Hydrothermal Oxidation of Polyethylene (PE) Plastic to Short-chain Fatty Acids (C₁ - C₅)

Wanning Zhou¹, Heng Zhong¹,²,a,* and Fangming Jin¹,³,b

¹ School of Environmental Science and Engineering, State Key Lab of Metal Matrix Composites, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China
² Research Institute for Chemical Process Technology, National Institute of Advanced Industrial Science and Technology, Nigatake4-2-1, Sendai, 983-8551, Japan.
³ Graduate School of Environmental Studies, Tohoku University, Aoba-ku, Sendai 980-8579, Japan.

*,a Corresponding author e-mail: zhong.h@sjtu.edu.cn, b fmjin@sjtu.edu.cn.

Abstract. In most of the past studies on disposal of waste plastic, due to the irreversible hazards for human environmental health (incineration), and the strict requirements of reaction conditions (pyrolysis, gasification), the cost of disposal and research also increases. In this study, we converted waste polyethylene (PE) plastic into high-value-added organic products by high-temperature water (HTW) to obtain C₁ to C₅ short-chain fatty carboxylic acids (formic acid, acetic acid, propionic acid, butyric acid and valeric acid). In addition, the reaction parameters (temperature, time, oxidant amount, pH) were investigated under hydrothermal conditions, and the yield for PE to short-chain fatty acids (C₁ -C₅) was optimized to 20%. Then the concentration of TOC and IC in the solution was used to measure the conversion and degradation of PE. In addition, the oil phase and solid residue after the reaction were also discussed in this research.

Keywords: Waste plastic treatment; polyethylene (PE); High-temperature water (HTW); Short-chain Fatty Acids; Hydrothermal.

1. Introduction

With the development of modernization, plastic have been widely used due to their advantages of wide applicability, durability, and low cost. However, treatment and disposal of waste plastic has become one of the fastest growing environmental problems in the world and is increasingly beyond human control. According to relevant studies, global plastic production has soared from 15 million tons in 1964 to more than 300 million tons in 2017.[1] As we all know, plastic is difficult to degrade in the natural environment due to its stable physical and chemical structures, therefore, it is urgent to treat this issue in a green, low-cost and highly-efficient way. Traditional disposal methods of waste plastic mainly include recycling, reusing, incineration and landfill.[2] Due to the aging of materials and impurities in waste plastic, recycled plastic can only be used to produce inferior products,[3] while a large amount of harmful substances such as dioxins, polychlorinated biphenyls and furans are produced during the incineration.[4] For landfill method, it is ultimately limited by geospatial space.[3] In recent years,
pyrolysis/gasification technology has attracted much attention due to its ability to convert various plastics into syngas/fossil fuels.[5] This technology do have superior environmental effects compared to incineration for no dioxins releasing into the air.[6] However, the pyrolysis/gasification process of plastics needs a high reaction temperature (400 – 1500 °C), and sometimes an anaerobic environment is even required.[6] In addition, expensive purification technologies are also indispensable during the large-scale synthesis process of gas/petrochemical products. As a result, new technology for a green, low-cost and highly-efficient plastic treatment is urgently demanded.

Water has been widely used as an ideal green solvent in chemical reactions due to its abundant reserve, non-toxic and environmental-benign characteristics. Especially, water at high temperatures (200 – 350°C) has unique properties as a reaction medium such as low dielectric constant, few and weak hydrogen bonds, and high isothermal compressibility compared to ambient liquid water [7]. Therefore, hydrothermal treatment which using high-temperature water (HTW) as the reaction medium is considered as an emerging and promising thermochemical technology for conversion of organic materials such as sludge, [8, 9] biomass [10, 11] and municipal waste [12] into value-added product. Our group has successfully achieved the hydrothermal oxidation of different biomass such as glucose, cellulose, and food wastes into various chemicals (formic acid, acetic acid, lactic acid, etc.) with H₂O₂ as the liquid oxidant. [13, 14] However, the study of hydrothermal oxidation of waste plastics into chemicals is limited. Under hydrothermal conditions, H₂O₂ could form highly active hydroxyl radicals to break down the stable long carbon chain contained in the plastics at a relatively low temperature and short time, which can greatly save time and reduce energy consumption. Therefore, in this paper, we studied the treatment of waste polyethylene (PE) plastic in HTW to produce value-added C₁₋C₅ short-chain fatty acids. Compared with traditional pyrolysis/gasification method, this process not only can be conducted at a relatively lower temperature but also achieved the production of low-molecular-weight organic acid products.

2. Experimental Section

2.1. Experimental Procedure

In this study, experiments of PE hydrothermal oxidation with H₂O₂ to high value-added organic compounds were conducted in a stainless steel (SUS-316) tubular batch reactor with an inner volume of 5.7 mL and a pressure limit of 20 MPa, which has been described in detail in our previous report [15]. The experimental procedure is described as follows. First, a certain amount of PE, H₂O₂ and deionized water were added into the reactor to provide a total filling rate of 35% (liquid volume: 2 mL). Then, the reactor was sealed and placed into a salt bath which had been preheated to desired reaction temperature. At desired reaction time, the reactor was taken out from the salt bath and immersed into a water bath (25 °C) immediately to quench the reaction.

For liquid sample collection, two different methods were used. One was collected directly after the reaction with a syringe and filtered through a 0.22 μm syringe filter, which was denoted as aqueous-phase sample. The other was denoted as oil-phase sample and was collected as follows. 1.5 mL DCM was injected into the reaction chamber after the reaction, then, the reactor was sealed and was shaken for 10 min in order to extract oil phase compounds. Finally, the underneath layer oil phase sample was collected with a syringe and also filtered with a oil phase syringe filter. Solid sample after the reaction was filtered, washed thoroughly with water, and then dried in vacuum for 12 h.

2.2. Analytic Method

The aqueous and oil phase samples were identified by a gas chromatograph-mass spectrometer (GC-MS, Agilent GC7890A-MS5975C) on an HP-Innowax and a HP-1 capillary columns (30 m × 0.25 mm × 0.25 mm), respectively.[16] The FA and AA in the products were quantified by a high-performance liquid chromatography (HPLC, Agilent 1200 LC) equipping with an UV detector and two Shodex KC-811 columns. The detail description of the HPLC testing method has been reported in our previous research.[17] PA, BA and VA were quantified by a gas chromatography-flame ionization detector (GC-
FID, Agilent GC7890A) equipped with a HP-Innowax capillary column (30 m × 0.25 mm × 0.25 mm).[16] The total organic carbon analyzer (SHIMADZU-TOC-VCPh) is used to measure the concentrations of total organic carbon, inorganic carbon and total carbon in aqueous solution. And the solid samples before and after the reaction were analysed by a Fourier transform infrared spectrometer (FTIR, Thermo Scientific Nicolet iS20) to analyse the change of functional groups and bond energy.

3. Results and Discussion

3.1. Aqueous Products

Initially, the possible aqueous products of PE hydrothermal oxidation were explored in the preliminary experiment (300 ℃, 30 min, 50% H₂O₂ supply, 35% water filling rate), and FA, AA, PA, BA and VA were obtained as main products (Fig. 1). Table 1 summarized the yield of C₁–C₅ organic acid products obtained at temperatures from 250 ℃ to 350 ℃. The total yield of products increased from 1.8% at 250 ℃ to 18.8% at 300 ℃, suggesting a certain temperature is necessary for the cleavage and oxidation of PE. However, a further increase in the temperature over 300 ℃, all the C₁–C₅ product yields decreased, especially for BA and VA. This is probably because the further decomposition of organic acids in HTW, which has been previously reported[18].

![Figure 1](a)HPLC and (b)GC-FID of liquid sample after the reaction of PE (reaction conditions: 2 mmol PE, 75% H₂O₂, water filling rate 35%, 300 ℃, 30min).

3.2. Oil phase Products

Considering that the oil extracted from PE has an outstanding potential as chemical raw material, the collected yellowish-brown oil after suspension of DCM was characterized by GC-MS. acids (C₆ ~ C₂₀) detected as one kind of the products were sequentially labeled on the corresponding peaks according to the retention time and the similarity index of mass spectrum >80% in Fig.2. From the analysis of products, we can conclude that the main oil phase organics can be classified to alkanes (C₁₂ ~ C₂₁), aldehydes (C₆ ~ C₁₆), ketones (C₆ ~ C₁₉), diketones (C₆ ~ C₁₆) and acids (C₆ ~ C₂₀), and the peak time sequence of these five types of products in GC-MS shows a certain regularity.
3.3. Solid Residue

It is observed from the experimental phenomenon that the color and amount of solid residue remained after the reaction are mainly related to the H$_2$O$_2$ supply. Fig. 3 is the solid residue collected after the reaction with H$_2$O$_2$ supply from 0% to 100%. From the pictures we can clearly see that as the oxidant increases, less solids remained after the reaction, and the color also appears white to yellow to brown and finally to black. The residue can be observed in the solution is a trace amount once the H$_2$O$_2$ supply is more than 100%, and there is no residue remained when it is over 125%.

![Figure 3. Solids after reaction at different H$_2$O$_2$ supplies (reaction conditions: 2 mmol PE, water filling rate 35%, 300°C, 30 min)](image)

4. Conclusion

In summary, we have found a method to deal with the waste PE plastic under hydrothermal conditions, the oil phase products after the reaction were explored to identify several major product types, and it can be considered that PE plastic is oxidized and degraded completely when the oxidant supply is more than 125%. Importantly, 20% yield of short-chain fatty acids (C1 ~ C5) was obtained as aqueous products in this research, as proofs, the concentration of TOC and IC in solution after reaction was analyzed to explore the formation and decomposition of products and measure the degradation degree.
of PE at the same time. Based on the functional groups and structure of the products, we tried to give a possible reaction pathway for the conversion of PE into short-chain fatty acids (C1 ~ C5). This research is devoted to the use of hydrothermal oxidation of waste PE plastic to obtain high value-added organic materials that can be used as chemical raw materials, and also provides a new way for the disposal of waste plastic of other chemical components.

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