



Controlling generation of benzenes and polycyclic aromatic hydrocarbons in thermolysis of polyvinyl chloride in CO₂

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ABSTRACT

This study emphasizes the control of benzene derivatives and polycyclic aromatic hydrocarbons (PAHs) in thermolysis of polyvinyl chloride (PVC) using CO₂. To this end, the generation of benzenes and PAHs from the thermolysis of PVC in N₂ was characterized and all experimental findings from the thermolysis of PVC in N₂ were used as the reference value to configure the role of CO₂ in the thermolysis of PVC. The formation of hydrogen chloride (HCl) followed by the subsequent dechlorination in the thermolysis of PVC in N₂ resulted in the high yield of charring compounds, providing a favorable condition for forming benzene derivatives and PAHs. However, the thermal degradation of PVC in CO₂ showed the genuine thermal degradation patterns. For instance, despite the presence of the source for oxygen, the formation of CO at temperatures higher than 600 °C was observed in the thermolysis of PVC in CO₂, suggesting that some unknown reactions between hydrocarbons from the thermolysis of PVC and CO₂ are initiated to form CO. In addition to these unknown reactions, the enhanced thermal cracking induced by CO₂ was observed. Two identified roles of CO₂ during the thermolysis of CO₂ was only limited at temperatures higher than 600 °C. However, despite no precise description for the mechanistic role of CO₂ at this stage of study, the formation of benzene derivatives and PAHs was effectively controlled in the presence of CO₂ at temperatures higher than 480 °C. Thus, these empirical findings in this study are necessary to further be investigated in the future, which offers a great venue offering a new means for modifying and/or controlling the harmful chemical species.

1. Introduction

The global production of polymers including elastomers exceeds 300 million tons per annum due to their cost-effective and versatile physico-chemical properties [1,2]. In light of the extraordinary functionalities and physico-chemical properties, their application has been found from diverse fields for substituting the conventional materials (e.g., wood and metal). Because of the massive generation of polymeric wastes, severe environmental problems have been realized worldwide [1,3]. Compared to other organic wastes (e.g., biomass and food waste), it is yet challenging to establish an environmentally viable platform for disposing polymeric wastes without significant environmental burdens due to their low biodegradability and invulnerable physico-chemical stability [1,4,5].

Over the last three decades, discarded polymers have also been recognized as one of the main streams for the emerging contaminants [6,7]. Some polymeric wastes containing hazardous monomers and additives (e.g., chlorinated compounds and phthalates) are also identified to be lethal and mutagenic to marine ecosystems and most living creatures including human beings [8–10]. Because waste polymers can adsorb chemical pollutants (e.g., persistent organic pollutants) in aquatic environments due to their intrinsic hydrophobicity [7,9,11], intake of these chemical-laden polymers and chemicals by marine creatures may result in the internal and chronic accumulation with the disturbance and the disorder of their health [12–14]. Similarly, they can act as one of the crucial contributors for impairing human health.

Therefore, it is desirable to establish an environmentally viable platform for disposing polymeric wastes. Considering the current

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energy problems associated with our heavy dependence on fossil fuels, disposing waste polymers while recovering energy can be the desirable end use [15,16]. Moreover, energy recovery from petro-derived wastes (i.e., polymers and elastomers) provides a means for enhancing the energy security in most developed countries. Polymeric wastes can be a promising and attractive feedstock for energy recovery because the heating value of petro-derived wastes is higher than coal (i.e., 32.5 MJ kg⁻¹ of anthracite) and roughly equivalent to petro-diesel (i.e., 44.48 MJ kg⁻¹) [4,17,18]. Considering the annual generation of petro-derived wastes (3 × 10⁸ tons), the possible energy recovery from polymeric wastes is equivalent of 0.3 billion tons of diesel, which amount is far exceeding than the total consumption of petro-diesel in Korea.

Among polymeric wastes, it is very challenging to establish an appropriate disposal platform for polyvinyl chloride (PVC) since it requires the stringent caution due to the high content of chloride. The conventional disposal methods for PVC have been mainly conducted via landfilling or incineration, which is not environmentally friendly. Chlorine in PVC can be readily transformed into chlorinated hydrocarbons during the hydrolysis and thermolysis steps, which serves as precursors of toxic contaminants like polychlorinated dibenzo-*p*-dioxins/furans, hydrogen chloride (HCl), and polychlorinated biphenyls [19–25]. Thus, water and soil pollution can be triggered by the long-term release of leachate in the landfilling site. The contamination of groundwater by the leachate containing chlorinated chemicals can violate drinking water standards [26]. In case of incineration of PVC, the high electronegativity of chlorine can be served to a radical scavenger during the incineration, blocking the oxidation of between oxidants and PVC [27,28]. Hence, this mass transfer limitation of oxygen simultaneously results in incomplete combustion, which provides the favorable conditions to expedite the generation of benzenes and polycyclic aromatic hydrocarbons (PAHs) [29,30]. In these respects, it is desirable to establish the means for suppressing these harmful chemical species during the disposal process of PVC.

To this end, the dechlorination process is conducted first, and then other process via stepwise pyrolysis, catalytic degradation, and mixture with adsorbent or alkaline additives are intentionally conducted [2,31,32]. Due to the technical incompleteness, the complete control for the generation of harmful chemical compounds during the thermal degradation of PVC cannot be achieved. Based on this rationale, it is desirable to establish a new and simple process without using any chemical additives such as catalyst. This study mainly emphasizes understanding of the generation of harmful chemical species such as benzene derivatives and PAHs in N₂ and CO₂. To do so, this study experimentally justifies that use of CO₂ as reaction medium plays a crucial role to mitigate the harmful chemical species.

2. Materials and methods

2.1. Chemicals

In this work, commercially available PVC (389293, Sigma-Aldrich) was used as the feedstock. The PVC was grinded with a Wiley Mill (Thomas Scientific) and its particle size was adjusted as ~355 μm. Proximate analysis of PVC was conducted with a programmable furnace (DAIHAN Scientific) in accordance with the Ref. [33]. Ultimate analysis of PVC was carried out by an elemental analyzer (Thermo-Fisher Scientific). The gross heating value of PVC was measured using a bomb calorimeter (IKA). All results are summarized in Table 1.

2.2. Thermo-gravimetric analysis (TGA) of the mixtures of PVC in N₂ and CO₂

Thermal degradation of PVC was conducted using a TGA (Netzsch) in N₂ and CO₂. The TGA tests were conducted from 20 to 900 °C (10 °C min⁻¹). Each gas flow rate (purge: 50 mL min⁻¹; protective

Table 1
Proximate, ultimate analysis, and heating value of PVC.

Proximate analysis (wt%)			Ultimate analysis (wt%)				Heating value (MJ/kg)
Moisture	Volatile matter	Fixed carbon	Ash	Carbon	Hydrogen	Chlorine	
0.14	86.99	12.87	0	37.77	4.80	57.43	19.02

gases: 100 mL min⁻¹) was controlled by the mass-flow controllers (MFCs) imbedded in the TGA. The sample loading was 10 ± 0.1 mg for each set of the TGA test. To ensure reproducibility, all TGA tests were conducted in triplicates.

2.3. Pyrolysis reactor setup

A batch-type quartz tubular reactor (25.4 mm of outer diameter (OD), 22 mm of inner diameter (ID), and 0.6 m of length) was used for a scale-up experimental work. Both ends of the tubular reactor (TR) were connected to ultra-torr vacuum fittings (Swagelok). The programmable tube furnace (DAIHAN Scientific) was used and its temperature was controlled by PID controller (Samwon Engineering). K-type thermocouple (Omega) was located at the center of the TR to ensure the experimental setting temperature and its deviation was less than 3 °C. 2 ± 0.05 g of sample was loaded at the center of the TR for each batch test. Like the TGA test, all experimental work was done in triplicate to ensure reproducibility. The flow rate (600 mL min⁻¹) of N₂ and CO₂ were controlled by MFCs (Brooks Instrument). Effluents from the TR were transferred into a micro gas chromatography (INFICON 3000A) using 0.25 in (6.35 mm) of the PTFE tubing (DAIHAN Scientific). The lag times of the gaseous products from the TR were calculated to be less than 2 s based on the volume of the transfer line (3 mL). The chiller (DAIHAN Scientific) was set to collect condensable hydrocarbons using a jacketed water circulation at 4 °C.

2.4. Analysis

The gases evolved from the TR were quantified using micro-GC with a thermal conductivity detector (TCD) equipped with a Mol-Sieve 5A capillary column (Agilent). Calibration data and QA/QC for the micro-GC are summarized in Supporting Information (Table S1). The collected condensable hydrocarbons from the TR were weighted for the overall mass balance from the TR. Moreover, the collected condensable hydrocarbons were quantified by a GC/TOF-MS (Agilent 7890B/ALMSCO) equipped with an Agilent HP-5MS column. Prior to the quantification, the condensed hydrocarbons were diluted by 20-fold with dichloromethane (Sigma-Aldrich, USA). Multiple calibrations were performed using indoor air standard (Lot No. XA22144U, SUPELCO, USA) and PAH-mix B (Lot No. LB04623, SUPELCO, USA). QA/QC for the GC/MS-TOF is reported in Table S2. The methods used for the micro-GC and GC/MS-TOF are detailed in Table S3.

3. Results and discussion

3.1. Thermal degradation of PVC in N₂ and CO₂

The TGA test was conducted at to investigate the effect of CO₂ on thermal degradation of PVC. Mass decay of PVC as a function of experimental temperature in N₂ (black color) and CO₂ (red color) was illustrated as two thermograms in Fig. 1. Differential thermogram (DTG) obtained from the thermolysis of PVC in N₂ and CO₂ was also incorporated to effectively differentiate any CO₂ effect on the thermal decomposition of PVC.

As described in Fig. 1, there were two distinctive mass losses that

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