure 1. Experimental setup.

design of the reactor increases the residence time of gas inside the reactor by establishing a high temperature environment in the char bed, thus improving the conversion efficiency and reducing the higher molecular weight compounds.

A lock hopper mechanism was used for fuel loading, thus helping in operating the reactor at marginally above the ambient pressure to allow air/oxygen and steam as reactants by isolating the reactor from the ambient. The lock hopper ensured leak proof operation during biomass feeding at regular intervals. An ash extraction system at the bottom of the reactor facilitates removal of ash/char at regular intervals. An electric boiler was installed for steam generation at saturated condition and pressure up to 0.4 MPa. Steam generated using an electric boiler was passed through an electrically heated super heater for further increasing the steam temperature to about 1100 K. Oxygen drawn from an oxygen cylinder (99% O<sub>2</sub> and balance N<sub>2</sub>) was premixed with superheated steam and supplied to the reactor. The reactor had a provision to supply the oxy–steam mixture at different bed height. Water scrubber was used for cooling and cleaning of syngas. The tar and water molecules in syngas were condensed and separated from the dry syngas during the cooling process. The cooled and cleaned gas was flared in a specially designed burner. Syngas and oxygen flow rates were measured using pre-calibrated flow meters. Steam and oxygen flow rates were regulated to achieve different SBR and ER values for the gasification process. The syngas composition (CO, CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub> fractions) was measured using the *Sick Maihak S 517* gas analyzer. The gas analyzer was calibrated with a calibration gas whose composition was similar to typical syngas composition. The gas composition data were acquired every 30 s. Eight K-type thermocouples were inserted in the reactor at intervals of 100 mm to measure the bed temperature in different

zones. The temperature data were acquired using the IO tech PDQ2 data acquisition system.

Casuarina wood chips (of size 20 mm × 20 mm × 20 mm) were used as a fuel for gasification. The wood chips were dried in an electric oven at 373 K to bring down the moisture content to less than 1%. The result of the ultimate analysis of dried casuarina wood samples is presented in Table III.

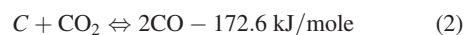
## 2.2. Methodology

In a downdraft configuration, consequent to the pyrolysis of biomass and combustion of volatiles, final gas composition, quality and yield depend largely on the reactions in the reduction zone. Typical reactions in the reduction zone are as follows:

Water gas reaction:



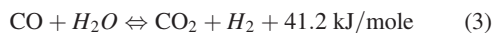
Boudouard reaction:



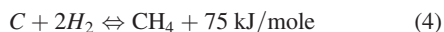
Water gas shift reaction:

Table III. Ultimate analysis result of dry casuarina wood.

Element	Mass fraction (%)
Carbon	52.02
Nitrogen	0.12
Sulfur	0.42
Hydrogen	6.55
Oxygen	41.43
Chemical Composition	CH <sub>1.4</sub> O <sub>0.6</sub>
Molecular weight	27.89 kg kmol <sup>-1</sup>



Methane reaction:



It is vital to identify that water gas (1) and water gas shift reactions (3) are responsible for the production of hydrogen. Present work uses steam as a gasifying medium to enhance hydrogen production using reactions (1) and (3). Water gas reaction (1) is highly endothermic that requires employing superheated steam to facilitate the water gas reaction for better char conversion and higher hydrogen yield.

Steam to biomass ratio in the present study is defined as the ratio of the amount of steam passed to the amount of biomass consumed in the given time, on a molar basis. Equivalence ratio (ER) is defined as the actual oxygen to fuel ratio divided by the stoichiometric oxygen to fuel ratio.

Thermodynamic analysis has been performed using NASA-SP 273 code for chemical equilibrium analysis, to establish the theoretical limits for oxygen–steam gasification of biomass. Analysis has been carried out to study the effect of process parameters such as temperature, SBR and ER. The results of equilibrium analysis and comparison with experimental results are discussed in Section 4.

Another important parameter for evaluating the process is the overall energy efficiency of the system. Nimit *et al.* [7] attempted efficiency evaluation as the syngas to solid fuel energy ratio.

$$\text{Syngas to solid fuel energy ratio} = \frac{\text{syngas yield} \times \text{HHV}_{\text{syngas}}}{\text{mass}_{\text{(solid fuel)}} \times \text{HHV}_{\text{solid fuel}}} \quad (5)$$

The previous relationship (Equation (5)) is not complete. The expression does not consider the energy input toward steam generation thereby overestimating the

$$\text{Hydrogen efficiency}(\eta_h) = \frac{n_{\text{H}_2} \times \text{LHV}_{\text{H}_2}}{\text{LHV}_{\text{BIOMASS}} + E_{\text{O}_2\text{-SEPARATION}} + E_{\text{SCRUBBER\_PUMP}} + Q_{\text{STEAM}} - (n_{\text{CO}} \times \text{LHV}_{\text{CO}} + n_{\text{CH}_4} \times \text{LHV}_{\text{CH}_4})} \quad (6)$$

efficiency. Nimit *et al.* [7] reported syngas to solid fuel energy ratio as high as 1.3. They also reported an increase in syngas to solid fuel energy ratio from 0.85 to 1.3 while increasing the temperature from 873 to 1173 K. It provides the information only on the higher syngas yield with temperature, without mentioning the extra energy input for generating steam at higher temperature. Thus, it is difficult to access the overall energy efficiency. Present work reports the overall energy efficiency of the system using two methods:

- On the basis of the amount of hydrogen generated, the first method defines the efficiency as the ratio of chemical energy in the hydrogen to the sum of all energy input in the form of energy content in biomass, enthalpy to raise steam, energy used in pumping water for scrubbing syngas and energy involved in separation of oxygen from the air. The energy used for separation of  $\text{H}_2$  from syngas has not been considered in the current analysis. CO and  $\text{CH}_4$  can very well be used as a fuel, to generate steam, after separation of  $\text{H}_2$  from the syngas. Energy required for  $\text{O}_2$  separation from air using pressure swing adsorption (95% purity, the rest being  $\text{N}_2$ ) is also accounted. The following equation has been used for the efficiency calculation:
- The second approach defines the gasification efficiency as the ratio of output energy to the input energy. The output energy is identified as the LHV of syngas and the input energy as the sum of energy content of biomass, enthalpy to raise steam, energy used in pumping water for scrubbing syngas and energy involved in separation of oxygen. The following equations have been used for the efficiency calculation:

Gasification efficiency ( $\eta_g$ )

$$= \frac{\text{LHV}_{\text{SYNGAS}}}{\text{LHV}_{\text{BIOMASS}} + E_{\text{O}_2\text{-SEPARATION}} + E_{\text{SCRUBBER\_PUMP}} + Q_{\text{STEAM}}} \quad (7)$$

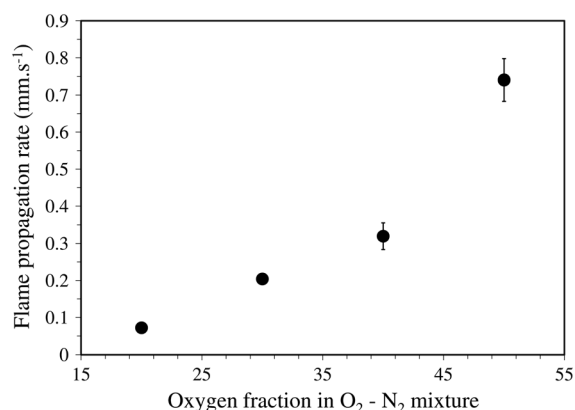
### 3. EXPERIMENTAL OBSERVATION AND RESULTS

Experiments were conducted using the open-top downdraft gasification system. For the startup of the gasifier system, initially, charcoal was loaded to a height of 300 mm (~350 g of wood charcoal) from the ignition nozzle and dry biomass (with moisture content <1%) above the char bed. The char bed was ignited from ignition ports using an ignition torch. A blower was used to provide the suction, so as to induce air

flow inside the reactor through the air nozzles. This procedure was adopted to ensure easy starting of the reactor. Having established combustible gas in the flare, the top of the reactor was closed (air supply was stopped), and gasifying media ( $\text{O}_2 + \text{H}_2\text{O}$ ) was supplied in controlled amounts through the designated ports. Steam flow rate was in the range of 2–5.5  $\text{g s}^{-1}$ , and oxygen fraction in the oxy–steam mixture was maintained between 11% and 22% for varying operating conditions. Temperature, gas composition of syngas, and flow rate of the reactant and the syngas were recorded.



Initial set of experiments were conducted to evaluate the performance of the gasification system with only oxygen as a reactant, toward focusing on flame propagation rate. Propagation of the reaction front into the fuel bed inside the reactor with air as the reacting media has been carried out. Propagation rate is a crucial parameter that would provide information on the establishing of appropriate thermal environment in the reactor bed helping toward enhancing the temperature along the length of the reactor, which has significant influence on the gas residence time and impacting the gas quality [18,19]. Tests were carried out with varying oxygen flow rates to ensure the right operating conditions for anchoring the flame front at a desired location, as in the case of air gasification. It was observed that, with oxygen, the propagation rates were unusually high. The flame front moved rapidly from the ignition nozzle at the bottom to the top of the reactor, where  $O_2$  was injected. It was observed that only surface pyrolysis was taking place, and very little volatiles were released for gas-phase exothermic reaction(s). The flame propagation into the unreacted bed with 100%  $O_2$  was over 100 times than that with air (around  $10 \text{ mm s}^{-1}$  for pure oxygen against  $0.1 \text{ mm s}^{-1}$  in air). Repeated tests clearly suggested that the propagation rates with 100% pure  $O_2$  from the top resulted in an undesirable situation for the stable reactor operation. To establish the role of a dilutant in controlling the propagation rate, nitrogen was used. Figure 2 presents data on flame propagation rate with  $O_2$  volume fraction in an  $O_2$ – $N_2$  mixture. The measured flame propagation rate was  $1 \text{ mm s}^{-1}$  at 50% oxygen, which is 10 times higher compared with that for the air (21%  $O_2$ ) gasification. This aspect has been studied by Dasappa *et al.* [18], wherein such behavior is attributed to the balance between heat generation and heat loss in the reaction zone and wherein the convective cooling of the influx of gasifying medium controls the temperature of the combustion zone. Further, it is evident that, with the reactant composition similar to that of air, the propagation rates obtained are similar to the results with air as the reacting medium. It is clear from these results that the fraction of oxygen supply has



**Figure 2.** Variation of flame propagation rate with oxygen volume in  $O_2$ – $N_2$  mixture.

a significant role to play in the propagation rates, which has influence on the mass flux, used toward designing the reactor [18].

From the results obtained using  $O_2$  in the  $O_2$ – $N_2$  mixture for gasification, it is evident that the flame propagation rate is significantly influenced by the dilutant. Using oxygen instead of air also can lead to issues such as ash fusion and problems related to material of construction due to increased flame temperature. This issue can be addressed using steam as an additional gasifying medium, which not only induces endothermicity but also enhances hydrogen yield, using water gas and water gas shift reactions ((1) and (3)).

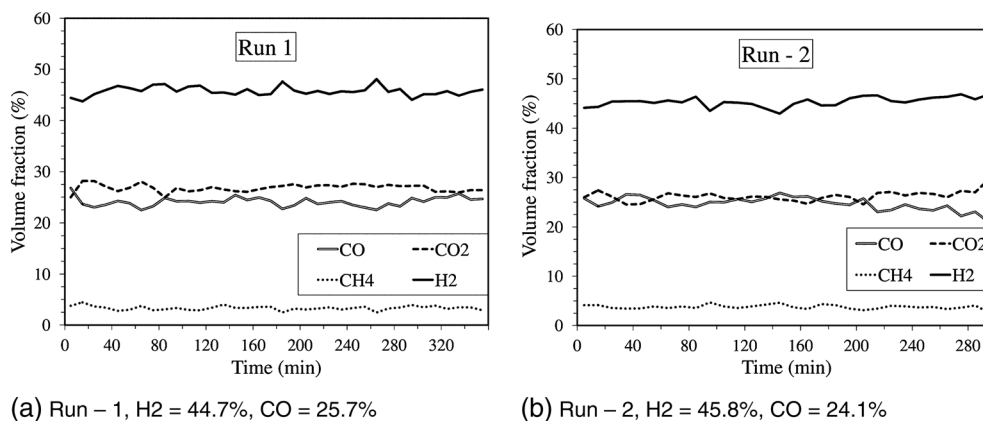
### 3.1. Experiments with oxy–steam

Experiments were conducted using oxygen and superheated steam as the gasifying medium. Provisions were made in the reactor to introduce oxy–steam mixture from the side nozzles at different height. Oxy–steam mixture was injected into the reactor at different bed heights, and performance was analyzed. Multiple nozzles across the periphery of reactor, at the given height, were designed to ensure the uniform distribution of gasifying media across the bed till center of the reactor. Introduction of oxy–steam mixture in the pyrolysis zone, just above the oxidation zone (at the bed height of maximum temperature), provided the stable operating condition. Syngas composition, hydrogen yield and performance parameters were monitored with varying SBR and ER. Experiments were conducted by varying SBR from 0.75 to 2.7 and ER ranging from 0.18 to 0.3.

Figure 3(a and b) shows the gas composition of two different set of experiments for oxy–steam gasifier operation at SBR of 1 with ER of 0.18. The gas composition measurement for about 5–6 h shows that the hydrogen volume fraction is in the range of  $45.24 \pm 0.76\%$  with  $24.94 \pm 1.16\%$  CO.

Experiments were conducted at similar operating conditions, such as ER and SBR, to evaluate consistency in the results and performance. Table IV presents the data from the set of experimental results using dry biomass with superheated steam. Figures 4 and 5 represent the mean values and respective standard deviation in results, showing a trend in some key results with varying SBR.

Reduction in average bed temperature was noticed with the increase in SBR. To maintain higher bed temperature ( $>1000 \text{ K}$ ), ER was increased with the increase in SBR. Higher hydrogen yield was obtained with the increase in SBR but with loss in energy efficiency. At SBR of 2.7 and an ER of 0.3,  $H_2$  of  $104 \text{ g/kg}$  of biomass with  $71.5\%$  gasification efficiency ( $\eta_g$ ) was obtained. Higher gasification efficiency of  $85\%$  was achieved with SBR of 0.75 and ER of 0.21 at lower hydrogen yield of  $66 \text{ g/kg}$  of biomass. Figure 4 shows the variation in  $H_2$  yield and gasification efficiency with SBR. The significant enhancement in hydrogen yield was noticed at higher SBR (SBR  $>1.5$ ). Detailed analysis of this observation is presented in Section 4.3.4.



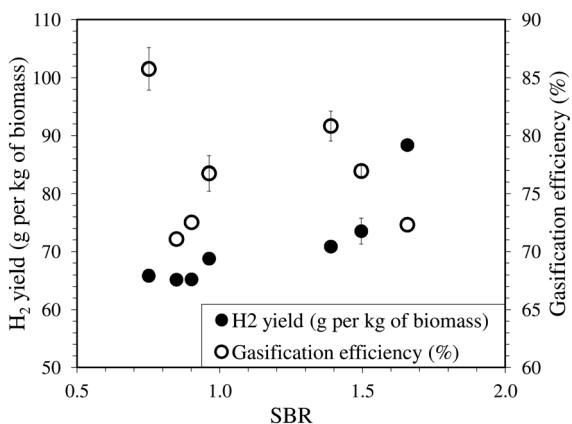
**Figure 3.** (a), (b) – gas composition using oxygen and superheated steam with dry biomass (steam to biomass ratio = 1, equivalence ratio = 0.18).

**Table IV.** Results, analysis and comparison while using wet biomass and dry biomass with superheated steam.

	Wet biomass			Dry biomass with superheated steam						
	0.75	1	1.4	0.75	1	1.4	1.5	1.8	2.5	2.7
H <sub>2</sub> O to biomass ratio	0.75	1	1.4	0.75	1	1.4	1.5	1.8	2.5	2.7
ER	0.3	0.34	0.36	0.21	0.18	0.21	0.23	0.27	0.3	0.3
H <sub>2</sub> yield (volume fraction, %) on dry basis	32	25	33	41.8	45.2	43.1	45.2	49.6	51.7	50.5
CO yield (volume fraction, %) on dry basis	32	24	27	27.6	24.9	26.5	24.9	17	12.8	13
H <sub>2</sub> yield (g kg <sup>-1</sup> of biomass) – Experimental result	47	52	63	66	68	71	73	94	99	104
H <sub>2</sub> yield (g kg <sup>-1</sup> of biomass) – Equilibrium analysis result	63	74	75	87	88	102	101	99	107	117
Percent of H <sub>2</sub> yield from moisture/steam (%) (65.5 g H <sub>2</sub> in biomass)	–	–	7	21.4	20.2	28	27.7	43.7	44.3	48.1
H <sub>2</sub> /CO	1	1.08	1.22	1.5	1.8	1.6	1.8	2.9	4.0	3.9
LHV (MJ Nm <sup>-3</sup> )	6.9	6.9	7	8.9	8.6	8.8	8.7	8	7.5	7.4
H <sub>2</sub> O volume fraction in syngas (%)	–	–	–	0.8	1.4	1.6	2	1.9	2.3	2.4
Fraction of heat available through CO + CH <sub>4</sub> in syngas for steam generation	–	–	–	4.2	2.7	2.2	1.9	1.3	0.8	0.8
Hydrogen efficiency (%) – (Equation (6))	51	46.1	42	73.7	63.2	67.2	63.5	70.5	61	63.7
Gasification efficiency (%) – (Equation (7))	61.5	57.2	55.8	85.8	76.8	80.8	77	79.5	69.5	71.5

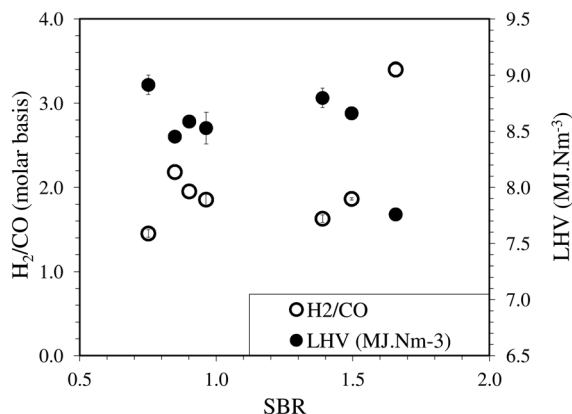
ER, equivalence ratio; LHV, lower heating value.

To evaluate the influence of SBR on the yield of hydrogen in the dry syngas, the total hydrogen content in the syngas was calculated as the sum of hydrogen in H<sub>2</sub> and CH<sub>4</sub>,



**Figure 4.** Variation of H<sub>2</sub> yield and gasification efficiency ( $\eta_g$ , Equation (7)) with steam to biomass ratios (SBR).

and hydrogen content in the tar and residual char was ignored. With the increase in SBR, the fraction of hydrogen in syngas contributed by steam was found to be increasing from 20.2% at SBR of 1 to 48.1% at SBR of 2.7 but at the cost of extra energy input for steam generation. CO and CH<sub>4</sub> mixture can be used as a fuel for steam generation, after separation from the syngas. The energy content in CO and CH<sub>4</sub> is found to be sufficient for raising steam at the required temperature (650 K) at lower SBR (SBR = 0.75–1.8) but not sufficient at higher SBR (SBR > 1.8). At higher SBR, CO yield obtained is lower, and extra heat needs to be supplied to generate steam, resulting in the loss of efficiency (Equations (6) and (7)). Figure 5 shows the variation of H<sub>2</sub> to CO ratio and LHV with SBR. H<sub>2</sub> to CO ratio was observed to be increasing with increasing SBR ratio. LHV is observed to be decreasing with the increase in SBR owing to the higher rate of reduction in the CO mole fraction compared with increment in the H<sub>2</sub> yield. The LHV of syngas is evaluated to be varying from 7.4 to 8.8 MJ Nm<sup>-3</sup>. Measuring tar content in the cold gas using wet method indicated less than 10 mg Nm<sup>-3</sup> of gas.



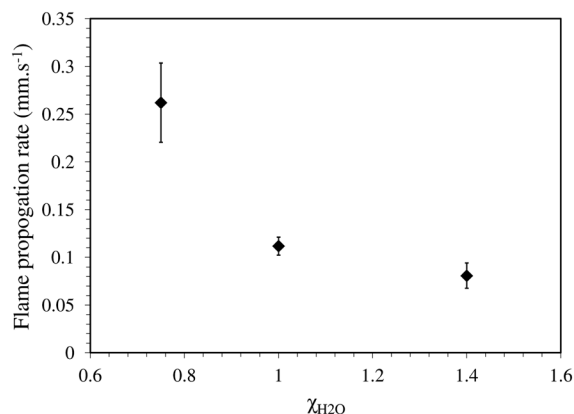
**Figure 5.** Variation of H<sub>2</sub> to CO ratio and lower heating value (LHV) with steam to biomass ratios (SBR).

Compared with hydrogen yield of 44 g/kg of biomass at SBR of 0.8 and ER of 0.24, as reported by Pengmei *et al.* [9], H<sub>2</sub> of 66 g/kg of biomass was achieved in the current work at SBR of 0.75 and ER of 0.21. Stable operation of oxy–steam gasification of wood chips was achieved with hydrogen yield as high as 104 g/kg of biomass at SBR of 2.7 and ER of 0.3. Gasification efficiency ( $\eta_g$ ) of 85.8% was achieved with SBR of 0.75 and ER of 0.21.

### 3.2. Experiments with wet biomass

Specific experiments were conducted by inducing H<sub>2</sub>O into the reaction mechanism by using moist wood chips. The moisture content in the wood chips was controlled by adding known amount of moisture to dry biomass in a controlled environment. This was used to induce endothermicity in an oxy-gasification system. On the other hand, it is supposed to reduce the necessity of generation of superheated steam, an energy intensive process. Tests were conducted to study the influence of moisture in controlling the flame propagation rates while using pure oxygen and adding extra reactant (H<sub>2</sub>O) for hydrogen production without spending energy in generating steam. The moisture content in the biomass was varied, with moisture to biomass ratio as 0.75, 1 and 1.4 on the molar basis and 0.6, 0.8 and 1.1 on the mass basis, respectively. Figure 6 presents the results from the experiments, showing flame propagation rate with varying moisture content in biomass. It was observed that the flame propagation rate reduced to values comparable with those for the air gasification (0.1 mm s<sup>-1</sup>) at moisture to biomass ratio of 1 on the molar basis (0.8 on mass basis).

At moisture to biomass ratio of 0.75, the peak bed temperature was over 1200 K and the hydrogen volume fraction was 32% (by volume). This amounts to a hydrogen yield of 47 g/kg of biomass. With an increase in the moisture content, the average bed temperature reduced, resulting in high methane and tar content (>200 mg Nm<sup>-3</sup>) in the cold gas. It was also observed that staged injection of oxygen with 10–15% of total oxygen supply being passed from the region around the ignition nozzle increased the



**Figure 6.** Variation of flame propagation rate using wet biomass with varying moisture content in biomass.  $\chi_{H_2O}$  = moisture content in biomass/biomass (molar basis).

reduction zone bed temperature, thereby reducing both methane and tar levels and subsequently increasing the hydrogen yield. Under these conditions, the maximum yield of hydrogen at 63 g/kg of biomass with 33% volume fraction was achieved, with moisture to biomass ratio of 1.4 and an ER of 0.37 with the average bed temperature of 975 K. Woody biomass has a natural property to imbibe moisture (water) but to a certain level till it becomes saturated. Under standard atmospheric conditions, dry casuarina wood absorbed maximum moisture amounting to H<sub>2</sub>O to biomass ratio of 1.4 only. Table IV presents the results of experiments with wet biomass. With an increase in the moisture to biomass ratio, H<sub>2</sub> yield increases with reduction in gasification efficiency ( $\eta_g$ ). With an increase in the moisture to biomass ratio from 0.75 to 1.4, the H<sub>2</sub> yield increased from 47 to 63 g/kg of biomass, and the gasification efficiency decreased from 61.5% to 55.8%. Similar to the results with superheated steam, CO volume fraction was found to be decreasing from 32% to 27% with an increase in moisture to biomass ratio from 0.75 to 1.4.

It is by comparing the performance with oxy–steam and dry wood at similar SBR of 1.4 that higher hydrogen yield of 71 g/kg of biomass was achieved at lower ER of 0.21. Gasification efficiency was also found to be on the lower side at 57% with wet biomass compared with 80.8% with dry biomass and oxy–steam.

### 3.3. Comparison of performance with dry and wet biomass

Table IV presents the comparison of data using wet biomass and dry biomass along with superheated steam. With the comparison of the results, it is evident that with superheated steam, higher yield of H<sub>2</sub> at 71 g/kg of biomass was obtained compared with H<sub>2</sub> at 63 g/kg of biomass with wet biomass at similar H<sub>2</sub>O to biomass ratio of 1.4. The gasification efficiency ( $\eta_g$ ), at all the considered biomass to moisture ratios, is higher for oxy–steam gasification with dry biomass as compared with gasification with wet biomass and oxygen. At the H<sub>2</sub>O to biomass



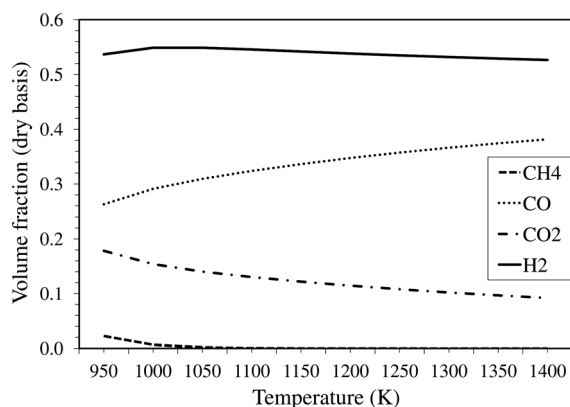
ratio of 1.4, the gasification efficiency was 55.8% with wet biomass as compared with 67% with dry biomass and injection of superheated steam. It was also observed that syngas has higher LHV while using dry wood with superheated steam than wet biomass. LHV of  $8.8 \text{ MJ Nm}^{-3}$  was obtained using superheated steam compared with  $7 \text{ MJ Nm}^{-3}$  with wet biomass at  $\text{H}_2\text{O}$  to biomass ratio of 1.4. Residual char was found to be higher while using wet biomass compared with superheated steam with dry biomass, which directly affects the conversion and energy efficiencies. Residual char obtained, at different  $\text{H}_2\text{O}$  to biomass ratio, was found to be between 8% and 12% (of input biomass by weight) in the case of wet biomass compared with 2–5% while using dry biomass and superheated steam at different SBR. It is by using wet biomass as fuel that higher tar and condensable HHC content were observed in hot gas in comparison with the usage dry biomass and superheated steam. Owing to high tar level with wet biomass, it was difficult to quantify the amount of  $\text{H}_2\text{O}$  scrubbed out, which has been calculated using elemental mass balance technique.

## 4. ANALYSIS AND DISCUSSIONS

### 4.1. Equilibrium analysis

#### 4.1.1. Effect of temperature

Above the temperature of 923 K, equilibrium analysis predicts no residue of solid carbon, indicating complete conversion of solid to gaseous fuel. Considering the three  $\text{H}_2$ -generating reactions individually (reactions (1), (3) and (4) as in Section 2), reactions (1) (in the forward direction) and (4) (in the reverse direction) approach completion at around 1000 K, whereas reaction (3) reduces the  $\text{H}_2$  level slightly with the increase in temperature [20]. Equilibrium analysis results also show a similar trend. Figure 7 presents the variation of syngas composition at different temperatures. Hydrogen content is seen to peak



**Figure 7.** Isothermal analysis at steam to biomass ratio of 1 and equivalence ratio of 0.05.

at about 1000 K, whereas beyond 1000 K, CO increases with a nominal reduction in  $\text{H}_2$  content.

#### 4.1.2. Effect of SBR

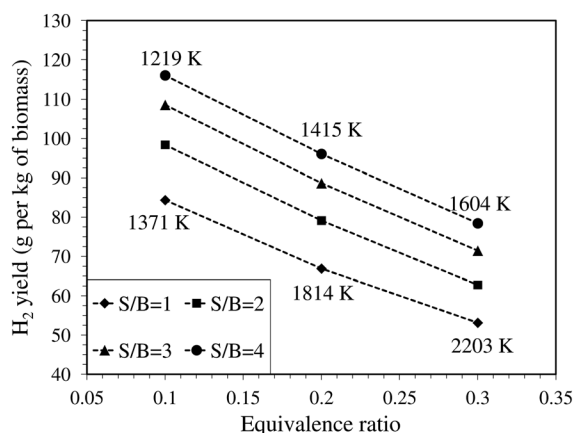
Steam to biomass ratio has a strong influence on syngas composition and overall efficiency. Figure 8 shows the variation in the  $\text{H}_2$  yield and adiabatic temperature for different SBR. Higher SBR provides extra hydrogen in the final syngas composition while reducing the tar content [21]. On the energy input aspect, increasing the SBR leads to higher energy input toward steam generation, thus influencing the overall efficiency. The adiabatic temperature decreases with increasing SBR due to the endothermicity of steam gasification (reaction (1)), whereas at a given ER, although increasing SBR increases the hydrogen yield, the process energy efficiency decreases because of the extra energy input toward steam generation.

#### 4.1.3. Effect of ER

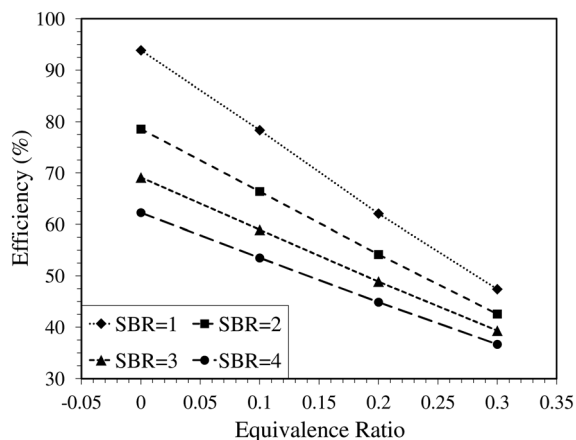
Steam gasification being an endothermic process,  $\text{O}_2$  as a part of the reaction medium, ensures sustaining the gasification process. Increasing the ER reduces the hydrogen generation, which contributes toward reduction in the efficiency as evident from Figure 9.

Adiabatic temperature above 1200 K is desirable, and therefore, the optimum-operating conditions were found to be at ER of 0.1 with steam injection at 1000 K and SBR in the range of 1–4. At an ER of 0.1, the efficiency of 94% with a lower  $\text{H}_2$  yield (84 g/kg of biomass) is found at SBR of 1, whereas efficiency drops to 54% with higher  $\text{H}_2$  yield (115 g/kg of biomass) at SBR of 4. This result further emphasizes the importance of choice of SBR to optimize both energy efficiency and  $\text{H}_2$  output.

Abuadala and Dincer [22] report similar thermodynamic studies employing EES software. Simulation results of a self-heated gasifier reactor of 0.08-m diameter and 0.5-m height with sawdust wood produce similar results. It is by varying the SBR from 0.1 to 0.4 and temperature from



**Figure 8.** Hydrogen output at different equivalence ratios and steam to biomass ratio (SBR) with respective adiabatic temperature at SBR of 1 and 4.



**Figure 9.** Gasification efficiency ( $\eta_g$ ) at different equivalence ratios and steam to biomass ratio (SBR).

1000–1500 K that the behavior of  $H_2$  yield and concentration with the change in SBR and temperature are found similar to the present analysis. Aduadala *et al.* [5] also report similar results, with the variation of temperature on  $H_2$  yield while simulating the gasification system under isothermal and equilibrium condition.

#### 4.2. Comparison of equilibrium analysis results with experimental results

Table V presents the comparison of hydrogen yield with equilibrium analysis at various moisture to biomass ratios using wet biomass. Gasification efficiency ( $\eta_g$ ) of 57.2% was achieved with moisture to biomass ratio of 1 and ER

**Table V.** Comparison of experimental and equilibrium hydrogen yield at different moisture to biomass ratios (molar basis) with wet biomass.

SBR	0.75	1	1.4
ER	0.3	0.34	0.36
$H_2$ yield (g/kg of biomass) experimental result	47	52	63
$H_2$ yield (g/kg of biomass) equilibrium analysis result	63	74	75
Difference in equilibrium and experimental results (%)	25.4	29.7	16

SBR, steam to biomass ratio; ER, equivalence ratios.

**Table VI.** Comparison of experimental and equilibrium hydrogen yield at different steam to biomass ratios (molar basis) with dry biomass and superheated steam.

SBR	0.8	1.0	1.4	1.5	1.8	2.5	2.7
ER	0.21	0.18	0.21	0.23	0.27	0.28	0.3
$H_2$ yield (g/kg of biomass) experimental result	66	68	71	73	94	99	104
$H_2$ yield (g/kg of biomass) equilibrium analysis result	87	88	102	101	99	107	117
Difference in equilibrium and experimental results (%)	24.1	22.7	30.4	27.7	5.1	6.8	11.1

SBR, steam to biomass ratio; ER, equivalence ratios.

of 0.34, with yield of hydrogen at 52 g/kg of biomass and average bed temperature of 975 K. Using higher moisture content in the fuel led to lower bed temperature and high methane and tar content, resulting in loss of efficiency and lower  $H_2$  yield.

Table VI presents the experimental results using dry biomass with superheated steam and compares hydrogen yield with equilibrium analysis results.

From Tables V and VI, it is identified that the difference in  $H_2$  yield between experimental and equilibrium results with respect to SBR.  $H_2$  yield is found to be approaching equilibrium results at higher SBR or  $H_2O$  to biomass ratio. This aspect is analyzed in detail in Section 4.3.4.

#### 4.3. Analysis of results

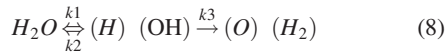
##### 4.3.1. Analysis and possible reason toward higher Hydrogen yield with superheated steam and dry biomass compared with wet biomass

Hydrogen yield is found to be substantially higher using superheated steam with dry biomass as compared with wet biomass (Table IV). Rate of pyrolysis plays an important role in the char yield and reactivity of char and hence hydrogen yield. Zanzi *et al.* [23] had studied the influence of temperature and rate of pyrolysis on gas and char yield using different biomass specimens. At temperatures less than 573 K, cellulose dehydrates to more stable compound anhydrocellulose, which gives higher char yield with low porosity. Above 573 K, cellulose depolymerizes, producing volatiles. Zansi *et al.* [23] inferred that high heating rates provide shorter residence time for dehydration, resulting in formation of less anhydrous cellulose and more volatiles. They found the reactivity of highly porous char, formed at rapid pyrolysis, with steam to be substantially higher than the char formed at slow pyrolysis. In the current work, steam injection at elevated temperature has reduced the residence time for dehydration, with rapid change in temperature from near ambient to around 675 K, yielding higher volatiles and lesser char with high reactivity. On the other hand, wet biomass induces extra endothermicity due to latent heat of vapourisation of water, in turn leading to the slower rate of pyrolysis and favoring the formation of anhydrous cellulose and lesser reactive char. Apart from the rate kinetics in reduction zone (discussed in the next section), higher yield of hydrogen with superheated steam is partially attributed to the above argument.

### 4.3.2. Increase in hydrogen yield with temperature and SBR

Results with varying moisture and SBR values strongly show the positive trend in hydrogen yield with the increase in H<sub>2</sub>O to biomass ratio. The hydrogen yield with oxy–steam is also found to be substantially high than using wet biomass and oxygen. Gasification is a heterogeneous reaction system where reaction rate kinetics plays a pivotal role to explain this behavior. Blackwood and McGrory [24] have studied the reaction rate kinetics of char–steam and char–CO<sub>2</sub> reactions. The rates of reaction of adsorbed H<sub>2</sub>O, H<sub>2</sub> and CO on the carbon surface are used to obtain the rate expression and have been used for biomass char by Dasappa [25] for single particle study and packed bed modeling. The following reactions and rate kinetics relations have been considered for the C + H<sub>2</sub>O reaction:

Reaction of char with H<sub>2</sub>O:



$$\omega_{C+H_2O}^{\dots} = - \frac{k_1 p_{H_2O} + k_4 p_{H_2} p_{H_2O} + k_5 p_{H_2O}^2}{1 + k_2 p_{H_2} + k_3 p_{H_2O}} \quad (11)$$

where,  $\omega_{C+H_2O}^{\dots}$  is the reaction rate of carbon per unit volume,  $k_1$  is the rate constant, and  $k_2$ ,  $k_3$ ,  $k_4$  and  $k_5$  are obtained from the detailed kinetic steps, with  $p_i$  being the partial pressure of the species with the following rate parameters.

$k_1 = 3.6 \times 10^7 e^{-E/RT} \text{ mol cm}^{-3} \text{ atm}^{-1}$ ;  $k_2 = 35 \text{ atm}^{-1}$ ;  
 $k_3 = 0.025 \times 10^{-6} \text{ atm}^{-1}$ ;  $k_4 = 2.1 \times 10^{-3} e^{-E_4/RT} \text{ atm}^{-1}$ ;  
 and  $k_5 = 91.8 e^{-E_5/RT} \text{ atm}^{-1}$ .

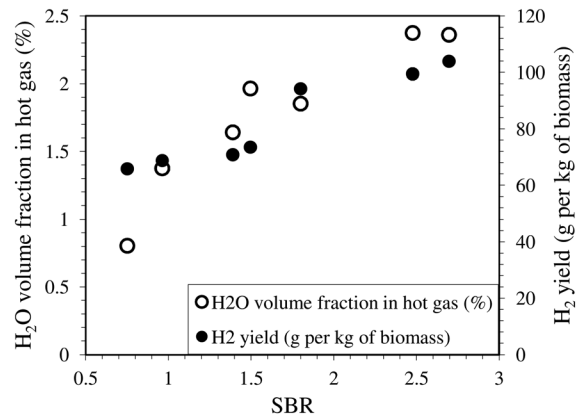
Rate kinetics of the char–steam reaction, as discussed previously, is further studied, and the influence of average bed temperature on reaction rate parameters of the rate equation (11) is analyzed. Table VII presents the numerical values of the rate constant terms in the rate equation (11) of char–steam reaction at different bed temperatures. The activation energy values ( $E_i$ ) for corresponding terms are adopted from the work of Dasappa *et al.* [25] on wood spheres (ficus). Considering the rate constant terms, the first and second terms in the numerator of the reaction rate equation (11) are related to the forward and backward reaction rates of reaction (8), respectively. The reverse reaction rate term ( $k_4$ ) is two orders of magnitude lower than the

forward reaction rate term ( $k_1$ ), which validates the usual assumption of the reverse reaction rate being negligible. The values of  $k_3$  and  $k_4$  in Table VII are found to be orders of magnitude lower than  $k_1$ ,  $k_2$  and  $k_5$ . It suggests that the second term in the numerator and third term in the denominator of the rate equation (11) can be ignored and simplified as

$$\omega_{C+H_2O}^{\dots} = - \frac{k_1 p_{H_2O} + k_5 p_{H_2O}^2}{1 + k_2 p_{H_2}} \quad (12)$$

The rate equation (12) clearly shows the increase in the overall reaction rate with increasing SBR, as the first ( $k_1 p_{H_2O}$ ) and third terms ( $k_5 p_{H_2O}^2$ ) in the numerator are directly proportional to the partial pressure of H<sub>2</sub>O ( $p_{H_2O}$ ) and to the square of  $p_{H_2O}$ , respectively. The values of the first and last terms in the numerator,  $k_1$  and  $k_5$ , are one and two orders of magnitude lower at 900 K compared with values at 1000 and 1100 K, respectively, which clearly shows the impact of average bed temperature on the overall rate kinetics.

From the experiments, it was observed that, with the increase in SBR from 0.75 to 2.7, volume fraction of the reactant H<sub>2</sub>O varied from 78% to 89% at the inlet condition. The H<sub>2</sub>O content in the hot gas outlet was found to be over four times higher at 2.4% at the SBR of 2.7 compared with 0.8% at the SBR of 0.75, calculated using mass and elemental balance technique. Figure 10 presents the variation of  $p_{H_2O}$  at outlet against SBR with the respective hydrogen yield. Although the  $p_{H_2O}$  changes continuously



**Figure 10.** H<sub>2</sub>O fraction in hot gas output and H<sub>2</sub> yield at varying steam to biomass ratio (SBR).

**Table VII.** Numerical values of the terms in the rate expression in char–steam reaction rate equation (11).

Temperature (K)	$k_1$	$k_2$	$k_3$	$k_4$	$k_5$
1100	$5.15 \times 10^{-5}$	35	$2.50 \times 10^{-8}$	$2.25 \times 10^{-7}$	$1.02 \times 10^{-4}$
1000	$3.36 \times 10^{-6}$	35	$2.50 \times 10^{-8}$	$9.02 \times 10^{-8}$	$2.58 \times 10^{-5}$
900	$1.20 \times 10^{-7}$	35	$2.50 \times 10^{-8}$	$2.95 \times 10^{-8}$	$4.83 \times 10^{-6}$

across the reacting bed, the change in the mole fraction of H<sub>2</sub>O at outlet provides an insight into the overall condition in the reaction bed. Figure 10 shows the increase in volume fraction of H<sub>2</sub>O in syngas and H<sub>2</sub> yield with SBR, clearly suggesting that the significant enhancement in char–steam reaction with SBR is in agreement with rate equation (12).

With the increase in SBR, bed temperature was found to be decreasing. Average bed temperature (over 500-mm bed height) was measured at the interval of every 5 s for 5–6 h. O<sub>2</sub> fraction in the reactant reflecting the ER was increased to maintain the desired bed temperature. Figure 11 presents the average bed temperature measured at various SBR, with the respective H<sub>2</sub> yield and ER. It is evident from Figure 11 that high bed temperature can be maintained by suitably increasing the ER resulting in enhanced H<sub>2</sub> yield at higher SBR.

To evaluate the cumulative effect of SBR and temperature on the reaction rate kinetics, the rate constants were calculated for the measured bed temperature for all the individual set of experiments. As discussed previously, the data labels of SBR indicate the respective proportional value of  $p_{H_2O}$ .  $k_1$  and  $k_5$  vary exponentially with temperature (Figure 12). The set of data points on the top right-hand side in Figure 12 clearly shows the cumulative impact of temperature and  $p_{H_2O}$  on the H<sub>2</sub> yield. The experimental trends with oxy–moisture and oxy–steam gasification, as summarized in Table IV, are found to be consistent with the rate kinetic equation (12).

Reduction in average bed temperature was noticed with the increase in SBR. Higher reaction rate with increased H<sub>2</sub>O input (partial pressure of H<sub>2</sub>O in the reacting system) as predicted and dependence of rate constants  $k_1$  and  $k_5$  on temperature lead to higher yield of H<sub>2</sub> with the increase in SBR using dry biomass and superheated steam compared with wet biomass. Equilibrium study also suggests a similar trend of increase in hydrogen yield with reduction in ER and increase in SBR (Section 3.1). The increase in H<sub>2</sub> yield with reduction in efficiency at higher SBR value is in agreement with the results of equilibrium studies (Figures 4, 8 and 9).

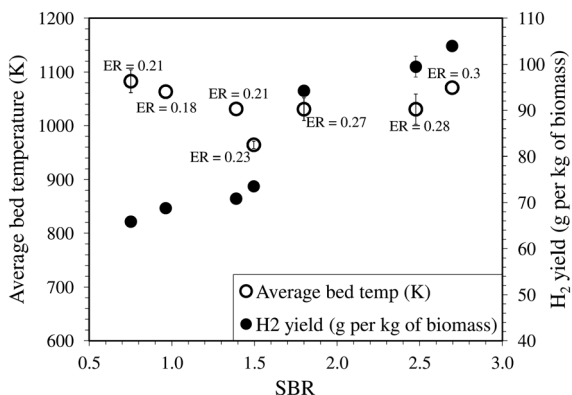


Figure 11. Average bed temperature and H<sub>2</sub> yield at varying steam to biomass ratio (SBR).

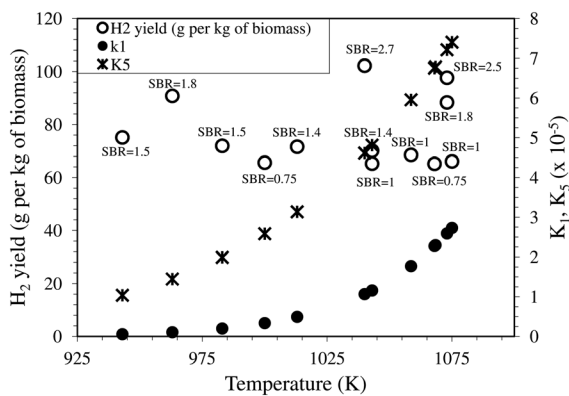
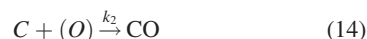
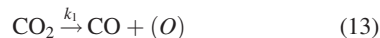


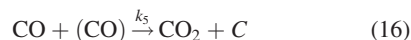
Figure 12. Variation of rate kinetic parameters  $k_1$  and  $k_5$  with the average bed temperature and respective H<sub>2</sub> yield.

### 4.3.3. Variation of H<sub>2</sub> to CO ratio with SBR

Another important result, from Table IV and Figure 5, is the increase in the H<sub>2</sub> to CO ratio from 1.5 to 4 on increasing the SBR from 0.75 to 2.7. H<sub>2</sub> mole fraction increases by about 24%, from nearly 42% to 52% in the given range of SBR (SBR = 0.75–2.7), whereas the CO fraction in syngas reduces by over 53%, from 28% to 13% in the given range. The water gas reaction (1) and the Boudouard reaction (2) are the reactions involved in production of CO, both being endothermic and heterogeneous in nature. The water gas shift reaction (3) on the other hand is a homogeneous reaction, oxidizes CO to CO<sub>2</sub> and produces H<sub>2</sub>, which is enhanced with an increase in partial pressure of H<sub>2</sub>O (SBR). If SBR had influenced only the water gas shift reaction (3) or the water gas reaction (1), then the H<sub>2</sub> fraction should increase with SBR at a higher rate in comparison to the rate of reduction in the CO fraction. It would, however, contradict the experimental results, which show an opposite trend. Analysis of experimental results needs further investigation in the complex behavior of char–steam and char–CO<sub>2</sub> reaction mechanism. Blackwood and McGrory [23] have studied the reaction rate kinetics of char–steam and char–CO<sub>2</sub> reactions independently. Char–steam reaction is already discussed in Section 4.2. The following reactions and rate kinetics relations have been considered for the C + CO<sub>2</sub> reaction: Reaction of char with CO<sub>2</sub>:



The retarding effect of CO is explained by the competition of CO with O for the active sites, that is,



$$\omega_{C+CO_2}^{***} = -\frac{k_1 p_{CO_2} - k_2 p_{CO}^2}{1 + k_3 p_{CO} + k_4 p_{CO_2}} \quad (17)$$



where,  $\omega_{C+CO_2}'''$  is the reaction rate of carbon per unit volume with the detailed rate parameters evaluated by Dasappa *et al.* [26] for biomass char.

$k_1 = 2.2 \times 10^9 e^{-E/RT}$  mol cm<sup>-3</sup> s<sup>-1</sup> atm<sup>-1</sup>,  $k_2$  is obtained from equilibrium,  $k_3 = 15.0$  atm<sup>-1</sup> and  $k_4 = 0.25$  atm<sup>-1</sup>.

As CO is a product of reaction (13) as well as of (14), the product of either reaction (C + H<sub>2</sub>O or C + CO<sub>2</sub>) influences the rate of the other reaction. On the similar thoughts, Roberts and Harris [27] have studied the reaction kinetics of char with H<sub>2</sub>O, CO<sub>2</sub>, as well as with the mixture of CO<sub>2</sub> and H<sub>2</sub>O. They concluded that the reaction rate with the mixture of reactant gasses was not the sum of the two pure-gas reaction rates. It is rather a complex combination of the two reactions that appear to be dependent on blocking of reaction sites by the relatively slow C–CO<sub>2</sub> reaction. The result suggests that there is a competition between CO<sub>2</sub> and H<sub>2</sub>O for active sites. The reduction in surface available to the H<sub>2</sub>O by the adsorbed C(O) species from the C–CO<sub>2</sub> reaction is cited as a likely reason for the decrease in the C–H<sub>2</sub>O reaction rate upon addition of CO<sub>2</sub>. The Langmuir–Hinshelwood style rate equation (18) for a mixture of CO<sub>2</sub> and H<sub>2</sub>O was proposed by Roberts and Harris, predicting the reaction rate in a mixture of gasses:

$$\omega_C''' = \omega_{C+CO_2}''' + \omega_{C+H_2O}''' \left( 1 - \frac{(k_1/k_3)p_{CO_2}}{1 + (k_1/k_3)p_{CO_2}} \right) \quad (18)$$

where,  $\omega_C'''$  is the reaction rate of char in a mixture of H<sub>2</sub>O and CO<sub>2</sub>, whereas  $\omega_{C+CO_2}'''$  and  $\omega_{C+H_2O}'''$  are the reaction rates of char with pure CO<sub>2</sub> and H<sub>2</sub>O, respectively.

The experimental results also suggest retardation of the Boudouard reaction (2) in the presence of H<sub>2</sub>O, as both CO<sub>2</sub> and H<sub>2</sub>O compete for the active sites for reaction. This supplements the findings of Roberts and Harris [27].

#### 4.3.4. Significant enhancement in hydrogen yield at higher SBR

As discussed in the previous sections, hydrogen yield and H<sub>2</sub> to CO ratio vary with SBR. Important findings from the present experiments and analysis are as follows:

- *Enhanced H<sub>2</sub> yield with SBR:* At lower SBR, the rate of increase in H<sub>2</sub> with SBR (SBR = 0.75–1.5) is low compared with the significant enhancement of H<sub>2</sub> yield noticed at higher SBR (SBR = 1.5–2.7) (Figure 12).
- *Hydrogen yield approaching equilibrium conditions with the increase in SBR:* With the analysis of the results in Tables V and VI, difference between equilibrium and experimental result is in the range of 24–30% at lower SBR compared with much lower differences, in the range of 5–11% at higher SBR.
- *Behavior of CO yield or H<sub>2</sub> to CO ratio:* Figure 13 presents the variation of H<sub>2</sub>/CO ratio with SBR. Significant reduction in H<sub>2</sub> to CO ratio is observed at higher SBR (SBR = 1.5–2.7) compared with reduction at lower SBR (SBR = 0.75–1.5).

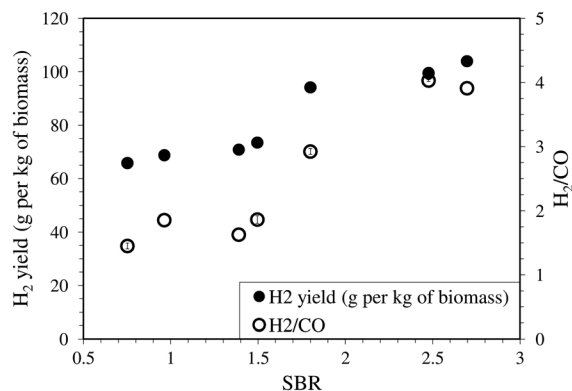


Figure 13. Variation of H<sub>2</sub> to CO ratio and H<sub>2</sub> yield with the steam to biomass ratio (SBR).

Analysis of water gas rate equation (12) alone will not be able to explain the observations presented earlier. These observations indicated the importance of water gas shift reaction (3) at higher SBR. Water gas shift reaction (3) is homogenous reversible reaction. High partial pressure of H<sub>2</sub>O shifts the water gas shift reaction equilibrium in favor of H<sub>2</sub> while consuming CO leading to higher H<sub>2</sub> to CO ratio. This is clearly observed at higher SBR. The char gasification is the rate-limiting step during gasification of biomass, and higher residence time is essential for completion of heterogeneous char reactions, whereas homogenous water gas shift reaction approaches equilibrium in the shorter residence time.

## 5. CONCLUSION

A downdraft fixed bed reactor is used for generation of hydrogen rich syngas using oxygen and steam as gasifying agents for the auto thermal conversion of biomass.

Experiments and analysis have shown that using dry biomass with superheated steam improved the H<sub>2</sub> yield, efficiency and syngas LHV compared with direct usage of wet biomass with oxygen. Comparison of using wet wood chips and dry wood with steam has shown that stable operation is achieved at ER of the order of 0.2 compared with ER of the order of 0.3 while using wet biomass argued because of the endothermicity. It is by using dry wood and oxy–steam as gasification agents that hydrogen of 104 g/kg of biomass is obtained compared with a maximum of H<sub>2</sub> at 63 g/kg of biomass with moist wood and oxygen. The gasification efficiency ( $\eta_g$ ) with oxy–steam gasification is 85.8% compared with 61.5% with wet biomass at H<sub>2</sub>O to biomass ratio of 0.75. Syngas with LHV of as high as 8.9 MJ Nm<sup>-3</sup> is obtained at lower SBR of 0.75 going down by 17% to 7.4 MJ Nm<sup>-3</sup> at higher SBR of 2.7, which is almost twice the energy content in producer gas obtained through air gasification. At lower SBR of 0.75, the low H<sub>2</sub> yield of 66 g/kg of biomass is achieved with higher gasification efficiency of 85.8% and higher LHV of 8.9 MJ Nm<sup>-3</sup>, and with an increase in SBR, H<sub>2</sub> yield increased to 104 g/kg of biomass with lower



efficiency of 71.5% and LHV of  $7.4 \text{ MJ Nm}^{-3}$ . An important result analyzed and reported is the variation in  $\text{H}_2$  to CO ratio, which is found to be less (1.5–1.8) in the lower SBR of 0.75–1.5 and significantly enhancing up to 4 at higher SBR of 1.5–2.7. At lower SBR values, the energy content in CO and  $\text{CH}_4$  yield is sufficient for raising steam. Current study emphasizes on the understanding of the reaction chemistry and overall behavior of the downdraft oxy–steam gasification system, enabling the control to achieve the desired output (efficiency,  $\text{H}_2$  yield,  $\text{H}_2$  to CO fraction and LHV of syngas) using process parameters such as SBR and ER.

## NOMENCLATURE

SBR	= steam to biomass ratio
ER	= equivalence ratio
$\omega'''$	= volumetric reaction rate ( $\text{mol cm}^{-3} \text{ s}^{-1}$ )
$\eta_{\text{h}}$	= hydrogen efficiency
$\eta_{\text{g}}$	= gasification efficiency
$n_i'''$	= number of moles of species 'i'
$\omega_{\text{C}+\text{H}_2\text{O}}'''$	= reaction rate of carbon per unit volume with $\text{H}_2\text{O}$ equation (17)
$\omega_{\text{C}+\text{CO}_2}'''$	= reaction rate of carbon per unit volume with $\text{CO}_2$ equation (18)
$k_1$	= rate constant
$k_2, k_3, k_4$ and $k_5$	= constants obtained from the detailed kinetic steps
$p_i$	= partial pressure of ith species
LHV <sub>x</sub>	= lower heating value of specie 'x' ( $\text{MJ kmol}^{-1}$ )
$E_{\text{O}_2\text{-SEPARATION}}$	= energy input in $\text{O}_2$ separation from air ( $\text{MJ kmol}^{-1}$ )
$E_{\text{SCRUBBER\_PUMP}}$	= energy input in scrubbing pump ( $\text{MJ kmol}^{-1}$ )
$Q_{\text{STEAM}}$	= energy input for steam generation ( $\text{MJ kmol}^{-1}$ )

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