Waste Management xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Improving the circular economy via hydrothermal processing of high-density waste plastics

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ARTICLE INFO

Article history:
Received 18 February 2017
Revised 19 May 2017
Accepted 1 June 2017
Available online xxxx

Keywords:
Hydrothermal liquefaction
Plastic monomers
Synthetic crude oil
Value added chemicals
Waste unrecyclable plastics

ABSTRACT

Rising environmental concerns on climate changes are causing an increasing attention on circular economies. The plastic economy, in particular, is in focus due to the accelerating consumption of plastics, mainly derived from virgin feedstock, combined with the lack of plastic recycling strategies. This work presents a novel outlook on the potential of using supercritical hydrothermal processing of waste plastic fractions for tertiary recycling. The study investigates hydrothermal processing of nine different, high-density types of plastics into original resin monomers and other value-added chemical compounds. The outlook presents conversion yields, carbon balances, and chemical details on the products obtained. It is found that all the investigated resins are prone to hydrothermal treatment, and that high yields of monomers and high value compounds (up to nearly 100%), suitable for chemicals and fuels applications, can be obtained. For instance, for polycarbonate, styrene-butadiene, poly(lactic acid), poly(ethylene terephthalate), and poly(butylene terephthalate), original monomeric compounds can be reclaimed for manufacturing new resins. The promising results presented demonstrate that hydrothermal processing of high-density plastics is a prospective technology for increasing the circularity of the plastic economy.

1. Introduction

Plastic production and consumption have increased dramatically over recent years, and with more than 300 million tons produced every year, plastic has become a global environmental concern. Striving for primary closed-loop recycling of plastics is ultimate, but has only been achieved for a very narrow plastic segment, such as clear PET bottles, for which dedicated collection schemes already exist [World Economic Forum, 2016]. The lack of primary recycling of plastics is challenged by many aspects, such as colors (dyes) and other contaminants, qualities, blends of different plastics, etc., and is manifested by the fact that only approximately 2% of all plastics is closed-loop recycled [World Economic Forum, 2016]. Secondary recycling of plastics into products of inferior qualities includes for example uni-coloring of mixed colored plastic, typically in black, but is limited mainly to fractions containing only a single type of plastic. Tertiary recycling, involving decomposition or depolymerization of the polymers for recovering of monomeric constituents or other valuable chemicals, is prospective for fractions of plastics were primary and secondary recycling is unviable [Al-Salem et al., 2009]. Tertiary recycling includes chemical depolymerization, solvolysis, catalytic and thermal cracking, pyrolysis, gasification, hydrogenation, etc. [Curlee and Das, 1998]. Whereas some types of polymers like polyesters, polyethers, polycarbonates, polyamides, are prone to solvolysis, such as hydrolysis (thermal and/or catalytic), others are more chemically resistant and require severe thermal conditions in order to decompose. For such polymers, including polyethylene and polypropylene, pyrolysis is suitable for converting the resins into basic chemicals and oils [Bockhorn et al., 1998; Onwudili et al., 2009]. Hydrothermal treatment is another thermochemical process identified as a highly cost competitive process for converting organic matter, e.g. wood, straw and sewage sludge, into value-added chemicals [De Jong, 2015; Zhu et al., 2014]. Hydrothermal processing of plastics at near and supercritical water conditions is an advanced tertiary technology, which has only scarcely been investigated [Sugano et al., 2009; Park et al., 2001; Watanabe et al., 1998]. Hydrolysis of Nylon 6 and Nylon 66 at near and supercritical conditions, without any added catalysts, was successfully applied for recovering high yields of monomers, such as caprolactam (85%) and apidic acid (>40%) [Meng et al., 2004; Iwaya et al., 2006]. Due to the bifunctionalities (thermal and chemical properties), a near or supercritical water environment is potentially useful for processing technically difficult waste, i.e. mixed types of plastics, and plastics contaminated with e.g. organic waste, which are otherwise incinerated. In fact, mixed fractions of plastics and plastics contaminated with organics are main challenges in plastic

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http://dx.doi.org/10.1016/j.wasman.2017.06.002
0956-053X/

waste management as they cannot be sorted and cleaned to their pure forms, which are requested aspects for their primary or secondary recycling [Gent et al., 2009].

As an alternative solution to incineration, we propose to processwaste plastic streams under supercritical water conditions and to recycle the plastic monomers for the production of new plastics along extraction of value added chemicals for usage in the chemical industry (Fig. 1). The flexibility of this hydrothermal process would allow the processing of different plastics regardless of color, sizes, purity, physical properties etc. within the same process.

In this paper, we demonstrate the usefulness of supercritical water for processing various types of high-density plastics. The objective is to screen hydrothermal processing of different types of pure plastics, individually, in order to obtain novel insight into decomposition trends and chemical recoveries for the various types of plastics. Ultimately, the expansion of the fundamental understanding, presented by this study, of how pure plastics decompose will improve the understanding and prediction of how undifferentiated plastic waste can be processed under supercritical water conditions.

2. Materials and methods

2.1. Materials

The high-density plastics used as feedstock in this study were: Poly(butylene terephthalate) (PBT), Polycarbonate (PC), Poly(ethylene terephthalate) (PET), Poly(lactic acid) (PLA), Poly(methyl methacrylate) (PMMA), Poly(oxymethylene) (POM), Poly(*p*-phenylene oxide) (PPO), Poly(vinyl alcohol) (PVA), Styrene-butadiene (SB). The plastics were purchased from major polymer producers: BASF, Chevron Phillips Chemical, LanXess, SABIC and Total Petrochemicals. All plastics were supplied in granular form, approximate size 3 mm, and then used as received without performing any pretreatment.

2.2. Experimental procedure

All pure plastics were processed, in duplicates, under hydrothermal process conditions. The experiments were carried out in micro-batch reactors (12 mL) submerged in a preheated fluidized sand bath (Techne SBL-2D). For each experiment, distilled water (5 g) and plastic (0.5 g, about 10 wt.%) were added to the reactor. None catalyst was necessary for the conversion. Reactors were sealed, purged with N_2 to remove residual O_2 and for leaking test, and then rapidly heated to 400 °C, developing a corresponding pressure of about 250 bar. The retention time was set to 15 min, including the heating period. During the reaction, temperature and pressure were both monitored and an agitation system provided the mechanical mixing inside the reactors. After 15 min, reactors were instantly cooled to room temperature in a water bucket.

2.3. Products recovery

The importance of the products recovery technique lies in the fact that products yields and quality are strictly dependent on the separation procedure and the solvents involved.

Once reactors were at ambient temperature, any eventual overpressure was vented through a top mounted valve. In some cases, such as for PLA processing, gases were collected for analysis. Reactors were then opened, and an aqueous phase containing soluble organics was collected and named as aqueous phase (AP). Acetone (≥95%, Cab Dan) was used to rinse reactors and to recover an oily phase. The collected mixture was vacuum filtrated and the solids (S) were dried in an oven (105 °C, 24 h) before being weighed. Then acetone was evaporated (40 °C, 556 mbar) in a rotary evaporator. Diethyl ether (DEE, ACS reagent, anhydrous, ≥99.0%, Sigma Aldrich) was added to extract the oily phase and then evaporated (40 °C, 990 mbar); the remaining oily phase was weighed and defined as synthetic crude oil (Fig. 2).

2.4. Products characterization

For some experiments, the gas phase composition was determined using a Gas Chromatograph (GC - Shimadzu, Tracera GC-2010 Plus). The GC was equipped with a micropacked column (Restek, length 2.0 m, I.D. 0.53 mm) and a BID detector. The oven was held at constant temperature of 85 °C. The total flow was 803 ml/min, split ratio was 1:200 and pressure was set to be the flow control mode (400 kPa). The injected volume was 0.1 mL.

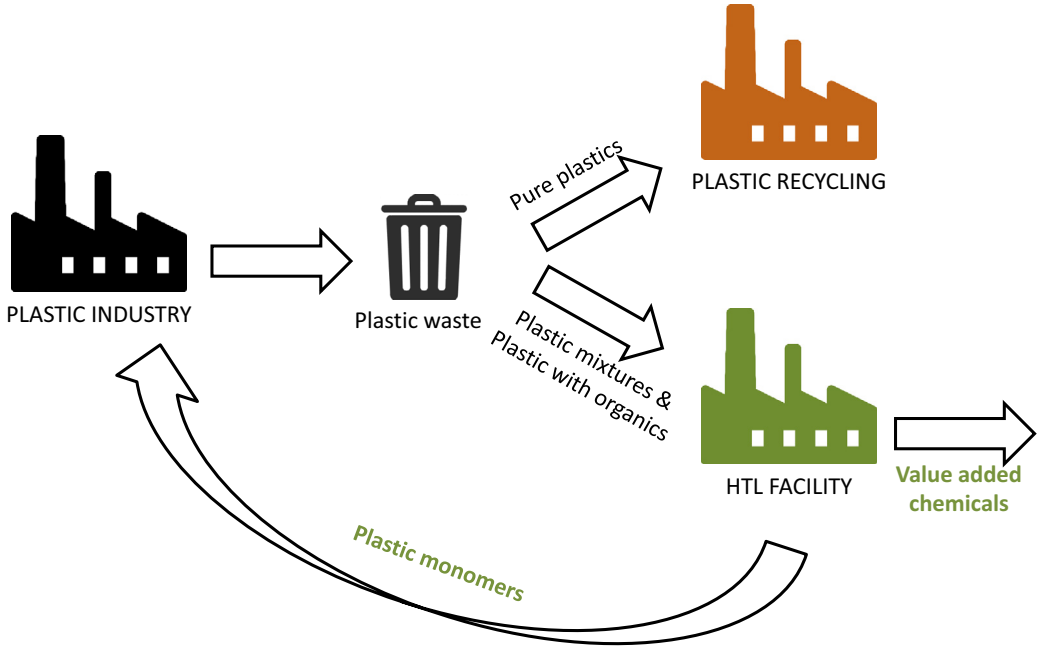

Fig. 1. Conceptual scheme for improving plastic economy via hydrothermal processing of unrecyclable plastics.

Please cite this article in press as: Helmer Pedersen, T., Conti, F. Improving the circular economy via hydrothermal processing of high-density waste plastics. Waste Management (2017), http://dx.doi.org/10.1016/j.wasman.2017.06.002