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TRANSFORMING SOLID WASTES INTO HIGH QUALITY BIOENERGY PRODUCTS: ENTROPY ANALYSIS

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ABSTRACT

Although energy analysis of a pyrolysis system improves the thermal efficiency of the process, it did not account for the quality of energy used and produced from the process. This paper presents the entropy of analysis of converting solid wastes into useable bio-products during pyrolysis. The entropy balance was performed on a continuous flow pyrolysis reactor system using pine pellets as a feedstock at the pyrolysis temperature of 773 K. An interesting conclusion was drawn from the results that the pyrolysis process converted low quality and high entropy biomass into high quality and low entropy energy products char, bio-oil, and gases. The analysis concluded that the both pyrolysis and combustion were the process of low entropy production and most part of the irreversibility or positive entropy production was mainly associated with condenser unit. The high quality energy producing pyrolysis process may be included as part of the future biorefinery.

Keywords: Pyrolysis, Bioenergy, Entropy, Solid waste

NOMENCLATURE

f	shape factor
\bar{h}_c	heat of combustion (kJ/kmol)
H	enthalpy (kJ/kmol)
HHV	higher heating values (MJ/kg)
k	thermal conductivity (W/m.K)
L	length of pyrolysis zone (m)
\dot{m}	mass flow rate (g/min)
\dot{Q}	rate of energy flow (kJ/min)
r	radius (m)
s	specific entropy (kJ/kmol.K)
\dot{s}	rate of entropy flow (kJ/min.K)
Δs	rate of entropy change (kJ/min.K)
T	temperature, K

Subscripts and superscripts

a ambient

ave	average
b	at the insulation material
bufferzone	in buffer zone
Biomass	due to biomass
Biooil	due to biooil
Char	due to char
Chemical	unbalanced part attributed to reaction
Condenser	in condenser unit
Conduction	due to conduction
exch	exchange
f	reactor wall at the outlet
gen	generated
genreactor	generated in pyrolysis reactor system
gencondenser	generated in condenser system
Heater	from heater through reactor wall
i	at the i^{th} zone
in	inflow
L	reactor wall at the inlet
Loss	loss in buffer zone
Nitrogenin	inflow of the nitrogen
Nitrogenout	outflow of the nitrogen
ow	outer wall
out	out flow
Pyrolysis	from heater through reactor wall
Radiation	due to radiation
Reactor	in pyrolysis reactor
samplei	sample (mass) in i^{th} zone
sample contacti	sample (T) in zone i

INTRODUCTION

The entropy analysis of biological systems validated the second law of thermodynamics [1] and will add a new dimension to bio-energy technology, providing a common platform to compare various biomass sources and bio-energy conversion technologies e.g. pyrolysis, gasification, densification and combustion etc. Although scientific theories postulated that crude oil and natural coal are the result of natural pyrolysis, the solid waste industry or bioenergy industries are either using combustion or gasification for energy production. Pyrolysis is the process of thermally cracking complex lignocellulosic solid wastes into liquid bio-product (bio-oil) and enriched carbon product (bio-char) in the absence of oxygen. Pyrolysis can be performed in either a batch or a continuous flow reactor. A number of studies published in various research journals showed only the energy balance during pyrolysis process [2, 3]. Although energy analysis of pyrolysis system improves the thermal efficiency of the process, it did not account for the quality of energy used and produced from the process. The main objectives of this work are to conduct an entropy balance on the pyrolysis process in addition to energy balance and to compare the quality of bio-oil produced from this process. This paper presents the entropy of analysis of converting solid wastes into useable bio-products during pyrolysis.

DESCRIPTION OF THE CONTINUOUS PYROLYSIS SETUP

The continuous pyrolysis reactor system used for the experiments was developed by [4]. Figure 1 shows the schematic of that system.

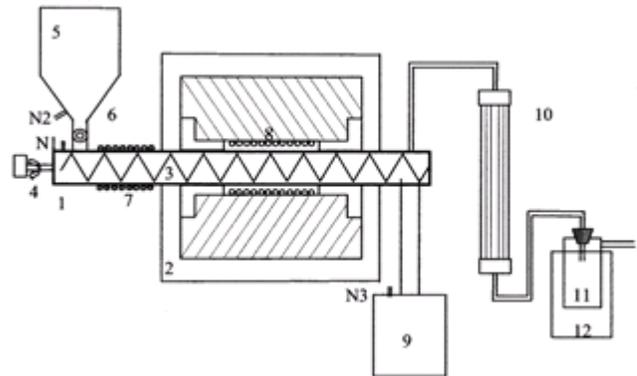


Fig. 1. Schematic represents the continuous pyrolysis reactor. The components are: (1) Main tube reactor, (2) Furnace, (3) Augur, (4) Motor to move the augur, (5) Hopper, (6) Feeder, (7) Cooling system, (8) Heating coil, (9) Char container, (10) Vertical tube condenser, (11) Bio-oil traps, and (12) Ice-cooled containers. The nitrogen was purged through inlets located at following locations: (N1) to the main reactor, (N2) to the hopper, and (N3) to the char container.

To study the thermodynamics of above system, a computer model was developed for the continuous flow reactor system [4]. During the formulation of the computer model, the main tube reactor was divided the reactor into nineteen zones as shown in Fig. 2. The length of each zone was 5 cm, which was equal to the pitch length of the augur shown in Fig. 1. Temperatures were measured at the end of cooling zone (zone # 4), at the beginning (zone # 9) and end (zone # 14) of heating zone and vapor and gas temperature at the exit (zone # 19) by installing thermocouples.

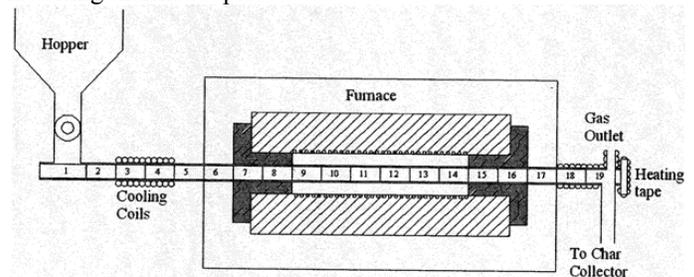


Fig. 2. The schematic diagram of a main reactor tube

SYSTEM CONSIDERATION AND EXPERIMENTS

The entropy balance for a continuous flow pyrolysis reactor system was performed using pine pellets at the pyrolysis temperature of 773 K. This reactor system was comprised of a feeder unit and two major heat exchanging units namely pyrolysis and condensing unit. Both heat exchanging units were considered to be open system located inside the infinite insulated system (Fig. 3).

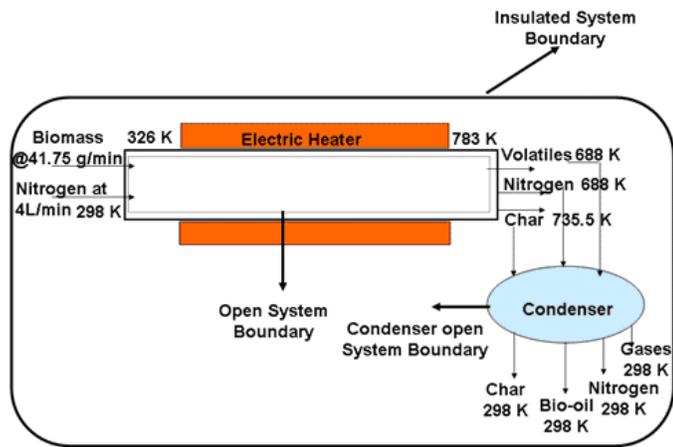


Fig. 3. System diagram of pyrolysis and condenser units

All zones than the two open systems were considered as buffer zone. In this pyrolysis unit (open system), the biomass entered into the reactor at 41.748g/min (calculated using bulk density 560 kg/m³ and 1.58 rpm auger speed) with nitrogen flow rate of 4 L/min. In steady state, the energy and entropy associated with the energy flowed to and from this open system to the surroundings in form of mass and heat. It is appropriate to mention here that the temperature profiles recorded at zone # 4 (298 K) and at zone # 14 (783 K) indicated no major decomposition beyond these zones. The secondary crackings of volatiles after zone # 14 were neglected during the entropy analysis.

The heat of combustion measured from bomb calorimeter was used as measure of free energy potential of the biomass, char, bio-oil, and gases. Heat of combustion of any biomass is a good estimation of heat of formation [5]. The heat of formation of biomass may be approximated to heat of combustion [5]. The heat of formation or enthalpy generally constitutes a major part of Gibbs free energy. If we ignore the TΔS part of Gibbs free energy it would introduce a maximum of 3% error for most of the biomass [5].

Heat flow from the reactor wall was computed from computer model [4] using various inputs including data obtained from Thermo-Gravimetric Analysis (TGA) and Differential Scanning Calorimeter (DSC). The TGA and DSC outputs were obtained for pine pellets from 298 K to 873 K at the heating rate of 283 K/min and nitrogen gas flow rate of 50ml/min. The use of TGA and DSC data automatically took care of heat exchanged (exothermic or endothermic) during chemical reaction. The output of this computer model included reactor and biomass temperature, amount of biomass left, and heat inflow/out flow in each zone. The output was used for performing energy and entropy balance.

To verify the possible error associated in the estimation of entropy production while using the heat of combustion, an entropy balance was performed for the combustion of methane. The entropy inflow due to methane into the combustion chamber was computed from three different cases: 1. using heat

of formation, 2. using heat of combustion, and 3. using standard tabulated values of entropy. The specific calculations for energy and entropy balance of the pyrolysis system and combustion of methane were discussed in following sections.

COMPUTATIONS FOR ENERGY AND ENTROPY BALANCES

This section is divided into five sub-sections for improved comprehension. The first sub-section describes the energy balance, the sub-second section explains the entropy balance for pyrolysis open system, the third sub-section covers the entropy balance when the pyrolysis and condenser unit together constitute the single open system, the fourth sub-section explains the calculations used to estimate the energy and entropy values shown in the sections one through three and the fifth sub-section details the entropy balance for the combustion of methane in the continuous system.

Energy flow from the pyrolysis open system

Energy flowed to and from the system due to mass and heat transfer. Each of these components of energy flow for pyrolysis of pine pellets were described below:

Energy flowed into the open system in following forms:

1. Biomass inflow into the system $\dot{Q}_{Biomass} = 772.236$ kJ/min
2. Nitrogen inflow at 25°C @ 4L/min $\dot{Q}_{Nitrogen} = 0.933$ kJ/min
3. Heat Flow from reactor walls due to heater $\dot{Q}_{Pyrolysis} : 23.522$ kJ/min

Energy flowed out of the system in following forms:

1. Char outflow at 462.5°C $\dot{Q}_{Char} = 403.28$ kJ/min
2. Nitrogen outflow at 415°C @ 4L/min $\dot{Q}_{Nitrogenout} = 24.248$ kJ/min
3. Bio-oil outflow at 415°C $\dot{Q}_{Biooil} = 492.69$ kJ/min
4. Gases out flow at 415°C $\dot{Q}_{Gases} : 83.21$ kJ/min
5. Heat loss into buffer zone $\dot{Q}_{Loss} : 5.43$ kJ/min
6. Radiation heat loss from zone # 17 $\dot{Q}_{Radiation} = 65.998$ kJ/min

Energy balance showed that there was a major unbalanced part of energy input in the system. Let us call it energy produced due to chemical process. This energy produced through chemical process was actually consumed by intermediate products of the pyrolytic reactions and stored in final products char, bio-oil, and gases in form of fuel potential.

$$\dot{Q}_{Biomass} + \dot{Q}_{Nitrogenin} + \dot{Q}_{Pyrolysis} + \dot{Q}_{Chemical} = \dot{Q}_{Char} + \dot{Q}_{Nitrogenout} + \dot{Q}_{Biooil} + \dot{Q}_{Gases} + \dot{Q}_{Loss} + \dot{Q}_{Radiation}$$

The energy balance shown above gave $\dot{Q}_{Chemical} = 278.165$ kJ/min. This energy didn't enter into the system but it increased the energy potential of the final products. The direction of this energy inflow was negative. We considered entropy input due to this increased potential but with negative sign. The entropy due to this increased potential flowed out of the system and was automatically included in entropy out flow due to gases, char, and bio-oil. Another way to take care of entropy flowed due to $\dot{Q}_{Chemical}$ would be to account it for entropy exchange due to chemical potential when stoichiometry of the chemical reaction was known.

Entropy production in the pyrolysis open system

The total entropy change of an insulated system was given by following equation:

$$\Delta \dot{S}_{total} = \dot{S}_{gen} = \Delta \dot{S}_{Reactor} + \Delta \dot{S}_{Condenser} + \Delta \dot{S}_{bufferzone} \quad (1)$$

In a steady state condition, the change in entropy at any point of buffer zone would be zero. The change in entropy of buffer zone was usually small relative to the entropy change of reactor and condenser and hence; may be disregarded. The total entropy change of an insulated system would be entropy change of a reactor plus entropy change of a condenser. So Eq. 1 was rewritten as:

$$\Delta \dot{S}_{total} = \dot{S}_{gen} = \Delta \dot{S}_{Reactor} + \Delta \dot{S}_{Condenser} \quad (2)$$

The reactor was an open system and an entropy balance for a reactor took the following form:

$$\Delta \dot{S}_{reactor} = \dot{S}_{in} - \dot{S}_{out} + \dot{S}_{gen} = \Delta \dot{S}_{exch} + \dot{S}_{genreactor} \quad (3a)$$

$$\Delta \dot{S}_{Condenser} = \dot{S}_{in} - \dot{S}_{out} + \dot{S}_{gen} = \Delta \dot{S}_{exch} + \dot{S}_{gencondenser} \quad (3b)$$

It was already assumed that the reactor along with the condenser was in a steady state, so heat exchanged through the boundaries of the reactor and condenser remained constant at any instant of time. This assumption made the term $\Delta \dot{S}_{total} = 0$. It means that total change in entropy of a reactor was equal to or greater than condenser but opposite in sign. If we assumed that each of these two open systems worked in steady state independently then net entropy change in each subsystem were zero and the Eq. 3a was reduced to Eq. 4.

$$\dot{S}_{in} - \dot{S}_{out} + \dot{S}_{genreactor} = \Delta \dot{S}_{exch} + \dot{S}_{genreactor} = 0 \quad (4)$$

The \dot{S}_{in} part of entropy exchange was due to following reasons in this system of study:

1. Entropy inflow due to biomass inflow $\dot{S}_{Biomass} = 2.59$ kJ/min.K

2. Entropy inflow due to nitrogen $\dot{S}_{Nitrogenin} = 3.132 \times 10^{-3}$ kJ/min.K
3. Heat flow from reactor walls $\dot{S}_{Pyrolysis} = 0.0324$ kJ/min.K
4. Entropy out flow due to increased potential stored in char, bio-oil $\dot{S}_{Potential} = -0.513$ kJ/min.K

The total entropy inflow was $\dot{S}_{in} = \dot{S}_{Biomass} + \dot{S}_{Nitrogenin} + \dot{S}_{Pyrolysis} + \dot{S}_{Potential} = 2.11$ kJ/min.K

The \dot{S}_{out} part of entropy exchange was due to following reasons in this paper:

1. Entropy outflow due to char outflow at 462.5°C
 $\dot{S}_{Char} = 0.548$ kJ/min.K
2. Entropy outflow due to Nitrogen outflow at 415°C @ 4L/min $\dot{S}_{Nitrogenout} = 0.0352$ kJ/min.K
3. Entropy outflow due to Bio-oil outflow at 415°C
 $\dot{S}_{Biooil} = 0.716$ kJ/min.K
4. Entropy outflow due to Gases out flow at 415°C
 $\dot{S}_{Gases} = 0.122$ kJ/min.K
5. Entropy outflow due to heat loss into buffer zone
 $\dot{S}_{Loss} = 0.0182$ kJ/min.K
6. Entropy out flow due to long wave radiation from zone # 17 $\dot{S}_{Radiation} = 0.157$ kJ/min.K

The total entropy outflow was $\dot{S}_{out} = \dot{S}_{Char} + \dot{S}_{Nitrogenout} + \dot{S}_{Biooil} + \dot{S}_{Gases} + \dot{S}_{Loss} + \dot{S}_{Radiation} = 1.596$ kJ/min.K

Substituting the values of inflow entropy and outflow entropy in Eq. 4:

$$\begin{aligned} \dot{S}_{in} - \dot{S}_{out} + \dot{S}_{genreactor} &= 1.893 - 1.6354 + \dot{S}_{genreactor} \\ &= 0.516 \text{ kJ/min.K} + \dot{S}_{genreactor} \end{aligned}$$

The entropy production in a continuous reactor is -0.516 kJ/min.K.

Considering Pyrolysis unit and condenser unit as a single open system

For an instance let us consider the pyrolysis zone and condenser unit as single open system. For such a system, the energy balance and entropy inflow will remain same but the temperature of char, bio-oil, and gases will be 298 K at the exit of the system. These considerations will make following changes in entropy out flow \dot{S}_{out} from the system:

1. Entropy outflow due to char outflow at 298 K $\dot{S}_{Char} = 1.353 \text{ kJ/min.K}$
2. Entropy outflow due to Nitrogen outflow at 298 K @ 4L/min $\dot{S}_{Nitrogenout} = 0.003132 \text{ kJ/min. K}$
3. Entropy outflow due to Bio-oil outflow at 298 K $\dot{S}_{Biooil} = 1.653 \text{ kJ/min K}$
4. Entropy outflow due to Gases out flow at 298 K $\dot{S}_{Gases} = 0.279 \text{ kJ/min. K}$
5. Entropy outflow due to heat loss into buffer zone $\dot{S}_{Loss} = 0.21 \text{ kJ/min K}$
6. Entropy out flow due to long wave radiation from zone 17 $\dot{S}_{Radiation} = 0.0159 \text{ kJ/min K}$

The total entropy outflow will be $\dot{S}_{out} = \dot{S}_{Char} + \dot{S}_{Nitrogenout} + \dot{S}_{Biooil} + \dot{S}_{Gases} + \dot{S}_{Loss} + \dot{S}_{Radiation} = 3.657 \text{ kJ/min K}$
 Substituting the values of inflow entropy and outflow entropy in Eq. 4:

$$\dot{S}_{in} - \dot{S}_{out} + \dot{S}_{int} = 1.596 - 3.657 + \dot{S}_{int} = -2.060 \text{ kJ/min.K} + \dot{S}_{int}$$

The entropy production in an open system where pyrolysis and condenser units were considered as single open system is 2.060 kJ/min.K.

Calculations for each component of entropy

1. Entropy inflow due to biomass inflow

$$\dot{S}_{Biomass} = 2.59 \text{ kJ/K.min}$$

Entropy inflow due to biomass inflow was

$\dot{S}_{Biomass} = \frac{\dot{Q}_{Biomass}}{T_a}$. Where $\dot{Q}_{Biomass}$ was the heat inflow due to biomass input and T_a was the ambient temperature equal to 25°C or 298 K. The value of $\dot{Q}_{Biomass}$ was computed as following:

$$\dot{Q}_{Biomass} = \dot{m}_{biomass} \times HHV_{Biomass} \quad (5)$$

$$\dot{Q}_{Biomass} = 41.748 \frac{\text{g}}{\text{min}} \times 4425.257 \frac{\text{cal}}{\text{g}} = 184.75 \text{ kcal/min}$$

$$\dot{Q}_{Biomass} = 184.75 \frac{\text{kcal}}{\text{min}} \times 4.18 \frac{\text{kJ}}{\text{kcal}} = 772.236 \text{ kJ/min}$$

Where $\dot{m}_{Biomass} = 41.748 \text{ g/min}$ is the biomass inflow into the reactor and the heating value of the biomass is 4425.257 cal/g. So, entropy inflow due to biomass flow can be computed as following.

$$\dot{S}_{Biomass} = \frac{\dot{Q}_{Biomass}}{T_a} = \frac{772.236 \text{ kJ/min}}{298 \text{ K}} = 2.59 \text{ kJ/min.K}$$

2. Entropy inflow due to nitrogen at 298K and 1 atm pressure

$$\dot{S}_{Nitrogenin} = 3.132 \times 10^{-3} \text{ kJ/min.K}$$

Entropy inflow due to nitrogen flow $\dot{S}_{Nitrogenin} = \dot{m}_{Nitrogen} (s_a)$ and energy inflow due to nitrogen inflow is $\dot{Q}_{Nitrogenin} = \dot{S}_{Nitrogenin} \times T_a$. Where T_a was the ambient air temperature or room temperature equal to 25°C, $\dot{m}_{Nitrogen}$ was the molar flow rate of nitrogen, and s_a was specific entropy of nitrogen at T_a and one atmospheric pressure. Calculations of entropy and energy inflow are given below based on following known data:

s_a = specific entropy of nitrogen at 298K = 191.502 kJ/K
 V_{Ta} = Volumetric flow rate of nitrogen at 298K = 4L/min
 Molar mass of nitrogen = 28.013 kg/kmol
 Density of nitrogen at Standard Temperature and Pressure (STP) = 1.2503 kg/m³
 At STP Temperature = 273 K and Pressure = 1 atm.

$$\text{Volume of 4L nitrogen at STP} = 273 \text{ K} \times \frac{4 \text{ L}}{298 \text{ K}} \times \frac{10^{-3} \text{ m}^3}{\text{L}} = 3.6644 \times 10^{-3} \text{ m}^3$$

$$\text{Moles of nitrogen} = \frac{\text{volume} \times \text{density}}{\text{Molar mass}} = \frac{3.6644 \times 10^{-3} \text{ m}^3 \times 1.2503 \text{ kg/m}^3}{28.013 \text{ kg/kmol}} = 1.63 \times 10^{-3} \text{ kmol}$$

$$\dot{S}_{Nitrogenin} = \dot{m}_{Nitrogen} (s_a) = 1.63 \times 10^{-4} \text{ kmol} \times 191.502 \text{ kJ/kmol.K} = 3.132 \times 10^{-3} \text{ kJ/min.K}$$

$$\dot{Q}_{Nitrogenin} = \dot{S}_{Nitrogenin} \times T_a = 3.132 \times 10^{-3} \text{ kJ/min.K} \times 298 \text{ K} = 0.933 \text{ kJ/min}$$

3. Entropy inflow due to heat flow into pyrolysis zone from reactor walls

$$\dot{S}_{Pyrolysis} = 0.03242 \text{ kJ/min.K}$$

Entropy inflow due to heat inflow from reactor wall is

$$\text{given by } \dot{S}_{Pyrolysis} = \frac{\dot{Q}_{Pyrolysis}}{T_i} = \frac{23.5216}{725.5} = 0.03242 \text{ kJ/min.K}$$

Where $T_i = 725.5$ (obtained by interpolation) was the temperature in middle wall tube thickness and $\dot{Q}_{Pyrolysis}$ was the heat input into the pyrolysis zone from the reactor wall that came into the reactor from the heater and can be computed as given below:

$$\dot{Q}_{Pyrolysis} = \dot{Q}_{Heater} \quad (6)$$

$$\dot{Q}_{Heater} = (T_{OW} - T_i) \times 2\pi \times k_{tube} \times \frac{L}{\ln(r_o / r_{mid})} \quad (6a)$$

$$\dot{Q}_{Conduction} = k_{tube} \times 2\pi r_{mid} \times \frac{(T_f - T_L)}{L} \quad (6b)$$

Where \dot{Q}_{Heater} was the heat input into the reactor wall that came into the reactor zone from the heater, $\dot{Q}_{Conduction}$ was the conductive heat loss through reactor wall to the cooling unit located at the inlet of the pyrolysis zone or conductive heat loss from zone five, T_{ow} was the outer wall temperature of the reactor, k_{tube} was the thermal conductivity of the stainless steel tube at a given temperature, L was the length of pyrolysis zone, r_0 was the outer wall radius, r_{mid} was the radius till middle wall tube thickness, T_f was the temperature of reactor wall towards exit and T_L was the temperature of reactor wall at the inlet point of pyrolysis zone.

Eqs. 6, 6a, and 6b look pretty simple; however, there was a practical difficulty in assuming pyrolysis zone as a single section due to temperature gradient at the outer wall of the reactor. To consider this gradient, the authors agreed to the zonation scheme [4] which assumed that open system under study was comprised of 12 sections each 5 cm long (from zone # 5 to zone # 19). For each section the energy balance was done separately as shown in Fig. 4.

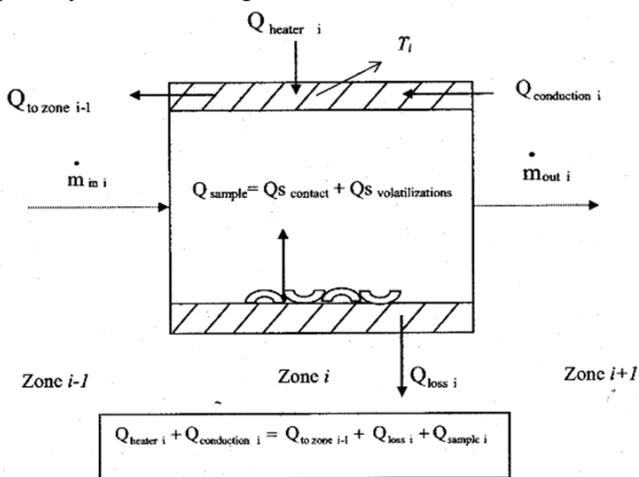


Fig. 4. Schematic representation of mass and energy balance in zone i [4].

$Q_{heater\ i}$ was the conduction input through the walls that comes in from the reactor. This heat input was only applied from zone # 9 to zone # 14 and was computed using Eq. 6a. $Q_{conduction\ i}$ and $Q_{conduction\ i-1}$ were the conduction input from zone $i+1$ and loss to zone $i-1$. $Q_{loss\ i}$ was the conduction loss through insulation material and it was applied to zone without heating elements. $Q_{sample\ i}$ was sample heat transfer in zone i . This sample heat transfer included sensible heat consumed by the sample and heat involved in the volatilization process. Computation of $Q_{sample\ i}$ can be done using equation given below.

$$\dot{Q}_{sample\ i} = \dot{m}_{biomass\ i} \times C_{Pbiomass} (\Delta T_{sample\ contact\ i}) + \dot{m}_{biomass\ i} \times DSC_i \quad (7)$$

$Q_{Sample\ i}$ = Heat consumed by biomass sample in i^{th} zone

Where $C_{Pbiomass} = 1.67 \text{ J/g.K}$ [3] was the specific heat of biomass, $\dot{m}_{Biomass\ i}$ was the average mass flow of biomass in i^{th} section, $\Delta T_{sample\ contact\ i}$ was the change in sample temperature in zone i and it was computed using TGA (Thermogravimetric data), and DSC_i was heat consume/evolved in the volatilization process and it came from DSC (differential scanning calorimeter data. Adding $Q_{heater\ i}$ for all zones would give \dot{Q}_{heater} .

Q_{Loss} was computed as sum of $Q_{Loss\ i}$ for different zones. In zone # 7, 8, 15, 16, 18, and 19 which were equipped with sleeves and insulation, $Q_{Loss\ i}$ took form of conduction, however, it took form of convection in zones # 5, 6, and 17. The computer model program developed by [4] was used to compute $Q_{heater\ i}$.

$\dot{Q}_{Conduction}$ was also obtained as heat loss to cooling units due to conduction from zone # 4 and # 3. The program took following inputs; temperature profile recorded via installed thermocouples (Fig. 5), TGA and DSC data. The TGA and DSC analysis of pine pellets were obtained by heating the samples from 25°C to 600°C at the heating rate of $10^\circ\text{C}/\text{min}$ and nitrogen gas flow rate of $50 \text{ ml}/\text{min}$. The output of the computer program included the sample mass entering and sample temperature in various zones. According to the output, following were the computed values:

$$\dot{Q}_{heater} = 392.03 \text{ W}$$

$$\dot{Q}_{Pyrolysis} = 392.03 \text{ W} = 23.5216 \text{ kJ}/\text{min}$$

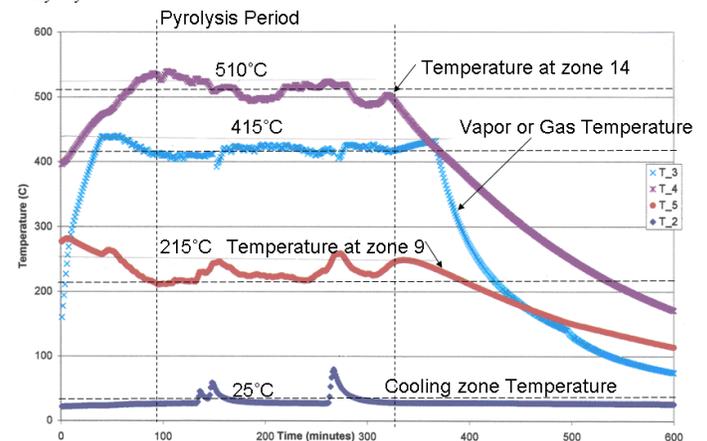


Fig. 5. A typical temperature profile of a pyrolysis unit.

Table 1. Heat input from heater through reactor walls

zone #	Heat input, Watt
9	94.12
10	93.11
11	95.09
12	63.12
13	19.98
14	26.61
Total	392.03

4. Entropy outflow due to char outflow at 462.5°C

$$\dot{S}_{Char} = 0.548 \text{ kJ/min.K}$$

$$\text{The entropy outflow due to char } \dot{S}_{Char} = \frac{\dot{m}_{char} \times HHV_{char}}{T_{Char}}$$

Where \dot{m}_{char} was the mass out flow rate of char, $HHV_{char} = 7000 \text{ cal/g}$ or 29.4 MJ/kg was the heating value of char, and $T_{Char} = 273+462.5 = 735.5 \text{ K}$ was the temperature of char. We didn't have data for the temperature of char but we know from experience that char temperature was generally higher than volatile and gas temperature. So, we took the average of surface temperature of reactor at the end of heating zone (510°C) and vapor/gas temperature (415°C) which was a reasonable assumption. The char yield was 33% of initial biomass, so $\dot{m}_{char} = 13.78 \text{ g/min}$. Energy and entropy outflow due to char outflow was calculated as shown below:

$$\dot{Q}_{Char} = \dot{m}_{Char} \times HHV_{char} = 13.78 \frac{\text{g}}{\text{min}} \times 7000 \frac{\text{cal}}{\text{g}} \times \frac{\text{kcal}}{1000\text{cal}} \times 4.18 \frac{\text{kJ}}{\text{kcal}} = 403.28 \text{ kJ/min}$$

$$\dot{S}_{Char} = \frac{\dot{Q}_{Char}}{T_{Char}} = \frac{403.28 \text{ kJ/min}}{(273 + 462.5)} = 0.548 \text{ kJ/min.K}$$

5. Entropy outflow due to Nitrogen outflow at 415°C @ 4L/min

$$\dot{S}_{Nitrogenout} = 0.0352 \text{ kJ/min.K}$$

Entropy outflow due to Nitrogen outflow at 415°C @ 4L/min $\dot{S}_{Nitrogenout} = \dot{m}_{Nitrogen} (s_f) = 1.63 \times 10^{-4} \text{ kmol/min} \times 217.5376 \text{ kJ/kmol.K} = 0.0352 \text{ kJ/min.K}$. Where T_f was temperature of the vapors at the exit of heating zone = 415°C or 688 K, $\dot{m}_{Nitrogen}$ was the molar flow rate of nitrogen = $1.63 \times 10^{-4} \text{ kmol/min}$, and $s_f = 216.2244 \text{ kJ/kmol.K}$ was specific entropy of nitrogen at T_f and one atmospheric pressure. Energy outflow due to nitrogen outflow was calculated as:

$$\dot{Q}_{Nitrogenin} = \dot{S}_{Nitrogenout} \times T_f = 0.0354 \text{ kJ/K.min} \times 688 \text{ K} = 24.248 \text{ kJ/min}$$

6. Entropy outflow due to Bio-oil outflow at 415°C

$$\dot{S}_{Biooil} = 0.772 \text{ kJ/min.K}$$

The entropy outflow due to bio-oil outflow

$$\text{was } \dot{S}_{Biooil} = \frac{\dot{m}_{Biooil} \times HHV_{biooil}}{T_f}. \text{ Where } \dot{m}_{Biooil} \text{ was the mass out}$$

flow rate of bio-oil, $HHV_{bio-oil}$ was the heating value of bio-oil, and $T_f = 688 \text{ K}$ was the temperature of bio-oil in vapor phase. The bio-oil yield was 55% of initial biomass, so

$\dot{m}_{Biooil} = 24.75 \text{ g/min}$. Energy and entropy outflow due to bio-oil outflow was calculated as shown below:

$$\dot{Q}_{Biooil} = \dot{m}_{Biooil} \times HHV_{biooil} = 22.96 \frac{\text{g}}{\text{min}} \times 5133.66 \frac{\text{cal}}{\text{g}} \times \frac{\text{kcal}}{1000\text{cal}} \times 4.18 \frac{\text{kJ}}{\text{kcal}} =$$

$$\dot{Q}_{Biooil} = 492.69 \text{ kJ/min}$$

$$\dot{S}_{Biooil} = \frac{\dot{Q}_{Biooil}}{T_f} = \frac{492.69 \text{ kJ/min}}{(688 \text{ K})} = 0.716 \text{ kJ/min.K}$$

7. Entropy outflow due to Gases out flow at 415°C

$$\dot{S}_{Gases} = 0.122 \text{ kJ/min.K}$$

Entropy outflow due to gases was

$$\dot{S}_{Gases} = \frac{\dot{Q}_{Gases}}{T_f} = \frac{83.21 \text{ kJ/min}}{688 \text{ K}} = 0.122 \text{ kJ/min.K}. \text{ Where } \dot{Q}_{Gases}$$

was the heat loss due to outflow of the gases produced during pyrolysis process and T_f was reactor temperature at zone # 19. Generally, $100 - (33 + 55) = 12\%$ of biomass was lost into gases according to law of mass conservation, which will be 12% of $41.748 \text{ g/min} = 5.976 \text{ g/min}$. Assuming heating values of gases

16.61 MJ/kg [7] would give total $\dot{Q}_{Gases} = 83.21 \text{ kJ/min}$.

8. Entropy outflow due to heat loss into buffer zone and into cooling unit

$$\dot{S}_{Loss} = 0.0182 \text{ kJ/min.K}$$

Entropy outflow due to heat loss into buffer zone

$$\text{was } \dot{S}_{Loss} = \frac{\dot{Q}_{Loss}}{T_b} = \frac{5.54}{298} = 0.019 \text{ kJ/min.K}. \text{ Where } T_b \text{ was the}$$

temperature of insulating material and \dot{Q}_{Loss} was the heat loss due to conduction into insulating material via reactor into non heating zone. T_b may be considered as atmospheric temperature.

The \dot{Q}_{Loss} can be computed as sum of \dot{Q}_{Lossi} for different zones. In zone # 7, 8, 15, 16, 18, and 19 which were equipped with sleeves and insulation, \dot{Q}_{Lossi} took form of conduction, however, it took form of convection in zone# 5, 6, and 17.

$$\dot{Q}_{Loss} = \sum_5^{19} \dot{Q}_{Lossi} + \dot{Q}_{Conduction} = 70.6413 + 19.842 = 90.4833 \text{ W} \\ = 5.5428 \text{ kJ/min} \quad (8)$$

\dot{Q}_{Lossi} and $\dot{Q}_{Conduction}$ were computed from thermal model developed by [4].

Table 2. Heat loss into buffer zone and into cooling unit obtained from [4] computer model.

Zone #	Conduction	Zone #	Convection, W	Zone #	Conduction to cooling, W
7	0.0294	5	2.336	3	-2.758
8	0.5896	6	-0.7843	4	22.6
15	6.682	17	39.5		
16	5.712				
18	7.811				
19	8.502				
Total	29.5896	Total	41.0571	Total	19.842

9. Entropy out flow due to increased potential stored in char, bio-oil

$$\dot{S}_{Potential} = -0.513 \text{ kJ/min.K}$$

Entropy out flow due to increased potential stored in char,

$$\dot{S}_{Potential} = \frac{\dot{Q}_{Chemical}}{T_{ave}} = \frac{-278.165 \text{ kJ/min}}{542.66} = -0.513$$

kJ/min.K. Since most of the biomass decomposed in zone # 11, so, we took the average of the sample temperature in zone # 11.

10. Entropy out flow due to long wave radiation from zone 17

$$\dot{S}_{Radiation} = 0.1571 \text{ kJ/min.K}$$

The entropy out flow due to long wave radiation was given by following expression:

$$\dot{S}_{Radiation} = A_{LR} * f * 1.33 * \sigma T^3 = 0.1571 \text{ kJ/min}$$

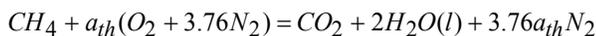
Where $A_{LR} = 2\pi r_0 L = 2\pi \times 0.51 \times 0.05 = 0.164 \text{ m}^2$, $\sigma = 5.67 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4$, $T = 596 \text{ K}$, and $L = 0.05 \text{ m}$. Let us consider the shape factor equal to 1. The heat released due to radiation from zone #

$$17 \text{ was } \dot{Q}_{Radiation} = A_{LR} f \sigma (T^4 - T_a^4) = 65.998 \text{ kJ/min.}$$

Entropy Balance for Methane Combustion Reaction

Determination of heat of combustion of methane

Heat of combustion is generally determined in a bomb calorimeter which reports a higher heating value or enthalpy of formation. **Assumption:** Enthalpy of formation of all the stable elements (O_2 , N_2 , H_2 , and C) has a value of zero at the standard reference state 298 K and 1 atm.



$\bar{h}_c = H_{\text{Product}} - H_{\text{Reactants}}$, where H_i is the enthalpy of formation of i^{th} substance.

From the standard table, the enthalpy of formation values for the product and reactant were obtained [6].

$$H_{\text{CH}_4} = -74,850 \text{ kJ/kmol} \quad H_{\text{CO}_2} = -393,520 \text{ kJ/kmol}$$

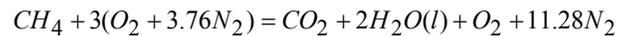
$$H_{\text{H}_2\text{O}(l)} = -285,830 \text{ kJ/kmol}$$

$$\bar{h}_c = (-393,520 \text{ kJ/kmol}) + 2 \times (-285,830 \text{ kJ/kmol}) - (-74,850 \text{ kJ/kmol}) = -890,330 \text{ kJ/kmol}$$

So, the heat of combustion of methane (-890,330 kJ/kmol) is 11.89 times higher than its heat of formation (-74,850 kJ/kmol). For complex biomass these two values are very close (5).

Entropy Balance for the methane in a continuous flow combustion chamber

According to "example 15-11 and 15-10" in the referred text, methane releases 871,400 kJ/kmol (Q_{out}) heat during the combustion process [6]. The methane after combustion process generates products (CO_2 , H_2O , O_2 , and N_2) at a flame temperature of 1789 K. Assuming the heat released and flame temperature as the measured value, the entropy of the combustion chamber can be performed for the following reaction.



Entropy inflow of the reactant due to

- 3 kmols of O_2 at 298 K and 1 atm, according to example 15-10 [6]: 654.06 kJ/kmol.K
- 11.28 kmols of N_2 at 298 K and 1 atm according to example 15-10 [6]: 2183.47 kJ/kmol
- Entropy inflow due to 1 kmol of methane at 298 K and 1 atm for three cases:
 - Using Heat of Formation = (-74850 kJ/kmol)/298 K = 251.1745 kJ/kmol.K
 - Using Heat of Combustion = (-890330 kJ/kmol)/298 K = 2987 kJ/kmol.K
 - Using standard entropy table = 186.16 kJ/Kmol.K

Total entropy inflow for the three cases of methane:

- Using Heat of Formation = 3088.705 kJ/kmol.K
- Using Heat of Combustion = 5825.21 kJ/kmol.K
- Using standard entropy table = 3023.69 kJ/Kmol.K

If the products are going out at the flame temperature and all the heat is stored in the products, then the entropy of products = 3989.71 kJ/kmol.K. The entropy outflow from the combustion chamber will be due to the flowing products according to the example 15-10 [6]:

Entropy outflow of the products due to

- One kmol of CO_2 at 1789 K and 1 atm: 325.19 kJ/kmol.K
- 2 kmol of H_2O at 1789 K and 1 atm: 551.72 kJ/kmol.K
- One kmol of O_2 at 1789 K and 1 atm: 287.15 kJ/kmol.K
- 11.28 kmol of N_2 at 1789 K and 1 atm: 2825.65 kJ/kmol.K

The total entropy outflow from the combustion chamber was 3989.71 kJ/kmol.K

Entropy produced during the combustion process for the three cases of methane

Entropy Production = Entropy of the products – Entropy of the reactants

- A. Entropy production calculated using Heat of Formation of methane = (3989.72 - 3088.705) kJ/kmol. K = 901.005 kJ/kmol.K
- B. Entropy Production calculated using Heat of Combustion of methane = (3989.72 - 5825.21) kJ /kmol. K = -1835.5 kJ/kmol.K
- C. Entropy Production calculated using standard entropy table = (3989.72 - 3023.69) kJ/Kmol.K = 966.02 kJ/kmol.K.

Entropy production when combustion chamber and condenser are considered a single system

In this case the combustion products leave the system at 298 K and 1 atm releasing 871, 400 kJ/kmol (Q_{out}) heat. The entropy inflow of the reactants in remains same; however the entropy outflow due to products changes to following according to example 15-11 [6]:

Entropy outflow of the reactant due to

- A. One kmol of CO₂ at 298 K and 1 atm: 235.57 kJ/kmol.K
- B. 1.57 kmol of H₂O (l) at 298 K and 1 atm: 109.77 kJ/kmol.K
- C. 0.43 kmol of H₂O at 298 K and 1 atm: 93.57 kJ/kmol.K
- D. One kmol of O₂ at 298 K and 1 atm: 226.81 kJ/kmol.K
- E. 11.28 kmol of N₂ at 298 K and 1 atm: 2179.63 kJ/kmol.K

The total entropy outflow from the combustion chamber was 2845.35 kJ/kmol.K

Entropy produced during the combustion and condensation process for the three cases of methane

Entropy Production = Entropy of the products – Entropy of the reactants + $Q_{out}/298\text{ K}$

- A. Entropy production calculated using Heat of Formation of methane = (2845.35 - 3088.705) kJ/kmol. K + 871400 kJ/kmol/ 298 K = 2680.806 kJ/kmol.K
- B. Entropy Production calculated using Heat of Combustion of methane = (2845.35 - 5825.21) kJ /kmol. K + 871400 kJ/kmol/ 298 K = -55.699 kJ/kmol.K
- C. Entropy production calculated using standard entropy table = (2845.35 - 3023.69 kJ/Kmol.K + 871400 kJ/kmol/ 298 K = 2746 kJ/kmol.K.

RESULTS AND DISCUSSION

Summarized energetics of this pyrolysis reactor open system was presented Table 3.

An interesting conclusion may be drawn from Table 3 that the pyrolysis process converted low quality and high entropy

biomass into high quality and low entropy energy products char, bio-oil, and gases. In light of this study, the entropy production in the pyrolysis unit open system was -0.516 kJ/min.K. To verify whether this negative entropy production is because of using the heat of combustion, the entropy balance was performed for standard chemical reaction for the combustion of methane [6]. The entropy inflow due to methane into the combustion chamber was computed from three different cases: 1. using heat of formation, 2. using heat of combustion, and 3. using standard tabulated values of entropy. We found that entropy production for case 1, 2, and 3 were 901.01 kJ/kmol.K, -1835.5 kJ/kmol.K, and 966.02 kJ/kmol.K respectively. Considering these results, it would be correct to conclude that pyrolysis process might produce some entropy.

For an instance let us consider the pyrolysis and condenser unit to be single open system. For such a system, the energy balance and entropy inflow will remain same but the temperature of char, bio-oil, and gases will be 298 K at the exit of the system. These considerations result the entropy production value of 2.060 kJ/min.K. Similarly, the entropy balance for methane combustion when combustion products are rejected at room temperature showed the entropy production value of 2680.806 kJ/kmol.K, -55.6989 kJ/kmol.K, and 2746 kJ/kmol.K for case 1, 2, and 3 respectively [6].

Table 3. Summarized energetics of pyrolysis unit open system.

Process	Inflow		Outflow	
	Energy, kJ/min	Entropy, kJ/min.K	Energy, kJ/min	Entropy, kJ/min.K
Biomass inflow 298 K and Char outflow at 735.5 K	772.236	2.59	434.511	0.591
Nitrogen inflow 298 K outflow 688 K	0.933	0.003	24.248	0.035
Heat flow from reactor walls (conduction inflow at 725.5 K from zone 9 to 14; conduction outflow at 298 K from zones 7, 8, 15, 16, 18, and 19; and convection out flow at 298 K from zones 5, 6, and 17).	23.523	0.032	5.430	0.018
Increased potential stored in char, bio-oil, and gases due to chemical reaction	467.419*	-0.8614		
Bio-oil outflow at 688 K			531.103	0.772
Gases out flow at 688 K			152.821	0.222
Energy out flow due to long wave radiation from zone 17 at 603.4 K			65.998	0.1571
Total	746.692	1.872	1214.111	1.795

* Obtained by difference of outflow and inflow.

CONCLUSION

This analysis not only describes the procedure for entropy analysis of the pyrolysis system but it also emphasize that the pyrolysis is the process of low entropy production and most part of the irreversibility or positive entropy production was

associated with condenser unit. This concluding statement of the study opens new avenues for improved condensers or for the direct use of pyrolysis products without condensing it. The high quality energy producing pyrolysis process may be included in bio-energy producing machine (Fig. 6) instead of using combustion, gasification or pyrolysis alone for energy production.

Future Bioenergy Producing Machine- K. Singh Model

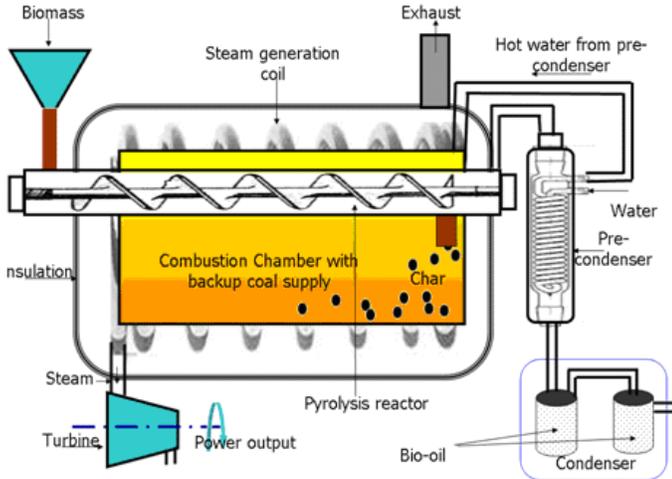


Fig. 6. A proposed pyrolysis unit design

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