Analysis of process parameters and assessing the possibility of utilizing the tail gases as energy sources for the pyrolysis of polyolefins

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Polyolefins (POs) represent ca. 65% of plastic waste (Abdy et al., 2022) and are suitable plastic types for the production of liquid fuels via pyrolysis technology. High-density polyethylene (HDPE), low-density polyethylene (LDPE), and polypropylene (PP) are together grouped as POs. High C/H ratio (ca. 6.6) and ash-free structure of pure POs (Kumagai et al., 2020) maximizes the liquid (i.e. pyrolysis oil) production while suppressing the production of solids (i.e. char) and gases (non-condensable gases) in pyrolysis conditions.

To produce fuel-like products from the pyrolysis of POs, the optimization of operational parameters (e.g. temperature, vapor residence time, and pressure) and units (e.g. feeder, reactor, and condenser types) is crucial. To resemble industrial processes, the design of a pyrolysis system should provide flexibility for optimization and favorableness for scaling-up. Systems involving batch and/or semi-batch reactors are frequently preferred for lab-scale due to their ease in operation, however, they are difficult to scale up. In contrast, for the maximization of the yield and enhancing the quality of the targeted products, continuous systems, which are adjustable and are easy to scale up, are preferred.

In this work, the literature reports, published between 1984 and 2021, focusing on the pyrolysis of POs performed in continuously and non-catalytically operated process systems were investigated. The ultimate goal is to determine the optimum process parameters maximizing the liquid yield during the pyrolysis of POs and investigating the suitability of gas products as energy sources for the process. In line with the industrial processes, a continuous pyrolysis setting was focused, while non-catalytic (NC) pyrolysis was chosen to explain trends in yields in the absence of any promoter (i.e. catalysts). 23 research articles were collected and deeply analyzed in terms of the reported product yields and energy values of the (by-)products. Figure 1, based on the reported results in the literature, shows the correlation between the *pyrolysis temperature* and the *yield of liquid* product (i.e. pyrolysis oil). The highest allowable temperature (600 °C), and the lowest expected yield of liquid product (70 wt.%) is set as criteria according to the results of TGA and DTG analyses, respectively. The data falling in the optimal zone for liquid production (cross-sectional area of dashed lines) were further examined with an aim of explaining the energy potential of the gas products (i.e. C1 to C4 hydrocarbons) as by-products. The total combustion energy of gases was calculated by Equation 1, where E_{gas} and CV are the total energy of gas products and the calorific value, respectively. The theoretical total energy requirement of a continuously operating process for the pyrolysis of 100 kg of POs is 280 MJ. This amount includes the energy needed for breaking the C-C bonds, heating, fusion, and evaporation of polymers (Abdy et al., 2022). The theoretical coverage of energy need for 100 kg POs was determined by Equation 2 (Dispons, 2006).

$E_{gas} = CV_{CH4} * Yield_{CH4} + CV_{C2H4} * Yield_{C2H4} + CV_{C2H6} * Yield_{C2H6} + CV_{C3H6} * Yield_{C3H6} + CV_{C4H8} * Yield_{C4H} + CV_{H2} * Yield_{H2}$……………………………………………………………………………….…………………*Eqn. 1*

% coverage for energy need = $(280000 / E_{gas}) * 100$…………………………………………….…...…………*Eqn. 2*

According to Figure 1, the liquid yield decreases at temperatures higher than 600 °C where the gas formation is favored due to excessive cracking reactions regardless of the plastic-type. At temperatures below 450 °C, which is lower than the highest degradation temperatures for POs, more than 90 wt.% of liquid is obtained. Typically, wax is the main component in the liquid at these temperatures (Abdy et al., 2022). However, using a reactor eliminating heat and mass transfer limitations or increasing the vapor residence time may lead to wax cracking and the production of lightweight fuels (C5-C15). Polyethylene (PE), represented by green markings in Figure 1, is pyrolyzed at the temperature range where the gas formation is favored. The major product was ethylene, hence the monomer recovery from the PE is the target for these studies (Kumagai et al., 2020). In Table 1, the calculations concerning the total energy required for the pyrolysis of 100 kg of POs is given. Both the yield and the composition of gas products are important for determining the energy required for pyrolysis. Gas yields ca. 5 wt.% were found to provide almost all energy required for the pyrolysis of POs. The elevated H_2 contents in the gas products lead to a decrease in the required total amount of gases (Kumagai et al., 2020). Thus, increasing the H_2 yield, in a well-optimized process, will provide sufficient energy for the pyrolysis of POs without sacrificing the liquid yield.

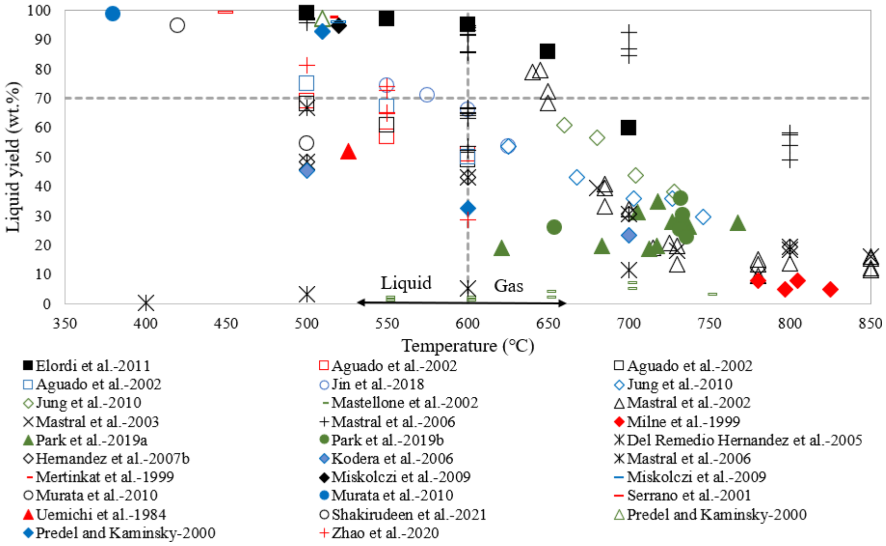

Figure 1. The correlation between liquid yield and pyrolysis temperature (**Black:** HDPE, **Red:** LDPE, **Blue:** PP, **Green:** PE).

Table 1. The analysis of by-products of data (obtained at below 600 °C and yielded more 70 wt.% of liquid) as energy source for pyrolysis of POs.

Plastic Type	Liquid yield (wt%)	Gas yield (wt%)	% Energy provided by gases for pyrolysis of 100 kg POs	Reference
HDPE	95-99	1-5	21-92	Elordi *et al.* (2011)
HDPE	85.5-97	14.4-2.1	7-250	Mastral *et al.* (2006)
HDPE	98.5	1.5	26	Artetxe *et al.* (2013)
HDPE	94.9	5.1	91	Miskolczi *et al.* (2009)
HDPE	94.9	5.1	69	Murata *et al.* (2010)
LDPE	99	1	18	Serrano *et al.* (2001)
LDPE	97.4	2.4	29	Mertinkat *et al.* (1999)
LDPE	75.8-89.2	10.8-24.2	228-443	Williams & Williams (1997)
LDPE	72.7-81.2	8.2-23.4	851-1592	Zhao *et al.* (2020)
PE	97.2-97.4	2.4-2.6	33	Predel & Kaminsky (2000)
PP	75	25	164	Aguado *et al.* (2002)
PP	71-74.4	22.7-28	321-247	Jin *et al.* (2018)
PP	95.8	4.2	74	Miskolczi *et al.* (2009)
PP	98.7	1.3	21	Murata *et al.* (2010)
PP	92.9	6.9	104	Predel & Kaminsky (2000)

For studies with single data point, a single value is given while a range is given for studies reporting multiple data.

Our intention for contributing to CORFU 2022 is to give a point of view for self-sustained continuous pyrolysis of POs by using a comprehensive literature review, combined with the experimental data generated in our research group. The ultimate goal is to come up with some recommendations and suggestions regarding the design of a pyrolysis process for the efficient conversion POs to alternative fuels on a commercial/industrial scale.

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