Slow Pyrolysis of Biowastes: Environmental, Exergetic, and Energetic Assessment

Daniela Zalazar-Garcia, Erick Torres, Germán Mazza

Abstract—Slow pyrolysis of a pellet of pistachio waste was studied using a lab-scale stainless-steel reactor. Experiments were conducted at different heating rates (5, 10, and 15 K/min). A 3-E (environmental, exergetic, and energetic) analysis for the processing of 20 kg/h of biowaste was carried out. Experimental results showed that biochar and gas yields decreased with an increase in the heating rate (43% to 36% and 28% to 24%, respectively), while the bio-oil yield increased (29% to 40%). Finally, from the 3-E analysis and the experimental results, it can be suggested that an increase in the heating rate resulted in a higher pyrolysis exergetic efficiency (70%), due to an increase of the bio-oil yield with high-energy content.

Keywords—3E assessment, biowaste pellet, life cycle assessment, slow pyrolysis.

I. INTRODUCTION

THE problem of the huge quantities of biowastes produced from the agro-industry, resulting from the rapid progress in both agricultural and industrial fields, acquires an important relevance due to the human population growth since it increases not only the food demand but also the environmental pollution associated with this industry.

San Juan Province, Argentina, is the principal pistachio (*Pistacia vera* var. Kerman) producer in this country, with around 1800 hectares cultivated and the production is continuously growing. In particular, pistachio cultivation generates important amounts of biowaste during the process of the fruit. The reuse of these wastes, in agreement with environmental policies and in the frame of sustainable industries, can reduce their accumulation and harmful health effects resulting from bad disposal [1]-[3]. These lignocellulolytic wastes are mostly composed mainly of lignin, cellulose, hemicelluloses [3].

The biowaste of pistachio production has some disadvantages for its valorization, such as low mechanical resistance structure, low energetic density, high moisture, and oxygen content, restricting its use for industrial-scale applications [4].

Biowastes can be converted into energy or biofuel using thermo-chemical processes, applying thermal energy for the biowaste conversion into valuable products of higher energetic value and/or energy. Pyrolysis is a thermochemical process and generates tri-state products, biochar, bio-oil, and biogas, at elevated temperatures under an inert atmosphere. They can be utilized for many high-value applications [5]. Biochar is constituted by carbon and ash. Biogas consists of CO, CO_2, CH_4, H_2, and other light hydrocarbons [6]. Oxygenates and aromatics hydrocarbons, water, and tars are the principal constituents of bio-oil [7], [8].

The performance of the pyrolysis process allows evaluating its sustainability and use of energy resources. In this sense, exergy analysis stands as an approach to detect the inefficient use of resources in different processes [3]. The term exergy is generally employed to describe the useful portion of the energy or work. Moreover, exergy is considered a general environmental indicator due to minimizing exergy losses is comparable to optimize the use of resources and minimize the emission of harmful products [9].

Bi et al. [10] reported that the greenhouse gas emissions during the biowaste pyrolysis are lower than those generated during the use of fossil fuel. Nevertheless, the environmental and performance assessment is difficult because several conditions affect pyrolysis. The temperature, heating rate, feedstock composition, and pyrolysis agent are the principal conditions that affect pyrolysis [7], [8].

Barry et al. [11] studied slow pyrolysis as a possibility to transform the sludge to biochar. They analyzed the influence of several parameters on the leaching of heavy metals contained in the biochar obtained. They determined the global warming potential, ecotoxicity of freshwater for various uses of biochar, as well as the energy required for several fractional moistures contained in raw materials using the Life Cycle Assessment (LCA).

The 4E (environmental, economic, energetic, and exergetic) analysis of slow pyrolysis process of different lignocellulosic wastes was carried out by Torres et al. [8]. They proposed a model based on a steady-state system during a residence time long sufficient to reach the thermodynamic equilibrium.

Cheng et al. [12] assessed the energy, climate change, and economic performance of slow pyrolysis of multiple feedstocks varying the operational variables using LCA. Data reported in the bibliography were used to carry out this study.

Considering the above-cited, this work presents a 3-E (exergetic, energetic, and environmental) analysis to predict the quality and efficiency of the biowaste pyrolysis process based on a study case concerning the continuous treatment of 20 kg/h

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World Academy of Science, Engineering and Technology
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of pistachio waste feedstock.

II. Materials And Methods

A. Materials

The biowaste used was the shell of pistachio (mesocarp) obtained during the harvest and processing from a regional pistachio producer located in the San Martin Department, San Juan Province (Cuyo Region), Argentina.

The mesocarp was milled and sieved until size in the range of 0.1-0.2 mm. Then, cylindrical pellets of 8 mm in diameter and 8 mm in height were produced by a mechanical press at room temperature. A pressure of 2 ton was applied during a holding time of 1 min.

B. Characterization

The ash and volatile matter were determined and the ASTM standards were used [13], [14]. The elemental analysis of the biowaste was carried out using a EuroEA3000 elemental analyzer. The higher heating value (HHV) was estimated according to the expression given by Sheng and Azevedo [15].

C. Experiments

Experiments were carried out in a lab-scale stainless-steel reactor described by Fernandez et al. [16]. The reactor was heated using electrical resistances and was thermally isolated with internal refractory walls. Inside the reactor, the biowaste pellet was introduced in a cylindrical basket. The heating rate, operating time, operating temperature were measured and recorded. The pyrolysis experiments were performed under a nitrogen (inert) atmosphere, with a flow rate of 100 mL/min, at different heating rates of 5 K/min, 10 K/min, and 15 K/min up to constant weight.

III. 3E Analysis

A. Environmental Analysis: LCA

The environmental analysis was focused principally on greenhouse gas emissions. In this context, the environmental analysis is represented by the LCA. The LCA is a recognized methodology to assess the environmental impacts of products and processes from "cradle to grave" [12].

To perform the LCA, 20 kg/h of biowaste feed was adopted, as described by Cerone et al. [17], for a pilot plant under continuous operation. These assumptions permit conceiving a study case in a continuous pyrolizer. It is assumed that the heat required for endothermic pyrolysis reaction is provided using 1.5 kWh of electric energy. Nitrogen flow fed to the reactor was 0.5 kg/min. SIMAPRO 8.0 using ReCiPe 2016 Endpoint (I) V1.03 was utilized to carry out the LCA.

B. Exergy Analysis

Exergy analysis allows to recognize the useful energy of a system and detecting thermodynamic inefficiencies [18]. It is important to note that the kinetic and potential energy were not taken into account in this study. Table I shows the equations that described the exergy analysis.

TABLE I
Expressions For Exergy Analysis

Exergy flow of stream [3], [18]

$$\dot{\varepsilon} = \dot{\varepsilon}_{ph} + \dot{\varepsilon}_{ch} \tag{22}$$

Physical exergy of a pure compound [18]

$$\dot{\varepsilon}_{ph,i} = \int_{T_0}^{T} C_{Pi}\, dT - T_0 \left(\int_{T_0}^{T} C_{Pi}/T \, dT \right) \tag{23}$$

Physical and chemical exergies of syngas [18]

$$\dot{\varepsilon}_{ph} = \sum_i y_i \left[\left(\int_{T_0}^{T} C_{Pi}\, dT \right) - T_0 \left(\int_{T_0}^{T} C_{Pi}/T\, dT \right) \right] \tag{24}$$

$$\dot{\varepsilon}_{ch} = \sum_i y_i \dot{\varepsilon}_{ch,i} + RT_0 \sum_i y_i \ln y_i \tag{25}$$

Chemical exergy of biowaste [8], [18]

$$\dot{\varepsilon}_{ch} = m\, \beta\, LHV \tag{26}$$

Factor β for biowaste, bio-oil, and biochar [8], [18]

$$\beta = (1.004 + 0.0016H/C - 0.3493O/C(1 + 0.0531H/C) + 0.0493N/C)/(1 - 0.4124O/C) \tag{27}$$

$$\beta = 1.0374 + 0.0159H/C + 0.0567O/C \tag{28}$$

$$\beta = 1.0437 + 0.1869H/C + 0.0617O/C \tag{29}$$

Exergy efficiency [8], [18]

$$\eta_{ex\,g} = \dot{\varepsilon}_{in}/\dot{\varepsilon}_{out} \tag{30}$$

Physic exergy flow [8], [18]

$$\dot{\varepsilon}_{ph} = \dot{\varepsilon}_{phT} + \dot{\varepsilon}_{phP} \tag{31}$$

$$\dot{\varepsilon}_{phT} = \Phi\, C_P[+(T - T_0) - T_0 \ln T/T_0] \tag{32}$$

$$\dot{\varepsilon}_{phP} = \Phi \frac{RT_0}{M} \ln P/P_0 \tag{33}$$

Exergy destroyed [3]

$$\dot{\varepsilon}_{destroyed} = \dot{\varepsilon}_{ph\,in} - \dot{\varepsilon}_{ph\,out} \tag{34}$$

Chemical exergy [3]

$$\dot{\varepsilon}_{ch} = \dot{\varepsilon}_{St} + \dot{\varepsilon}_{mix} \tag{35}$$

Flow exergy associated with compound mixing [3]

$$\dot{\varepsilon}_{St} = \Phi \sum_{i=1}^{n} x_i b_i^0 / M_i \tag{36}$$

Exergy wasted [3]

$$\dot{\varepsilon}_{Wasted} = \dot{\varepsilon}_{ch\,in} - \dot{\varepsilon}_{ch\,out} \tag{37}$$

The physical exergy (24) changes because the pressure was not considered in this work due to the pyrolysis process was carried out at constant pressure (atmospheric) [19].

Equation (24) shows that the resulting T_{fs} value is the temperature at the external surface of the pellet evaluated at the final condition that is taken as the condition for the evaluation of the different exergetic parameters, linking the two parts of the study carried out in this paper.

The physical exergy of the biowaste was neglected because it entered into the reactor at room temperature, $T_0 = 298$ K.

Biochar and bio-oil compositions were obtained from the correlations reported by Torres et al. [8].

As pointed out before, the calculations were carried out based on 20 kg/h of biowaste fed.

C. Energy Analysis

The energy analysis was carried out considering the energy contained in products, in the incoming biowaste, and the energy of heat supplied to the reactor. The base of 20 kg/h was used. Table II shows the equations that described the energy analysis.

The incoming energy, as expressed in (39), is the energy contained in the biowaste pellets and the energy of heat supplied to the reactor. The outgoing energy is the energetic content in products (40) [20]. Moreover, the total heat supplied to the reactor was calculated using (45) [8].

World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:16, No:8, 2022

IV. RESULTS AND DISCUSSION

A. Biowaste Characterization

Table II shows the results of the proximate and elemental analysis and predicted values of HHV of the pistachio mesocarp. The contents of carbon and hydrogen are in agreement with Demiral et al. [21], 50.20% C, 6.32% H, 0.69% N. These authors reported an ash content of 1.41% slightly higher than 1.3%.

TABLE II
RESULTS OF PROXIMATE AND ELEMENTAL ANALYSIS OF PISTACHIO
MESOCARP (D.B, WT%). PREDICTED VALUES OF HHV

$C_{biowaste}$ (%)	47.9 ± 2.09
$H_{biowaste}$ (%)	6.2 ± 0.70
$N_{biowaste}$ (%)	1.0 ± 0.11
$S_{biowaste}$ (%)	0.2 ± 0.04
$O_{biowaste}$ (%)[a]	42.7 ± 1.9
Ash (%, dry basis)	1.3 ± 0.14
Volatile matter (%, total weight)	72.2 ± 4.50
Fixed carbon (%, dry basis)	22.1 ± 1.42
Weight loss at 378 K (%, total weight)	4.3 ± 0.52
$HHV_{biowaste}$ (MJ/kg)	20.15 ± 2.34

[a]by difference

B. Pellet Pyrolysis

Table III presents the results of the experimental data, which show the influence of the heating rate on pellet decomposition under an inert atmosphere. Also, the biochar yield decreases when increasing the heating rate [8]. Similar behavior is present for the gas. On the other hand, the results of obtained bio-oil yields contrasted with values previously reported in the literature [22], [23]. It was also observed that at higher heating rates, the bio-oil yields increased [24]. In addition, when the heating rate increases, the secondary carbonization reactions decrease because the biochar formation reactions are promoted at low temperatures [24]. Hence, biochar yield decreased with an increase in the heating rates (Table III). Biochar yields were 43%, 40%, and 36.5% at 5 K/min, 10 K/min, and 15 K/min, respectively.

TABLE III
EXPERIMENTAL MASS YIELD OF PYROLYSIS PRODUCTS AT DIFFERENT
HEATING RATES

β [K/min]	Biochar (wt. %)	Bio-oil (wt. %)	Gas (wt. %)
5	43 ± 2	29 ± 3	28*
10	40 ± 3	34 ± 4	26*
15	36 ± 3	40 ± 2	24*

Yields values are mean (n = 3) ± SD
*by difference

C. Energy, Exergy, Environmental (3E) Assessment

The 3E analyses were applied to the study case defined in previous sections for this part of the work. A feedstock of 20 kg/h and the experimental product yields at 5 K/min, 10 K/min, and 15 K/min was used to perform the energy, exergy, and environmental analysis.

1. LCA Results

The emissions determinate for greenhouse gas to air are shown in Table IV. Results indicated that CO_2 and H_2O presented the highest emissions. The emission of CO_2 was produced by three causes: combustion of biochar, bio-oil, and gas produced from slow pyrolysis. The fossil fuel source that was generated by nitrogen production required for the inert atmosphere in the reactor, and electricity production for heating reactor; and biogenic sources, which was generated during nitrogen production.

TABLE IV
EMISSIONS OF GREENHOUSE GAS TO AIR

Emissions	Source
CO_2 emission: 1180 g	Combustion of slow pyrolysis products: 943 g
	Fossil fuel: 218 g
	Biogenic sources: 19.8 g
CH_4 emission: 4 g	Slow pyrolysis of biowaste pellet: 4 g
Emission of nitrogen oxides: 487 mg	Nitrogen required for an inert atmosphere in the reactor: 373 mg
	Electricity from reactor consumption: 114 mg
O_3 (Ozone) emission: 2.17 mg	Nitrogen-tube for an inert atmosphere in the reactor: 2.17 g

*Analyzing 1 kg of biochar produced from slow pyrolysis of biowaste

An alternative for the use of biochar can be a soil amendment [25], [26], and carbon activated in rum production [27]. LCA indicated that the use of biochar as a soil amendment or carbon-activated could reduce the emissions of greenhouse gas [28]. The emission of CH_4 gas was only caused by slow pyrolysis in the produced gas. The emission of nitrogen oxides was created by nitrogen and electricity production, while the emission of ozone was generated only by nitrogen production according to SIMAPRO databases. Another important aspect to improve could be the use of alternatives energy sources such as concentrated solar energy to supplying the pyrolysis heat of reaction [28].

2. Exergy Analysis

Table V shows the results of the exergy analysis. It indicated that the higher efficiency occurred at a heating rate of 15 K/min, with 70%. The increase in heating rate causes an increase in bio-oil exergy. This condition favors the bio-oil yield, even though the LHV value of the bio-oil (20 MJ/kg) is lower than the LHV value corresponding to the biochar (30 MJ/kg). In addition, as the heating rate increased from 5 K/min to 15 K/min, the bio-oil yield increased by 34%, while the biochar decreased by 17%. The gas contributions to the product exergy were not significant.

TABLE V
EXERGY OF PYROLYSIS PRODUCTS AND EXERGETIC EFFICIENCY

β (K/min)	Bio-oil Exergy (MJ/h)	Biochar Exergy (MJ/h)	Gas Exergy (MJ/h)	Exergetic Efficiency
5	127	253	2.67	0.65
10	147	236	2.50	0.68
15	171	211	2.25	0.70

3. Energetic Analysis

Fig. 1 shows the results of the energy analysis. The higher energy content is associated with the production of biochar.

World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
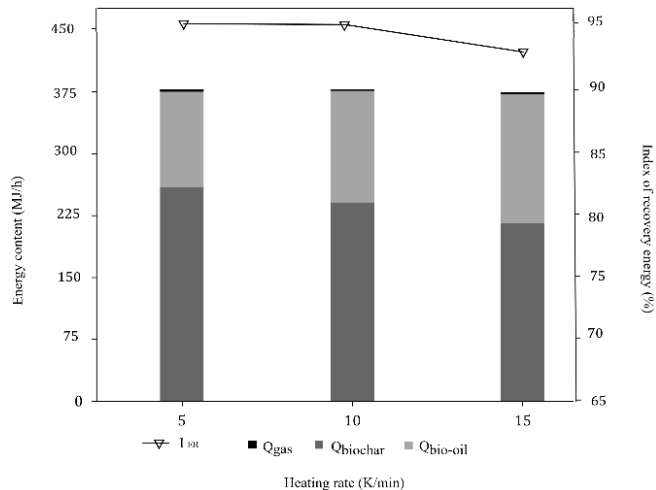Vol:16, No:8, 2022

Fig. 1 Energetic content of pyrolysis products and Index of recovery energy at 5 K/min, 10 K/min, and 15 K/min on a basis of 20 kg/h of biowaste

Values of the percentage of Index of recovery energy were within the 68-57% range for heating rates comprised between 5-10 K/min, respectively. The percentage of gas represents less than 1%. The Index of recovery energy (IER) values of slow pyrolysis at different heating rates ranged from 93.6% to 94.5%. These results indicate that almost all of the energy content of biowaste was transformed into energetic products. However, the IER of recovery energy decreased with the increase of the heating rate. This indicates that the pyrolysis of biowaste was not fully achieved under the operating conditions studied.

V. CONCLUSIONS

In this work, the 3E analysis (energy, exergy, environmental) was carried out.

Regarding LCA, the results showed the sources of emission of greenhouse gas during slow pyrolysis. Consequently, it is possible to reduce the environmental impact by using alternative unit operations and other pyrolysis agents different from nitrogen gas; or obtaining products as biochar used as a soil improver, which does not require combustion. For this work, the CO_2 and CH_4 emissions were 1180 and 4 g per kilogram of biochar, respectively.

In energy terms, the pyrolysis process is more efficient because higher heating rates cause an increase in the yield of bio-oil with high-energy content. The indexes of recovery energy were 94.5%, 94%, and 93.6% at 5 K/min, 10 K/min, and 15 K/min, respectively. About exergy analysis, a higher exergetic yield was obtained for slow pyrolysis at 15 K/min. This result suggested that the process becomes more efficient with the increase of bio-oil, due to an increase in its mass and its high energy content. However, bio-oil increases the emission of greenhouse gas.

This work proposes a beginning for future research involving the optimization between pyrolysis processes that are energy efficient and those having low emissions of greenhouse gases.

NOMENCLATURE

Symbol

b_i^0	Standard energy, MJ/h
C	Carbon content, %
$C_{biowaste}$	Carbon content of biowaste, %
Cp_i	Heat capacity of component "i", J/(kg K)
H	Hydrogen content, %
$H_{biowaste}$	Hydrogen content of biowaste, %
$HHV_{biowaste}$	Higher heating value of biowaste, MJ/kg
HHV_i	Higher heating value of i-th component, MJ/kg
i	i-th component
M_i	Molecular weight
m	Flow, kg/h
N	Nitrogen content, %
$N_{biowaste}$	Nitrogen content of biowaste %
P0	Reference pressure
P	Pressure
O	Oxygen content, %
$O_{biowaste}$	Oxygen content of biowaste, %
R	Universal gas constant, $8.3144 \times 10{-3}$ kJ/(mol K)
$S_{biowaste}$	Sulfur content of biowaste, %
T	Temperature, K
T_0	Initial temperature, K
x_i	Mols of i-th component, kmol
y_i	Molar fraction, of component "i"

Greek letters

$\eta_{ex\,g}$	Exegetic efficiency of gas
ε	Exergy, MJ/h
εch	Chemical exergy, MJ/h
εch_i	Chemical exergy of component "i", MJ/h
εph	Physical exergy, MJ/h
ε_{phT}	Physical exegetic due to temperature change, MJ/h
ε_{phP}	Physical exegetic due to pressure change, MJ/h
β	Correlation factor
$\varepsilon wasted$	Exergy of wasted, MJ/h
$\varepsilon_{ch\,in}$	Chemical exegetic input, MJ/h
$\varepsilon_{ch\,out}$	Chemical exegetic out, MJ/h
ε_{prod}	Products exergy, MJ/h
ε_{in}	Input exergy, MJ/h
$\varepsilon_{destroyed}$	Exergia destroyed, MJ/h
Φ	Molar quantity
ε_{mix}	Exergy due to mixing, MJ/h
ε_{St}	Exergy standard, MJ/h

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World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:16, No:8, 2022

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