Thermochemical Degradation of Polypropylene: Energy and Exergy Analysis in a Tubular Reactor

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ABSTRACT

One method to evaluate the energy behavior is energy and exergy analysis. These analyses applied to waste-to-energy conversion technologies provide the information on operating conditions, facilitating energy optimization processes. In this study, an energetic and exergy analysis was used on the thermochemical degradation process of polypropylene in a tubular reactor at 600 °C with a speed of 15 °C min^{-1}. The experimental data used in this work were taken from the study by Parku et al. (2020). According to the results, energy efficiencies of up to 43% and exergy efficiencies of 38% were achieved, and it was also observed, according to what was reported, that the products obtained from pyrolysis contain a high calorific value and can be used as alternative fuels.

Keywords: tubular reactor, exergy, energy, PP, thermal degradation.

INTRODUCTION

The increase in energy demand, climate change, the high disposal of solid waste, and the shortage of oil sources have begun to drive researchers in various areas to seek solutions to all these problems. An exciting route is through the energy recovery of all waste, thus reducing solid contaminants and producing an alternative energy source (Barbarias et al., 2018). The technology for energy recovery used in various countries is through the incineration of waste. However, its energy efficiency tends to be low compared to a traditional coal-burning plant (Tang et al., 2016). In addition, the incineration of solid waste puts the environment at risk, since it tends to emit highly polluting gases such as acid, mercury, dioxins, and furan dioxins, furan (Yutao Zhang et al., 2020). For this reason, some researchers propose an alternative method known as pyrolysis.

Pyrolysis is a thermochemical process in which carbon-based compounds, such as some municipal solid waste (MSW), can be degraded and converted into combustible products (Cruz et al., 2022). Pyrolysis applied to plastic waste has been studied and reported by various researchers (Ali et al., 2011; Cardona & Corma, 2000; Elordi et al., 2009; Garforth et al., 1998; Kim & Kim, 2004; Lin et al., 2010; Miskolczi et al., 2009; Scott et al., 1990; Yoon et al., 1999), and the results shown indicate that up to 80 wt% conversions can be obtained, thereby producing fuel products similar to diesel and gasoline, density (0.8 MJ/kg), viscosity (above 2.96 mm^2/s), cloud point (-18 °C), flash point (30.5) and calorific value of (40 MJ/kg) (Rehan et al., 2016). In addition,

another benefit of pyrolysis is the low emission of polluting gases, such as dioxins.

Considering all its benefits, it is crucial to establish a theoretical methodology that allows the energetic evaluation of the thermochemical degradation process and the improvement in the energy efficiencies of the process, involving, in turn, the different experimental schemes and operating parameters to which it is carried out – pyrolysis. That is why this work arose, based on the results reported by Parku et al. (2020), to establish a theoretical evaluation for the energy-exergy efficiencies of the polypropylene pyrolysis in a tubular reactor.

Table 1. Input data

Products	Units	Qty
PP	g	twenty
Liquid (heavy and light oil)	%	63
Gas	%	27
Char	%	2.5
Electrical power supply	W/h	300
Dead state conditions		
T0	K	298
T	K	873
R	J mol-1 K-1	8.3144
P	kPa	14.8
P0	kPa	14.7

## METHODOLOGY AND MATERIALS

Materials

The development of this work was based on the results obtained by Parku et al. (2020), in which the thermochemical degradation of PP was evaluated at different temperatures (450, 488, 525, and 600 °C) and different heating rates (15 and 180 °C/min) in a tubular reactor. Therefore, only the results at 600 °C with a heating rate of 15 °C/min (slow atm) are considered for this case. The input data is shown in Table 1.

Figure 1 describes the experimental scheme used in all the tests. It is a tubular reactor

approximately 1 m long with an internal diameter of 60 mm. It contains two K-type thermocouples, one located in the middle of the reactor and another on the wall of the reactor. For the slow pyrolysis tests, the PP sample was introduced into the reactor before being heated. The gaseous products were separated and condensed in 4 crystal vessels and subsequently collected for quantification.

Theoretical evaluation for the energy and exergy analysis of the thermochemical degradation process

The data obtained from the pyrolysis of polypropylene in the tubular reactor are used for
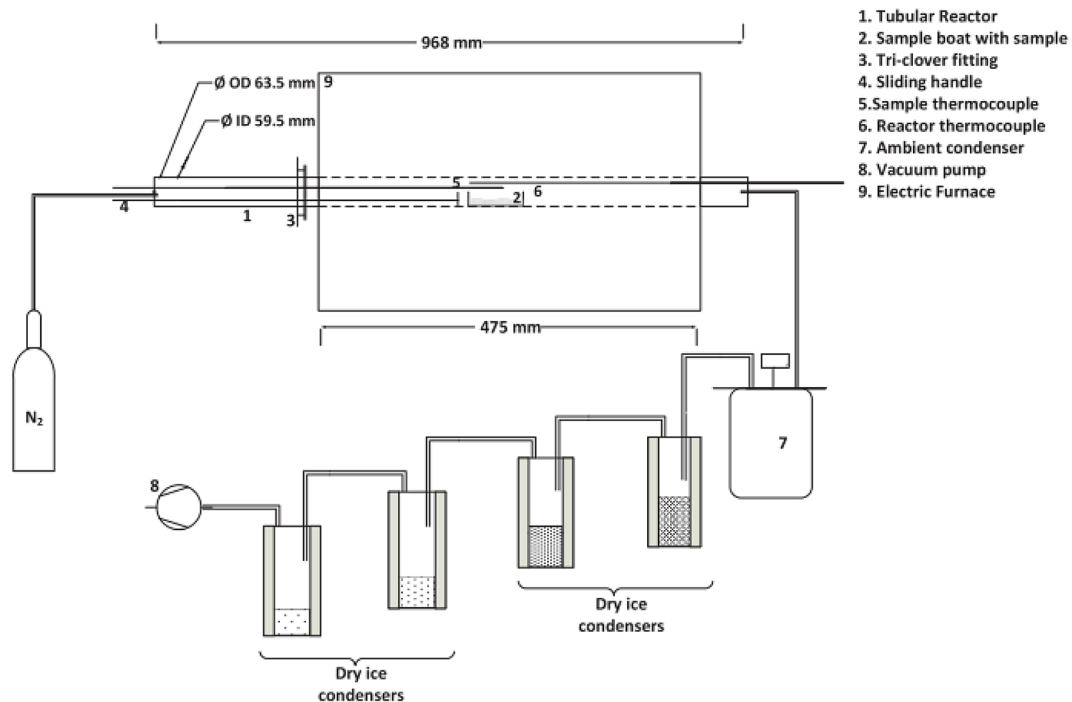
Figure 1. Experimental scheme used by Parku et al. (Parku et al., 2020)

energy and exergy analysis. The input and output products are represented in Figure 2, while the theoretical methodology is described below.

Energy efficiency based on the first law

According to Zhang et al. (Yutao Zhang et al., 2020), the steady-state energy balancecan be calculated through the first law;therefore, pyrolysis can be expressed as:

$$E_{int} = E_{out} + E_{loss} \tag{1}$$

where: E_{int} – the total input energy;
  E_{out} – the output energy;
  E_{loss} – represents the energy losses in the pyrolysis process.
  The input and output energies can be expressed as:

$$E_{int} = Q_{pw} + Q_s \tag{2}$$

$$E_{out} = Q_{liq} + Q_{gas} + Q_{char} \tag{3}$$

where: Q_{pw} – the energy contained in the plastics;
  Q_s – the demand for electrical energy required by the system, and the subscripts, liquid, solid, and gas, are the output energies of these products; the energy balance can be rewritten as shown below:

$$Q_{pw} + Q_s = Q_{liq} + Q_{gas} + Q_{char} \tag{4}$$

The energy recovered from the pyrolysis of plastic waste, is calculated by Equations 5 and 6, taking into account the calorific values (Lopez et al., 2011; Mei et al., 2016).

$$Q_{pw} = HHV_{pw} \tag{5}$$

$$E_{out} = X_i + HHV_i \tag{6}$$

where: Q_{pw} – the energy contained in the plastic waste;
  HHV_i – the higher calorific power of the fractions (liquid, gas, solid);
  X_i – the mass yield of the pyrolysis products per kilogram of plastic waste.
  The calculation of energy efficiency of the pyrolysis process based on the first law will be calculated using Equation 7:

$$\eta = \frac{Q_{recovery}}{Q_{pw} + Q_s} \tag{7}$$

Exergy analysis based on the second law

Exergy can be defined as the maximum work potential of a system in an environment balanced with the environment. This concept is based on the second law of thermodynamics (Boateng et al., 2012; Yaning Zhang et al., 2015). The sum of all exergies in a system, canbeexpressedas:

$$e_x = e_x^{ph} + e_x^{ch} + e_x^{ki} + e_x^{po} \tag{8}$$

where: e_x^{ph} – the physical exergy (MJ/kg);
  e_x^{ch} – the chemical exergy (MJ/kg);
  e_x^{ki} – the kinetic exergy (MJ/kg);
  e_x^{po} – the potential exergy (MJ/kg).
  The kinetic and potential exergy can be considered irrelevant due tobeing relatively tiny (Wang et al., 2016; Yaning Zhang et al., 2015). Therefore, Equation 8 is to be approximated by:

$$e_x = e_x^{ph} + e_x^{ch} \tag{9}$$

The physical exergy of gaseous products can be calculated as shown below (Tang et al., 2016; Yaning Zhang et al., 2015):

$$e_{x,gas}^{ph} = \sum n_i[(h - h_0) - T_0(s - s_0)] \tag{10}$$

$$h - h_0 = \int_{T_0}^{T} C_p dT \tag{11}$$

$$s - s_0 = \int_{T_0}^{T} \frac{C_p}{T} dT - R ln \frac{p}{p_0} \tag{12}$$

where: n_i – the molar yield of the gas components "i" (mol/kg);
  s – the specific entropy (KJ/kmol K);
  h – the specific enthalpy (KJ/kmol) of the gas component "i" under operating conditions, respectively;
  h_0 – the specific enthalpy;
  s_0 – the specific entropy of the component "i" of the gas at a standard environmental reference;
  R – the specific heat at constant pressure (J/mol K) and the general gas constant (8.3144 J/mol K).

The specific heat constant at constant pressure (Cp) can be calculated according to the next correlation (Wang et al., 2016):

$$C_p = A + BT + CT^2 + DT^3 + ET^4 \tag{13}$$

The A~E constants are coefficients of the specific heat at constant pressure, which are listed in Table 2. The equation 14 is used to determine the chemical exergy of the gas (Yaning Zhang et al., 2015).

$$e_{x,gas}^{ch} = \sum y_i e_{ch,i}^0 + T_0 R \sum y_i ln y_i \qquad (14)$$

where: y_i – the molar fraction of the gas component "i";

$e_{ch,i}^0$ – the chemical exergy standard of the gas component "i", it can be seen in Figure 3. The evaluation of the chemical exergy of the pyrolytic liquid and plastic waste can be obtained based on its lower heating value (LHV) (Eq. 15, 16):

$$e_{x,pw}^{ch} = \beta_0 LHV_{pw} \qquad (15)$$

$$e_{x,liquid\ oil}^{ch} = \beta_1 LHV_{liquid\ oil} \qquad (16)$$

where: $LHV_{liquid\ oil}$ – a lower heating value than the pyrolytic liquid and are correlation factors of plastic residues and pyrolytic liquid based on the latest analysis. Therefore, they are estimated by (Tang et al., 2016; Wang et al., 2016).

$$ß_0 = \frac{1.044 + 0.0160\frac{H}{C} - 0.3493\frac{O}{C}\left(1 + 0.0531\frac{H}{C}\right) + 0.0493\frac{N}{C}}{1 - 0.4124\frac{O}{C}} \qquad (17)$$

$$ß_1 = 1.0401 + 0.1728\frac{H}{C} + 0.0432\frac{O}{C} \qquad (18)$$

where: C, H, O, and N constants are the mass fractions of carbon, hydrogen, nitrogen, and oxygen. These are shown in Table 3. The total exergy efficiency of the thermochemical degradation of plastics according to the exergies obtained from the products can be defined by:

$$\psi = \frac{e_{liquid} + e_{gas} + e_{char}}{e_{pw} + e_s} x100\% \qquad (19)$$

where: ψ – the exergy efficiency of the pyrolysis process;

e_{pw}, e_s – the energy to degrade the plastic residue and energy required by the reactor to bring it to reaction conditions.
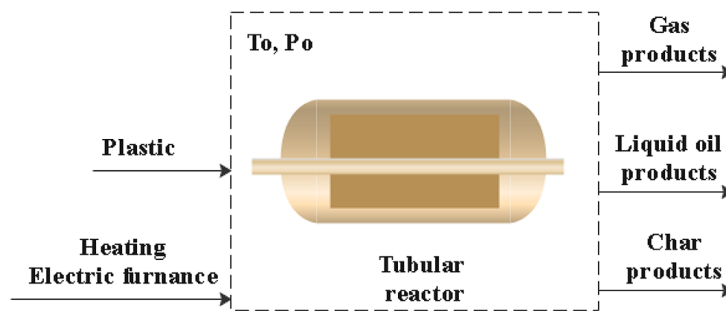

Figure 2. Int and output of products in the tubular reactor

Table 2. Coefficients of specific heat capacity of gases at constant pressure (Yutao Zhang et al., 2020)

Gas	A	B(x10-2)	C(x10-5)	D(x10-9)	E(x10-11)	Temperature range (°C)
H2	29.1100	-0.1916	0.4003	-0.8704	-	0-1527
CH4	19.8900	5.0240	1.2690	-11.0100	-	0-1527
CO	28.1600	0.1675	0.5372	-2.2220	-	0-1527
CO2	22.2600	5.9810	-3.5010	7.4690	-	0-1527
C2H4	3.9500	15.6400	-8.3440	17.6700	-	0-1527
C2H6	6.9000	17.2700	-6.4060	7.2850	-	0-1527
C3H6	3.1500	23.8300	-12.1800	24.6200	-	0-1527
C3H8	-4.0400	30.4800	-15.7200	31.7400	-	0-1527
1-C4H10	3.9600	37.1500	-18.3400	35.0000	-	0-1527
TR-2-C4H8	40.3120	13.4720	16.8770	-211.4000	6.3263	-73-1227
1-C4H8	24.9150	20.6480	5.9828	-141.7000	4.7053	-73-1227
Iso-C4H8	32.9180	18.5460	7.7876	-146.4000	4.6867	-73-1227
Cis-C4H8	29.1370	14.0080	19.1090	-237.2000	7.0962	-73-1227

Table 3. The ultimate analysis, HHVs, H/C ratio of liquid oils, and the carbon distribution of pyrolysis products (Yutao Zhang et al., 2020)

Run	Carbon distribution (wt%)			Ultimate analysis				H/C	HHV (MJ kg⁻¹)
	Liquid oil	Gas	Char*	C	H	oh	N		
SMP-0%	55.3±1.3	44.0±0.7	0.6±0.8	88.0	8.1	3.0	0.9	1.1	39.1
SMP-5%	56.6±1.5	41.9±0.9	1.5±1.1	88.8	8.3	2.1	0.8	1.1	41.0
SMP-10%	58.2±0.9	39.2±0.8	2.6±0.6	89.2	8.6	1.4	0.80	1.2	41.3
SMP-15%	62.2±0.8	34.2±1.2	3.6±0.6	88.9	9.7	0.6	0.8	1.3	42.9
SMP-20%	51.6±1.7	45.4±0.8	3.0±1.1	90.4	8.7	0.2	0.7	1.2	42.0
PE-15%	47.6±1.8	43.6±0.9	8.8±1.2	87.2	11.8	0.7	0.3	1.6	43.4
PP-15%	78.1±1.0	16.5±0.8	5.4±1.1	87.0	12.5	0.1	0.4	1.7	44.0
PS-15%	90.6±1.3	7.1±0.8	2.2±0.9	91.9	7.6	0.3	0.2	1.0	40.8
Diesel[b]	-	-	-	86.6	13.3	0.0	-	1.8	44.9
Gasoline[c]	-	-	-	85.8	14.2	-	-	2.0	43.9

Note: [a] calculated by difference, [b] ref (Ayanoglu and Yumrutas, 2016a), [c] ref (Ayanoglu and Yumrutas, 2016b).

RESULTS

Yields and chemical composition

According to the results obtained by Parku et al. (2020), all trials showed high conversion rates, above 80 wt%. Furthermore, it was observed that the temperature tends to decrease the liquid yields, while the percentage of gaseous yield increases both for low and high heating rates. Regarding the influence of the heating rate, a tendency to obtain a higher liquid yield was shown for the tests carried out at lower ramps (Figure 3).

In terms of the reported chemical composition of the PP pyrolysis, it is observed in the results that in all the tests, a higher concentration of C_1-C_3 compounds was obtained, and a lower concentration of C_4-C_5, CO, and CO_2 compounds. This can be mainly due to the reaction mechanisms involved in the formation of new compounds (Figure 4).

Energy and exergetic efficiency

The energy content of the pyrolysis products is shown in Figure 5a. The energy balance was calculated using equation 4. The energy in the pyrolytic liquid was 736 kJ according to the liquid yield obtained, which was 73 wt%. On the other hand, the energy contained in the gas was 126.4 kJ for a gas yield of 27 wt%. Therefore, gaseous products are considered a leading energy source with the potential to supply part of the energy demand required for the pyrolysis process (Brown
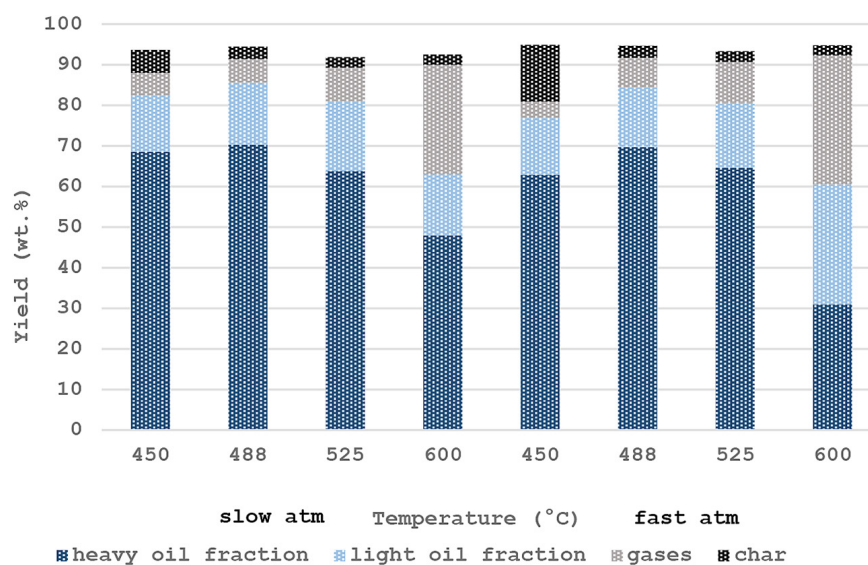
Figure 3. Yields of the products obtained from the pyrolysis of PP, obtained from (Parku et al., 2020)
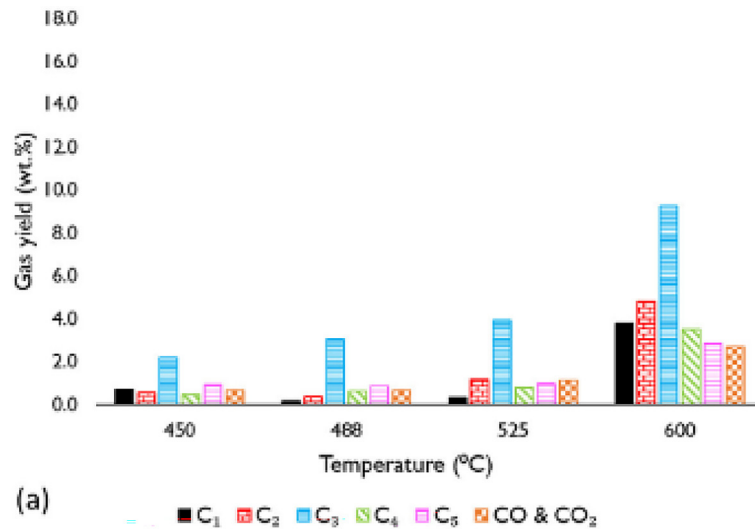
Figure 4. Chemical composition of gases. They are obtained from (Parku et al., 2020)

et al., 2017). Regarding the energy losses, there was a total of 1 121 kJ, which is part of the energy demand for heating the furnace that is lost in the cooling process.

The exergy value for the pyrolytic liquid was 617.3 kJ, subject to the H/C ratio described in equation 17; depending on this, the exergy value can increase or decrease (Figure 5b). The value of the exergy for the gas was 157.8 kJ. This value is subject to the distribution of the chemical composition of the gas, which is shown in Figure 4.

The energy and exergy efficiencies are shown in Figure 6. For the energy efficiency, there was a result of 43.97% and a value of 38.35% for the
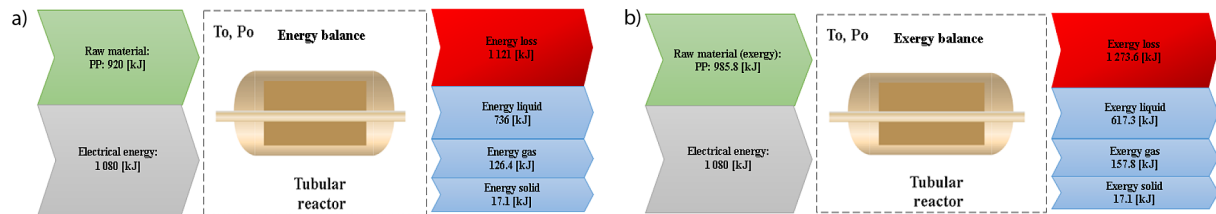

Figure 5. Sankey diagram for the energy balance (a) and exergy balance (b) of the pyrolysis process in a tubular reactor
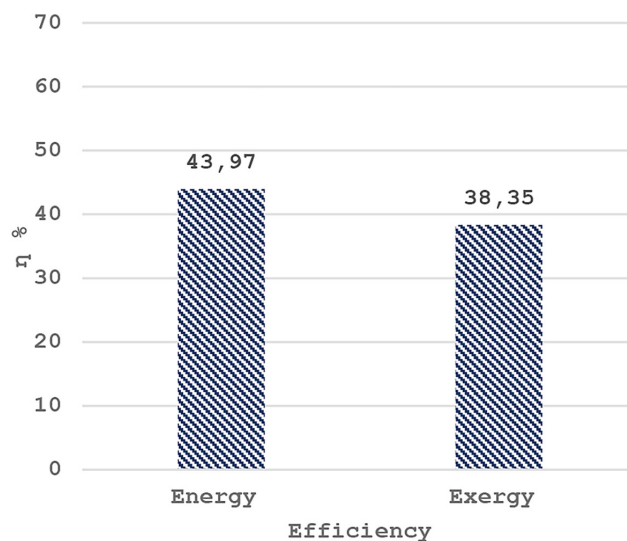

Figure 6. Energy and exergy efficiency of the PP pyrolysis process

exergy efficiency, which turned out to be lower. This is mainly because the environmental conditions of the process are considered in an exergy analysis. For this reason, the energy efficiencies fail to reflect the energy potential of the products, contrary to the exergy potential.

CONCLUSIONS

The energy analysis showed an efficiency of 43.97%, and an efficiency of 38.35% was obtained for the exergy analysis. The difference between them is mainly due to the environmental conditions considered in the exergy evaluation. In both cases, it was observed that more than half of the input energy was lost during the pyrolysis process. This is mainly due to the heating process required for the thermochemical degradation of PP. According to the study, it was observed that the gas could supply part of the energy demanded by the process. An interesting study would be a pyrolysis gas recirculation system for heating the reactor, analyzing the efficiencies of this implementation.Moreover, different degradation temperatures can be evaluated since,lower temperatures require less energy demand, which would allow increasing both energy and exergetic efficiencies.

The energy and exergyanalyses presented in this work are aimedat guiding the optimization of waste conversion processes into energy products.

Acknowledgments

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