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Partial oxidation treatment of waste polyvinyl chloride in critical water: Preparation of benzaldehyde/acetophenone and dechlorination

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A B S T R A C T

In this work, a partial oxidation treatment process in critical water was developed for high-efficiency dechlorination of waste polyvinyl chloride and the recovery of high value-added chemical feedstock. The partial oxidation treatment of waste polyvinyl chloride was performed at the temperature range of 200–400 °C with the mass ratio of 32 (waste polyvinyl chloride-to-oxygen). Fourier Transform Infrared Spectroscopy and Gas Chromatography-Mass Spectrometer were utilized to characterize solid residue and oil products. The chlorine in aqueous phase was measured by ion chromatography to determinate the dechlorination efficiency. The results indicated that 85.5% of the chlorine in waste polyvinyl chloride could be transferred into aqueous phase at 250 °C, and approximately 95% could be transferred at 300 °C. The temperature of critical water had a significant effect on chemical composition of oil products of waste polyvinyl chloride after the partial oxidation treatment. Two important chemical feedstock, benzaldehyde and acetophenone, could be selectively prepared from waste polyvinyl chloride by the partial oxidation treatment in critical water at lower temperature condition. The summation of the relative peak area of benzaldehyde and acetophenone from the results of Gas Chromatography-Mass Spectrometer could reach 91.74% and 91.68% at 300 °C and 350 °C. The further increase of partial oxidation treatment temperature could enhance the reactivity of oxygen involved in the system and initiate more side reactions, resulting in that many impurity compounds were generated, including phenol/phenol derivatives, naphthalene, aliphatic alkanol, and cyclanone. The purity of benzaldehyde and acetophenone in oil products decreased when the partial oxidation treatment temperature exceeded 350 °C, and the additional value of decomposition products was lowered. This result showed that the partial oxidation treatment of waste polyvinyl chloride in critical water was beneficial for both dechlorination and resources recovery.

1. Introduction

Polyvinyl chloride (PVC) is one of the five great general plastics, and plays an important role in our daily life (Yu et al., 2016). Global plastics production capacity of PVC was about 61 million tons in 2013 (Attenberger et al., 2014). In China, the production capacity of PVC reached 30 million tons in 2013, and accounted for 25% of all synthetic resins (Attenberger et al., 2014). Generally, PVC products have long service life in comparison with other plastics. However, they will eventually become solid waste. The degradation of the large amount of waste PVC is slow in natural conditions, which not only brings serious harm to the environment, but also causes the waste of resources (Sadat-Shojai and Bakhshandeh, 2011).

Traditional treating methods of waste PVC include landfill, incineration and physical recovery (Goodman, 2014). Landfill occupies land and brings the waste of resources, and the toxic substances in waste PVC can be easily leached into the environment and cause huge harm to soil and groundwater (Baishya and Mahanta, 2013). Incineration is the burning of waste PVC in specific devices and the recycling of calories. The advantage of incineration is obvious waste minimization. But incineration of waste PVC can result in liberation of harmful gases such as dioxins and chlorinated organic compounds to the environment (Suresh et al., 2017). The physical recovery method has the advantage of low

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investment and cost, however, the requirement for the quality of waste PVC is very high (Sadat-Shojai and Bakhshandeh, 2011). Currently, chemical recovery is regarded as a promising approach for the recycling and reutilization of waste PVC (Zhao et al., 2017). Chemical recovery method is the transformation process of waste PVC into a product by chemical reaction under certain conditions. The chemical recycling and reutilization of waste PVC with safe dechlorination treatment have become the research focus and attracted the most attention of researchers around the world. Pyrolysis is a typical chemical recycling method, and is widely used in waste PVC recycling (Zhou et al., 2016a, 2016b). Pyrolysis is a heating process without oxygen, and waste PVC can be decomposed to low molecular weight products including liquids and gases, which can be reused as fuel or chemical feedstock (Cao et al., 2016). One potential problem in the pyrolysis of PVC is that the generated oil products contain significant amount of Cl, which can cause severe unit corrosion and the release of toxins during the combustion of oil products (Bidoki and Wittlinger, 2010). Recently, it was found that the chlorinated hydrocarbons in the oil products could be suppressed to some extend by adding some catalysts in pyrolysis process (Al-Salem et al., 2017). However, the chemical composition of oil products derived from waste PVC by pyrolysis is very complicated. It is difficult to obtain chemical feedstock from pyrolytic products of waste PVC by purification and separation. Hence, the additional value of oil products derived from pyrolysis is relatively low.

In recent years, critical water (CW) system has been extensively applied in the decomposition of high molecular materials (Arturi et al., 2017). CW has the advantage of fast reaction rates without the limitation of mass transfer (Wan et al., 2015). The low molecular weight hydrocarbons decomposed from polymer materials can easily disperse in liquid phase, restraining the formation of coke (Bermejo and Cocero, 2006). To obtain Cl-free oil products from waste PVC, the treatment of PVC using CW under oxygen-free system has been performed (Takeshita et al., 2004). It was found that the decomposition of waste PVC in CW could be divided into three stages: $T < 250\,°C$, $250\,°C < T < 350\,°C$ and $350\,°C < T$. Most of the Cl in waste PVC could be transferred into aqueous phase, avoiding the formation of chlorinated hydrocarbons in oil products. However, the chemical composition of the obtained oil products from waste PVC by CW treatment under oxygen-free environment is very complicated and the selectivity of decomposition products is relatively low, decreasing the additional value of oil products as chemical feedstock. On the other hand, the oxidation treatment of waste PVC in alkaline water with high O_2 pressure condition was performed (Yoshioka et al., 2000). The decomposition reaction and dechlorination could be highly accelerated under oxygen-rich condition and the products were mainly HCl, oxalic acid, benzenecarboxylic acid, and CO_2. In our previous study (Xiu et al., 2014), the dechlorination of PVC and the removal of brominated flame retardants from waste printed circuit boards could be achieved simultaneously by a subcritical water oxidation co-treatment process, and the products were CO_2 and HCl. The products decomposed from PVC were significantly influenced by the oxidation and ambient condition in the reaction system. It is promising to recover valuable chemical feedstock from waste PVC and obtain high dechlorination efficiency simultaneously by controlling appropriate oxidation process. This work intends to develop a partial oxidation treatment (POT) system in subcritical water (sub-CW) and supercritical water (SCW) for the decomposition/dechlorination of waste PVC and the preparation of new and high value-added oil products. The major objective of the present work is to evaluate the effect of partial oxidation conditions on the oil product characteristic and the dechlorination efficiency of waste PVC in POT process. Based on this, an eco-friendly approach for recovering high value-added oil products from waste PVC with high dechlorination efficiency by POT in sub-CW/SCW is proposed.

2. Materials and methods

2.1. Materials and chemicals

Waste PVC used in this work was obtained from Xi'an Zhengjiu Co., Ltd. (China). The PVC is rigid PVC and the formulation information from manufacturer is as follows: PVC resin 100 phr, dioctyl phthalate (DOP, plasticizer) 1.5 phr, tin mercaptide (thermal stabilizer) 2 phr, stearic acid (lubricant) 0.5 phr, and acrylic processing aid 1 phr. Before treatment, waste PVC was cut into small pieces with the size of $2\,cm \times 2\,cm$. After that, waste PVC pieces were washed by deionized water and dried for subsequent experiments. All chemicals used in this work were purchased from Chemical Reagent Company of Beijing in analytical grade and used without any further treatment.

2.2. Schematic drawing and POT experiments in sub-CW/SCW

Schematic drawing of the treatment of waste PVC by partial oxidation process in sub-CW/SCW is shown in Fig. 1. The POT experiments were performed by using a 400-mL high-pressure reactor made of 316 alloy. The reaction conditions of each experiment are presented in Table 1. In a typical POT experiment, waste PVC pieces and a certain volume of deionized water were introduced into the reactor. Then the reactor was closed to be heated. After the reactor was closed, the oxygen content above the reaction liquid in the reactor was calculated to be 90 mg, and the oxygen content in the reaction liquid (deionized water) was around 2 mg. Hence, the total oxygen content in the reaction system was around 92 mg. The POT reaction temperatures were controlled at 200, 250, 300, 350, 374, and 400 °C. The reaction temperatures of 400-1 and 400-2 are 400 °C. The difference between the two experiments is solid-to-liquid ratio. The solid-to-liquid ratio of 400-1 and 400-2 was calculated to be 1:65 g/mL and 1:97 g/mL. The POT time was controlled at 60 min. The pressure inside the reactor was monitored by a pressure gauge attached to the reactor. The pressure value inside the reactor depends on the reaction temperature and the volume fraction. When the reactor was heated to the selected temperature, the pressure value inside the reactor was defined as the initial pressure. When the residence time reached the selected value, the pressure value inside the reactor was defined as the final pressure. The reaction was terminated by a cold water bath. Then the gaseous phase product was collected and passed through a

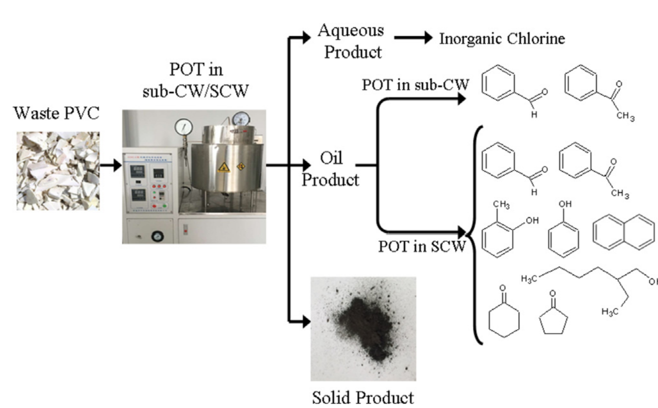

Fig. 1. Schematic drawing of the treatment of waste PVC by partial oxidation process in sub-CW/SCW.