



Parametric Analysis of Hydrogen-rich gas from Sawdust Gasification

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Abstract – In the present study the air and steam gasification of biomass to produce hydrogen-rich gas or syngas (H_2 and CO) was investigated. The influence of the air and steam on yield and product composition was studied at the temperature range of 600 to 1200°C. The highest amount of hydrogen present during air gasification is 25% with equivalence ratio of 0.3. The addition of steam increases the hydrogen from 25% to 55% in the temperature range of 700 to 800°C. Higher temperature resulted in the formation of high amount of H_2 and CO production, higher carbon conversion efficiency and dry gas yield. The Lower Heating Value (LHV) of the gas from the sawdust is higher in steam gasification with 0.2 – 0.4 kg of steam and lower range was observed in air gasification. Steam gasification in the range of 0.2 – 0.4 kg of steam is found to yield high amount of H_2 and CO gas at a temperature range of 700 to 800°C.

Keywords – Air steam gasification, biomass, equivalence ratio, hydrogen rich gas, lower heating value.

1. INTRODUCTION

Sustainable energy plays an important role in the world due to increase in energy demand. Biomass is considered to have more potential as fuel for transportation. The biomass is more attractive as it is environment friendly with no net carbon dioxide to the atmosphere. Biomass is commonly recognized as an important renewable energy source. The chemical energy is stored in the biomass with the help of photosynthesis process. The biomass can be used to produce heat from combustion process, gas from gasification, liquid from pyrolysis and methane from fermentation. Biomass is recently being used in the production of hydrogen rich gas which is suitable for fuel cells.

The other reason to use the renewable sources of energy is due to fast depletion of fossil fuels. The production of H_2 largely depends on fossil fuels via steam methane reforming and coal gasification. These also lead to increase in the amount of CO_2 [16]. To achieve the maximum yield of H_2 and CO gas from air and steam gasification of sawdust, the optimum temperature, equivalence ratio, steam ratio and composition of gasifying medium has to be determined. The lower heating value (LHV) of fuel gas may indicate better utilization of fuel. In this paper, the effects of gasification temperature and gasification medium on the product gas yield and its lower heating value are analysed.

2. MODELS TO ANALYSE BIOMASS GASIFICATION

There are two models used for analysing the process of gasification. The kinetic modelling predicts the values more accurately but it is very complex for computation

process. The various approaches in kinetic model are discussed by Corella *et al.* [14]. The other model viz equilibrium models which is independent of design process and it shows the thermodynamic limit of gasifier performance under different conditions. The data required for the models are Gibbs free energy, enthalpy formation, heat capacity. The composition formed and LHV of the producer gas is unchanged with various operating conditions. The value obtained from the model may be used in the gasifier design and improved the process of gasification.

2.1 Literature Survey on Equilibrium Approaches

The model based on minimization of Gibbs free energy to predict the performance of gasifier. The non-stoichiometric equilibrium model was developed by Lie *et al.* [1] to predict the performance of a CFB coal gasifier. The model showed the flexibility to use various type of fuel. The result showed that, to accelerate the reaction in gas phase higher pressure is needed. Residence time, mass transfer, particle size and hydrodynamics are the basic in the carbon conversion. In his model the effect of chemical equilibrium was not included. Li *et al.* [2] modified the model prediction at 1100 K with an equivalence ratio of 0.22 – 0.54 in the temperature range of 970 – 1090 K and proved good agreement with the experimental data.

In downdraft gasifier the equilibrium model was investigated for the gasification process by Zainal *et al.* [4]. In his model the calorific value of producer gas with effects of temperature and moisture content in the gasification zone were studied. It showed less deviation in the value, compared to the equilibrium model. The influence of temperature was studied in the equilibrium model by Altafini *et al.* [5]. The wood waste gasification was utilized in this model. The model predicted showed the effect on product gas composition with increase in temperature range.

A simple model developed by Ruggiero *et al.* [6] included the chemical equilibrium. The model predicted the gas composition, lower heating value of gas, gross

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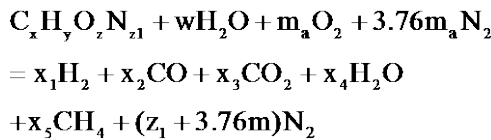
efficiency of the gasifier and exergy efficiency. The value of experimental data is compared with predicted model data and showed less variation in the value.

2.2 Thermodynamic Equilibrium

The reactions at which reactant and product are zero and do not change with time is referred to as thermodynamic equilibrium. It helps to provide information on various products formed during the solid, liquid and gaseous state at varying operating conditions of the gasifier. The thermodynamic equilibrium model predicted by Watkinson *et al.* [9] showed the gas composition and the yield. They used coal as the fuel. The equilibrium model values showed less deviation with experimental value. At higher temperature the equilibrium model deviates. The model predicted by Altafini *et al.* [5] shows the reactions occur at higher temperature and deviation from the experimental value. The value predicted shows some useful information on gas composition. To determine the gas formed during the gasification process the commercial packages equilibrium software FactSage 6.3 was utilized and it is based on non-stoichiometric equilibrium approach.

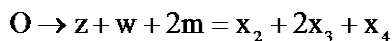
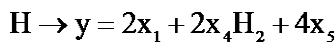
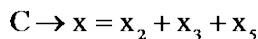
2.3 Stoichiometric Equilibrium Approach

In this method the approach is based on various reactions involved during the gasification process and their equilibrium constant. It includes balancing of reactant and product value. The value obtained can be solved by algebraic equation. The general stoichiometric equation:



where $C_x H_y O_z N_{z1}$ is the chemical representation of biomass and x , y , z and $z1$ are C, H, O and N mole determined from the ultimate analysis of biomass.

Balancing of carbon, hydrogen and oxygen



2.4 Non - Stoichiometric Equilibrium Approach

The non-stoichiometric models are based on the Gibbs free energy minimization. The reaction mechanisms are not involved in the approach, $\Delta G=0$.

The approach does not rely on the identification of any stoichiometric equation. The Gibbs energy is a function of moles present in the fuel. The compositions of biomass and reactant gas stream are needed for the analysis. The complex mathematical theories are involved in minimization of Gibbs free energy. Jarungthammachote *et al.* [10] pointed out complex theories in minimizing the Gibbs free energy. There are set of equations for all chemical species that are involved in the analysis including the equation of atomic balance for each element, total number of moles, the equations of variation and the energy balance around the gasifier.

2.5 Model Derivation with Basic Equation

The Gibbs free energy of a system with fixed T and P can be expressed as a linear combination of the chemical potential of each component in the system.

$$G = \sum_i x_i \mu_i \quad (1)$$

G is minimum when the system reaches the equilibrium

$$\mu_i(T, P) = \mu_i^0(T) + RT \ln a_i \quad (2)$$

$a_i = p_i$ (For gaseous species)

$$a_i = p_i = (x_i / X) P \quad (3)$$

$$\begin{aligned} G / RT = \sum_{i=1}^m x_i^g \left[\left(g^0 / RT \right)_i^g + \ln P + \ln(x_i^g / X) \right] \\ + \sum_{i=1}^s x_i^c \left(g^0 / RT \right)_i^c \end{aligned} \quad (4)$$

The equilibrium constant K_f is the function of temperature only

$$\Delta g^0 = -RT \ln k_f$$

$$\frac{\Delta g^0}{RT} = -\ln k_f \quad (5)$$

The mass balance relation can be written as

$$\sum_{i=1}^m a_{ij}^g x_i^g + \sum_{i=1}^m a_{ij}^c x_i^c = b_j \quad (j=1,2,\dots,l) \quad (6)$$

$$\begin{aligned} \left(g^0 / RT \right)_i^g + \ln P + \ln(x_i^g / X) \\ - \sum_{j=1}^l L_j a_{ij}^g = 0 \quad (i=1,2,\dots,m) \end{aligned} \quad (7)$$

$$\left(g^0 / RT \right)_i^c - \sum_{j=1}^l L_j a_{ij}^c = 0 \quad (i=1,2,\dots,s) \quad (8)$$

Expanding the Equations 3 and 6 in Taylor series

$$\begin{aligned} \sum_{i=1}^m a_{ij}^g y_i^g + \sum_{i=1}^m a_{ij}^c y_i^c - b_j + \sum_{i=1}^m a_{ij}^g (x_i^g - y_i^g) \\ + \sum_{i=1}^m a_{ij}^c (x_i^c - y_i^c) = 0 \quad (j=1,2,\dots,l) \end{aligned} \quad (9)$$

$$\begin{aligned} \left(g^0 / RT \right)_i^g + \ln P + \ln(y_i^g / Y) - \sum_{j=1}^l L_j a_{ij}^c + (x_i^g / y_i^g) \\ - (X / Y) = 0 \quad (i=1,2,\dots,m) \end{aligned} \quad (10)$$

$$\text{Where } Y = \sum_{i=1}^m y_i^g$$

$$x_i^g = -f_i + y_i^g \left[(X / Y) + \sum_{j=1}^l L_j a_{ij}^g \right] \quad (i=1,2,\dots,m) \quad (11)$$

Where

$$f_i = y_i^g \left[\left(g^0 / RT \right)_i^g + \ln P + \ln(y_i^g / Y) \right] \quad (i=1,2,\dots,m)$$

Summation of Equation 7 gives

$$\sum_{j=1}^l L_j \sum_{i=1}^m y_i^g a_{ij}^g = \sum_{i=1}^m f_i \tag{12}$$

Quantity C_j , which serves as a correction term in case where initial guess of mole numbers does not satisfy mass balance relations, is defined as:

$$C_j = \sum_{i=1}^m y_i^g a_{ij}^g - b_j \quad (j=1,2,\dots,l)$$

Substituting Equations 7 and 9 in Equation 5 gives:

$$\sum_{k=1}^l L_k r_{jk} + [(X/Y) - 1] \sum_{j=1}^l y_i^g a_{ij}^g + \sum_{j=1}^l y_i^c a_{ij}^c = \sum_{i=1}^m a_{ij}^g f_i - C_j$$

$$\text{Where } r_{jk} = r_{ki} = \sum_{i=m}^m (a_{ij}^g a_{ik}^g) y_i^g \quad (j, k = 1, 2, \dots, l)$$

3. METHODS OF DATA PROCESSING

3.1 Methods of Data Processing

The lower heating value (LHV) of hydrogen-rich gas is calculated by,

$$\begin{aligned} \text{LHV}(\text{MJ/N m}^3) = & (\text{CO} \times 126.36 + \text{H}_2 \times 107.98 + \\ & \text{CH}_4 \times 358.18 + \text{C}_2\text{H}_2 \times 56.002 \\ & + \text{C}_2\text{H}_4 \times 59.036 \\ & + \text{C}_2\text{H}_6 \times 63.772) / 1000 \end{aligned}$$

where, CO, H₂, CH₄, C₂H₄ and C₂H₆ are the molar percentages of components of hydrogen-rich gas, and old gas efficiency is:

Cold gas efficiency

$$= \frac{\text{LHV of fuel gas (kJ/Nm}^3) \times \text{fuel gas production (Nm}^3/\text{kg)}}{\text{Lower heating value of biomass fed in the system (kJ/kg)}}$$

3.2 Simulation Parameters

The major parameters involved in the simulation are

- (1) Biomass type;
- (2) Gasification medium; and
- (3) Temperature and pressure of gasification.

3.3 Biomass Type

There are various types of biomass fuels available all over the world. Vassilev *et al.* [11] highlighted an extended overview of the chemical composition of various biomasses. Data for chemical composition of 86 varieties of biomass, including traditional and complete proximate, ultimate and ash analyses (21 characteristics) were used to describe the biomass system. In this study the biomass fuel - sawdust is taken since it has high amount of carbon and hydrogen content with less amount of ash composition [12]. The approximate molecular formula for the biomass along with composition in terms of dry ash free basis is given in Table1.

3.4 Gasification Medium

The partial oxidation is an essential part in the gasification process. To gasify the fuel the supply of oxidiser (air or steam) should be lower than the stoichiometric quantities. The oxygen in the air is used to oxidise the fuel and nitrogen as inert. Air ratio or equivalence ratio is defined as the ratio between the actual air fuel ratio and stoichiometric air fuel ratio by mass. The other medium of gasification is steam. The steam supplied is expressed as kg of steam per kg of sawdust. In air gasification the air ratio is varied from 0.2 to 0.5. During steam gasification, the amount of steam supplied is varied from 0.2 to 0.8 kg per kg of steam.

3.5 Temperature and Pressure Gasification

The Gibbs free minimization mainly depends on the temperature and pressure gasification. Most of biomass gasification model and experiment was conducted in the range of 700 to 950°C [2, 4, 5, 7]. In this simulation the temperatures are varied in wide range from 600 to 1200°C. The wide range allows to understand the variation of product formation with the change in the temperature. The pressure used in this model is atmospheric pressure. Since it is equilibrium approach the size of sawdust is not important.

Table 1. Proximate and ultimate analysis of sawdust.

Sl No.	Parameter	DF(% wt)	DAF(% wt)
01	Carbon	49.2	49.7
02	Hydrogen	5.99	6
03	Nitrogen	0.82	0.83
04	Sulphur	0.03	0.03
05	Oxygen	42.98	43.44
06	Ash	0.98	
07	Moisture	42	
08	Volatile matter (dry)	80.05	

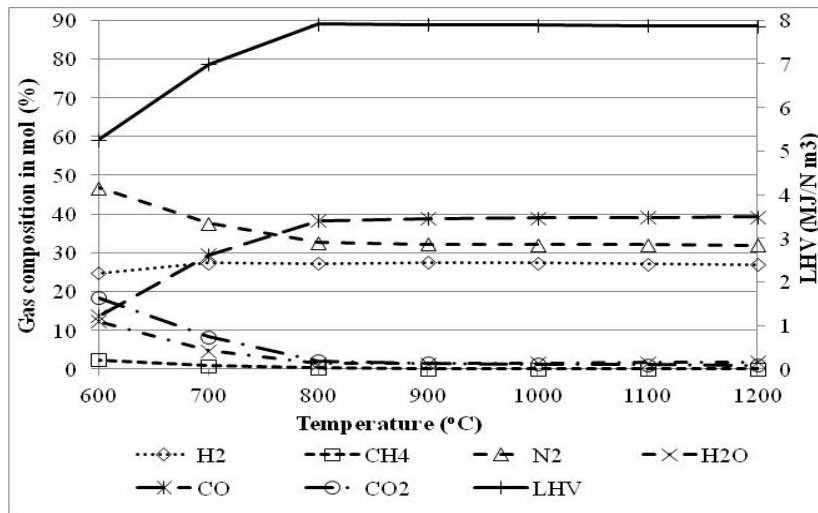
4. RESULTS AND DISCUSSION

4.1 Effect of Air Gasification

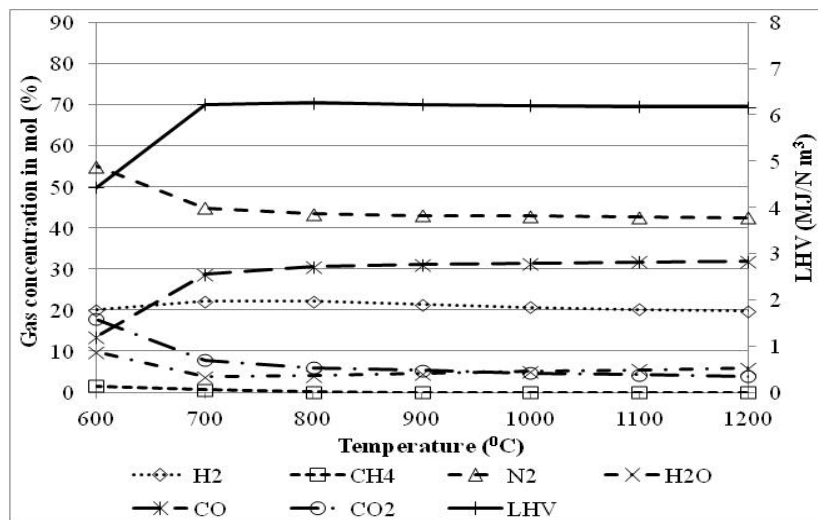
The air ratio plays an important role in the production of H_2 and CO gas. The non-stoichiometric equilibrium model developed by Li *et al.* [2] shows the product gas composition based on air ratio. It showed that the CO rich gas was produced at an air ratio of 0.2 – 0.3 and for hydrogen rich gas, the air ratio is in the range of 0.15 – 0.25 with temperature range from 800 to 1000°C.

Figure 1 shows process of the sawdust air gasification for the air ratio of 0.2 – 0.5 with varying temperature. The amount of CH_4 decreases gradually from 2.4% to 0.8% with an increase in the air ratio from 0.2 to 0.5 at 600 °C. The CH_4 finally becomes zero for all air ratios above 700°C. The amount of H_2 produced

varies from 8% to 27%. The amount of hydrogen increases with an increase in the temperature up to 800°C and beyond that temperature the hydrogen slowly decreases. It is mainly because of cracking of heavier hydrocarbons and tar at higher temperature. At higher temperature the process of gasification is fast. The amount of oxygen required to burn the fuel is insufficient and hence the formation of CO_2 is less at higher temperature. The value of CO increases to 39% until the temperature reaches 800 °C. The lower heating value shows a maximum of 7.9 $MJ/N\ m^3$ at temperature of 800°C for an air ratio of 0.2. The LHV decreases with increase in an air ratio. The same was trend observed from Gómez-Barea *et al.*[18].

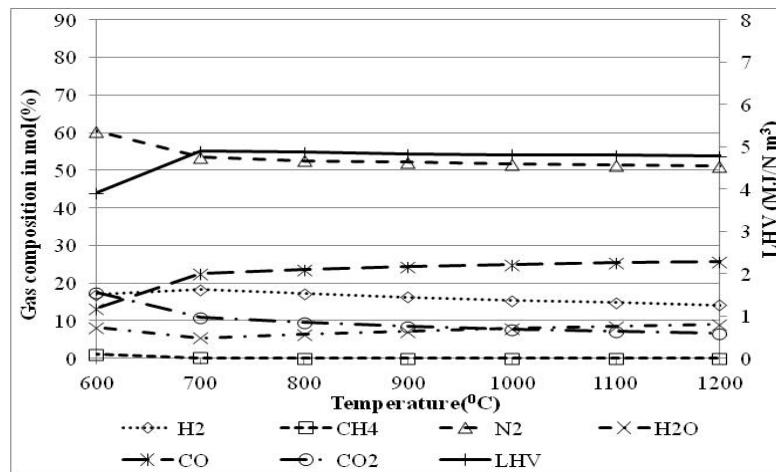


(a)

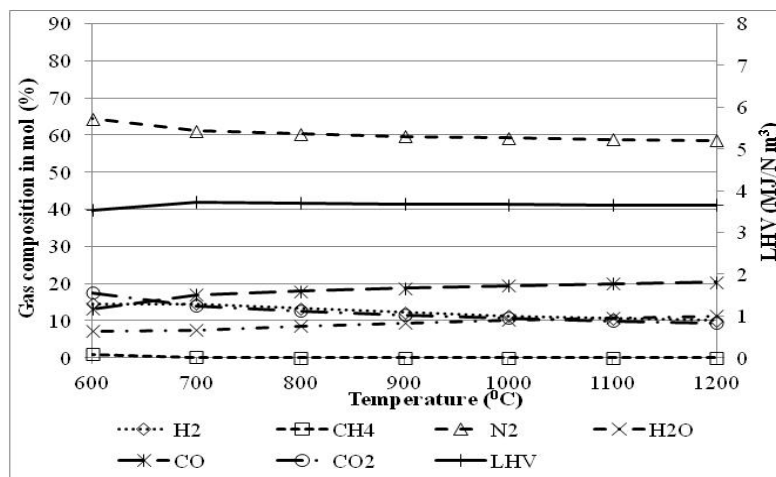


(b)

Fig. 1. Gasification of sawdust with air gasification to an air ratio a) 0.2 b) 0.3.



(c)



(d)

Fig. 1. Gasification of sawdust with air gasification to an air ratio c) 0.4 d) 0.5.

4.2 Temperature Effect

The other major factor that influences the production of hydrogen is temperature. The product gas formed mainly depends on the operating temperature as reported by Natarajan *et al.* [3]. They used rice husk in fluidized bed reactor. It shows that the concentration of H₂ and CO increases with an increase in temperature for a given equivalence ratio. The higher temperature results in lower rate of hydrogen production which is due to decomposition of CO₂. In Figure 1 for the entire air ratio the amount of hydrogen increases with an increase in temperature and starts to decrease beyond 900 °C. At lower temperature the formation of methane decreases the formation of hydrogen [17], [20]. It is also evident from Figure 1 which shows higher CH₄ and lower hydrogen below 700 °C. The amount of hydrogen is maximum the temperature range of 750 – 850 °C for both air and steam gasification.

The increase in temperature from 600 to 800 °C also increases the heating value of the fuel as shown Figures 1 and 2. Li *et al.* [2] also noticed the same trend in the increase of heating value when they gasified the sawdust. The increase in heating value of product gas indicates better conversion of solid fuel to gaseous fuel.

The heating value at higher temperature indicated rate of carbon conversion.

4.3 Air Ratio

The equivalence ratio also shows some effects in the product gas formed during gasification process. The amount of hydrogen produced varies in both air and steam gasification at equivalence ratio. It shows that the amount of hydrogen formed is more at lower equivalence ratio in air gasification [17]. The equivalence ratio was varied from 0.2 to 0.5 during air gasification. Hydrogen content is more in the order for the equivalence ratio of 0.2 > 0.3 > 0.4 > 0.5. The equivalence ratio also affects other gases formed during the gasification process. The various gas formed during the gasification of fuel with varying equivalence ratio is seen from Fig. 1. The LHV of fuel gas decreases with an increase in Equivalence ratio and from Figure 1 the product gas formed shows decrease in trend. Higher amount of oxygen also causes decrease in quality of fuel. It is also confirmed by Lv *et al.* [13]. The introduction of steam into biomass fuel increases the quality of fuel and the percentage of hydrogen present in the fuel. Figure 2 also shows an improvement percentage of hydrogen production with steam

introduction. The experimental study done by Turn *et al.* [8] shows higher yield of hydrogen was based on the equivalence ratio.

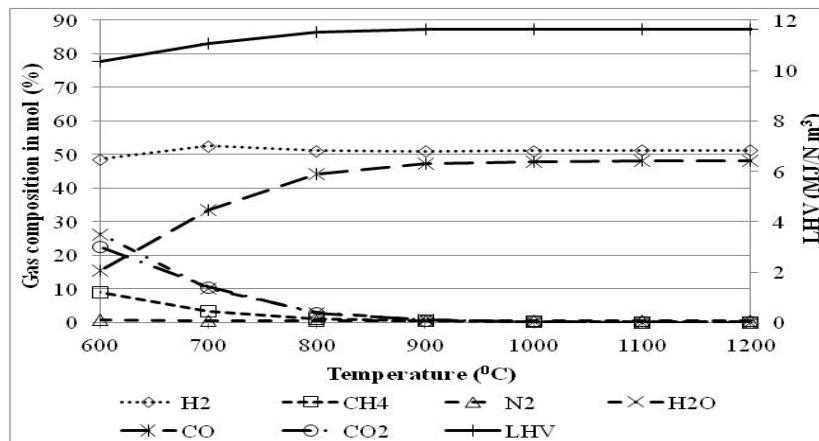
4.4 Effect of Steam Gasification

To improve the presence of hydrogen in the product gas or to produce more amount of hydrogen from fuel the introduction of steam is adopted. The quality of gas also improves with the introduction of steam. Over the range of 0.2 to 0.8 kg of steam per kg of biomass the highest amount of hydrogen is about 54%. Steam gasification shows higher in hydrogen production and quality of fuel gas compared to air gasification. The quality of fuel gas decreases with an increase in the amount of steam supplied and further the production of hydrogen is same. From Figure 2 the result also shows that higher amount of steam decreases the quality of fuel. Increase in temperature shows improved hydrogen production [19]. Higher temperature shows formation of other gases and decreases the quality of fuel. The formation of CO increases with an increase in temperature. The introduction of steam lowers the operating temperature since the system is supplied by an external heat source. This low in temperature causes high amount of tar content. Lv *et al.* [13] shows the effect of air steam gasification in fluidised bed. The experimental results show that introduction of steam increased the quality of

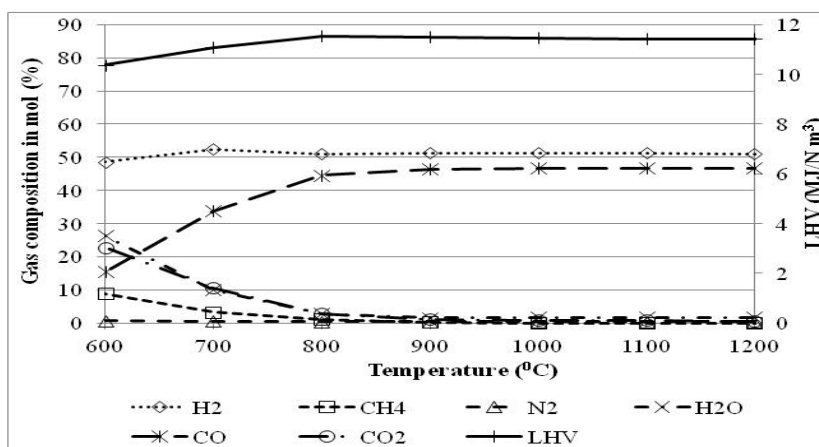
fuel but excessive steam will cause decrease in temperature and quality of fuel. The variation of gas composition occurs when the steam to biomass is more. Li *et al.* [2] also shows that injection of steam into biomass improves the gas quality at a given O/C molar ratio.

4.5 Highest Hydrogen Production

The concentration of hydrogen is more in steam gasification. The steam reforming and water gas shift reaction causes higher amount of hydrogen production. The amount of hydrogen also increases with an increase in the temperature until the methane is converted to hydrogen. The H₂ concentration increases with an increase in steam-biomass ratio as reported by Florin *et al.* [15]. The maximum yield of hydrogen is about 55% for the steam ratio of 0.8 kg. The maximum yield of hydrogen in air gasification is 27% at air ratio of 0.2. The higher temperature shows less concentration of steam to biomass ratio. Turn *et al.* [8] also showed that at higher temperature less product gas sensitive to steam biomass ratio. The experiment performed by Lv *et al.* [7] shows an increase in hydrogen production with an increase in temperature for equivalence ratio of 0.22 and steam to biomass ratio 2.7. The value is closes to our value of steam to biomass ratio of 0.2 kg of steam and 0.2 – 0.3 equivalence ratios.

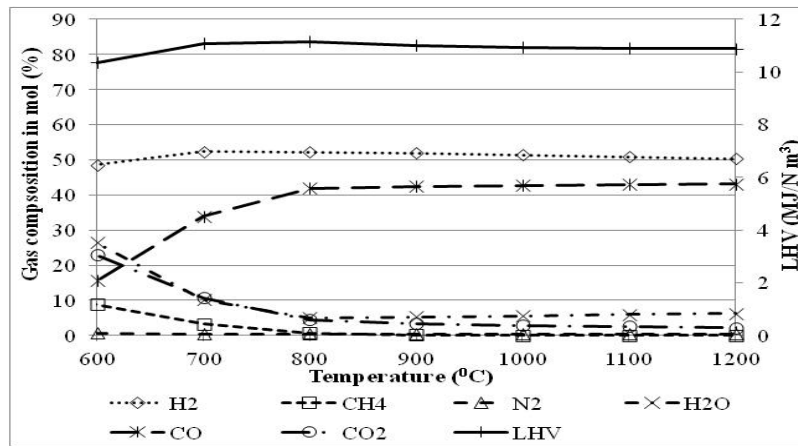


(a)

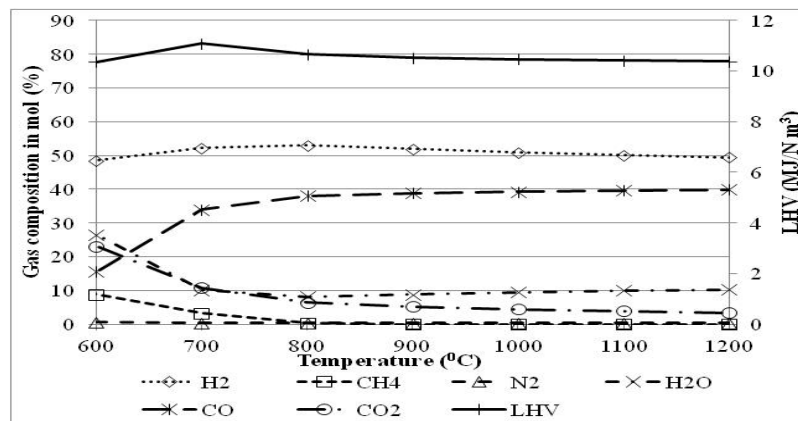


(b)

Fig. 2. Gasification of sawdust with steam ratio a) 0.2 b) 0.4



(c)



(d)

Fig. 2. Gasification of sawdust with steam ratio c) 0.6 d) 0.8.

5. CONCLUSION

A thermodynamic equilibrium analysis of biomass gasification was carried out at temperature range of 600 to 1200°C for sawdust with air and steam as gasification medium. The effects of process parameters such as temperature, equivalence ratio, gasification medium were studied on biomass air-steam gasification. The results at air steam gasification of biomass to produce hydrogen-rich gas or syngas (H₂ and CO) was investigated. The maximum volume percentage of hydrogen gas observed at equivalence ratio of 0.2 – 0.3 within temperature range of 800 to 1000 °C was about 25%.

The introduction of steam increases the hydrogen percentage and quality of the fuel gas. An increase in temperature increases the hydrogen percentage but higher temperature shows less sensitivity to the steam to biomass ratio. The amount of hydrogen in the steam gasification increases from 25 to 55% in the temperature range of 700 to 800 °C compared to the air gasification. Increase in temperature also yields increase in quality of gaseous fuel. Higher temperature results in higher H₂ and CO production, higher carbon conversion efficiency and higher dry gas yield. The lower heating value of the product gas from the sawdust is higher in steam

gasification with 0.2 to 0.4 kg of steam per kg of biomass and reduces with excess amount of steam.

Steam gasification of sawdust with 0.2 to 0.4 kg in the temperature range of 700 to 800 °C of steam is found to produce gaseous fuel of 11MJ/Nm³ due to higher percentage of H₂ and CO.

NOMENCLATURE

- a_{ij} jth element in ith substance
- b_j the total number of moles of the jth element
- c condensed phase
- g gas phase
- l total number of elements
- m number of substances in gas phase at equilibrium
- m_a number of moles of oxygen supplied in air
- p partial pressure
- s number of substances condensed phase at equilibrium
- w Moisture content of feed, kg/kg (dry basis)
- x Number of moles of carbon
- x_i Number of moles of a ith substance or species in the mixture
- y Number of moles of hydrogen
- z Number of moles of oxygen
- z_l Number of moles of nitrogen

μ_i	chemical potential of i^{th} species
C	Carbon
DF	Dry Fuel
DAF	Dry Ash Free
G	Gibbs free energy
H	Hydrogen
LHV	Lower heating value of product gas, MJ/Nm ³
L_j	Lagrangian multipliers
N	Nitrogen
O	Oxygen
P	total pressure
R	ideal gas characteristic constant
S	Sulphur
T	absolute temperature
X	total number of moles in the gas phase
Y	dry gas yield, Nm ³ /kg.

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