Valorisation of multi-component plastic waste via hydrothermal liquefaction: A comprehensive analysis of interactions between PET and PA6 depolymerization

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Introduction

Since its invention in the early 20th century, synthetic plastic has revolutionized industries worldwide, driven by continuous advancements in polymer chemistry and composite materials. The versatility and low production costs of plastics have fueled their exponential growth and widespread use. However, this rapid expansion has led to a parallel increase in plastic waste generation. Alarmingly, over 90% of plastics are derived from fossil fuels, and recycling remains highly inefficient; 79% of plastic waste ends up in landfills or polluting natural environments, both on land and at sea (Plastic Europe, 2022).

Mechanical recycling struggles with contaminated and complex plastic waste, leading to limited recovery and downcycling. In contrast, chemical recycling breaks down polymers to recover and purify raw materials, enabling the recycling of a broader range of difficult-to-recycle post-consumer plastics.

Among the technologies for chemical recycling, hydrothermal liquefaction (HTL) offers a promising alternative by converting plastics into valuable raw materials. HTL is a thermochemical depolymerization process that occurs in liquid water at medium temperatures (250-374°C), high pressures (4-25 MPa), and with dry solid loading ranging from 5 to 30 wt.% (Ghadge et al., 2022). HTL performance strongly depends on the polymer structure: polyolefins, lacking active hydrolysis sites, remain inert in subcritical conditions but yield high amounts of oil under supercritical conditions (>374°C) (dos Passos et al., 2020). Condensation polymers like polyethylene terephthalate (PET) and nylon 6 (PA6), containing heteroatoms, can be efficiently hydrolyzed into their monomers even in subcritical conditions, unlocking the potential to recycle more diverse and challenging plastic waste (Darzi et al., 2022).

PET and PA6 are important polycondensation polymers commonly used in plastic materials. These blends have a broad range of applications, including food packaging, automotive components, flexible films, and synthetic fibers. The efficient decomposition of PET into terephthalic acid (TPA) and ethylene glycol (EG) (Jaime-Azuara et al., 2023), and PA-6 into ε-caprolactam (CL) (Iwaya et al., 2006) has been observed under HTL conditions, utilizing various catalysts, solvents, and high temperatures. However, it is not yet known how the interaction between PET and PA-6 in mixed polymer systems might change with variations in their percentage composition, the amount of dry matter, and the processing time and temperature. This study aims to explore these variables for the first time, addressing this gap in understanding, which is particularly relevant for undifferentiated polymer mixtures and real waste streams.

Material and methods

This study aims to evaluate the performance of HTL on mixture of PA6 and PET under different process conditions. Reactions were performed in fast-heating 20 ml batch reactors using a fluidized sand bath. Four most critical parameters were investigated - temperature (300-340°C), residence time (10-30 minutes), dry solid loading (10-20 wt.%) and PET/(PET+PA6) mass ratio (0.25-0.75) – following a design of experiments (DoE) with center composite circumscribed (CCC) method described in Table 1.

Table 1. DoE with CCC parameter description.

Factor name	Units	- Alpha	-1	0	1	+ Alpha
Temperature	°C	280	300	320	340	360
Dry matter	%	5	10	15	20	25
PET	%	0	0.25	0.5	0.75	1
Time	min	0	10	20	30	40

PA6 and PET were analyzed through FTIR, TGA and CHNS. For each experiment (performed in duplicate), a total of 10 g of slurry were loaded into the reactor at the desired dry matter composition and PET-PA6 mass ratio. The reactors were submerged in a preheated sand bath at setpoint temperature and for the desired residence time. Afterwards the reactor was quenched to room temperature in water. Gas mass determination was performed by weight difference after venting. The residual content of solids and liquid were separated and collected by centrifugation. The aqueous phase (AP) was collected and stored at 4 °C until further analysis. The solid phase was treated with a 1M NaOH solution to solubilize the TPA. The fraction that remained insoluble was dried overnight at 105 °C and labeled as the ‘Unconverted plastic’. The TPA in the alkaline solution was subsequently precipitated by lowering the pH to 1 with concentrated H_2SO_4. After filtration, the precipitate was filtrated and dried overnight at 105 °C, yielding the ‘TPA-rich phase’. The AP rich in CL and EG were analyzed and quantified through HPLC. TPA rich solids were quantified and analyzed using various analytical techniques, including GC-MS (solubilized in pyridine and derivatized with BSTFA), CHNS, and TGA.

Results and discussion

For the sake of representativeness, the distribution of products at the mean point of the DoE is illustrated in Figure 1. A remarkable recovery of TPA was achieved, as confirmed by the GC-MS chromatogram presented in Figure 2, with TPA constituting approximately 90% of the total yield in the TPA-rich phase. The liquid fractions, predominantly enriched in EG and CL, along with trace levels of minor impurities, offer promising potential for valorization through complementary processing strategies, thereby contributing to the realization of a sustainable zero-waste system. Material losses, primarily represented by gaseous emissions and unconverted solids, were determined to be of limited significance, further underscoring the efficiency of the process.

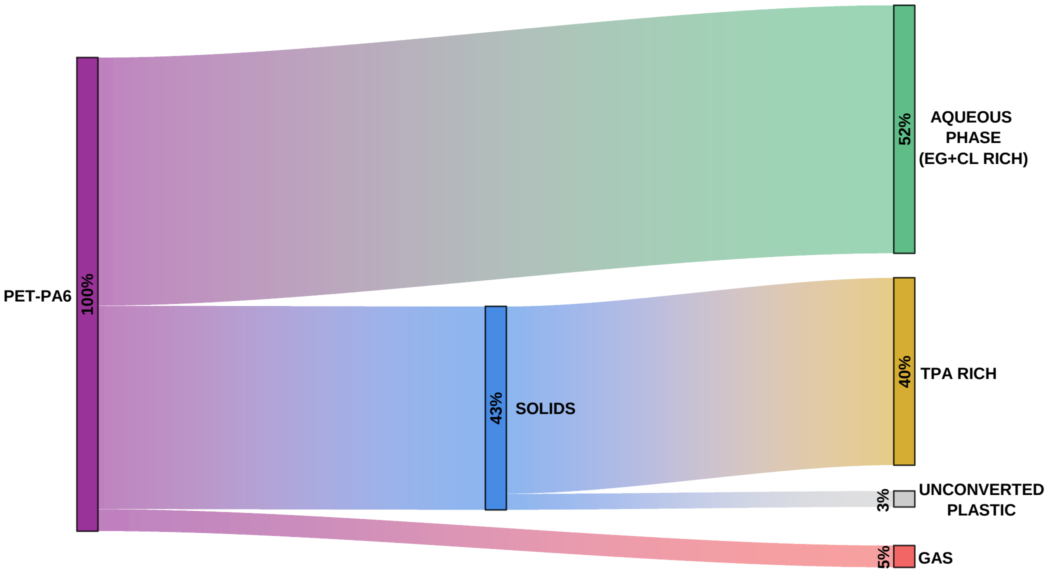

Figure 1. Sankey diagram of HTL products distribution after a reaction at 320 °C, 15 % dry solid loading, 1:1 PET/PA ratio and 20 min residence time.

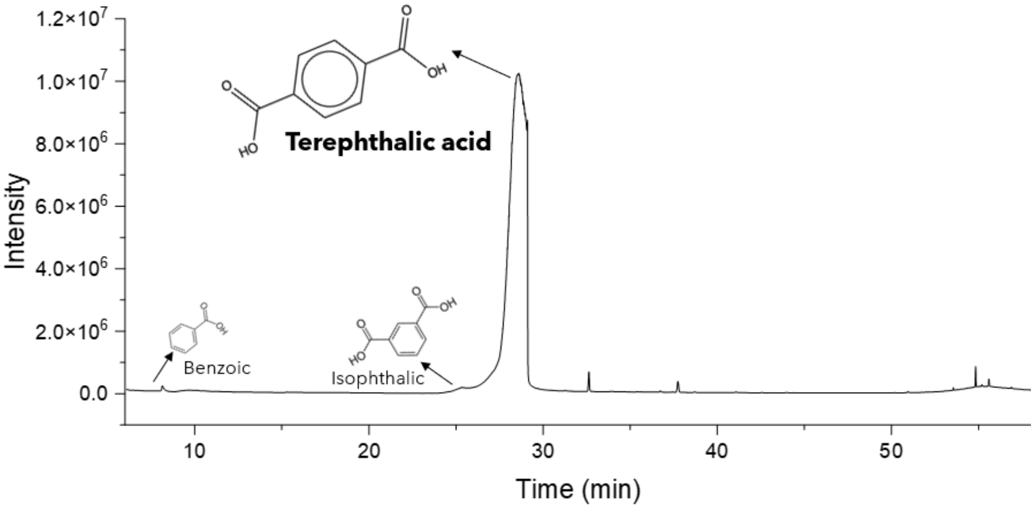

Figure 2. GC-MS chromatogram of TPA rich solids

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