

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/ijhydene

First and second law thermodynamic analysis of air and oxy-steam biomass gasification



K. Sandeep, S. Dasappa*

Center for Sustainable Technologies, Indian Institute of Science, Bangalore 560 012, India

ARTICLE INFO

Article history:

Received 7 July 2014

Received in revised form

12 September 2014

Accepted 22 September 2014

Available online 19 October 2014

Keywords:

Exergy analysis

Thermodynamic analysis

Hydrogen

Syngas

Oxy-steam gasification

Carbon boundary point

ABSTRACT

Gasification is an energy transformation process in which solid fuel undergoes thermochemical conversion to produce gaseous fuel, and the two most important criteria involved in such process to evaluate the performance, economics and sustainability of the technology are: the total available energy (exergy) and the energy conserved (energy efficiency). Current study focuses on the energy and exergy analysis of the oxy-steam gasification and comparing with air gasification to optimize the H₂ yield, efficiency and syngas energy density.

Casuarina wood is used as a fuel, and mixture of oxygen and steam in different proportion and amount is used as a gasifying media. The results are analysed with respect to varying equivalence ratio and steam to biomass ratio (SBR). Elemental mass balance technique is employed to ensure the validity of results. First and second law thermodynamic analysis is used towards time evaluation of energy and exergy analysis. Different component of energy input and output has been studied carefully to understand the influence of varying SBR on the availability of energy and irreversibility in the system to minimize the losses with change in input parameters for optimum performance. The energy and exergy losses (irreversibility) for oxy-steam gasification system are compared with the results of air gasification, and losses are found to be lower in oxy-steam thermal conversion; which has been argued and reasoned due to the presence of N₂ in the air-gasification. The maximum exergy efficiency of 85% with energy efficiency of 82% is achieved at SBR of 0.75 on the molar basis. It has been observed that increase in SBR results in lower exergy and energy efficiency, and it is argued to be due to the high energy input in steam generation and subsequent losses in the form of physical exergy of steam in the product gas, which alone accounts for over 18% in exergy input and 8.5% in exergy of product gas at SBR of 2.7. Carbon boundary point (CBP), is identified at the SBR of 1.5, and water gas shift (WGS) reaction plays a crucial role in H₂ enrichment after carbon boundary point (CBP) is reached. Effects of SBR and CBP on the H₂/CO ratio is analysed and discussed from the perspective of energy as well as the reaction chemistry. Energy density of syngas and energy efficiency is favoured at lower SBR but higher SBR favours H₂ rich gas at the expense of efficiency.

Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

* Corresponding author.

E-mail addresses: sdasappa@cgpl.iisc.ernet.in, s.dasappa@gmail.com (S. Dasappa).

<http://dx.doi.org/10.1016/j.ijhydene.2014.09.134>

0360-3199/Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

| Nomenclature | |
|-----------------------|---|
| $E_{O_2_SEPARATION}$ | energy spent for O_2 separation from air, kJ/kg |
| Ex_{in} | total exergy input during gasification, kJ/kmole |
| $E_{AUXILIARY_UNIT}$ | energy spent on the auxillary units of gasifier. eg. water pump, water chiller, kJ/kg |
| Ex_{steam} | exergy spent on steam generation and superheating, kJ/kmole |
| Q_{STEAM} | energy spent on steam generation and superheating, kJ/kg |
| Ex_{char} | exergy of char, kJ/kmole |
| η_{en} | energy efficiency of gasifier, % |
| e_{DB}^{CH} | chemical exergy of dry biomass, kJ/kg |
| Ex | exergy, kJ/mole |
| x_i | mole fraction of ith specie |
| Ex_{ph} | physical exergy, kJ/kmole |
| s | entropy, kJ/(kmole K) |
| Ex_{ch} | chemical exergy, kJ/kmole |
| s_0 | entropy at SRS, kJ/(kmole K) |
| h_i | enthalpy of ith specie, kJ/mole |
| $s_{i,0}$ | entropy of the ith specie at SRS, kJ/(kmole K) |
| $h_{i,0}$ | enthalpy of ith specie at SRS, kJ/kmole |
| I | irreversibility |
| R | universal gas constant, 8.314 kJ/(kmole K) |
| Abbreviation | |
| T_0 | temperature at SRS, K |
| CBP | carbon boundary point |
| $\epsilon_{i,0}$ | standard chemical exergy of ith specie at SRS, kJ/kmole |
| LHV | lower heating value |
| Ex_{gas} | exergy of hot syngas, kJ/kmole |
| ER | equivalence ratio |
| $Ex_{H_2O_gas}$ | exergy of H_2O in hot syngas, kJ/kmole |
| SBR | steam to biomass ratio (on mole basis) |
| Ex_{O_2} | exergy spent in O_2 separation from air, kJ/kmole |
| SRS | standard reference state |
| Ex_{ch_mix} | component of exergy lost in, kJ/kmole gas due to mixture |
| SMFR | superficial mass flux rate, kg/(m ² s) |

Introduction

With the growing demand for renewable fuel to substitute the fossil fuel, biomass gasification is emerging as an important technology to fill the gap [1]. Conversion of solid fuel to gaseous fuel helps in providing alternate fuel for many like IC engines, gas turbines, fuel cells etc. Apart from energy plantation; agro residue, municipal waste and organic industrial waste provides sustainable ways to extract energy from waste. Sadhan and Dasappa [2] have researched on one of the challenging issues of electrification in rural areas away from the power grid network. Based on the life cycle cost analysis, their study examined the economic feasibility of

decentralized off-grid renewable energy systems. Using 10 to 120 KW open top downdraft gasification system for study, they have found biomass gasification as a promising solution for rural electrification which is more cost effective than solar photovoltaic system and even grid extension [2]. Apart from the demand and usefulness, energy efficiency is one of the most important criteria to assess the performance and techno-economic viability of any technology.

In the gasification process, the first law of thermodynamics preserves the total energy of the system in converting solid to gaseous fuel in gasification is governed by the first law of thermodynamics, while the second law restricts the availability of energy (exergy) transformation of energy into useful form. In the case of gasification process, evolution of gaseous species increases the entropy and introduces irreversibility in the overall thermo-chemical conversion process. During the course of conversion, apart from the process irreversibility, the transformation of chemical energy in the solid fuel partly to thermal energy as sensible heat cannot be converted to desired output i.e., chemical enthalpy in the gaseous species. Evaluating the energy efficiency based on the energy output to the energy input and identifying the energy loss from the system to the environment is appropriate while considering the device. This approach may not be sufficient while evaluating the process and the device together as a system. Identifying the internal losses arising due to the irreversibility is important towards understanding any energy conversion process and probably helps in redesigning the system elements. Exergy analysis thus helps in evaluating the conversion process and provides an insight towards optimizing, by minimizing the losses, if any.

Peters et al. [3] have analysed the exergy efficiency of a fast pyrolysis bio-oil production plant using Aspen Plus software. Based on the analysis they have found the exergy efficiency is 71.2% and have also identified the components for the exergy losses. The areas that had been identified for improvement were biomass drier, milling process for size reduction and heat exchanger used for pre-heating the combustion air.

In the area of biomass gasification, researchers have performed exergy analysis based on equilibrium analysis [4–9]. Abuadala et al. [4] reports thermodynamic studies employing Engineering Equation Solver (EES) software. With the focus on H_2 production, from a gasifier reactor of 0.08 m diameter and 0.5 m height using sawdust as the fuel, exergy and energy efficiencies were estimated. The heat loss from the reactor was modelled assuming isothermal condition. Tar, generally an issue for gasification process and its utilization [10–14], was considered as a useful product (fuel) and modelled as benzene molecule in the system. Effects of varying the SBR (Steam to Biomass ratio) from 0.2 to 0.6 were studied, by varying steam flow rate from 4.5 kg/s to 6.3 kg/s and biomass feed rate from 10 kg/s to 32 kg/s. In the analysis, temperature was varied between 1000 and 1500 K and its influence on the H_2 yield, exergy and energy efficiency was also studied. The maximum exergy efficiency reported is about 65% with minimum near SBR of 0.4, and the authors have shown maximum specific entropy generation is between 0.37 and 0.42. The lower value of the exergy efficiency has been argued due to the increase in internal irreversibility with the varying SBR. Abuadala et al. [4] have also argued the saturation of H_2 yield

at around SBR of 0.7 without attributing any specific reason. It is evident that in the temperature range of 1000–1500 K, char-steam reaction plays a significant role and H_2 yield increases significantly till carbon boundary point (at SBR of 1.5). Prins et al. [5] also reported carbon boundary at SBR of 1.3. It is not evident why the equilibrium values at higher SBR's were not used in the analysis by Abuadala et al. [4].

Prins et al. [5] have carried out extensive analysis on availability and irreversibility for the biomass gasification process. They have compared the exergy efficiencies of air and steam gasification with pyrolysis. Equilibrium studies were employed using non-stoichiometric method based on minimizing the Gibbs free energy. Steam gasification proved to be more efficient process compared to air gasification and pyrolysis. Steam gasification efficiency was reported to be 87.2%, compared to 80.5% for air gasification. In the case of pyrolysis, the efficiency was 76.8%. They have also analysed the physical, chemical exergy and sensible enthalpy of gas separately and variation with steam to biomass ratio (SBR) and equivalence ratio (ER). In the case of air gasification, Prins et al. have also identified the carbon boundary (at ER of 0.25), beyond which no carbon is available for gasification. Beyond the carbon boundary point, the efficiency decreases and losses are credited to oxidation of fuel gas to CO_2 and H_2O leading to higher sensible heat and lower chemical energy in product gas. Similarly, in the case of steam gasification, carbon boundary has been identified at SBR of 1.3 beyond which introducing extra steam leads to loss in input energy used in steam generation. The coupling of exothermic oxidation of carbon with endothermic water-gas and Boudouard reaction is argued for the better efficiency of gasification over pyrolysis. The authors have not clearly identified reasons towards higher efficiency achieved in the case of steam gasification over air gasification.

Silva and Rouboa [6] conducted thermodynamic analysis for oxygen enriched air gasification of pine wood. The oxygen fraction in gasifying media was increased from ambient condition (21% O_2) to 40% O_2 on the mole basis; the balance being N_2 . They found increase in exergy and energy efficiencies with O_2 fraction. Exergy efficiency of 76% with 21% O_2 increased to over 83% with 40% O_2 while H_2 and CO mole fraction in the product gas decreased from 22% to 11% and 19% to 14% respectively. Increase in reaction zone temperature with increase in O_2 fraction has been cited as the reason for higher efficiencies. Specific reasons towards the reduction of H_2 and CO with the increase in O_2 percent are not discussed. Also, the given argument for the higher efficiencies at higher O_2 fractions seems inconsistent based on the work of Karamarkovic and Karamarkovic [8] who presented the analysis of exergy and energy efficiencies with the variation in temperature.

It is evident from the literature on exergy and energy analysis of gasification system that the analyses are largely based on equilibrium calculation, while experimental reports are limited [4–9]. However, it is important to note that thermodynamic equilibrium model cannot approximate the process due to complex nature of the heterogeneous reaction system [15]. The heterogeneous reactions that occur inside the reactor are both diffusion and kinetic limited depending upon the reactants [15]. The gas composition, quality and efficiency of a gasification system depends significantly on the residence

time of the reacting species at the given temperature which inherently depends on the reactor geometry, design and process parameters [16]. Hence, experimental investigation is important.

The present work is focused on evaluating the first and second law efficiency based on the experiments using a downdraft gasification system. The results from an auto-thermal oxy-steam/air gasification system are used to evaluate the exergy and energy efficiencies using wood chips as the fuel. Effect of variation in SBR and ER on the gasification efficiency and losses in the system are discussed. Comparison of the oxy-steam gasification and air gasification process is also discussed. Carbon boundary point (CBP) is identified and the reason for significant enhancement in the H_2/CO ratio beyond CBP is discussed. The choice of SBR for higher H_2 yield and syngas with higher energy density and efficiency is analysed.

Materials and methods

Experiments were conducted using a scaled down version of an open-top downdraft gasifier (Fig. 1) developed at the Indian Institute of Science (IISc) [17–20]. The reactor was modified with the lock-hopper assembly for feeding the biomass; thus isolating the system from the ambient, as oxygen and steam were introduced at slightly above ambient pressure. Steam was generated at around 0.4 MPa using an electric boiler and further superheated to about 650 K using electric heater. Oxygen cylinder (99% O_2 and balance N_2) was used for O_2 supply and premixed with superheated steam and supplied to the reactor. The reactor had a provision to introduce the oxy-steam mixture at different heights. Water scrubber was used for cooling and cleaning of syngas. The cooled and cleaned gas was flared in a specially designed burner. Syngas and oxygen flow rates were measured using pre-calibrated flow metres. Steam and oxygen flow rates were regulated to achieve different SBR and ER values for the gasification process. The syngas composition (CO , CO_2 , CH_4 and H_2 fractions) was measured using the Sick Maihak S 517 gas analyser. The gas analyser was calibrated with a calibration gas whose composition was similar to the typical

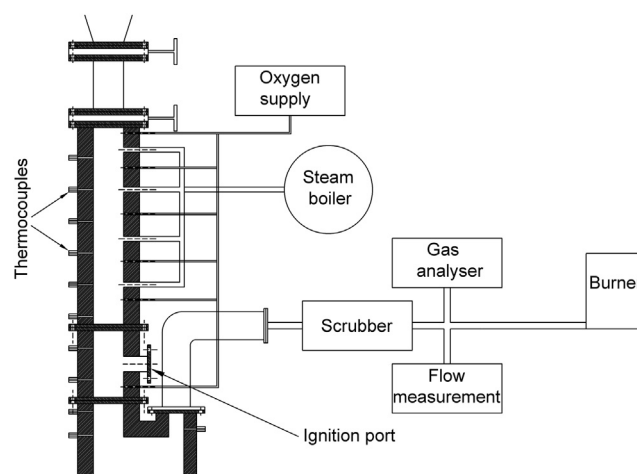


Fig. 1 – Experimental setup.

syngas composition. The gas composition data was acquired every 30 s. K-type thermocouples were used to measure the temperature and the data was acquired using the IO tech PDQ2 data acquisition system.

For the initial startup, approximately 350 g of wood charcoal was loaded to a height of 300 mm from the gasifier ignition nozzle and dry casuarina wood (with moisture content <1%) above the char bed. Using an ignition torch, char bed was ignited through ignition ports. A suction blower was used to draw air flow inside the reactor through the air nozzles to ensure easy ignition of the reactor. In the case of air gasification, having established combustible gas in the flare, the system was operated in suction mode. Temperature, gas composition of syngas and flow rate of the reactant and the product gas were recorded. For oxy-steam gasification, top of the reactor was closed (air supply was stopped), and gasifying media as per the design ($O_2 + H_2O$) was supplied in controlled amounts.

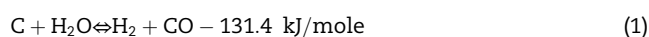
The current work adopts the operational parameters for the air gasification from Dasappa et al. and Mahapatra and Dasappa's work [16,21,22] for optimum performance of the air gasification process. Dasappa et al. [16] studied the influence of the superficial mass flux rate (SMFR) on the flame propagation rate, gas quality and the performance of open-top downdraft gasifier with air as a gasifying medium. Mahapatra and Dasappa [21–23] have also done similar work to analyse the performance of the gasifier and tar level with the variation in particle size and air mass flux rate. Using casuarina wood chips, SMFR of $0.1 \text{ kg/m}^2\text{s}$ was used in the present study.

Wood chips of approximately 20 mm overall dimensions were dried to moisture content to less than 1% in an electric oven at 373 K. Ultimate analysis of dried casuarina wood samples is presented in Table 1.

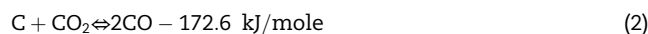
Methodology and approach

Gasification of biomass, in a downdraft gasifier configuration, involves pyrolysis, combustion of volatiles and the reduction of char with the reaction with product of volatiles. The final gas composition and yield depends largely on the reactions in reduction zone. Typical reactions in the reduction zone are:

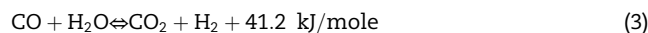
Water gas reaction



Boudouard reaction



Water gas shift reaction



Methane reaction



Depending on the type of gasifying agent (air/oxygen/steam), fraction of H_2 , CO , CH_4 , CO_2 , H_2O and N_2 in the gaseous fuel product varies.

Water gas (1) and Boudouard (2) reactions are highly endothermic and coupling it with the exothermic combustion of volatiles with oxygen makes the system more thermodynamically sustainable. In other words, supplying heat externally to the reactor involves loss in exergy. Prins et al. [5] have also argued on the similar lines while finding pyrolysis process less efficient than gasification.

Water gas (WG) (1) and water gas shift (WGS) reaction (3) are the major reactions involved in the gasification process leading to H_2 and CO yield. Water gas reaction (1) is highly endothermic that requires superheated steam to facilitate better char conversion and higher hydrogen yield. Dasappa [15] had studied the wood char reaction with the steam, CO_2 and mixture of O_2-N_2 extensively, and after careful study of char-steam reaction at atmospheric pressure, they derived simplified reaction rate expression (5), suggesting the increase in the overall reaction rate with increasing SBR. 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_2O (p_{H_2O}) and to the square of p_{H_2O} respectively.

$$\omega_{C+H_2O}^m = \frac{k_1 p_{H_2O} + K_5 p_{H_2O}^2}{1 + K_2 p_{H_2}} \quad (5)$$

where, $\omega_{C+H_2O}^m$ is the reaction rate of carbon per unit volume, k_1 is the rate constant, and K_2 and K_3 are obtained from the detailed kinetic steps, with p_i being the partial pressure of the species with the following rate parameters. $k_1 = 3.6 \times 10^{13} e^{-E_1/RT} \text{ mol}/(\text{m}^3 \text{ s})$; $K_2 = 35 \text{ Pa}^{-1}$ and $K_3 = 9.18 \times 10^7 e^{-E_3/RT} \text{ mol}/(\text{m}^3 \text{ s})$, $E_1/R = 30000.3 \text{ K}$, $E_3/R = 15,083 \text{ K}$.

It is evident from the equation (5) that with the increase in SBR, the partial pressure of H_2O and hence the char-steam reaction rate increases, with the higher H_2 yield in the product, while there is a tradeoff between the energy input to raise steam to the overall gain in the energy and H_2 yield.

Elemental mass balance technique has been employed to use experimental data for the analysis. Biomass and air or oxygen-steam is considered as input; all of which were measured during the experiment [17]. Gas composition was measured on dry basis. To account for condensed H_2O during gas cooling process, species balance of C, H and O was used, based on exit gas composition.

Energy efficiency analysis for gasification

Energy efficiency is evaluated as the ratio of output energy to the input energy. Output energy is identified as the lower

Table 1 – Ultimate analysis result of dry casuarina wood.

| Element | Mass fraction (%) |
|----------------------|------------------------------|
| Carbon | 52.02 ± 1.0 |
| Nitrogen | 0.12 ± 0.012 |
| Sulphur | 0.42 ± 0.002 |
| Hydrogen | 6.55 ± 0.03 |
| Oxygen | 41.43 ± 0.5 |
| Chemical Composition | $CH_{1.4}O_{0.6}$ |
| Molecular weight | $27.89 \text{ kg kmol}^{-1}$ |

heating value (LHV) of syngas and the energy content in the residual char. The input energy is calculated as the sum of energy content of biomass, energy requirement of auxiliary units of gasifier (water pumps, scrubbers, blower, etc), enthalpy to raise steam and energy involved in separation of oxygen from the air. In the current work, oxygen cylinder is used for the experiments but the total energy used in the oxygen separation from air is calculated based on the data from literature. Energy efficiency is obtained using.

$$\text{Energy efficiency } (\eta_{\text{en}}) = \frac{\text{LHV}_{\text{SYNGAS}} + \text{LHV}_{\text{CHAR}}}{\text{LHV}_{\text{BIOMASS}} + E_{\text{O}_2\text{-SEPARATION}} + E_{\text{AUXILIARY_UNIT}} + Q_{\text{STEAM}}} \quad (6)$$

Exergy efficiency analysis for gasification

Energy balance of the biomass gasification can be represented as:

$$\sum E_{\text{in}} = \sum E_{\text{out}} + I$$

where, E_{in} and E_{out} represent the input exergy and output exergy, and I represent the irreversibility induced during the conversion process.

Exergy or the available energy in any gaseous species is the sum of chemical and physical exergy (equation (7)). Physical exergy depicts the change in enthalpy of particular gaseous specie from standard state to the given pressure and temperature and also accounts for the loss in entropy in the process (equation (8)). Chemical exergy of the mixture is the standard chemical exergy mixing of all the constituents (1st term in equation (9)) and the loss in entropy due to mixing of different species of gases (2nd term in equation (9)).

$$\begin{aligned} \text{Exergy efficiency} &= \frac{Ex_{\text{SYNGAS}} + Ex_{\text{CHAR}}}{Ex_{\text{BIOMASS}} + Ex_{\text{O}_2\text{-SEPARATION}} + Ex_{\text{STEAM}}} \\ &= \frac{(Ex_{\text{ph}} + Ex_{\text{ch}})_{\text{SYNGAS}} + Ex_{\text{CHAR}}}{Ex_{\text{BIOMASS}} + Ex_{\text{O}_2\text{-SEPARATION}} + (Ex_{\text{ph}} + Ex_{\text{ch}})_{\text{O}_2 + \text{H}_2\text{O}}} \\ &= \frac{\sum (x_i \cdot Ex_0 + RT_0 (x_i \cdot \ln x_i)) + \sum (x_i (h - h_0) - x_i T_0 (s - s_0)) + Ex_{\text{char}}}{Ex_{\text{BIOMASS}} + Ex_{\text{O}_2\text{-SEPARATION}} + \sum_{\text{O}_2, \text{H}_2\text{O}} (x_i \cdot Ex_0 + RT_0 (x_i \cdot \ln x_i) + x_i (h - h_0) - x_i T_0 (s - s_0))} \end{aligned} \quad (11)$$

$$Ex = Ex_{\text{ch}} + Ex_{\text{ph}} \quad (7)$$

$$Ex_{\text{ph}} = \sum ((h_i - h_{i,0}) - T_0 (s_i - s_{i,0})) \quad (8)$$

$$Ex_{\text{ch}} = \sum x_i \epsilon_{i,0} + RT_0 \sum (x_i \ln x_i) \quad (9)$$

Chemical exergy of the mixture is always lower than of the sum of standard chemical exergy of the individual species due to the irreversibility caused during mixing of gases (2nd term in the equation (9), also called as exergy of mixing, is always negative).

Thermodynamic data for the exergy of gaseous species are derived from the standard data book [24], except for the solid fuel, i.e., biomass and char. Estimation of the chemical exergy of biomass involves a combination of various organic compounds, in varying amount, having numerous different elements and closely bounded by complex bonds. Researchers [25,26] have adopted different techniques to evaluate the chemical exergy of biomass. Rant [27] proposed the exergy for solid biomass fuels to be evaluated as a constant factor of the

calorific value of the fuel. Szargut and Styrylska, and Song et al. [25,26] have considered statistical correlations based on the lower heating value of the biomass and fraction of C, H and O. Song et al. have used the similar technique to evaluate standard exergy values of different biomass species [26]. Based on Szargut's Reference Environmental (R.E.) model [28], Song et al. arrived at simplified method to evaluate exergy value of dry biomass formulated in equation (10).

$$\begin{aligned} e_{\text{DB}}^{\text{CH}} &= 1812.5 + 295.606C + 587.354H + 17.50 + 17.735N \\ &\quad + 95.615S - 31.8A \end{aligned} \quad (10)$$

where, $e_{\text{DB}}^{\text{CH}}$ is the chemical exergy of dry biomass, and C, H, O, N and S are respective elemental constituents in biomass and A is the ash content, all in wt%.

Using the equation (10), standard exergy of wood is calculated as 20.8 MJ/kg for the dry casuarina wood used in the present work.

Exergy efficiency is evaluated using equations 7–11.

The terms in the numerator and denominator in the equation (11) are analysed separately using the experimental data. Parametric studies are carried out to assess impact of change in SBR on efficiency and to compare efficiencies of air and oxy-steam gasification process.

Observations and results

Product gas composition, mass flow rates of the fuel and reactants along with the gas temperature was used to arrive at energy input and efficiency for varying SBR and ER. With the

increase in SBR, reduction in bed temperature was noticed; not a desirable condition for ensuring good gas quality; both composition as well as tar in the gas. With the increase in steam flow rate, oxygen supply i.e., ER was increased to maintain the higher average bed temperature. Experiments were conducted by varying SBR from 0.75 to 2.7 and ER ranging from 0.16 to 0.3. Longer duration gasifier operations were conducted to ensure stability in operation towards achieving consistency in result.

Table 2 summarizes the experimental results. Based on the elemental composition (C,H and O as in Table 1), casuarina wood contains about 65 g of H₂/kg of biomass and through air gasification 45.7 g H₂/kg of biomass has been realized in the gaseous fuel (Table 2). It is evident from the results in Table 2 that the oxy-steam gasification process has enhanced H₂ fraction in the gas. Compared with air gasification, the H₂ fraction in the syngas is more than double. The H₂ yield is found to be increased with SBR, whereas CO fraction shows the reverse trend. The maximum yield of H₂ at 104 g per kg of biomass with 50.6% mole fraction on dry basis has been achieved.

Tables 3 and 4 presents the exergy and energy efficiency. The exergy and energy efficiencies of air gasification process are found to be comparable to the oxy-steam gasification process at lower SBR of 0.75. Exergy efficiency is found to be reduced with the increase in the SBR. Maximum exergy efficiency of 85% is obtained at the lower SBR of 0.75; which reduces to 69.2% at the higher SBR of 2.7. Similar trends are observed for energy efficiency too. At any given SBR the energy efficiency is found to be lower than the exergy efficiency. Close examination of the data presented in Table 3 suggests that the exergy input in the steam generation increases significantly from the 6.1% of the total exergy input at SBR of 0.75 to 18.4% at higher SBR of 2.7. For the same operating conditions the exergy input fraction in O₂ generation shows a modest increment from 5.1% to 6.3% in the same SBR range to maintain average bed temperature high. The physical exergy fraction in the output gas for air gasification is 3.2% compared to oxy-steam gasification which increases from 5.9 to 11.3% with the increase in SBR from 0.75 to 2.7. On the contrary, the chemical mixture exergy fraction in the gas during air gasification is found to be 3.2% compared to oxy-steam gasification, which shows a modest increment with SBR from 1.7% to 2.8% in the given range of SBR.

From the analysis as presented in Table 4, it is evident that during the air gasification, the energy yield in output gas per kg of biomass and the calorific value is significantly lower than the results obtained during oxy-steam gasification. The calorific value of gas during the oxy-steam gasification process is found to be decreasing from 8.91 MJ/Nm³ to 7.43 MJ/Nm³ with the increase in SBR from 0.75 to 2.7.

Analysis and discussion

The results from the analysis are further analysed at the sub-process levels occurring during the gasification process.

Exergy analysis

All the components in the equation (11) are evaluated separately to provide an insight on the system losses. Fig. 2 gives the schematic representation of the exergy flow.

From Table 3, the highest exergy efficiency recorded was at 86% with the SBR of 0.96 and then the value reduced to 69% at the SBR of 2.7. The component of sensible heat in the gas is identified as physical exergy, which is lost during the gas cooling process and is one of the major factors in the deviation of energy efficiency from exergy efficiency. Physical exergy in the syngas was found to be increased from about 6% to 12% with increase in SBR from 0.75 to 2.7, while the physical exergy is found to be quite low with a value of 3.2% in the case of air gasification (Table 3). The data clearly suggests the reduction in energy efficiency at higher SBR due to the extra loss in sensible heat or physical exergy in syngas. Presence of unreacted steam in the hot syngas is found to be contributing significantly to the physical exergy, which increases from 13% to 76% of physical exergy in product gas. The exergy of mixture also contribute to the losses and were found to be roughly 2% of total exergy of syngas and no significant variations were observed with the change in SBR. Mixture exergy in the case of air gasification was found to be higher at 3.2%, and is argued due to the presence of large fraction of N₂ in product gas, where N₂ accounts for 35% of the total mixture exergy in the product gas.

Fig. 3 presents the exergy input fraction in O₂ and steam generation with change in SBR. Exergy input for O₂ separation and steam generation were roughly same for low SBR, but with the increase in SBR, the steam exergy increased significantly from 6% to over 18%. Marginal increase in oxygen level to maintain the bed temperature had shown no significant impact on the exergy input.

Energy analysis

Similar to exergy efficiency, energy efficiency was also found to be decreased with the increase in SBR. Efficiency reduced from 80% to about 66% with the increase in SBR from 0.75 to 2.7. Efficiency in the case of air gasification is 80%, slightly lower compared to oxy-steam gasification. The fraction of energy input in oxygen separation accounts for over 5%–8% for the range of SBR used in the experiment, even though in absolute terms the input energy spent almost double to little

Table 2 – Results: H₂ and CO yield.

| SBR | 0 (Air) | 0.75 | 0.86 | 0.96 | 1.39 | 1.5 | 1.66 | 1.8 | 2.43 | 2.52 | 2.7 |
|--|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| H ₂ yield (% dry gas) | 18.2 ± 0.2 | 41.8 ± 0.1 | 44.8 ± 0.4 | 45.8 ± 0.1 | 43.1 ± 0.2 | 45.2 ± 0.3 | 51.1 ± 0.2 | 48.9 ± 0.1 | 51.6 ± 0.2 | 51.8 ± 0.1 | 50.6 ± 0.3 |
| CO yield (% dry gas) | 17.1 ± 0.2 | 28.8 ± 0.3 | 26.1 ± 0.1 | 24.1 ± 0.2 | 26.6 ± 0.1 | 25 ± 0.1 | 15 ± 0.1 | 17.2 ± 0.2 | 12.4 ± 0.1 | 13.3 ± 0.1 | 12.9 ± 0.1 |
| H ₂ yield (g/kg of biomass) | 45.7 ± 0.4 | 65.6 ± 0.2 | 65.3 ± 0.7 | 68.6 ± 0.2 | 70.8 ± 0.4 | 72.7 ± 0.6 | 88.4 ± 0.5 | 94 ± 0.2 | 98.5 ± 0.3 | 99 ± 0.2 | 104 ± 0.6 |

Table 3 – Exergy analysis of gasification process.

| SBR | 0 (Air) | 0.75 | 0.86 | 0.96 | 1.39 | 1.5 | 1.66 | 1.8 | 2.43 | 2.52 | 2.7 |
|--|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Energy efficiency (%) | 80 ± 0.1 | 80.3 ± 0.2 | 75.2 ± 0.1 | 73.5 ± 0.1 | 76.3 ± 0.3 | 73.5 ± 0.2 | 68.1 ± 0.1 | 77 ± 0.1 | 64.7 ± 0.2 | 65.8 ± 0.2 | 65.6 ± 0.3 |
| Exergy efficiency (%) | 83.1 ± 0.1 | 85 ± 0.2 | 83.1 ± 0.1 | 85.7 ± 0.1 | 80.3 ± 0.3 | 76.6 ± 0.2 | 84.3 ± 0.1 | 83.9 ± 0.1 | 79.6 ± 0.2 | 77.8 ± 0.2 | 69.2 ± 0.3 |
| Ex _{ph} /Ex _{gasv} (%) | 3.2 ± 0.03 | 5.9 ± 0.04 | 6.5 ± 0.03 | 6.6 ± 0.05 | 6.9 ± 0.03 | 7.3 ± 0.02 | 8.1 ± 0.05 | 8.6 ± 0.06 | 10.6 ± 0.07 | 11.1 ± 0.05 | 11.3 ± 0.06 |
| Ex _{H₂O_gas} /Ex _{gasv} (%) | 0.8 ± 0.01 | 0.8 ± 0.02 | 1.6 ± 0.01 | 1.7 ± 0.02 | 2.3 ± 0.01 | 3 ± 0.01 | 3.2 ± 0.02 | 4.1 ± 0.02 | 6.7 ± 0.05 | 8.5 ± 0.04 | 8.6 ± 0.06 |
| Ex _{steam} /Ex _{inv} (%) | 0 | 6.1 | 6.9 | 7.7 | 10.6 | 11.3 | 12.4 | 13.2 | 16.1 | 17.4 | 18.4 |
| Ex _{O₂} /Ex _{in} (%) | 0 | 5.1 | 4.9 | 4.5 | 5.1 | 5.5 | 5.1 | 5.8 | 6.1 | 6.3 | 6.3 |
| Ex _{H₂O_gas} /Ex _{ph} (%) | 24.1 ± 0.01 | 13.7 ± 0.01 | 25.4 ± 0.02 | 25.9 ± 0.03 | 33.2 ± 0.02 | 41.1 ± 0.01 | 39.4 ± 0.02 | 47.4 ± 0.03 | 68.2 ± 0.03 | 76.2 ± 0.02 | 76 ± 0.03 |
| Ex _{Ch_mix} /Ex _{gas} (%) | 3.2 ± 0.01 | 1.7 ± 0.01 | 1.9 ± 0.01 | 1.9 ± 0.01 | 2 ± 0.01 | 2.1 ± 0.01 | 2.2 ± 0.01 | 2.4 ± 0.01 | 2.5 ± 0.01 | 2.7 ± 0.01 | 2.8 ± 0.01 |

Table 4 – Energy analysis of gasification process.

| SBR | 0 (Air) | 0.75 | 0.86 | 0.96 | 1.39 | 1.5 | 1.66 | 1.8 | 2.43 | 2.52 | 2.7 |
|--|-------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| ER | 0.25 | 0.21 | 0.17 | 0.18 | 0.21 | 0.23 | 0.22 | 0.25 | 0.28 | 0.29 | 0.3 |
| Energy spent in O ₂ separation (MJ/kg of biomass) | NA | 1.5 | 1.2 | 1.3 | 1.5 | 1.5 | 1.6 | 1.8 | 2 | 2.1 | 2.1 |
| Energy spent in steam generation (MJ/kg of biomass) | NA | 2.2 | 2.6 | 2.8 | 4 | 4 | 4.8 | 5.2 | 7 | 7.3 | 7.8 |
| Fraction of input energy in O ₂ separation (%) | NA | 6.9 | 5.6 | 5.8 | 6.4 | 6.3 | 6.5 | 7.2 | 7.4 | 7.8 | 7.5 |
| Fraction of input energy in steam generation (%) | NA | 10.3 | 12.2 | 13 | 17.4 | 17.5 | 20 | 21.3 | 26.5 | 27.1 | 28.5 |
| Energy in syngas (MJ/kg of biomass) | 13.72 ± 0.3 | 17 ± 0.2 | 14.6 ± 0.3 | 15.8 ± 0.3 | 17.5 ± 0.2 | 17.5 ± 0.4 | 16.2 ± 0.2 | 18.9 ± 0.2 | 17.1 ± 0.3 | 17.7 ± 0.2 | 18 ± 0.4 |
| LHV of syngas (MJ/Nm ³) | 4.96 ± 0.2 | 8.91 ± 0.1 | 8.45 ± 0.2 | 8.63 ± 0.1 | 8.82 ± 0.1 | 8.68 ± 0.2 | 7.8 ± 0.1 | 7.75 ± 0.1 | 7.42 ± 0.1 | 7.53 ± 0.1 | 7.43 ± 0.2 |
| Fraction of output energy in form of H ₂ (%) | 42.5 ± 0.2 | 46.5 ± 0.2 | 53.6 ± 0.3 | 52 ± 0.4 | 48.4 ± 0.2 | 48.5 ± 0.2 | 65.3 ± 0.2 | 62.5 ± 0.1 | 69 ± 0.2 | 68.1 ± 0.1 | 67.4 ± 0.3 |
| Energy Efficiency (%) | 80 ± 0.1 | 80.3 ± 0.2 | 75.2 ± 0.1 | 73.5 ± 0.1 | 76.3 ± 0.3 | 73.5 ± 0.2 | 68.1 ± 0.1 | 77 ± 0.1 | 64.7 ± 0.2 | 65.8 ± 0.2 | 65.6 ± 0.3 |

NA – not applicable.

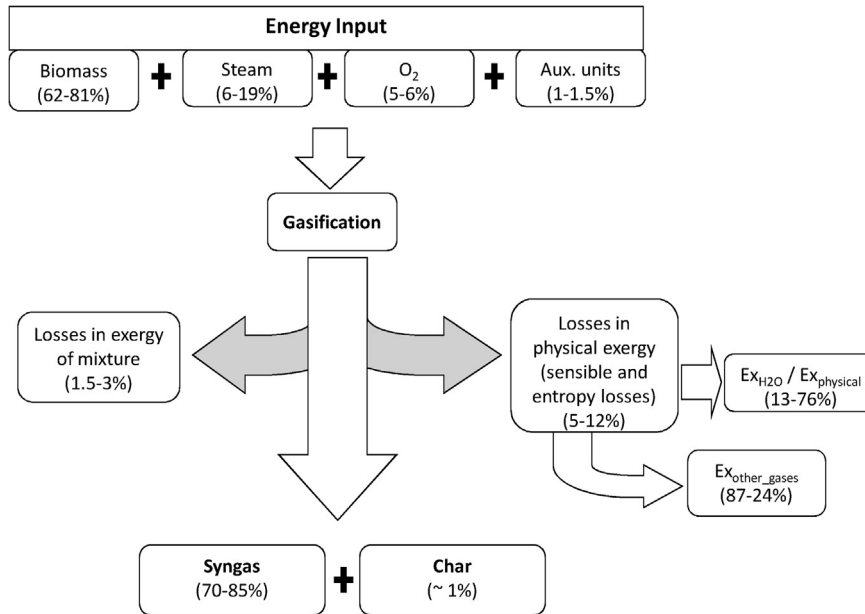


Fig. 2 – Schematic depicting typical exergy analysis for oxy-steam gasification.

over 2 MJ per kg of biomass at higher SBR from around 1 MJ at lower SBR of 0.85. As expected, energy input for steam generation and superheating varies substantially with the SBR. Energy input fraction for steam generation increased almost three times with 10.3% at SBR of 0.75 to about 28.5% at SBR of 2.7.

Differences in exergy and energy efficiency

Fig. 4 presents the exergy and energy efficiency for air gasification and oxy-steam gasification with the varying SBR. Data for air gasification is plotted at SBR = 0. Decrease in energy and exergy efficiency with SBR is evident from Fig. 4. As expected, the 2nd law exergy efficiency is evaluated to be higher than First law energy efficiency. The differences are attributed to the loss in sensible heat of the hot gas.

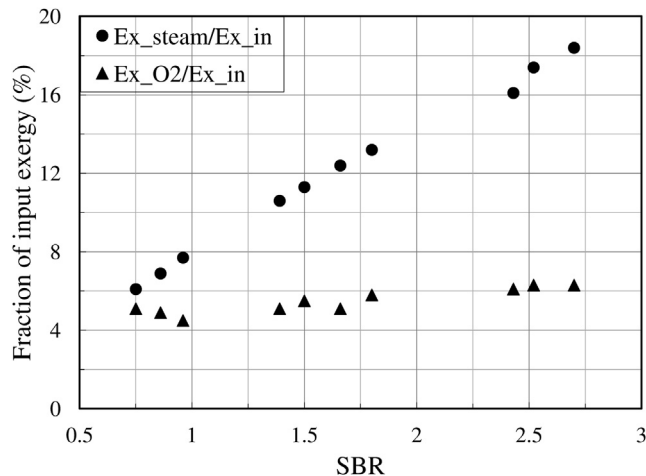


Fig. 3 – Fraction of exergy input in O₂ and steam generation Vs SBR.

Comparison of efficiencies for air and oxy-steam gasification

The thermo-chemical process involving air and oxy-steam gasification generates gaseous fuel. It is interesting and also important to analyse the overall process efficiency in these cases

- The exergy loss due to the mixing of gases in the case of air gasification is about 3.2% of total hot gas exergy value compared to 1.7% in case of oxy-steam gasification at lower SBR of 0.75.
- Total exergy (chemical and physical) in the hot gas due to N₂ itself accounts for 3.3% which directly translates to loss in energy efficiency.
- Loss in efficiency due to H₂O accounts for 0.8%, which is comparable to that in the case of oxy-steam gasification at lower SBR of 0.75.

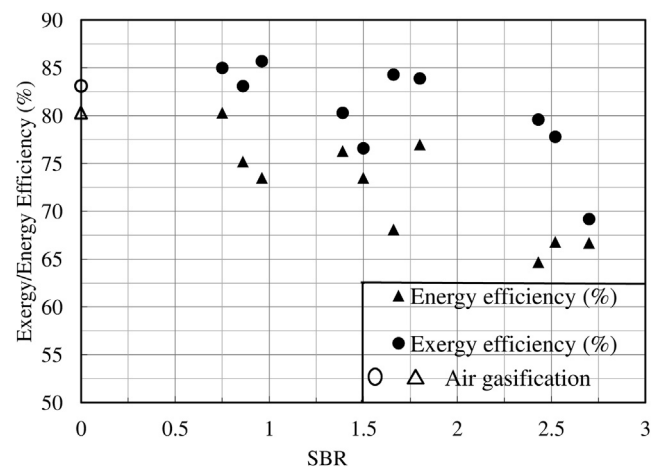


Fig. 4 – Variation in energy and exergy efficiency with SBR (Air gasification data point is at SBR = 0).

The analysis suggests that the presence of N₂ in the product gas contributes significantly towards the losses, while in the case of oxy-steam gasification, the H₂O fraction in the hot gas leads to the similar losses at lower SBR, which makes air gasification a less efficient process. It also justifies and reasons the results presented by Silva and Rouboa [6] on the numerical studies for the oxygen enriched air gasification with pine wood suggesting the higher exergy efficiency at lower N₂.

Carbon boundary point (CBP) and effects on LHV, gas composition and efficiencies at SBR >1.5

It is evident from the equation (5) that with the increase in SBR, the rate of char-steam reaction and hence the carbon conversion increases. Researchers have found that in the gasification system, the carbon boundary point (when residual carbon approaches 0%) is achieved at a certain ER and temperature for optimal efficiency and the system performance [5,7,8]. In the equilibrium studies, Prins et al. identified the carbon boundary for the biomass-steam gasification at SBR of 1.3 [5]. Fig. 5 presents the percent of carbon conversion with SBR. It can be clearly observed that the carbon conversion inside the reactor increased with SBR and reached CBP at SBR of 1.5 i.e., residual carbon approaching zero.

- a. Mass and elemental balance technique has been used to evaluate carbon boundary. Only 87% of carbon conversion was observed at SBR of 0.75 and conversion rate increasing with SBR. Complete carbon conversion was observed at SBR of 1.5 (Fig. 5). Beyond SBR of 1.5, no carbon being left for reaction with steam, extra steam reacts with CO (reaction 3) to yield H₂ and CO₂. As a result, significant enhancement in H₂ yield is observed with the proportional loss in CO output. Fig. 6 plots the H₂/CO ratio with SBR which clearly shows the significant increase in H₂/CO ratio after SBR >1.5.
- b. The WGS reaction is mildly exothermic and calorific value of H₂ is less than CO (on molar basis) which simply implies that once the carbon boundary is reached, no extra fuel gas is generated but chemical energy is transferred from CO to H₂. It results in higher yield of H₂ at the expense of chemical energy or efficiency.

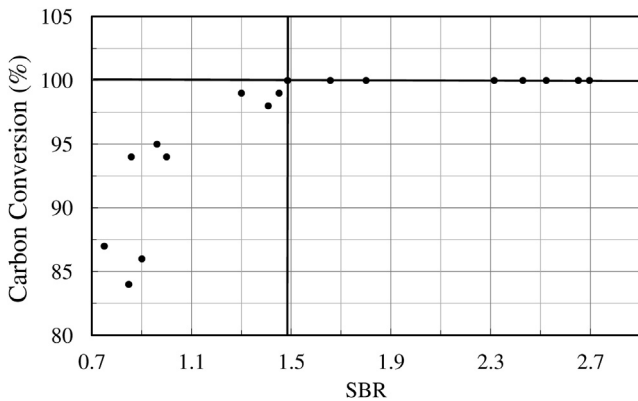


Fig. 5 – Char (carbon) conversion Vs SBR and CBP (the intersection of 2 lines at the SBR of 1.5).

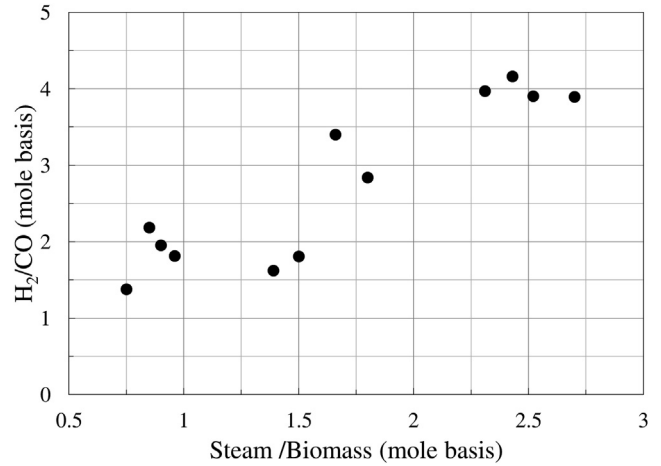


Fig. 6 – Variation in H₂/CO ratio with SBR.

- c. The total energy yield in syngas per unit biomass increases with SBR due to more carbon getting converted to fuel gas, but the calorific value of syngas (per unit volume or mass) reduces at higher SBR. Fig. 7(a) clearly shows the improvement in energy yield saturates at around 18 MJ/kg

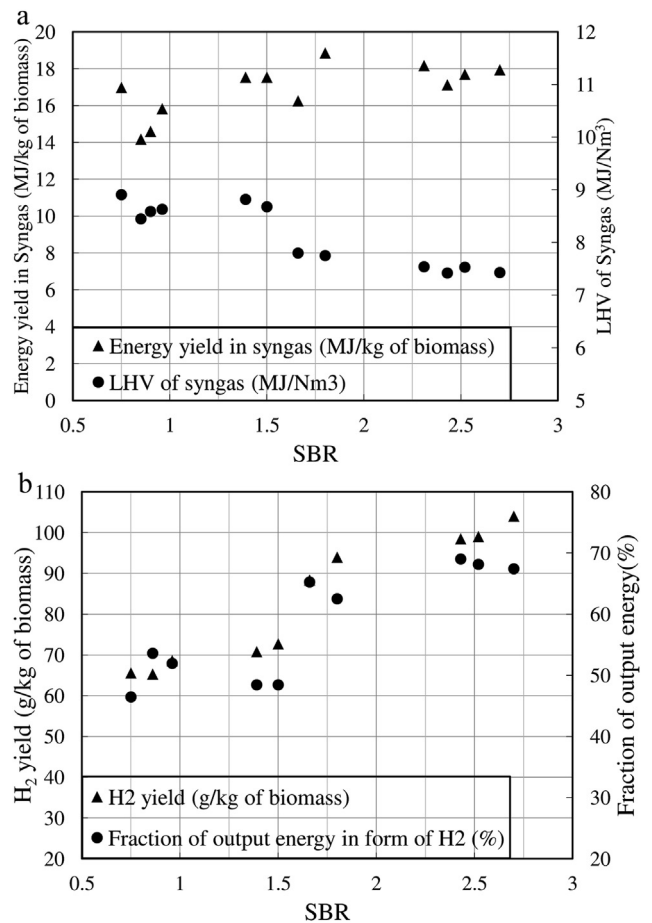


Fig. 7 – (a) – Variation in energy yield of syngas per kg of biomass and syngas calorific value with SBR. (b) – Variation in H₂ yield and fraction of energy in H₂.

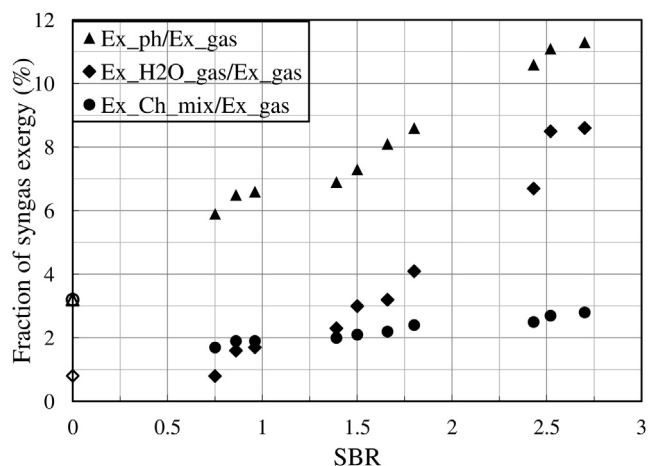


Fig. 8 – Variation in various product gas exergy components with SBR.

of biomass once the carbon boundary is reached. On the other hand, LHV of syngas decreases gradually with increase in SBR after CBP is reached (at SBR of 1.5). Fig. 7(b) clearly shows the sudden jump in H₂ yield and energy fraction in form of H₂ with SBR.

Effect of SBR on efficiency

As explained in Fig. 4, the variation in SBR has significant effect on the overall efficiency. Once the CBP is reached (at SBR = 1.5), the efficiency gradually decreases with SBR. Apart from the extra energy input in the steam generation, the conversion of CO to H₂ is responsible for the reduction in efficiency, as discussed in the section 5.5(b), at higher SBR. Variation of different components of exergy losses in the process with SBR is presented in Fig. 8. H₂O in the hot gas is found to be rising substantially with SBR. Exergy in H₂O alone accounts for 13.7–76% of the total physical exergy or 0.8–8.6% of the total exergy of syngas. Also, physical exergy in the formulation (equation (8)) accounts for the enthalpy rise and increase in the entropy at elevated temperatures which is a loss during energy efficiency evaluation. With the increase in SBR, physical exergy fraction in syngas exergy increases from 5.9 to 11.3%.

Conclusion

The paper presents an in-depth study of the energy transformation during the gasification of biomass using exergy analysis based on the experimental results of air and oxy-steam gasification in a 50 kW_{Th} downdraft reactor configuration. Sub-components contributing to the exergy flow are studied and causes of irreversibility and inefficiencies have been identified. Presence of N₂ in the reaction system is attributed towards slightly lower efficiency level in air gasification compared to oxy-steam gasification at lower SBR. The current study provides scientific basis towards the increase in efficiency in the oxygen enriched air gasification as reported by Silva and Rouboa [7].

Variation in energy efficiency, LHV and H₂ yield with SBR have been studied and analysed. Elemental mass technique has been employed to identify the CBP at SBR of 1.5 and ER of 0.23. Syngas energy yield per kg biomass was found to be increased, though marginally, with SBR till CBP after which it saturates, due to enhanced solid-to-gas conversion till CBP is reached. The sudden rise in H₂/CO ratio at SBR value more than 1.5 (after reaching CBP) is argued due to WGS reaction playing the major role. On the other side the calorific value of syngas was found to be gradually decreased with SBR after CBP due to the WGS reaction converting high energy CO molecule to comparatively lower energy H₂ molecule. Apart from CO conversion; the high exergy and energy input in steam generation with the increase in SBR and substantial exergy output in the form of unconverted H₂O adds to the system inefficiencies. Exergy and energy analysis suggests operating at lower SBRs for high energy syngas at better efficiency, but to operate at higher SBRs for high H₂ yield and syngas with high H₂/CO ratio.

REFERENCES

- [1] S Dasappa. Handbook biomass gasification – 2nd ed.. Edited by H.A.M. Knoef. Published by Biomass Technology Group BV, The Netherlands. [chapter 22]: 479–509.
- [2] Mahapatra S, Dasappa S. Rural electrification: optimising the choice between decentralised renewable energy sources and grid extension. *Energy Sustain Dev* 2012;16(2):146–54.
- [3] Peters JF, Petrakopoulou F, Dufour J. Exergetic analysis of a fast pyrolysis process for bio-oil production. *Fuel Process Technol* 2014;119:245–55.
- [4] Abuadala A, Dincer I, Naterer GF. Exergy analysis of hydrogen production from biomass gasification. *Int J Hydrogen Energy* 2010;35:4981–90.
- [5] Prins MJ, Ptasinski KJ, Janssen FJJG. Thermodynamics of gas-char reactions: first and second law analysis. *Chem Eng Sci* 2003;58:1003–11.
- [6] Silva VB, Rouboa A. Using a two-stage equilibrium model to simulate oxygen air enriched gasification of pine biomass residues. *Fuel Process Technol* 2013;109:111–7.
- [7] Ptasinski KJ, Prins MJ, Pierik A. Exergetic evaluation of biomass gasification. *Energy* 2007;32(4):568–74.
- [8] Karamarkovic R, Karamarkovic V. Energy and exergy analysis of biomass gasification at different temperatures. *Energy* 2010;35:537–49.
- [9] Sues A, Juras M, Ptasinski KJ. Exergetic evaluation of 5 biowastes-to-biofuels routes via gasification. *Energy* 2010;35:996–1007.
- [10] Turn S, Kinoshita C, Zhang Z, Ishimura D, Zhou J. An experimental investigation of hydrogen production from biomass gasification. *Int J Hydrogen Energy* 1998;23(8):641–8.
- [11] Pengmei LV, Yuana Zhenhong, Longlong Maa, Chuangzhi Wua, Yong Chena, Jingxu Zhu. Hydrogen-rich gas production from biomass air and oxygen/steam gasification in a downdraft gasifier. *Renew Energy* 2007;32(13):2173–85.
- [12] Lucasa C, Szewczyk D, Blasiaka W, Mochida S. High-temperature air and steam gasification of densified biofuels. *Biomass Bioenergy* 2004;27:563–75.
- [13] Wei Ligang, Xu Shaoping, Zhang Li, Liu Changhou, Zhu Hui, Liu Shuqin. Steam gasification of biomass for hydrogen-rich gas in a free-fall reactor. *Int J Hydrogen Energy* 2007;32:24–31.

- [14] Umeki Kentaro, Yamamoto Kouichi, Namioka Tomoaki, Yoshikawa Kunio. High temperature steam-only gasification of woody biomass. *Appl Energy* 2010;87:791–8.
- [15] Dasappa S. Experimental and modeling studies on the gasification of wood-char [Ph.D. thesis]. India: Indian Institute of Science; 1999.
- [16] Dasappa S, Paul PJ, Mukunda HS, Rajan NKS, Sridhar G, Sridhar HV. Biomass gasification technology — a route to meet energy needs. *Curr Sci* 2004;87(7):908–16.
- [17] Sandeep K, Dasappa S. Oxy–steam gasification of biomass for hydrogen rich syngas production using downdraft reactor configuration. *Int J Energy Res* 2014;38:174–88.
- [18] Mukunda HS, Dasappa S, Shrinivasa U. Open-top wood gasifiers. *Renewable energy – sources for fuels and electricity*, edited by TB Johansson, H Kelly, AKN Reddy, and RH Williams. Washington DC: Island Press, 699–728.
- [19] Dasappa S, Shrinivasa U, Baliga BN, Mukunda HS. Five-kilowatt wood gasifier technology: evolution and field experience. *Sadhana* 1990;14(3):187–212.
- [20] Dasappa S, Subbukrishna DN, Suresh KC, Paul PJ, Prabhu GS. Operational experience on a grid connected 100kWe biomass gasification power plant in Karnataka, India. *Energy Sustain Dev* 2011;15(3):231–9.
- [21] Mahapatra S, Dasappa S. Experiments and analysis of propagation front under gasification regimes in a packed bed. *Fuel Process Technol* 2014;121:83–90.
- [22] Mahapatra S, Dasappa S. Influence of surface area to volume ratio of fuel particles on gasification process in a fixed bed. *Energy Sustain Dev* 2014;19:122–9. <http://dx.doi.org/10.1016/j.esd.2013.12.013> [Available online].
- [23] Dasappa S, Paul PJ. Gasification of char particles in packed beds: analysis and results. *Int J Energy Res* 2001;25(12):1053–72.
- [24] Sonntag Richard E, Borgnakke Claus. *Thermodynamics databook*. 2nd ed. Wiley India Pvt Ltd; 2013. p. 25–75.
- [25] Szargut J, Styrylska T. Approximate evaluation of the exergy of fuels. *Brennst Wärme Kraft* 1964;16(12):589–96.
- [26] Song G, Shen L, Xiao J. Estimating specific chemical exergy of biomass from basic analysis data. *Ind Eng Chem Res* 2011;50:9758–66.
- [27] Rant Z. Towards the estimation of specific exergy of fuels. *Allg Warmetech* 1961;10:172–6.
- [28] Szargut J, Valero A, Stanek W. Towards an international legal reference environment. In: *Proceedings of ECOS 2005*; 2005. p. 409–17. Trondheim, Norway.