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OLIVE MILL WASTE WATER SLUDGE VALUATION THROUGH BIO-OIL PRODUCTION

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Abstract - The production of olive oil has a huge socio-economic significance in the Mediterranean region. However, the extraction of olive oil generates huge quantities of wastes which have negative impacts on land and water environments because of their phytotoxicity. Olive mill waste water sludge (OMWWS) is one of the major pollutants in olive oil industry. To prevent the severe effects arising from OMWWS, it is necessary to convert this pollutant into useful products such as bio oil, biochar and biogas. Pyrolysis is one of the most prominent thermo-chemical conversion technologies available today because it produces solids, condensable vapors and non-condensable gaseous products at the same time. In our work, pyrolysis of olive mill waste water sludge takes place at 450°C and the products are gradually cooled in two condensers connected in series. Bio oil is condensed in 1st condenser at 90 °C while water vapors are condensed in 2nd condenser at 10°C. A simulation model is developed for the pyrolysis of olive mill water sludge based on the experimental results using Advances System for Process Engineering (ASPEN) Plus. This tool is used here to conduct energy and exergy analysis of the process for each component used in pyrolysis depending upon chemical and physical properties of biomass and operating conditions. As high temperatures are involved in this process especially hot gases, there is a potential of heat recovery for the condensing system using an adsorption cooling machine. Exergy efficiency of the process shows that energy is conserved in the process.

Keywords - Energy, Exergy, Pyrolysis, ASPEN Plus, Fluidized Bed Reactor

I. INTRODUCTION

Fossil fuels remain the major cost efficient and reliable source of energy that currently assure the production of required product quality. Statistics from the past decade show that more than 25% of the world energy mainly from diesel and gasoline is consumed in the transportation industry [1] [2]. Despite the numerous socio-economic benefits of fossils fuels as primary energy resources, they have brought global environmental problems [3]. To tackle this global emerging problem, the quest to produce energy from carbon neutral resources is getting much more attention for the last two decades. Among other techniques, fast pyrolysis remains the highest widely used process to convert biomass into liquid fuels [4] [5]. Depending upon operating conditions, pyrolysis can be categorized into slow, intermediate and fast pyrolysis. Operating parameters include temperature of reactor, residence time, heating rate and biomass particle size [6] [7]. The type of biomass dictates the properties of bio oil produced by fast pyrolysis [8]. Many researchers have developed simulation models using ASPEN Plus for different biomasses to determine the maximum yield of bio oil [9]. Production of bio oil by fast pyrolysis has received tremendous attention for the following reasons [10] [11].

- Bio oil is a renewable source of energy suitable for power generation purposes.
- It can be easily stored and transported.
- It has higher HHV than the gasification products.

- It can replace the conventional fuel for automobile applications.

So far, Aspen Plus has been used to maximize the products yield for pyrolysis and gasification processes but there has not been any attempt to retrieve heat from high temperature products in fast pyrolysis [12] [13].

The aim of the modelling of pyrolysis process in Aspen Plus is to determine the potential of heat recovery after the cyclone. The energy analysis will enable us to integrate an adsorption machine in the system to cool down the products thus minimizing energy consumption. The exergy analysis will give an idea about the efficiency of process to produce high energy content products.

II. METHODOLOGY

A. Pyrolysis Model development in Aspen Plus

Aspen Plus is a modeling tool extensively used in chemical and process engineering. The capability of this simulation tool ranges from mass, energy and exergy balance, chemical equilibrium, reaction kinetics, heat transfer and optimization of the process. It has the ability to handle conventional and non-conventional solids. The researchers use Aspen Plus for predictive yields of biomass pyrolysis [14] [9] [12]. Pyrolysis process modeled in ASPEN Plus® V10 is shown in figure. OMWWS, Biochar, carrier gas (CG) and fluidizing gas (FG) are fed into the RYield reactor. Nitrogen is used as carrier gas and fluidizing gas. Pyrolysis of olive mill waste water

takes place at 450°C. The pyrolysis products enter the cyclone which is kept at 350°C to avoid the premature condensation of bio oil. Char is separated from other gaseous products in the cyclone. The char free gases and vapors are passed through 1st condenser where they are cooled from 350°C to 90°C. Bio oil vapors are condensed in the 1st condenser. The water is used in the first condenser

which is heated from 60 to 67°C. This heated water can be used to drive an adsorption machine. The condensed bio oil is separated from non-condensable gases and water vapors in SSPLIT unit. After separation of bio oil, pyrolysis products are passed through 2nd condenser where water vapors are condensed at 10°C.

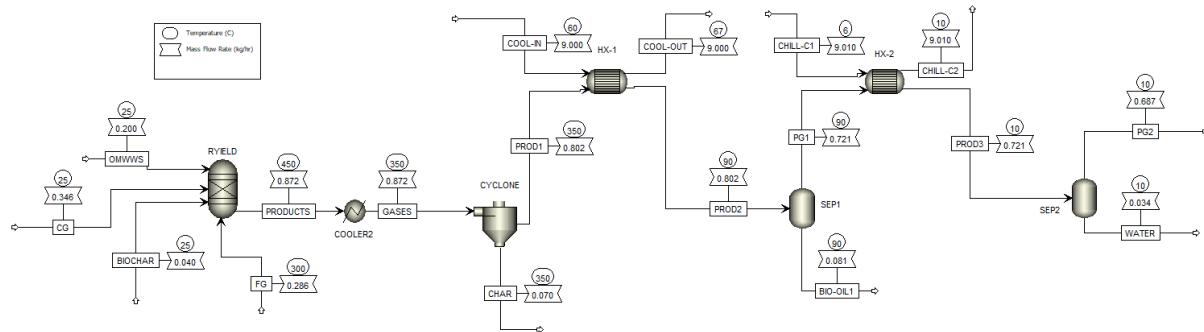


Fig. 1. Flow sheet of pyrolysis of OMWWS

Operational parameters of the pyrolysis of olive mill waste water sludge are given in table 1 [15].

| Unit block/Stream | Temperature (°C) |
|---------------------------------------|------------------|
| Biomass | 25 |
| Carrier gas (Nitrogen) | 25 (102 kPa) |
| Fluidizing gas (Nitrogen) | 300 (125 kPa) |
| Pyrolysis temperature | 450 |
| Cyclone temperature | 390 |
| 1 st condenser temperature | 90 |
| 2 nd condenser temperature | 10 |

Table 1. Operational parameters

Masses and temperatures of reactants and products for pyrolysis reactor are given in table 2.

| Pyrolysis Reactor | | | |
|----------------------------------|------------------------|-----------------------|------------------------|
| Input | | Output | |
| Component | Mass flow rate (kg/hr) | Component | Mass flow rate (kg/hr) |
| Biomass (25°C) | 0.2 | Steam (450°C) | 0.039 |
| Biochar (25°C) | 0.04 | Bio oil (450°C) | 0.081 |
| Carrier gas (25°C, 1.02 bar) | 0.346 | Biochar (450°C) | 0.070 |
| Fluidizing gas (300°C, 1.25 bar) | 0.286 | Pyrolysis Gas (450°C) | 0.050 |
| | | Nitrogen (450°C) | 0.632 |
| Total | 0.872 | Total | 0.872 |

Table 2. Mass balance for pyrolysis reactor

Pyrolysis products are obtained in the form of non-condensable gases, bio oil and water vapors and solids. The gas phase includes CO, CO₂, H₂, CH₄ and some light hydrocarbons. The vapors include water molecules and organic compounds which have a wide range of boiling points and molecular weights. Biochar mainly consists of solid carbon and ash. Characteristics of OMWWS, bio oil and biochar are shown in the table 3 [15] [16].

| Attribute | Biomass | Biochar | Bio oil |
|--|---------|---------|---------|
| <i>Proximate analysis (wt. %)</i> | | | |
| Moisture | 4.08 | 4.0 | - |
| FC | 22.21 | 75.3 | - |
| VM | 64.43 | 19.3 | - |
| Ash | 13.36 | 1.4 | - |
| <i>Ultimate analysis (wt.%) dry ash free basis</i> | | | |
| Ash | 13.36 | 1.4 | 0 |
| Carbon | 52.89 | 82.9 | 76.67 |
| Hydrogen | 7.16 | 3.3 | 11.78 |
| Nitrogen | 1.96 | 0.32 | 2.74 |
| Sulfur | 0.6 | 0.03 | 0 |
| Oxygen | 24.03 | 13.38 | 8.82 |
| HHV (MJ) | 25.64 | 21.34 | 37.5 |

Table 3. Biomass and biochar attributes

Experimental measurements of products of pyrolysis of OMWWS at 450°C are given in table 4 [15].

| Product | Yield (wt.%) |
|----------------------|--------------|
| Organic liquid yield | 33.21 |
| Aqueous liquid yield | 16.29 |
| Char yield | 29.59 |
| Gas yield | 20.91 |

Table 4. Products yield on mass basis

| Component ID | Type | Component Name | Alias |
|--------------------------------|-----------------|-----------------|-----------------------------------|
| OMWWS | Nonconventional | | |
| Biochar | Nonconventional | | |
| Ash | Nonconventional | | |
| C | Solid | CARBON-GRAFITE | C |
| H ₂ O | Conventional | WATER | H ₂ O |
| H ₂ | Conventional | HYDROGEN | H ₂ |
| N ₂ | Conventional | NITROGEN | N ₂ |
| CL ₂ | Conventional | CHLORINE | CL ₂ |
| S | Conventional | SULFUR | S |
| O ₂ | Conventional | OXYGEN | O ₂ |
| CO | Conventional | CARBON-MONOXIDE | CO |
| CO ₂ | Conventional | CARBON-DIOXIDE | CO ₂ |
| CH ₄ | Conventional | METHANE | CH ₄ |
| C ₂ H ₆ | Conventional | ETHANE | C ₂ H ₆ |
| C ₄ H ₁₀ | Conventional | N-BUTANE | C ₄ H ₁₀ -1 |

| | | | |
|-------------|--------------|--------------------------|--------------|
| PENTADECANE | Conventional | N-PENTADECANE | C15H32 |
| 8-HEP-01 | Conventional | 8-HEPTADECENE | C17H34-N4 |
| 1-HEP-01 | Conventional | 1-HEPTADECENE | C17H34-D1 |
| N-HEP-01 | Conventional | N-HEPTADECANE | C17H36 |
| N-HEX-01 | Conventional | N-HEXADECANOIC-ACID | C16H32O2 |
| 2-ETH-01 | Conventional | 2-ETHYLHEXADECANOIC-ACID | C18H36O2-N18 |
| OLEIC-01 | Conventional | OLEIC-ACID | C18H34O2 |
| ETHYL-01 | Conventional | ETHYL-OLEATE | C20H38O2-N1 |

A list of components used in the simulation is shown in table 5. The components are categorized into conventional, non-conventional (biomass, biochar, ash) and pure solids (C). Conventional components have a known chemical formula while non-conventional solids are without any known chemical formula. Conventional solids which do not contribute in phase equilibrium calculations are listed as solid [17].

The pyrolysis process is modelled by using two unit blocks; Ryield and SSsplit. In this work, a simplified pyrolysis reactor based on experimentally measured pyrolysis yields is modelled. Yield of each component in kg/kg of input is given in table 6.

| Component | Yield (kg/kg of input materials) |
|--------------------------------|-------------------------------------|
| CHAR | 0.08 |
| H ₂ O | 0.044 |
| H ₂ | 0.00046 |
| CO | 0.0039 |
| CO ₂ | 0.045 |
| CH ₄ | 0.0011 |
| C ₂ H ₆ | 0.0058 |
| C ₄ H ₁₀ | 0.0015 |
| N ₂ | 0.72514 |
| N-PENTADECANE | 0.0012 |
| 8-HEPTADECENE | 0.0015 |
| 1-HEPTADECENE | 0.0012 |
| N-HEPTADECANE | 0.0018 |
| N-HEXADECANOIC-ACID | 0.0068 |
| 2-ETHYLHEXADECANOIC-ACID | 0.0026 |
| OLEIC-ACID | 0.05 |
| ETHYL-OLEATE | 0.028 |

Table 6. Products yield

B. Property Models

Peng-Robinson is used as the global thermodynamic method in this model. For enthalpy of char and biomass, HCOALGEN model is used and DCOALIGT model is used for density of biomass and char. Stream class MCINCPSD is used because of presence of both conventional and non-conventional solids with particle size distribution (PSD).

C. Exergy

Exergy is defined as the maximum theoretical work which can be achieved from a substance if it is brought to the equilibrium with the environment.

Aspen Plus calculates the thermal exergy of pyrolysis products but fails to calculate the chemical exergy of biomass and bio oils so it will be calculated manually. Exergy is the sum of physical and chemical exergies.

$$E_x = E_x^{ph} + E_x^{ch} \quad (1)$$

Physical energy is attributed to temperature of the substance. It is quite significant for liquids and gases but very low for solids. It can be computed as follows.

$$E_x^{ph} = (h - h_o) - T_o(s - s_o) \quad (2)$$

Chemical exergy of biomass on the basis of higher heating value (HHV) can be expressed as follows [18].

$$E_x^{ch} = 1.047 \times HHV \quad (3)$$

Chemical exergy of bio-oil, and biochar can be calculated with following equation [19].

$$E_x^{ch} = \beta \times m \times LHV \quad (4)$$

Where β is defined as the ratio between chemical exergy and mass fraction of H/C, O/C, N/C and S/C. LHV is lower heating value of the substance. β for biochar and bio oil is given in the following relations.

$$\begin{aligned} \beta_{biochar} &= 1.0437 + 0.1896 \frac{z_H}{z_C} + 0.0617 \frac{z_O}{z_C} + \\ &0.0428 \frac{z_N}{z_C} \end{aligned} \quad (5)$$

$$\begin{aligned} \beta_{bio-oil} &= 1.0401 + 0.1728 \frac{z_H}{z_C} + 0.0432 \frac{z_O}{z_C} + \\ &0.2169 \frac{z_S}{z_C} (1 - 2.0628 \frac{z_H}{z_C}) \end{aligned} \quad (6)$$

The chemical exergy of a mixture of gases can be computed by following equation [20].

$$E_x^{ch} = n \sum x_i (ex_i^{ch} + RT_o \Delta_i x_i) \quad (7)$$

Exergy efficiency can be defined by the following relation [19]

$$\Psi = \frac{E_x, biooil + E_x, biochar + E_x, gas}{E_x, biomass + Electricity} \quad (8)$$

Standard chemical exergies of some gases can be found in table 7 [20] [21].

| Gas | E _x ^{ch} (kJ/kmol) |
|--------------------------------|--|
| H ₂ | 236,100 |
| CO | 275,100 |
| CO ₂ | 19,870 |
| CH ₄ | 831,650 |
| C ₂ H ₆ | 1,495,000 |
| C ₄ H ₁₀ | 2,804,000 |

Table 7. Standard Chemical Exergy of SOME gaseses at 25°C, 0.1 mpa

III. RESULTS AND DISCUSSION

The pyrolysis of OMWWS was carried out in Aspen Plus at 450°C. Mass flow rate of each component is given in table 8.

The products of pyrolysis of OMWWS are cooled down from 350°C in cyclone to 90°C in first condenser to condense the bio oil vapors. Cooling the products gives us the possibility to recover heat

between cyclone and 1st condenser. It is clear from figure that 285 kJ/hr of energy or 108 kJ/hr of physical exergy is retrieved in the 1st condenser. About 0.081 kg/hr of bio oil is condensed in 1st condenser. In the second condenser, products are cooled from 90°C to 10°C and water vapors (0.034 kg/hr) are condensed in 2nd condenser. The net energy exchanged in 2nd condenser is 151 kJ/hr. The exergy flow is 6.70 kJ/hr at this point. Energy and exergy flows for three components are shown in figure 2.

| Component | Products (kg/hr) |
|--------------------------------|------------------|
| CHAR | 0.06976 |
| H ₂ O | 0.038368 |
| H ₂ | 0.000401 |
| CO | 0.0034 |
| CO ₂ | 0.03924 |
| CH ₄ | 0.00095 |
| C ₂ H ₆ | 0.00505 |
| C ₄ H ₁₀ | 0.001308 |
| N ₂ | 0.6323220 |
| N-PENTADECANE | 0.0010464 |
| 8-HEPTADECENE | 0.00130 |
| 1-HEPTADECENE | 0.0010464 |
| N-HEPTADECANE | 0.0015696 |
| N-HEXADECANOIC-ACID | 0.0059296 |
| 2-ETHYLHEXADECANOIC-ACID | 0.0022672 |
| OLEIC-ACID | 0.0436 |
| ETHYL-OLEATE | 0.024416 |

Table 8. Mass flow rate for each product

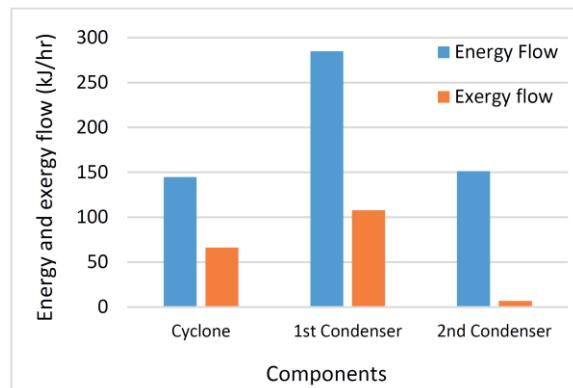


Fig. 2. Energy and exergy flow across different components

Physical exergy flow across each component is shown in figure 3. It is obvious that maximum exergy is available at 1st condenser (HX-1).

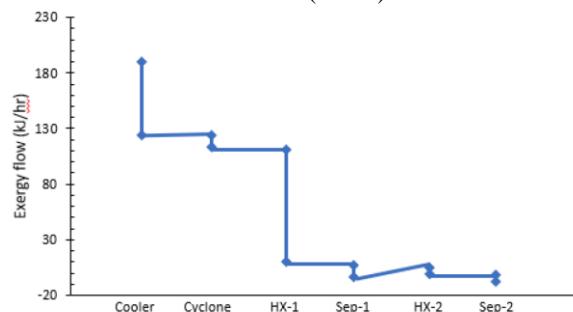


Fig. 3. Physical exergy flow across each component

The exergy efficiency for bio oil was calculated to be 60% which is a significant indicator for the pyrolysis

process. The exergy efficiency for all products was found to be 99.1% for the pyrolysis of OMWWS. It indicates that exergy was conserved in the process. The very little difference can be attributed to the electricity used in the pyrolysis reactor which was not considered.

IV. CONCLUSION

Aspen Plus V10 was used to develop a simulation thermal model for energy and exergy analysis of the pyrolysis of OMWWS as a function of operating conditions, chemical and physical properties. While cooling the non-condensable gases from 350°C to 90°C in first condenser the cooling water in heat exchanger was heated from 60°C to 67°C and a net 285 kJ/hr of energy transfer took place. At this point 108 kJ/hr of physical exergy is available to be retrieved. In the second condenser the products were cooled down from 90°C to 10°C resulting in condensing of water vapors. The hot water in the first condenser is suitable to drive an adsorption machine for cooling the products in the second condenser. The exergy efficiency shows that exergy was conserved in the process and products possess a high energy content for different applications.

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