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Exergy Analysis on Pyrolysis Process of Oil Palm Empty Fruit Bunch

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Abstract. Exergy analysis is useful to evaluate the effectiveness of energy conversion process. This study is aimed to evaluate the effectiveness of oil palm empty fruit bunch conversion by pyrolysis process using the exergy analysis compared to the theoretical of the cellulose pyrolysis. The effect of pyrolysis temperature was evaluated based on the amount of selected syngas produced. The results show that increasing the temperature of pyrolysis from 473 K until 723 K will increase the concentration of H₂ and CH₄, but it will reduce the concentration of CO. Based on exergy efficiency, the optimum composition of gases that can be produced in the pyrolysis process of 1 mol cellulose are 3 mol of H₂, 5 mol of CO, and 1 mol of CH₄ at a temperature of 723K. The maximum amount of exergy efficiency is 96.33% in the reaction 2. Based on Gibbs free energy, the maximum value of hydrogen will be produced start at temperature 628K.

1. Introduction

Hydrogen is a chemical element that has great potential as an energy carrier in the future. Hydrogen has the highest energy content compared to other common fuels (about three times more than gasoline). In addition to its high energy content, the source of this element is available abundantly, as in biomass. Many studies noted that hydrogen may be the only alternative fuel that can reduce the country's dependence on foreign oil while significantly reducing greenhouse gases. Chen (2008) states that fuel cell technology can be used as transportation fuel, or primary energy generation, while hydrogen is a vital fuel in the technology. Therefore, any technology to produce hydrogen efficiently with the lowest cost becomes very important and indispensable to be studied.



Biomass is a renewable energy source that can be converted to hydrogen. Thermochemical reaction, such as pyrolysis is one of the available mechanism. Specific characteristics from biomass will affect its role in producing the hydrogen. The composition of the products can be controlled using process control. Normally, the fraction of hydrogen produced by pyrolysis method is very small compared to other gases. A technology to enrich H₂ composition through this pyrolysis process is necessary. This technology can be developed through a thermodynamic analysis of the process. In general, the products produced in a thermochemical process can be predicted through thermodynamic approaches and simulations.

Energy balance is an important concept to analyse the performance of a system. This concept is based on the first law of thermodynamic which is often called as the law of energy conservation. The first law of thermodynamic states that energy cannot be created or destroyed. Therefore, energy balance in a system must be maintained. When the system changes from the initial states to a equilibrium state (final state), the system can absorb or release energy into its environment.

The equilibrium state is a situation where there is no change in the system, or between the system and the environment. At equilibrium, temperature and pressure are uniform throughout the system. In practice, the total energy content in a situation (beginning or end) is very difficult to determine, so the thermodynamic approach is often based on energy difference between the initial and final conditions (Burghardt, 1993).

The second law of thermodynamic states that besides having quantity, energy also has quality. A real process will take place in the direction of decreasing the energy quality. Although there is no loss of energy quantity, the energy quality always decrease during the process. The amount of this energy quality is called exergy. Energy and exergy analysis is useful to evaluate the effectiveness of energy conversion process.

2. Methodology

This study is aimed to evaluate the effectiveness of oil palm empty fruit bunch conversion by pyrolysis process using the exergy analysis compared to the theoretical of the cellulose pyrolysis. An exergy analysis must consider input and output of the system. In the pyrolysis system, the input that get into its system is cellulose, while the outputs are gas, bio-oil, and biochar products. But in this study, the analysis is focused only on syngas product. In the system, there will always exergy loss, but in this study the value will be ignored.

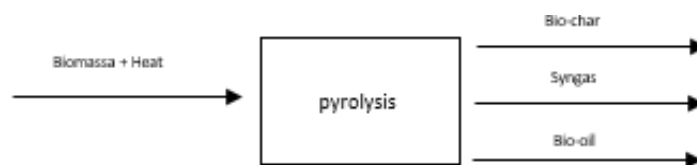


Figure 1. Scheme of biomass pyrolysis system

The composition of cellulose pyrolysis products is calculated based on the Gibbs free energy of several possible reactions that can occur during the cellulose pyrolysis process. The reaction with the smallest amount of free energy Gibbs is a reaction that will occur during the process. The composition from that reaction is the maximum gas composition from cellulose pyrolysis. The composition produced for each reaction that may occur during the process will be analyzed based on the exergy efficiency of the syngas. The reaction with the greatest exergy efficiency value is the best reaction. The composition will be compared to the experiment data. The experiment data in this study were carried out using secondary data from [1]. The experiment data used palm oil empty fruit bunch (EFB) as feedstock. EFB contains more

cellulose than hemicellulose and lignin. Proximate and ultimate analysis, lignocellulose analysis, and pyrolysis product of palm oil empty fruit bunch shown at table 1, 2, and 3, respectively.

Table 1. Proximate and ultimate analysis *

Analysis	Value
Proximate	
Water content _{db} (%)	1.7
Volatile matter (%)	75.7
Ash (%)	7.27
Fixed Carbon (%)	17.44
Ultimate	
C (%)	60.4
H (%)	7.6
O (%)	29.8
N (%)	2.2
S (%)	0
HHV (MJ/kg)	18.74

Table 2. Lignocellulose analysis of palm oil empty fruit bunch [1]

Component	EFB (%)
Cellulose	56.05
Hemicellulose	17.63
Lignin	5.97
Other components	20.35

Table 3. Pyrolysis product of palm oil empty fruit bunch [1]

Temperature (K)	Initial mass (g)	Solid product (g)	Bio-oil (g)	Gas (g)
473	152,9	60,13	10,92	81,85
523	152,9	65,35	11,59	75,96
573	152,9	54,49	16,51	81,9
623	152,9	62,94	14,53	75,43
673	152,9	50,54	23,8	78,56
723	152,9	50,39	14,15	88,36

The Gibbs free energy value states the spontaneity of a reaction process where the smaller the Gibbs energy value, the more spontaneous the reaction will be. However, to ensure that the reaction can continue, the Gibbs free energy value must exceed its equilibrium limit or be less than 0. In equilibrium, the total Gibbs free energy of a gas emission can be stated as follows:

$$\Delta G = \Delta H_{f,i,T} - T\Delta S \quad (1)$$

where $H_{f,i,T}$ is enthalpy formation at T, S is entropy and G is gibbs free energy value.

2.1 Exergy analysis

According to Wang et al (2016), exergy does not obey conservation law due to the unavoidable irreversibility of reaction processes. Exergy balance equation can be established with these assumption : pyrolysis is a control volume unit, input exergy is from biomass, output exergy is from product gas, bio-oil, and bio-char, and the irreversibility (internal exergy loss) is in the lost part.

$$Ex_{biomass} = Ex_{gas,T} + Ex_{bio-oil,T} + Ex_{biochar,T} + Ex_{loss,T} \quad (2)$$

This study only focus on the exergy efficiency of syngas on biomass exergy so that the amount of bio-oil exergy, biochar exergy, and exergy loss will be temporarily ignored. The total exergy value equals to sum of all kinds of exergy value [3]

$$E_x = E_x^{po} + E_x^{ki} + E_x^{ph} + E_x^{ch} \quad (3)$$

where E_x is energy total while E_x^{ki} , E_x^{po} , E_x^{ch} , and E_x^{ph} are kinetic exergy, potential exergy, chemical exergy, and physical exergy, respectively. The potential exergy and kinetic exergy values are slight enough so that in this study those values can be neglected. Equation (3) can be equation (4).

$$E_x = E_x^{ph} + E_x^{ch} \quad (4)$$

Physical exergy of pyrolysis gas :

$$Ex^{ph} = m ((h - h_0) - T_0(s - s_0)) \quad (5)$$

where m is mass value (kg), h is enthalpy (MJ/kg), h_0 is standard enthalpy of gases at T_0 (MJ/kg), s_0 is standard entropy of gases at T_0 (MJ/kg.K), and T_0 is standard temperature (298K). The standard enthalpy, and entropy of some gases are shown at table 3.

The specific enthalpy and entropy of gases at T can be determined with equation (6) until equation (11)

$$h = h_0 + \int_{T_0}^T C_p dT \quad (6)$$

$$h - h_0 = \int_{T_0}^T C_p dT \quad (7)$$

$$\int_{T_0}^T C_p dT = aT + \frac{b}{2}T^2 + \frac{c}{3}T^3 + \frac{d}{4}T^4 \quad (8)$$

$$s = s_0 + \int_{T_0}^T \frac{C_p}{T} dT \quad (9)$$

$$s - s_0 = \int_{T_0}^T \frac{C_p}{T} dT \quad (10)$$

$$\int_{T_0}^T \frac{\Delta C_p}{T} dT = a \ln T + bT + \frac{1}{2}cT^2 + \frac{1}{3}dT^3 \quad (11)$$

where C_p is specific enthalpy of each component, a until d values are coefficient of constant pressure specific heat capacity of some gases, which is shown at table 5.

Table 4. Standard enthalpy and entropy [2]

Gas	h _o (MJ/kg)	S _o (MJ/kg.K)
H ₂	4.23400	0.00464
CO	0.30961	0.00706
CO ₂	0.21282	0.00763
CH ₄	0.00000	0.00665
C	0.00000	0.00020
H ₂ O	0.55022	0.01048

Table 5. Coefficients of constant pressure specific heat capacity of some gases [2]

Gas	A	b (10 ²)	c (10 ⁵)	d (10 ⁹)	Range (K)
H ₂	29.11	-0.1916	0.4003	-0.8704	273-1800
CO	28.16	0.1675	0.5327	-2.222	273-1800
CO ₂	22.26	5.981	-3.501	7.469	273-1800
CH ₄	19.89	5.024	1.269	-11.01	273-1800
H ₂ O	32.22	0.192	1.055	-3.593	273-1800

Chemical exergy of pyrolysis gas :

$$Ex^{ch} = me^{ch} \quad (12)$$

where m is mass of gas (kg), and e^{ch} is standard chemical exergy of gas (MJ/kg) which is shown at table 6.

Table 6. Standard chemical exergy of some gases [3]

Gas	e^{ch} (MJ/kg)
CO	275.1
H ₂	236.1
C	410
CH ₄	831.65
H ₂ O	1.3
CO ₂	19.87

HHV value and exergy of biomass can be determined with equation (13) and (14), respectively :

$$e_{DB}^{CH} = 1812.5 + 295.606C + 587.354H + 17.506O + 17.735N + 95.615S - 31.8A \quad (13)$$

$$HHV = -1.3675 + 0.3137C + 0.7009H + 0.0318(100 - C - H - A) \quad (14)$$

where $Ex_{biomass}$ is chemical exergy of biomass in dry base (kJ/kg) and HHV is its high heating value (MJ/kg). H, C, O, and N (%) are the value of ultimate analysis of palm oil empty fruit bunch [9].

Exergy efficiency of cellulose gas product can be determined with equation (15). The gas measured in the secondary data used are only CO, H₂, and CH₄ so that the other gases are ignored. So, equation (15) can be equation (16)

$$\psi_{gas,T} = \frac{Ex_{CO,T} + Ex_{H_2} + Ex_{CH_4} + Ex_{H_2O} + Ex_{CO_2}}{Ex_{biomass}} \quad (15)$$

$$\psi_{gas,T} = \frac{Ex_{CO,T} + Ex_{H_2} + Ex_{CH_4}}{Ex_{biomass}} \quad (16)$$

3. Result And Discussion

3.1 Composition of maximum syngas produced from cellulose pyrolysis

Table 7 shows the product result of each reaction that may occur during the process of cellulose pyrolysis. The reactions are based on the stoichiometric equation for pyrolysis of 1 mol cellulose. Based on the table 6, the maximum amount that can be produced for each CO, H₂, CH₄, H₂O, CO₂, and C are 5 mol, 2 mol, 2 mol, 1 mol, and 3 mol respectively. The distribution of each products is different for each possible reaction. This study expect maximum hydrogen so, the reaction that is expected to occur should be reaction 1 with the moles of H₂, CO, and C are 5 moles, 5 moles, and 1 mol in a row.

Table 7. Maximum pyrolysis product of 1 mol cellulose

	Cellulose	CO (mol)	H ₂ (mol)	CH ₄ (mol)	H ₂ O (mol)	CO ₂ (mol)	C (mol)
Reaction 1	C ₆ H ₁₀ O ₅ → 5CO + 5H ₂ + C	5	5	0	0	0	1
Reaction 2	C ₆ H ₁₀ O ₅ → 5CO + CH ₄ + 3H ₂	5	3	1	0	0	0
Reaction 3	C ₆ H ₁₀ O ₅ → 4CO + CH ₄ + C + 2H ₂ + H ₂ O	4	2	1	1	0	1
Reaction 4	C ₆ H ₁₀ O ₅ → 3CO + CO ₂ + 2CH ₄ + H ₂	3	1	2	0	1	0
Reaction 5	C ₆ H ₁₀ O ₅ → 3CO + CH ₄ + 2C + H ₂ + 2H ₂ O	3	1	1	2	0	2
Reaction 6	C ₆ H ₁₀ O ₅ → 2CO + CO ₂ + 2CH ₄ + C + H ₂ O	2	0	2	1	1	1
Reaction 7	C ₆ H ₁₀ O ₅ → 3CO + 3H ₂ + 3C + 2H ₂ O	3	3	0	2	0	3
Reaction 8	C ₆ H ₁₀ O ₅ → 2CO + CO ₂ + 3C + 4H ₂ + H ₂ O	2	4	0	1	1	3

The simulation of each reaction based on the Gibbs free energy value has been conducted at 298 – 950 K. Figure 2 shows the effect of the temperature changes on the Gibbs free energy value of the cellulose pyrolysis process. At 298 -668 K, reaction 6 is the reaction with the smallest Gibbs free energy value but at 668-950 K, the reaction with the smallest Gibbs energy change to reaction 8. Maximum product produced from reaction 8 are 2 mol CO, 1 mol CO₂, 3 mol C, 4 mol H₂, and 1 mol H₂O. It means that based on the Gibbs free energy value,

the maximum amount of hydrogen reaches maximum at 4 moles and start at 668 K for 1 mol of cellulose.

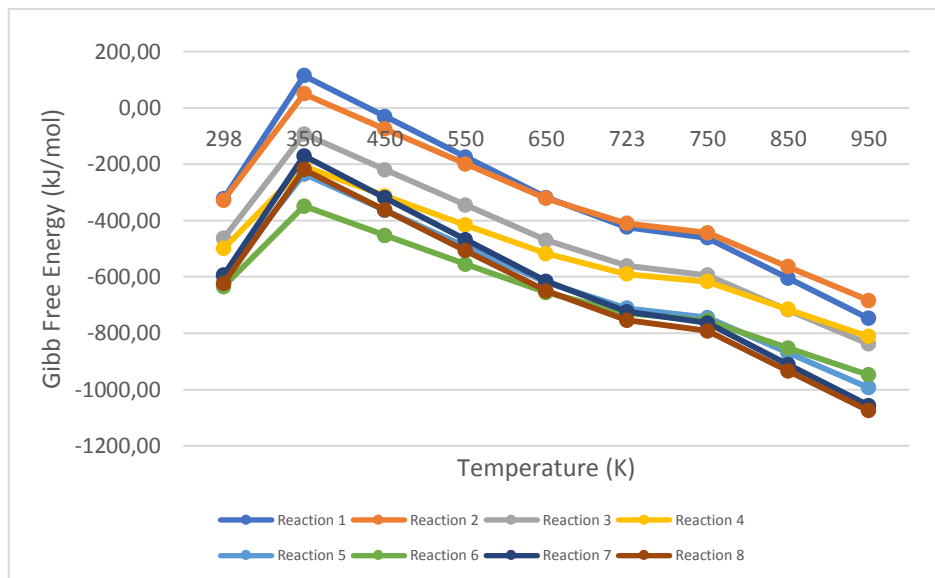


Figure 2. Gibbs free energy of cellulose pyrolysis

Table 8. Gas product of palm oil empty fruit bunch pyrolysis

Temperature (K)	CO (mol)	H ₂ (mol)	CH ₄ (mol)
473	2.805	0.042	0.201
523	2.101	0.648	0.990
573	2.130	0.929	1.274
623	2.236	0.474	0.742
673	1.622	2.155	1.801
723	1.731	2.332	2.202

Table 8 shows the gas product result of palm oil empty fruit bunch pyrolysis that has been conducted by [1] at 473 – 723 K. The result shows that the temperature will increase the amount of CH₄ and H₂. It is occurred because tar decomposes into CH₄ and H₂ at high temperature. This result is consistent with the result from Sukiran et al (2014) where increase the temperature in pyrolysis process will increase the amount of CH₄ and H₂ concentrations. As for CO, the concentration decreases with increase the temperature. This is due to characteristic of the CO that will more be released in the decomposition of the hemicellulose component. The cellulose component decomposes at low temperature.

At temperature 723 K, gas composition produced from 56.05% cellulose of palm oil empty fruit bunch are 1.731 mol of CO, 2.332 mol of H₂, and 2.332 mol of CH₄. Those amounts are still smaller than the simulation result. It shows that the pyrolysis process from [1] is still not optimal.

3.2 Maximum hydrogen from pyrolysis cellulose based on exergy analysis

Table 9 shows the exergy of each gas product can be produced from each reaction that may occur during the pyrolysis process of 1 mol of cellulose at 723K compared to the gas product of oil palm empty fruit bunch from experiment data. The result shows that reaction 8 with the maximum hydrogen produces the smallest amount of gas product exergy, which is 9.6412 MJ/kg. It means that the gas composition of reaction 8 is actually not optimum to be produced in the pyrolysis process compared to the composition of other possible reactions.

Table 9. Exergy total of syngas product of 1 mol cellulose pyrolysis at 723 K

	Cellulose	Exergy (MJ/kg)					Total
		CO	H ₂	CH ₄	H ₂ O	CO ₂	
Reaction 1	$C_6H_{10}O_5 \rightarrow 5CO + 5H_2 + C$	8.6417	7.4319	0.0000	0.0000	0.0000	16.0736
Reaction 2	$C_6H_{10}O_5 \rightarrow 5CO + CH_4 + 3H_2$	8.6417	4.4591	5.1834	0.0000	0.0000	18.2842
Reaction 3	$C_6H_{10}O_5 \rightarrow 4CO + CH_4 + C + 2H_2 + H_2O$	6.9134	2.9728	5.1834	0.0438	0.0000	15.1133
Reaction 4	$C_6H_{10}O_5 \rightarrow 3CO + CO_2 + 2CH_4 + H_2$	5.1850	1.4864	10.3668	0.0000	0.1682	17.2064
Reaction 5	$C_6H_{10}O_5 \rightarrow 3CO + CH_4 + 2C + H_2 + 2H_2O$	5.1850	1.4864	5.1834	0.0876	0.0000	11.9424
Reaction 6	$C_6H_{10}O_5 \rightarrow 2CO + CO_2 + 2CH_4 + C + H_2O$	3.4567	0.0000	10.3668	0.0438	0.1682	14.0355
Reaction 7	$C_6H_{10}O_5 \rightarrow 3CO + 3H_2 + 3C + 2H_2O$	5.1850	4.4591	0.0000	0.0876	0.0000	9.7318
Reaction 8	$C_6H_{10}O_5 \rightarrow 2CO + CO_2 + 3C + 4H_2 + H_2O$	3.4567	5.9455	0.0000	0.0438	0.1682	9.6142
Experiment data [1]	--> Oil palm empty fruit bunch [1]	3.1699	3.6723	12.0915	-	-	18.9337

Table 10. Exergy efficiency of syngas product of 1 mol cellulose pyrolysis at 723 K

	Cellulose	Syngas ex (MJ/kg)	Total	Ex
			input ex (MJ/kg)	Efficiency (%)
Reaction 1	$C_6H_{10}O_5 \rightarrow 5CO + 5H_2 + C$	16.0736	18.9800	84.69
Reaction 2	$C_6H_{10}O_5 \rightarrow 5CO + CH_4 + 3H_2$	18.2842	18.9800	96.33
Reaction 3	$C_6H_{10}O_5 \rightarrow 4CO + CH_4 + C + 2H_2 + H_2O$	15.1133	18.9800	79.63
Reaction 4	$C_6H_{10}O_5 \rightarrow 3CO + CO_2 + 2CH_4 + H_2$	17.2064	18.9800	90.66
Reaction 5	$C_6H_{10}O_5 \rightarrow 3CO + CH_4 + 2C + H_2 + 2H_2O$	11.9424	18.9800	62.92
Reaction 6	$C_6H_{10}O_5 \rightarrow 2CO + CO_2 + 2CH_4 + C + H_2O$	14.0355	18.9800	73.95
Reaction 7	$C_6H_{10}O_5 \rightarrow 3CO + 3H_2 + 3C + 2H_2O$	9.7318	18.9800	51.27
Reaction 8	$C_6H_{10}O_5 \rightarrow 2CO + CO_2 + 3C + 4H_2 + H_2O$	9.6142	18.9800	50.65
Experiment data	→ Oil palm empty fruit bunch [1]	18.9337	24.4600	77.41

Calculation of gas product exergy efficiency has also been done for each possible reaction and experimental data. The amount of theoretical exergy input is derived from the biomass exergy and heat needed to reach a temperature of 723K, whereas the exergy input from experiment data is only from biomass exergy. The heater input energy is not recorded during the process, so the exergy from the heater is ignored. In the experiment data, the gas components produced are only 3 main gases. Those are CO, H₂, and CH₄ gases. The result shows that the highest exergy efficiency is generated from reaction 2 which is 96.33%. The highest exergy efficiency from reaction 2 shows that 3 mol of hydrogen is the optimum amount which actually must be produced from the pyrolysis process of 1 mol of cellulose, while the other gas composition being 5 mol of CO, and 1 mol of CH₄.



Figure 3. Exergy efficiency of syngas product at 723 K

4. CONCLUSION

Increasing the temperature of pyrolysis will increase the concentration of H_2 and CH_4 , but it will reduce the concentration of CO . Based on exergy efficiency, the optimum composition of gases that can be produced in the pyrolysis process of 1 mol cellulose are 3 mol of H_2 , 5 mol of CO , and 1 mol of CH_4 at a temperature of 723K. The maximum amount of exergy efficiency is 96.33% in the reaction 2

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