Use of Supercritical Water for Degradation of Polyethylene Waste

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Abstract The degradation of polyethylene (PE) waste using supercritical water (SCW) has been studied. The colored PE waste was degraded in SCW at 425 °C and 450 °C and at reaction times ranging from 15 min to 4 h, and the effect of temperature and reaction time on product yield was investigated. The degradation products were separated into the oil, gas, aqueous and intermediate phases. The obtained products in the oil and gas phase were analyzed using GC/MS, while the total carbon in the aqueous phase was determined by TOC analyzer. It was found that the oil phase was mostly composed of hydrocarbons, while the gaseous phase contained various gases such as CO2, and light hydrocarbons from C1-C6. TC value in aqueous phase decreased with increases in the temperature and reaction time.

Keywords: polyethylene, waste, supercritical water, recycling, plastics.

University of Maribor Press

DOI https://doi.org/10.18690/978-961-286-353-1.5
ISBN 978-961-286-353-1

1 Introduction

Currently, great attention is being paid to the development of recycling technology for waste packaging, since plastic waste that is not recycled represents a major ecological and economic problem. Production of plastics is expected to increase in the coming years, and waste plastics already pollute drinking water, poison aquatic animals and cause health problems (Anuar Sharuddin *et al.*, 2016; Helmer Pedersen and Conti, 2017). Degradation of plastics is very slow in the natural environment. Plastic waste in the environment can decompose for several hundred years, and consequently, pollution with plastics does not decrease (Anuar Sharuddin *et al.*, 2016; Moore, 2008). Waste plastic can be recycled in many ways. The four main recycling techniques are primary, mechanical (secondary), chemical (tertiary) and quaternary (energy recovery) (Helmer Pedersen and Conti, 2017). Primary recycling refers to the processing of plastics where the product is later used for a purpose similar to that of the original plastics (Achilias *et al.*, 2012; Rahimi and García, 2017). Mechanical recycling or secondary recycling is a process where the polymer is separated from the respective contaminants and can be easily converted into granules with conventional extrusion (Achilias *et al.*, 2012; Rahimi and García, 2017). Chemical or tertiary recycling is a process where waste plastics can be converted into petrochemical components or lead to complete depolymerization to monomers or partial depolymerization to oligomers and other chemical substances. Quaternary recycling or energy recovery is a method where waste plastics are incinerated (Achilias *et al.*, 2012; Helmer Pedersen and Conti, 2017; Rahimi and García, 2017).

One of the most effective methods for chemical recycling is based on the use of sub- and supercritical water, as an environmentally friendly medium. Decomposition of plastics in subcritical and supercritical water is a very effective method for converting plastic waste into a wide range of useful products without expensive and harmful organic solvents (Zhang *et al.*, 2007). Subcritical water (SubCW) is known as hot water under pressure, above boiling point (100 °C) and below the critical point (374 °C, 221 bar). With the increase in temperature and pressure above the critical point, water enters the supercritical area (Haghighi and Khajenoori, 2013; Zhang *et al.*, 2007).

Supercritical water (SCW) provides quick and complete reactions. The increase in degradation of polyethylene in supercritical water is partly due to the dissolution of high molecular hydrocarbons in it. In the supercritical state, water has excellent transport properties (like gases), such as high compressibility, high diffusion co-efficient and low viscosity. The ionic product of SCW is also very low. Thus, it is especially suitable for reactions with free radicals, such as decomposition of plastic waste into oil and gasses. In the supercritical state, the dielectric constant of water is as low as for nonpolar organic solvents. SCW thus easily dissolves non-polar organic compounds that are not dissolved in water at room temperature and atmospheric pressure (Su *et al.*, 2004; Zhang *et al.*, 2007).

Polyethylene (PE) is one of the most commonly used plastics in the world and is mainly used for packaging. It is a lightweight, durable thermoplastic with low density and a low melting point. PE is resistant to atmospheric effects and is a good insulator, since it has low electrical and thermal conductivity (Kumar *et al.*, n.d.). Its basic use is in packaging, such as plastic bags, plastic foil, bottles, baby toys, pipes, electrical equipment and more. As a result, it represents the largest share of waste plastic.

The aim of this research was to investigate the degradation of colored PE waste in SCW. The effect of different reaction parameters, such as reaction temperature, pressure and reaction time on products yield was studied.

2 Experimental part

2.1 Materials and apparatus

The colored PE waste (Fig. 1) was used as a raw material. The particle diameter of the PE waste was around 4-5 mm.

Figure 1: The colored PE waste.

The decomposition of colored PE waste in SCW was performed in a high-temperature, high-pressure batch reactor, shown in Figure 2. The experiments were carried out at high temperatures (425 °C and 450ºC) and high pressures for different reaction times (15 to 240 minutes).

Figure 2: High temperature, high pressure batch reactor.

The reaction mixture of PE and water in a ratio of 1/5 (g/mL) was transferred to the reactor, and a magnetic stirrer was added. The reactor was tightly sealed, and the thermocouple connected. A heating wire was wrapped around the reactor and insulated with glass wool for faster heating and to prevent heat loss. To prevent oxidation, before heating, the reactor was purged three times with nitrogen. When the reactor reached the desired temperature, temperature was maintained constant until the desired reaction time. After completion of the reaction, the heating wire and glass wool were removed, and the reactor was immediately cooled down in an ice bath. When the reactor cooled to room temperature, the generated gas was discharged into special gas bags. The reactor was disassembled, and the resulting decomposition products transferred from the reactor to the beaker. The oil (or wax) phase was transferred to a container and weighed. 20 mL of dichloromethane was added to the remaining liquid phase, then filtered, as it contained solids, which were dried on filter paper and weighed. The liquid phase mixture was stirred well to separate the phases. In the upper phase, there was an aqueous phase, in the middle an intermediate phase, while the lower phase represented dichloromethane and the

remainder of the oil phase. The lower phase was evaporated on a rotary evaporator to remove the solvent, and the residue was weighed and added to the oil phase.

2.1.1 Products analysis

The oil/wax and gas products were analyzed by gas chromatography coupled to a mass spectrometer (GC/MS), while the content of total carbon (TC) in the aqueous phase was determined with a TOC analyzer.

3 Results and discussion

The decomposition products of PE waste in SCW were separated into the oil, gas, aqueous and intermediate phases. The intermediate phase was formed, since dyes and additives in the PE waste were probably converted into ash particles. Figure 3 shows the effect of temperature and reaction time on the yield of decomposition products. With increasing temperature and reaction time, the yield of gases in all cases increased, while the yield of oil at 450 °C decreased. In the case when PE waste degraded at low temperature (425 °C) and for the short reaction time (15 and 30 min), the yield of oil first increased, owing to the slower degradation of PE waste in SCW, and then with prolongation of the reaction time began to decrease. The highest yield of oil was found at a temperature of 450 °C and a reaction time of 15 min and was higher than 98 %. The oil products contained mostly hydrocarbons (alkanes and alkenes). As the temperature and reaction time increased, the yield of gas products increased from 0.6 to 3.6 %, where at 450 °C and 240 min, the maximum yield of gas was achieved. In the gaseous phase, the CO_2 and light hydrocarbons such as methane, ethene, ethane, propene, propane, butene, butane, pentene, pentane, hexene and hexane appeared in detectable content.

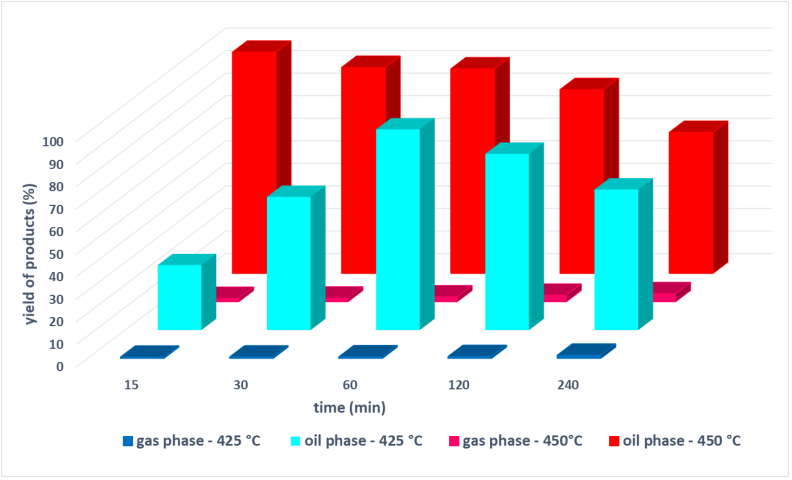

Figure 3: Effect of temperature and reaction time on product yield.

In the aqueous phase, determined TC values were higher at temperature of 450 °C than at 425 °C (Fig. 4). At the temperature of 425 °C, the concentration of TC increased with a prolonged reaction time; however, at the higher temperature (450 °C), the concentration of TC decreased with longer reaction times. The reason for this was that organic substances were converted to gases at higher temperatures and longer reaction times.

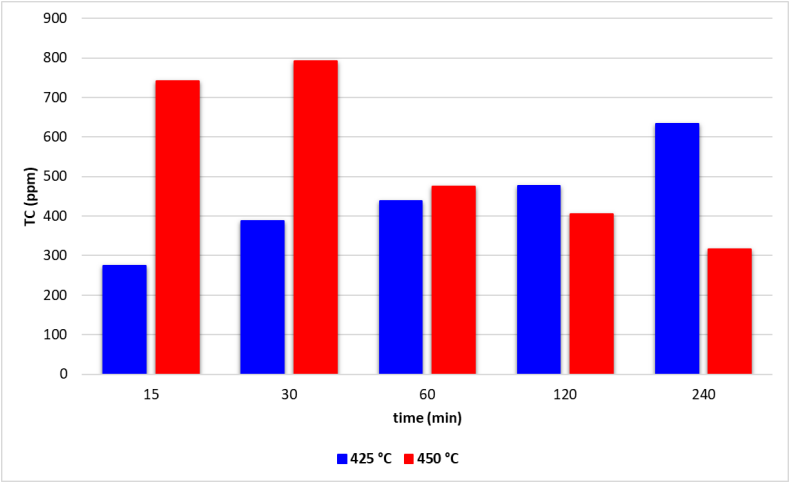

Figure 4: Total carbon (TC) values of aqueous phase products.

3 Conclusions

Supercritical water is an excellent medium for degradation of PE waste to useful products. Under the operating conditions researched, the main product was the oil phase that contained mostly alkanes and alkenes. The highest yield of oil was achieved at 450 °C, at a very short reaction time (15 min) and was higher than 98 %. The yield of the gas phase was generally low (< 4 %) and increased with increasing temperature and reaction time. The gaseous and oil phases contained many interesting substances that could be reused (energy, fuel). By this method, the degradation of waste plastics would help to reduce the amount of waste plastics, which burden the environment, and the resulting degradation products could be used for further applications.

Acknowledgment

This work was financially supported by the Slovenian Research Agency (ARRS) in the framework of Research Programmes P2-0046 (Separation processes and product design) and P2-0032 (Process systems engineering and sustainable development).

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