Towards closed-loop recycling of multilayer and coloured PET plastic waste

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Keywords: PET plastic Waste, Recycling, Hydrolysis, Multilayer.
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Introduction

Plastics are indispensable in today's modern life due to their great functionality and low production costs. Whereas the production processes of plastics are very mature, the current recycling market is still in its infancy, often limited to open-loop recycling towards bulk applications. Because of their negative impact on the environment, plastic also gained a negative perception, despite the service they provide during their lifetime. Therefore, there is a growing demand for sustainable technologies towards closed-loop plastic waste recycling. One of the issues impeding high end recycling is the presence of multilayers which are used to improve physicochemical properties of plastics (Kaiser et al., 2018). For example, polyethylene terephthalate (PET) is extensively laminated with other types of polymers such as polyolefins and ethylene vinyl alcohol (EVOH) especially in food packaging applications due to its limited properties related to permeation of oxygen and sealing (Kaiser et al., 2018). Although recycling rates of monolayer PET bottles are high (>57%) in Europe, those of PET trays and films are significantly lower due to the presence of broad range of colours, additives, and multilayer structures (Petcore Europe, 2016). Therefore, there is a growing demand for an efficient chemical recycling processes towards closed-loop recycling of complex PET waste streams. Although chemical recycling processes have been studied vastly, there is no detailed kinetic study available on the alkaline hydrolysis of PET in mild degradation conditions. Moreover, the reported kinetic studies are mainly limited to pure PET pellets, which is typically different compared to more complex real PET plastic waste in terms of composition and shape, amongst others. This work presents a selective hydrolysis of multilayer and coloured PET plastic waste at mild conditions, allowing the recovery of pure PET monomers and the constituent polyolefin layers without any degradation (Ügdüler et al., 2020). This presentation includes optimization of the selective hydrolysis conditions, comparison of the reaction kinetics of different types of real PET waste streams as well as an LCA in order to investigate the environmental sustainability of the proposed process.

Materials and Methods

The experimental parameters of hydrolysis were optimized through kinetic tests performed on pure PET pellets under different conditions: at temperatures 50 and 80 °C, at 5, 10 and 15 wt% NaOH concentrations and at 20, 60 and 100 vol% ethanol to water volume ratios. The degradation kinetics of PET was followed through gas chromatography-flame ionization detector (GC-FID) measurements based on the change in ethylene glycol (EG) concentration in the hydrolysis medium.

Once the degradation conditions were optimized, kinetic tests were performed on real post-consumer samples from bottles, transparent monolayer and multilayer PET at different particle sizes (lower than 0.05 cm, 0.05–0.1 cm, 0.1–0.16 cm, 0.2–0.25 cm, 0.25–0.315 cm, 1 cm and 4 cm). For each sample, a two-step alkaline hydrolysis was conducted at optimal degradation conditions and their degradation kinetics were analysed through GC-FID measurements. After alkaline hydrolysis of PET waste, unreacted LDPE polymer films were separated from the solution via vacuum filtration and the filtrate was acidified using concentrated sulphuric acid to obtain terephthalic acid (TPA) as a monomer.

The composition and crystallinity of PET waste was analyzed using polarized optical microscopy (POM) and differential scanning calorimetry (DSC), respectively. The purity of obtained monomers was characterized via proton-Nuclear Magnetic Resonance (^{1}H-NMR) and UV-VIS spectrophotometer.

Results and Discussions

The experimental parameters affecting the PET hydrolysis such as temperature (50–80 °C), ethanol (EtOH) to water ratio (20–100 vol%) and NaOH concentration (5–15 wt%) have been optimized by using pure PET pellets.

According to the results, rise in temperature from 50 °C to 80 °C increases the hydrolysis rate more than two-fold. In terms of NaOH concentration, it is observed that PET degradation yield increases from 35% to 58% with the increase in NaOH concentration from 5 to 10 wt%. However, further increase in the NaOH wt% results in decrease of the PET conversion yield due to possible deposition of excess NaOH on the PET sample surface. The results show that the EtOH to water volume ratio also has an important effect on the PET conversion. Increase in the volume percentage of EtOH from 20 vol% to 60 vol% results in increase in the PET conversion from 30% to 95%. Based on these experimental kinetic data, the best-fit kinetic model was selected among different solid-state kinetic models in order to describe the degradation kinetics. It has been observed that the diffusion model supports the obtained kinetic data, thus it is selected as a best-fit kinetic model for the hydrolysis of PET and it is also used to explain the kinetics of post-consumer PET waste.

The optimized hydrolysis conditions were also tested on the post-consumer PET waste e.g. bottles, monolayer trays and films having different thicknesses, specific surface area and crystallinity. The highest PET conversion (~95%) was obtained with pure PET at the smallest particle size (<0.05 cm), followed by PET films, bottles and trays, respectively. Among different PET samples, the slowest conversion was obtained with multilayer trays due to their higher thickness and lower specific surface area and the fact that only one side of the particle is accessible for hydrolysis, limiting degradation rate. In terms of particle size, it has been observed that PET conversion percentage decreases with an increase in the particle size for all types of PET samples. Similar to the kinetics of pure PET grades, the diffusion kinetic model showed the best-fit to describe the kinetics of post-consumer PET waste. By using this model, the effect of particle size and the type of sample on the rate constant (k) was investigated. It has been observed that the increased particle size, thickness and crystallinity of the samples and also the existence of other polymer layers result in lower degradation yields, thus lower rates (Ügdüler et al., 2020).

In this study, also a potential process scheme to scale up the hydrolysis process was proposed, including removal of colours from postconsumer plastic waste (Figure 1). It is shown that via this proposed process it is possible to obtain pure monomers even from black coloured PET samples. Furthermore, due to mild degradation conditions constituent polymer layers of multilayer PET samples such as polyolefins can be recovered without any degradation.
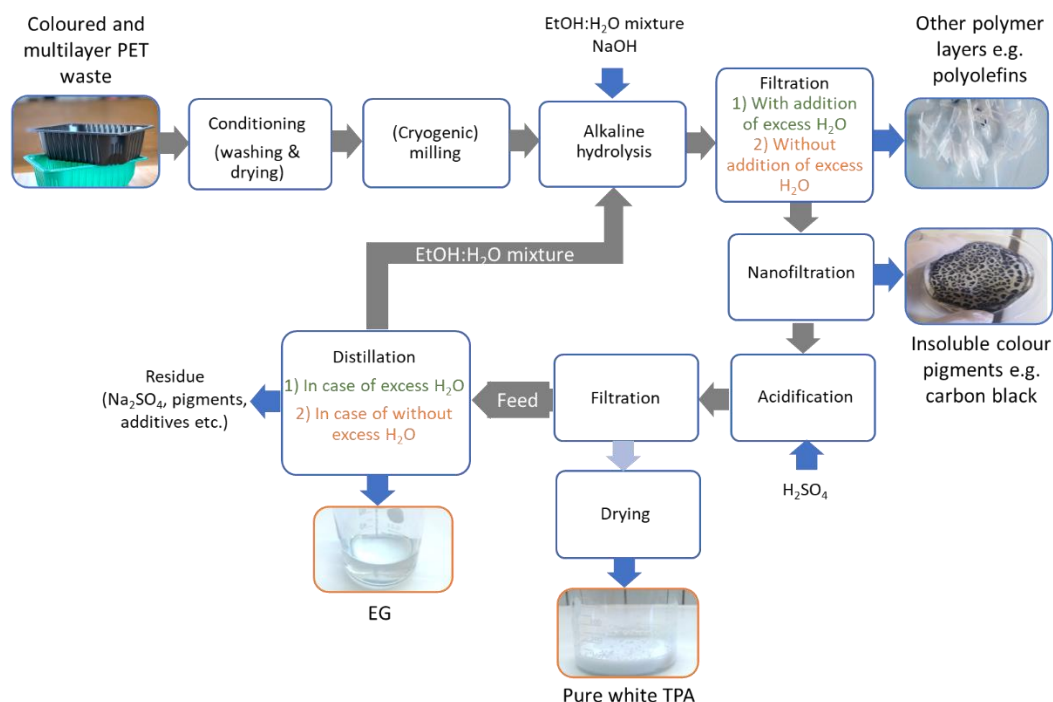

Figure 1. Possible flowsheet for separation of colours and polyolefins while obtaining pure PET monomers.

In addition to technical feasibility, the environmental impact of the process has been assessed through an LCA at different solid/liquid (S/L) ratios for two hydrolysis scenarios: with and without excess water addition during purification of the monomers. Based on this assessment, addition of excess water causes higher energy consumption during EG recovery, as such increasing the carbon footprint of the process. Therefore, using selective filtration without addition of excess water would increase the environmental feasibility of the process. Similarly, at low S/L ratio, higher amount of energy is consumed per kg of post-consumer PET treated, increasing the carbon

footprint of the process. Concluding, relying on industrial optimization, we can state that the proposed alkaline hydrolysis process is promising towards chemical recycling of complex PET plastic waste.

Acknowledgement

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