Irreversibilities in High Temperature Biomass Gasification

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ABSTRACT

The use of biomass for energy production is accompanied by possible ecological drawbacks such as limitation of land or water usage and competition with food production. For biomass-based systems such as gasifiers, a key challenge is to develop efficient conversion technologies. In view of the considerable interest in the gasification process worldwide, it is necessary to have a prior modeling and prediction of the gasifier's performance. This paper addresses the gasifier performance analysis based on the second law of thermodynamics thus quantifying gasifier degree of irreversibilities in biomass gasification for high temperatures, in the range 800K – 1400K. When this law and exergy concepts were evoked, it revealed the existence of inevitable losses, the process irreversibilities. The exergetic analysis model took into account the conservation of energy and mass to establish the losses. The model evaluated the efficiency, which is the maximum amount of work that can be obtained from energy interaction and is the highest realizable taking into account of the irreversibilities. The exergy contained in the biomass is converted into chemical exergy of the product gas, physical exergy, the rest is the unavailable energy due to process of irreversibilities. It is observed that values of irreversibilities reduces as the equivalent ratio increases in the case of chemical exergy based efficiency, values lies between 13.68% and 13.36% as temperature varies from 800K to 1400K. For the case of chemical and physical exergy, the irreversibility values also decrease with increase of temperature from 20.27% at 800K to 20.06% at 900K.

Key words: Biomass, Exergy Analysis, High Temperature Gasification, Irreversibilities

1.0 INTRODUCTION

In recognition of energy being a global need, it has also been realized that in the 20th and 21st centuries, world population and modernization increase shall increase the utilization of fossil fuels energy resources (IEA, 2010). The world population and its economic growth sustenance need to address issues on conserving the environment due to the consumption of fossil fuels, the use of which contribute to global warming. The use of sustainable energy sources such as renewable energies may be part of the solution. In the renewable energy sources dominated by biomass, solar, wind and micro/mini hydro, it has been shown that biomass is seen to be promising as is predicted to be a future dominant energy source in the years between 2020 and 2060 preceded by solar (Krothapalli, 2006). The efficient method for converting biomass materials into useful gas energy is via the gasification process since the gas produced can be combusted at higher temperatures. Previous efforts have been to study gasification process at temperature levels below 750°C referred to as low temperature agent gasification, (LTAG). Under this temperature regime some tars tend to remain as residue due to non cracking into gaseous components. At higher temperatures, above 750°C, the predominant phenomenon is the high temperature agent gasification, (HTAG), the gas yield increases and the tar yield decreases with increasing temperature (Hernandes *et al*, 2010).

The development of efficient technologies for biomass gasification requires a correct application of thermodynamics tools. Thermodynamics process analysis is based on energy and mass balances emanating from the first law of thermodynamics. The energy balance method makes the energy analysis possible by quantifying energy conversion processes and efficiency of energy conversion in a system process. Further thermodynamics analysis involves the use of the second law of thermodynamic. Since by the second law of thermodynamics there is a loss of energy during a thermodynamics process, an account should be taken on qualifying the energy degradation through the process due to dissipation by deploying the second law of thermodynamics analysis (Melsert and Jeter, 2010). In using the second law of thermodynamics for gasification process, an account of losses caused by the process irreversibilities can be determined. Irreversibility is a thermodynamics characteristics capable of quantifying the useful work that can be produced by a system or the amount of work needed to undertake a process. In determination of the values of irreversibility, an analogous consideration from the concept of effectiveness in availability shall be deployed.

Availability is the theoretical maximum amount of work which can be obtained from a system at any state p_1 and T_1 when operating at reference point's pressure, p_o and temperature T_o. The availability function for a steady state system at a temperature T, an enthalpy h and entropy s at any point *i* is given by:

$$b_i = h_1 - T_i s_i \tag{1}$$

With this function, the maximum theoretical amount of work that is available for steady flow system is given by:

$$W_{\max} = (h_1 - T_o s_1) - (h_o - T_o s_o) = b_1 - b_o \tag{2}$$

In considering a process executed between system states 1 and 2, effectiveness concept in the availability is necessary and is given by:

$$\zeta = \frac{h_2 - h_1}{b_2 - b_1} \tag{3}$$

In this expression the difference between maximum theoretical efficiency of 1 and ζ is the degree of irreversibility as a function of $(b_2\text{-}b_1)$. This philosophy of accounting for system irreversibilities is used to account for process irreversibilities by considering the system of energy interactions for process streams. The determination of the irreversibilities is by the way of accounting for the exergy efficiencies. By means of the exergy balance the exergy analysis is extended to simulate the availability analysis whose basis is also anchored in the second law of thermodynamics (Ganapthy *et al.*, 2009; Cao *et al*, 2005).

Among the available tropical biomass sources, palm oil plant is common in various areas. The plant is of many industrial opportunities and social benefits to the people. Oil palms are grown on a 25 to 30 years rotation before being removed to give way for new plants. At felling the average oil palm has reached a height of 12 – 15 m with a stem diameter of 350 mm. An average 30 year old oil palm has a stem volume of 1.6 m^3. After felling palm stems are mostly shredded on the spot, dried, and either left to decay or burnt. One hectare of oil palm plantation can produce about 50-70 tonnes of biomass residues such as stems.

This biomass shall be used in the model analysis for the evaluation of gasifiers' performance parameters.

2.0 METHODOLOGY

The central part of the biomass gasification process is the gasifier since it is one of the least efficient unit operations in the whole biomass to energy technology chain with more than 60% of the irreversibilities. Therefore in this work the gasification process unit for analysis of irreversibilities is presented. Figure 1 shows a schematic representation for high temperature air gasification arrangement. It is assumed that the gasifier operates as pseudo-homogeneous reactor at atmospheric pressure. The ideal situation presumes adequate residence time in the gasifier to allow pyrolysis products to burn and subsequently achieve equilibrium state in the reduction zone before exiting the gasifier at a temperature T_R (Altafini *et al.*, 2003; Kasembe *et al.*, 2008).

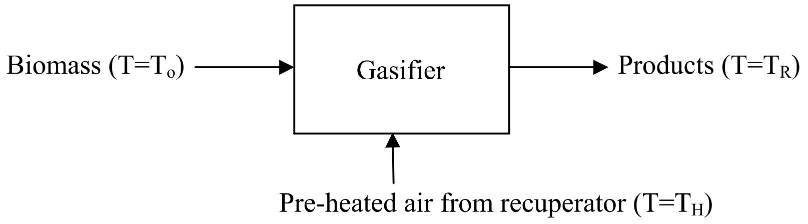

Figure 1: Schematic diagram of a pseudo-homogenous HTAG

Jarungthammachote and Dutta (2008) described the important chemical reactions in the gasifier as Oxidation, Boudouard, Water gas, Methanation, Water-gas shift, and Methane reforming as:

Oxidation reaction: $C+O_2 \rightarrow CO_2$; (4)

$C + \frac{1}{2} O_2 \rightarrow CO$; $CO + \frac{1}{2} O_2 \rightarrow CO_2$; (5)

Boudouard reaction: $C + CO_2 \rightarrow 2CO$ (6)

Water gas reaction: $C + H_2O \rightarrow CO + H_2$ (7)

Methanation reaction: $C + 2H_2 \rightarrow CH_4$ (8)

Water-gas shift reaction: $CO + H_2O \rightarrow CO_2 + H_2$ (9)

Methane reforming reaction: $CH_4 + H_2O \rightarrow CO + 3H_2$ (10)

In this presentation, the following assumptions are considered, also as presented by Kasembe *et al.* (2008): The chemical equilibrium between gasifier products is reached and evaluated at atmospheric pressure (1 bar); Ashes are not considered (Small amount 1%); and Heat losses are neglected (Adiabaticity)

2.1 THE MODEL

In consideration of Figure 1, the exergy balance of the biomass gasification process dictates that exergy values of all streams entering must be conserved by the total sum of the exergy values leaving the process and the process irreversibilities, this is expressed by Equation 11;

$$\sum_{IN} \varepsilon_j = \sum_{OUT} \varepsilon_k + I \tag{11}$$

Where $\sum_{IN} \varepsilon_j$ and $\sum_{OUT} \varepsilon_k$ are the exergy flow of all entering and leaving material streams respectively and I is the irreversibility and the degree of irreversibilities I is given by:

$$\frac{I}{\varepsilon_{in}} = \frac{\varepsilon_{in} - \varepsilon_{out}}{\varepsilon_{in}} = 1 - \frac{\varepsilon_{out}}{\varepsilon_{in}} \tag{12}$$

The total exergy of the streams is dependent upon its chemical as well as its physical composition and is given by Equation 13:

$$\varepsilon_{ch,gas} + \varepsilon_{ph,gas} \tag{13}$$

The biomass and gasifying agent exergy are respectively, $\varepsilon_{ch,\ biomass}$ and $\varepsilon_{ph,\ med}$:

Therefore
$$I = 1 - \frac{\varepsilon_{ch,gas} + \varepsilon_{ph,gas}}{\varepsilon_{ch,biomass} + \varepsilon_{ph,med}} \tag{14}$$

2.2 Evaluation of Parameters

(i) The chemical exergy of the gas ($\varepsilon_{ch,gas}$)

The chemical exergy $\varepsilon_{ch,gas}$ of the gas is determined by:

$$\varepsilon_{ch,gas} = \sum_i \chi_i \varepsilon_{ch,i} + R_o T_o \sum_i \chi_i \ln \chi_i \tag{15}$$

Where χ_i and $\varepsilon_{ch,i}$ are the mole fraction and chemical exergy of individual gas component i respectively, R_o is the universal gas constant (8.314kJ/kmolK) and T_o is the standard temperature (298K) . The values of $\varepsilon_{ch,i}$ for syngas composition component (H_2, CO, CO_2, H_2O, CH_4 and N_2) are obtained from Kotas (1985) . The biomass involved in the gasification is represented by a general formula $CH_xO_yN_z$ and the gasification equation is represented as:

$$\begin{aligned} &CH_xO_yN_z + wH_2O + m(O_2 + 3.76N_2) \rightarrow \\ &n_{H_2}H_2 + n_{CO}CO + n_{CO_2}CO_2 + n_{H_2O}H_2O + n_{CH_4}CH_4 + (z/2 + 3.76m)N_2 \end{aligned} \tag{16}$$

where x, y, and z are the number of atoms of hydrogen, oxygen, and nitrogen per number of atom of carbon in the feedstock respectively. These are derived from the feedstock charaterisation of its chemical composition using a proximate and ultimate analys, results provided in Table 1. w is the amount of moisture per kmol of feedstock and m as number of moles for air to be used in gasification process.

Tabel 1: Expermental values for Palm stem biomass

Proximate analysis (%), dry basis	Moisture	Volatile matter	Fixed carbon	Ash		
	9.10	81.20	15.30	3.50		
Ultimate analysis (%), dry basis	C	H	O	N	S	Cl
	47.50	5.90	42.50	0.28	0.13	0.18
Formulae $CH_xO_yN_z$	*x*	*y*	*Z*			
	1.48	0.67	0.01			

(ii) The physical exergy of the gas ($\varepsilon_{ph,gas}$) and Pre-heated air exergy (ε_{med})

The physical exergy $$\varepsilon_{ph,gas} = (h_R - h_o) - T_o(s_R - s_o) \tag{17}$$

Pre-heated air exergy $$\varepsilon_{med} = (h_H - h_o) - T_o(s_H - s_o) \tag{18}$$

Where h and s are enthalpy and entropy of the gas mixture at a given temperature and pressure, h_o and s_o are the values of these functions at standard temperature T_o (298K) and pressure (1 bar). The subscript R stands for exit gas from the gasifier and H is for the hot gas from the recuperator. The h and s values for the medium, air, (gas from the recuperator) and gas mixture are temperature dependent and the values used in this work are those from Stull and Prophet (1971), the JANAF Thermodynamic Tables as reported by Strehlow (1985). The temperature of the hot gas from the recuperator was varied from 800K to 1400K.

(iii) The biomass fuel exergy ($\varepsilon_{ch,biomass}$)

The biomass fuel exergy, $\varepsilon_{ch,biomass}$, is from Szargut and Syrylska (1964) as reported by Ptasinski et al. (2007);

$$\varepsilon_{ch,biomass} = \beta LHV_{biomass} \tag{19}$$

where $LHV_{biomass}$ is the lower heating value of biomass, β is a factor dependent upon mass fraction of oxygen, carbon, hydrogen and nitrogen in the feedstock (*Ptasinski et al.*, 2007)

The Matlab equation solver program and Maple programs was used to calculate the formulated model equations to obtain the values of irreversibilities.

3.0 RESULTS AND DISCUSSIONS

The elemental analysis of the palm oil plant is characterized by high oxygen content of 42.5 %, which grossly affect its calorific value. The sample Carbon content was 47.5% and hydrogen to 5.9 %, while the concentrations of nitrogen, sulphur and chlorine were marginal at 0.28 %, 0.13% and 0.18 % respectively. The model results for lower heating value of the biomass was 22,271 kJ /kg. The experimentally determined value was 22.88% lower at 16,182 kJ/kg.

The effect of gasification temperatures of 800K to 1400K and equivalence ratios of 0.3, 0.35 and 0.4 on the efficiency values based on heating value of the gas, chemical exergy and the ones based on chemical and physical exergy are presented to quantify the irreversibilities.

Figure 2 shows effect of temperature on second law efficiency based on chemical exergy at various equivalence ratios. The results show that high temperatures and equivalent ratio increase favoured the second law efficiency based chemical exergy. An increase from 82.27% to 82.36 is observed at about the temperature range between 1100K and 1200K with an equivalence ratio of 0.4. This means that the irreversibilities of about 17.73% to 17.63% are encountered in this range.

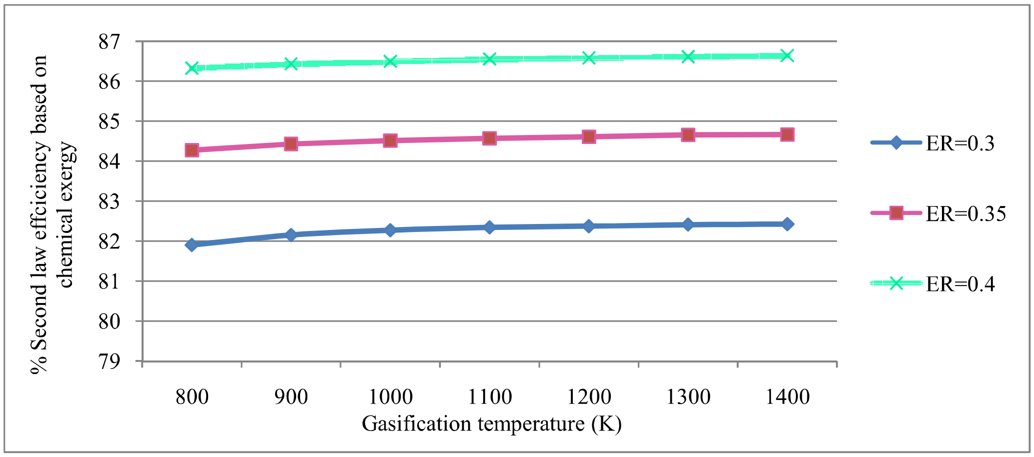

Figure 2: Effect of temperature on second law efficiency based on chemical exergies at various equivalent ratios

Figures 3, 4 and 5 compare the efficiency values based on Lower heating values, chemical exergy and the one which is based on chemical and physical exergy respectively. Efficiency values based on chemical exergy are observed to be higher (highest value of 86.64% at 1400K with an equivalence ratio of 0.4) than the efficiencies based on chemical and physical exergy (higher value of 79.94% at 900K with equivalence ratio of 0.4) and efficiencies base based on heating values (higher value of 64.03% at 1400K equivalence ratio of 0.3). Although efficiencies based chemical exergy and the ones based on heating value of the material increase with an increase in temperature, the case is different for efficiencies based on chemical and physical exergy, where the increase is up to a temperature of 900K, and then a slight decrease occurs. This is because some of exergy is present in the form of physical exergy, used to heat the reactants. This represents exergy losses (irreversibilities) of which can be minimized by altering the ratio of physical and chemical exergy in the product gas.

The values of irreversibilities deducted from the values of efficiencies. It is noted that the values of irreversibilities reduce as the equivalence ratio increases in the case related to chemical exergy, values lies between 13.68% and 13.36% as a temperature is increased. For the case related to chemical and physical exergy, the irreversibility values also tend to decrease with an increase of temperature of up to 900K to a value of 20.06% and from there, a small increment is observed.

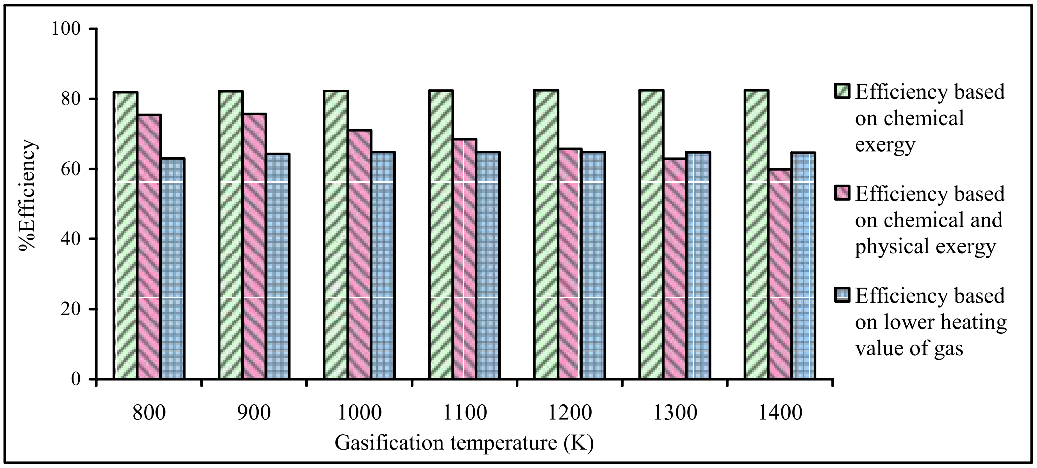

Figure 3: Effect of temperature on efficiencies at an equivalent ratio of 0.3

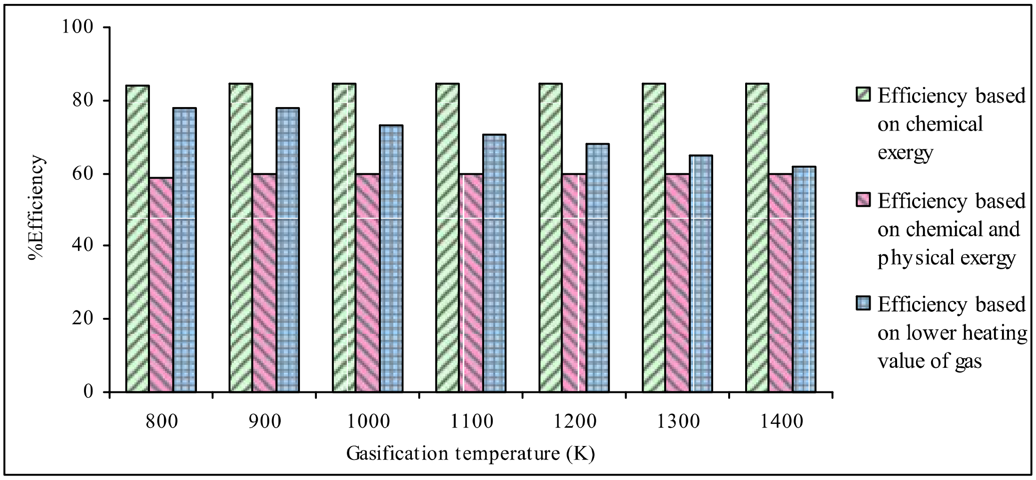

Figure 4: Effect of temperature on efficiencies at an equivalent ratio of 0.35

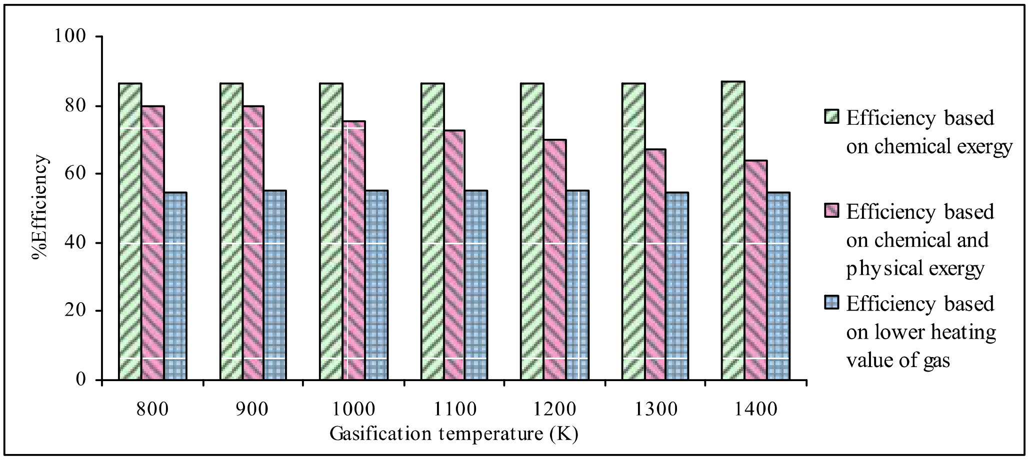

Figure 5: Effect of temperature on efficiencies at an equivalent ratio of 0.4