EXERGY ANALYSIS OF HIGH TEMPERATURE BIOMASS GASIFICATION

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Abstract: Biomass gasification is considered as one of the most promising thermo-chemical technologies but the gasifier unit renders itself to internal inefficiencies. This paper addresses the gasifier performance analysis using the exergy analysis modeling which utilizes both the first and second laws of thermodynamics. An exergy model incorporating a chemical equilibrium model is developed. Gasification is envisaged to be carried out at atmospheric pressure of 1 bar with the typical biomass feed, sugarcane bagasse, represented by the formula $CH_{1.42} O_{0.65} N_{0.0026}$ at the temperature range of 800-1400K. In the model, the exergy contained in the biomass was converted into chemical exergy of the product gas, physical exergy, the rest was the unavailable energy due to process of irreversibilities (losses). The model evaluated the product gas molar concentrations and efficiency. The results from the model showed that the mole concentration of H_2 increased from 9.8% to 23.7% and the formation of CO_2 ranges from 5.6% to 12.1%. While this is the case for H_2 and CO_2, CO mole concentration is reduced from 26.9% to 17.4%. The maximum efficiencies value obtained based on chemical energy and physical exergy was lower than the efficiency value based on chemical exergy (84.64% vs. 76.94%). This is because the sensible or physical heat (used for drying biomass) is less beneficial for the efficiency based on total exergy. Hence, the gasification efficiency can be improved by increasing the temperature with the change of equivalence ratio (ER) and with the addition of heat in the process.

Keywords: Biomass; Efficiency; Equilibrium Model; Exergy Analysis; High Temperature Gasification

INTRODUCTION

The efficient method for converting biomass materials into useful gas energy source is via the gasification process. When compared to conventional combustion technologies, biomass gasification can offer a greater reduction potential on the formation of CO_2 and NO_x compounds [1]. Hence, thermo gasification products can offer relatively higher equipment efficiency when used in electricity generation compared to direct combustion application for the same [2]. 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 [3].

The development of efficient technologies for biomass gasification is governed by tools deployed to achieve the maximum energy available from the system. For a given set of operating conditions, syngas production from biomass gasification can be improved through optimization of the operating parameters and efficiencies. This approach can be done by the application of the thermodynamic analysis concept of exergy. The concept is based on

the second law of thermodynamics which represents another step in the plant systems analysis in addition to those of mass and the enthalpy balances. The aim of the exergy analysis therefore is to identify the magnitudes of exergy losses in order to improve the existing systems, processes or components, or to develop new processes or systems [4] as reported by Ganapathy [5]. The analysis allows one to quantify the loss and efficiency in a process due to the loss in energy quality.

When evaluating exergy in the absence of nuclear, magnetic, electrical, and surface tension effects, the total exergy of a system (ε) can be divided into four components: physical exergy, kinetic exergy, potential exergy and chemical exergy, each having two parts which are; the thermo-mechanical contribution and the chemical contribution. Thermo-mechanical exergy, or physical exergy, is the maximum amount of work that can be achieved by a state of a substance as it comes into thermal and mechanical equilibrium with the environment. Neglecting kinetic and potential energy contributions, the molar specific physical exergy of a species at temperature T and pressure p are defined by Eq. 1:

$$\varepsilon_{ph} = \left(h - h_o\right) - T_0 \cdot \left(s - s_o\right) \qquad (1)$$

where h and s are the molar specific enthalpy and molar specific entropy, and the subscript "o" denotes the state of the environment.

The concept of standard chemical exergy was introduced by Szargut and Styrylska [6] so that chemical exergy values could be compiled and used for multiple exergy analyses. The standard chemical exergy is computed at standard temperature and pressure (298.15 K and 101.325 kPa) as the environment conditions. The chemical exergy of a gas stream of multiple components can be computed by summation of their partial chemical exergies, as given in Eq. 2:

$$\varepsilon_{ch} = \sum_i \chi_i \varepsilon_{ch,i} + R_o T_o \sum_i \chi_i \ln \chi_i \qquad (2)$$

where χ_i and $\varepsilon_{ch,i}$ are the mole fraction and chemical exergy of individual gas component i respectively, Ro is the universal gas constant and To is the standard temperature.
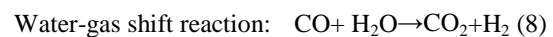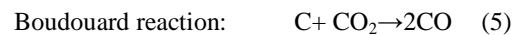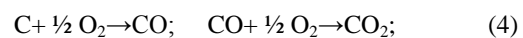
For a fuel containing carbon, hydrogen and oxygen, at a fixed pressure, the evaluation the exergic efficiency of the gasifier system is determined by varying its temperature and equivalence ratio (ER), where for this work a high temperatures gasification regime of 800K – 1400K and equivalence ratio (ER) between 0.3 and 0.4, shall be utilized. Sugar bagasse biomass shall be used in the analysis of this work

since the global drive towards renewable energy has recognized it as a large second generation bio-energy resource and readily-available fuel which could be utilized to generate electricity. Sugar plant is one of the major agricultural products worldwide, with approximately 1500 million tonnes produced annually. Each tonne of cane is estimated to produce about 130 kg of dry bagasse, giving a world supply of 200 million tonnes per annum. The specific energy of this biomass material is about 19 GJ t^{-1}..This represents a potential global energy source of 3.8 x 10^9 Gigajoules. If converted to electricity at an efficiency of 20%, it would supply 200 x 10^6 MWh per annum, meeting the total electrical power needs of a country like Australia [7].

METHODOLOGY

Fig. 1 shows a schematic representation for high temperature air gasification arrangement. The gasification process units for analysing the gasifier efficiency comprises of the recuperator, gasifier unit alongside with the inlet of the gas from the gasifier to the cyclone. 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 [8, 9].

The gasifier unit is one of the least efficient unit operations in the whole biomass to energy technology chain to less than 30% [10] and an analysis of the efficiency of the gasifier alone can substantially contribute to the efficient improvement. Hence [11] described the important chemical reactions in the gasifier as Oxidation, Boudouard, Water gas, Methanation, Water-gas shift, and Methane reforming as referred in Eq. 3 to Eq. 9:

Oxidation reaction: $C + O_2 \rightarrow CO_2$;   (3)

$C + \frac{1}{2} O_2 \rightarrow CO$; $CO + \frac{1}{2} O_2 \rightarrow CO_2$;   (4)

Boudouard reaction: $C + CO_2 \rightarrow 2CO$ (5)

Water gas reaction: $C + H_2O \rightarrow CO + H_2$ (6)

Methanation reaction: $C + 2H_2 \rightarrow CH_4$ (7)

Water-gas shift reaction: $CO + H_2O \rightarrow CO_2 + H_2$ (8)

Methane reforming reaction:

$CH_4 + H_2O \rightarrow CO + 3H_2$ (9)

In these schemes, the assumptions made are: (i) The chemical equilibrium between gasifier products is reached and evaluated at atmospheric pressure (1 bar); (ii) Ashes are not considered (Small amount 1%); (iii) Heat losses are neglected (Adiabaticity) and (iv) there are no chars with the exit gasifier products.
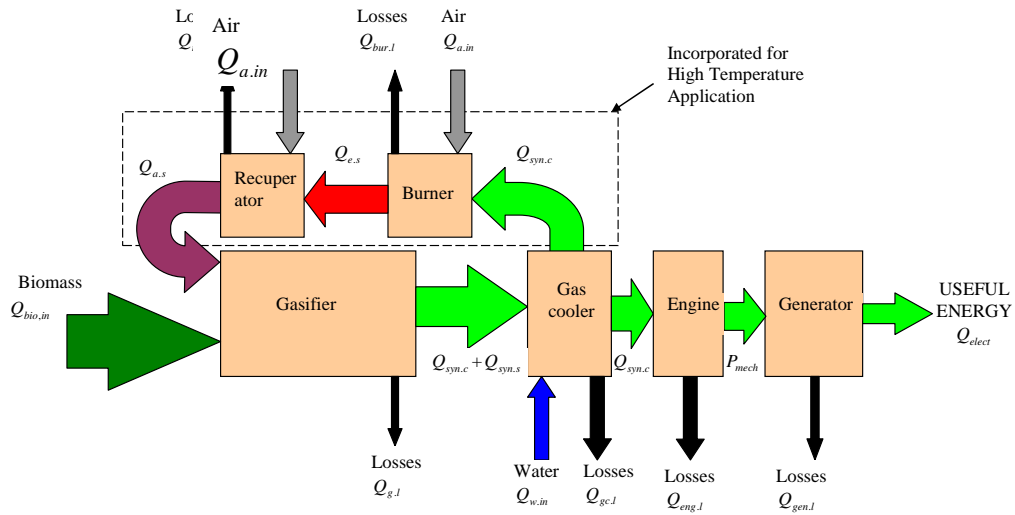
Figure 1: Conceptual diagram of energy balance in high temperature air gasification system

Table 1: Comparison between this model and Gautam model results for biomass material at a temperature of 800°C (1073K)

Gas Specie	This Model	Gautam Model	Deviation between the two models
Hydrogen (%)	15.7	16.8	0.065
Carbon monoxide (%)	22.03	22.5	0.0208
Carbon dioxide (%)	8.7	9.2	0.054

Table 2: Expermental values for Sugarcane Bagasse

Biomass type	Ultimate analysis (%), dry basis				Proximate analysis (%), dry basis				High Heating Value
	C	H	O	N	Moisture	Volatile matter	Fixed carbon	Ash	HHV (kJ/kg)
Sugarcane Bagasse	48.10	5.90	42.40	0.15	9.00	80.50	16.20	3.30	17,330

Realizing that the biomass enters the gasifier at ambient conditions, only chemical exergy is available in biomass, air do not react and enters the gasifier at high enthalpies, only physical exergy exist, the leaving gas from the gasifier shall have the chemical and physical exergy, therefore the exergy efficiency shall result in the expression given in Eq. (10):

$$\eta_{ex} = \frac{\varepsilon_{product}}{\varepsilon_{inputs}} = \frac{\varepsilon_{ch,gas} + \varepsilon_{ph,gas}}{\varepsilon_{ch,biomass} + \varepsilon_{ph,med}}$$

(10)

From which:

$$\varepsilon_{ch,gas} = \sum_i \chi_i \varepsilon_{ch,i} + R_o T_o \sum_i \chi_i \ln \chi_i \quad (11)$$

$$\varepsilon_{ph,gas} = (h_R - h_o) - T_o(s_R - s_o) \quad (12)$$

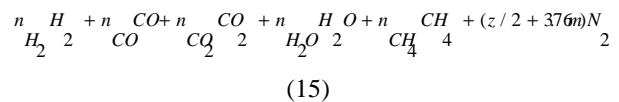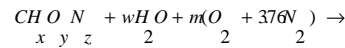$$\varepsilon_{ph,med} = (h_H - h_o) - T_o(s_H - s_o) \quad (13)$$

$$\varepsilon_{ch,biomass} = \beta LHV_{biomass} \quad (14)$$

$$\beta = \frac{1.044 + 0.0160Z_H - 0.3493Z_O[1 + 0.0531Z_H] + 0.0493Z_N}{1 - 0.4124Z_O}$$

(15)

where: $\varepsilon_{product}$ is exergy of the product gas ($\varepsilon_{ch,gas}$ and $\varepsilon_{ph,gas}$) and ε_{input} is the exergy of the input which is biomass $\varepsilon_{ch,biomass}$ and preheated air ($\varepsilon_{ph,med}$). χ_i and $\varepsilon_{ch,i}$ are the mole fraction and chemical exergy of individual gas component i respectively, Ro is the universal gas constant (8.314kJ/kmolK) and To 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 [12]. 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 To and pressure (1 bar). The subscript R stands for exit gas from the gasifier and H is for the hot gas from the recuperator. These values are from Stull and Prophet (1971) [13] and the JANAF Thermodynamic Tables as reported by Strehlow [14]. $LHV_{biomass}$ is the lower heating value of biomass, β is a factor dependent upon mass fraction of oxygen, carbon, hydrogen and nitrogen in the feedstock [15]. Z_H is H/C, Z_O is O/C, and Z_N is N/C and H/C, O/C and N/C represent atomic ratios of fuel components H, C, O and N in the solid fuel.

The model pre-assumes the biomass for analysis to be represented by a general biomass formula, $CH_xO_yN_z$, 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. On the

understanding that the biomass feedstock would imperatively constitute moisture of varying level which shall be involved in the gasification process in accordance to the following procedure:

$$CH_xO_yN_z + wH_2O + m(O_2 + 3.76N_2) \rightarrow$$

$$n_{H_2}H_2 + n_{CO}CO + n_{CO_2}CO_2 + n_{H_2O}H_2O + n_{CH_4}CH_4 + (z/2 + 3.76m)N_2$$

(15)

In order to obtain the amount of moisture per kmol of feedstock, w, and ash content in the biomass, the output of proximate analysis shall be necessary. On the other hand, the determination of x, y and z depend on the concentrations of the elements C, H, O and N in the biomass. These are obtained from the biomass ultimate analysis. This pre-analysis is necessary for the determination of the products of gasification; nCO, nCO_2, nCH_4, nN_2 and nH_2 which can finally be determined by performing mass/mole balance from the above Eq. (16) in addition to methanation Eq. 9 and water -gas shift Eq. 10. This is done by assuming the thermodynamic equilibrium where the equilibrium constants for all chemical reactions of ideal gases at 1 atm can be obtained. The Matlab equation solver program and Maple programs were used to calculate the formulated model equations to obtain the gaseous concentrations and exergy efficiency values.

MODEL VALIDATION, RESULTS AND DISCUSSIONS

Model Validation

The model validation on the effect of temperature on gas composition at an equivalence ratio of 0.4 is by the model data reported by Gautam [2] at a temperature of 800°C (1073K) for the material with the following composition: Carbon 50%, Hydrogen 6%; Oxygen 44%. The comparison between the model results for the case is in Table.

From the above Table, it is observed that the gas composition values for this model and the Gautam model values varies to a maximum of less than 7%. The concentration values for carbon monoxide and hydrogen for this model are close to those from the Gautam model and have small deviation of 0.0208 and 0.065 respectively. The carbon dioxide concentration value for this model is low by 0.054 which is mostly desirable.
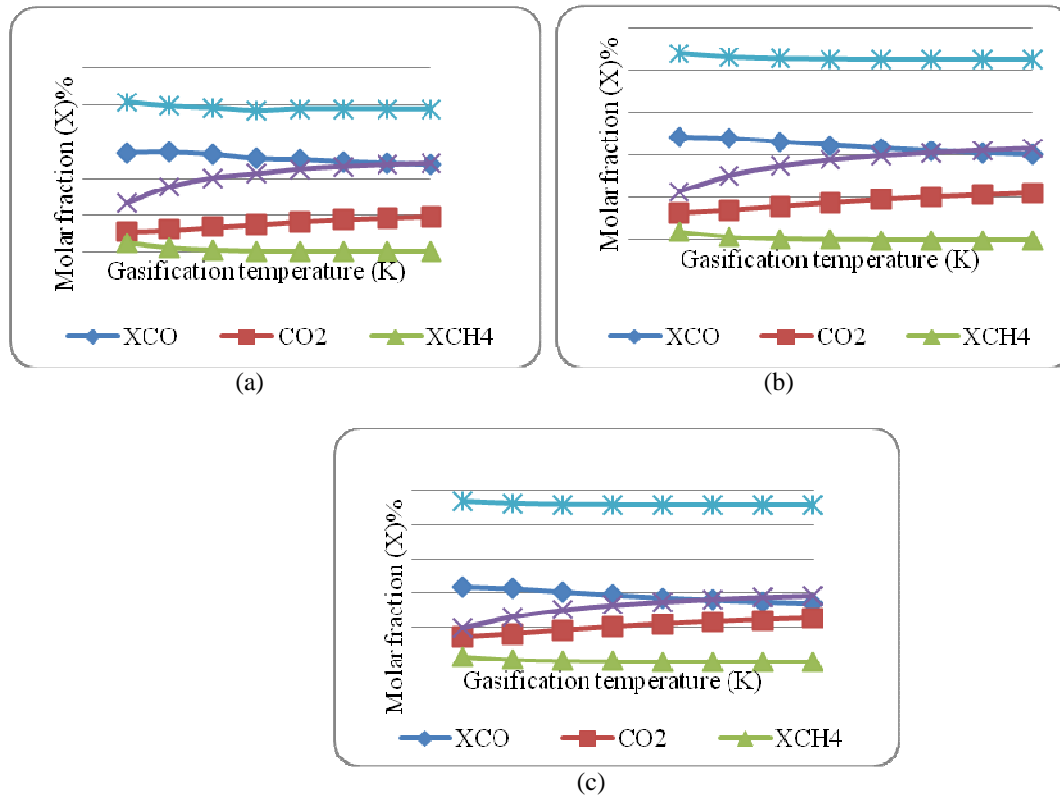
Figure 2: Effect of temperature on molar composition for CO, CH_4, CO_2 and H_2 gases from sugar bagasse at an equivalent ratio (ER) of (a) 0.3(b) 0.35 (c) 0.4

Results and Discussions

The elemental analysis and calorific value

The sugar baggase biomass derived from ultimate and proximate analysis presented in Table 2 has a formula $CH_{1.42} O_{0.65} N_{0.0026}$. The elemental analysis of the sugar baggase is characterized by high oxygen content of 42.4%, which grossly affect its calorific value fuel [15]. The sample Carbon content was 48.1% and hydrogen to 5.9 %, while the concentration of nitrogen was marginal at 0.15 %. The model results for lower heating value of the biomass was 22,368kJ/kg kJ /kg. The experimentally determined value was 23% lower at 17,330 kJ/kg. This variation is because the model assumes steady state condition which is not the case in practice. In addition the model does not include the endothermic reactions involving sulphur, nitrogen and chlorine. The ash content value was low (less than 10%) and observed to be almost close the literature reviewed values [16].

Effect of temperature and equivalence ratio on molar compositions for CO, CH_4, CO_2 and H_2

Carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2) and methane (CH_4) are major gases produced from biomass gasification. The molar composition of CO, CH_4, CO_2 and H_2 the in syngas from the biomass gasification process was calculated via equilibrium modeling.

(a)

(b)

(c)
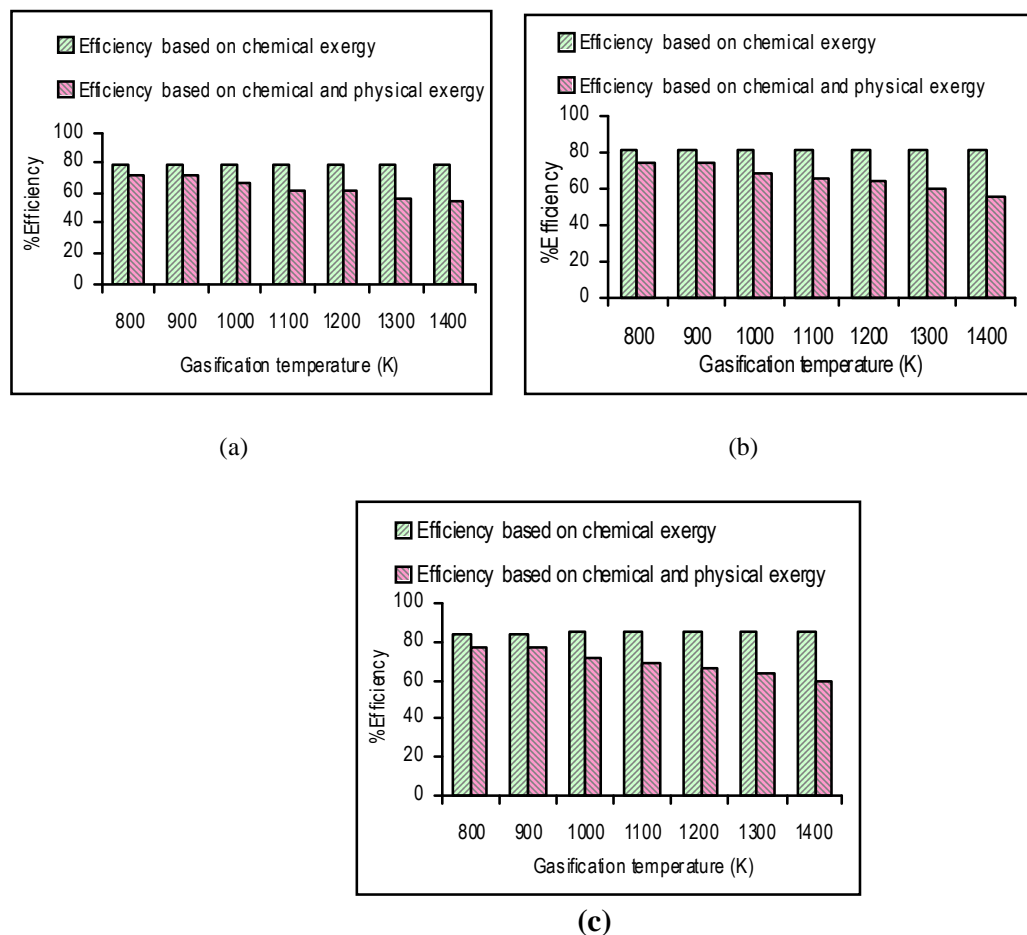
Figure 3: Effect of temperature on efficiencies at equivalence ratios of: (a) 0.3; (b) 0.35; and (c) 0.4 for sugar bagasse

These syngas composition are computed from running the model at a temperature between 800K and 1400K at an interval of 100K at a constant equivalent ratio. Then the equivalence ratio for all of these simulations is varied in the values between 0.27 and 0.43, and the selected values to run the model are 0.3, 0.35 and 0.4 for the sugar baggase. In Fig. 2 (a) to 2(c), it is noted that the higher value for H_2 and CO_2 molar concentrations are observed at a higher temperature of 1400K and for CO is at a lower temperature of 800K. The concentration of H_2 increased from 9.8% to 23.7% and the formation of CO_2 ranges from 5.6% to 12.1%. While this is the case for and CO_2, CO concentration is reduced from 26.9% to 17.4%. Decrease trend in the formation of CO is exhibited during gasification although there is high concentration of it in each syngas product formation batch. The reduction in CO production in

this study may have been due to the comparatively lower temperature than 850– 900°C (1123-1173K) for the Boudouard reaction to predominate. A similar trend of results is pronounced by [17]. In this study CH_4 concentration reduces as the temperature is increased. The CH_4 molar concentration values for ranges from 2.5% to 0.016%. However, the equilibrium modeling prediction was always less than 0.15% for biomass at a temperature of more than 1050K. Similar observations were reported in other thermodynamic modeling studies by [11, 19]. CH_4 predictions from thermodynamic equilibrium modeling are significantly lower than those encountered in practical gasification tests. Typical CH_4 concentration in downdraft gasifiers is 2-5 % [2].

Effect of temperature and equivalence ratio on Second Law Efficiency based on chemical exergy; and chemical physical exergy

Fig. 3(a) to 3(c) compare the efficiency values based on chemical exergy and the one which is based on chemical and physical exergy. Efficiency values based on chemical exergy are observed to be higher (highest value of 84.6% at 1400K with an equivalence ratio of 0.4) than the efficiencies based on chemical and physical exergy (higher value of 76.9% at 900K with equivalence ratio of 0.4). Although efficiencies based chemical exergy 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 the combustibles in the product gas are minimized because some of the exergy which is present in the form of physical exergy, used to heat the reactants. This represents exergy losses (irreversibilities) and can be minimized by altering the ratio of physical and chemical exergy.

CONCLUSION

Exergy analysis was applied to high temperature gasification process for obtaining the gasifier efficiency. The exergy content of the process streams was calculated using Matlab and Maple programs, incorporating mole concentrations of gasues product, chemical exergy and physical exergy efficiency values of a sugar bagasse samples. The results indicates that, the concentration of H_2 increased from 9.8% to 23.7% and the formation of CO_2 ranges from 5.6% to 12.1%. While this is the case for and CO_2, CO concentration is reduced from 26.9% to 17.4%. Efficiency values based on chemical exergy are observed to be higher (highest value of 84.64% at 1400K with at an equivalence ratio of 0.4) than the efficiencies based on chemical and physical exergy (higher value of 76.94% at 900K at the same equivalence ratio of 0.4).

ACKNOWLEDGEMENT

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