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Research article

Upgrading of non-condensable pyrolysis gas from mixed plastics through catalytic decomposition and dechlorination

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ABSTRACT

The non-condensable pyrolysis gas from plastic pyrolysis is a suitable fuel and precursor for chemical synthesis. Depending on downstream applications, the selective removal of unsaturated hydrocarbons and HCl released from polyvinyl chloride (PVC) is required. This study investigated the selective decomposition of unsaturated hydrocarbons with simultaneous dechlorination of non-condensable pyrolysis gas using a catalytic sorbent containing 5% NiO loaded on $CaCO_3$ support (Ni-Ca) and pristine $CaCO_3$ (Ca) at different temperatures, doses of catalytic sorbent and HCl contents. As a result, Ca removed 98.8% of HCl and decomposed 89% of alkynes and 23% of dienes at 700 °C. When applying Ni-Ca, the HCl removal was above 99% at all studied temperatures, while 90% decomposition of alkenes, dienes and alkynes was achieved, depending on temperature, Ni-Ca dose and HCl content. The higher HCl content in gas (43 mg against 13 mg) negatively influenced the catalytic activity of Ni-Ca, while increasing the selectivity towards the decomposition of alkenes, dienes and alkynes compared to alkanes. At 700 °C, 99.6% removal of unsaturated hydrocarbons by Ni-Ca was attained at only 10.1% conversion of alkanes. Thus, depending on the applied catalytic sorbent, either selective decomposition of alkynes and dienes (over Ca) or a mixture of unsaturated hydrocarbons (over Ni-Ca) was achieved with the simultaneous HCl removal from non-condensable pyrolysis gas.

1. Introduction

Owing to a high accumulation rate and availability in large quantities, plastic waste is a suitable feedstock for energy applications and chemical syntheses. During thermal decomposition in the absence of oxygen (pyrolysis), plastics are converted into liquid hydrocarbons, non-condensable gas and coke. The state-of-the-art of plastic pyrolysis has been extensively presented in the recent reviews [1–3]. The technology has been also implemented at large scale plants, among which are Sapporo Plastic Recycling plant by Klean Industries Inc. and Syntrol plant by GRT Group SA with ~15,000 t/year capacities. Liquid hydrocarbons can be utilized as fuel either directly or after post treatment that improves the product quality [4,5]. Non-condensable pyrolysis gas from plastics represents 10–90% of total product yield, depending on treatment conditions and feedstock [6,7], and is typically burnt [8]. However, proper utilization of non-condensable gas can provide economic benefits to the operators of pyrolysis plants.

Recently, the suitability of pyrolysis gas from plastics as a replacement of natural gas has been demonstrated [9]. Unlike natural gas, pyrolysis gas from plastics contains a mixture of alkanes, alkenes, dienes and alkynes. For the operation of gas engines, gas turbines and fuel cells, the removal of unsaturated hydrocarbons is desired. Owing to the high reactivity, unsaturated hydrocarbons can form soot, rubber-like materials and gums during combustion process [10–12]. The high reactivity of unsaturated hydrocarbons also results in carbon deposition on solid oxide fuel cells, which decreases electrical performance and increases mechanical degradation of anodes [13].

In other applications, alkenes (e.g., ethylene and propylene), which are present in large quantities in pyrolysis gas, can be used as precursors for chemical syntheses. For the utilization of these hydrocarbons, the removal of alkynes from pyrolysis gas is desired owing to poisoning of catalysts and/or formation of explosive acetylides with catalysts (e.g., Ziegler-Natta, silver- and copper-based catalysts) [14,15]. Thus, depending on downstream applications, selective decomposition of undesirable hydrocarbons containing in pyrolysis gas is essential.

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Pyrolysis gas obtained from mixed plastic waste typically contains HCl that originates from the thermal decomposition of polyvinyl chloride (PVC). PVC usually represents 2–10% fraction of total mixed plastic waste. The released HCl is a prime cause of equipment corrosion and compromises the performance of solid oxide fuel cells [16,17]. Therefore, the acceptable HCl concentration in pyrolysis gas is low and the upstream removal of HCl is highly required.

Currently, the removal of HCl is typically carried out separately from removal of unsaturated hydrocarbons. This is done by applying alkali and alkali earth sorbents either to a pyrolyzer [18,19] or in a downstream scrubber [20]. Another study utilized a two-stage pyrolysis process for the removal of HCl [21]. At the first stage, relatively low temperature is used in order to decompose PVC and capture HCl, while at the second stage higher temperatures are used in order to decompose other polymers. However, the dechlorination process affects the characteristics and quality of pyrolysis products [22] and the produced gas may require further treatment [18] to remove residual HCl before the final-end fuel application.

Catalytic decomposition of hydrocarbons present in non-condensable pyrolysis gas from plastics into hydrogen and carbon nanotubes has been previously demonstrated [23–26]. The main focus of these studies was to maximize the conversion efficiency of all hydrocarbons in order to increase H_2 and carbon yields. For utilization of non-condensable pyrolysis gas in other applications, the selective removal of unsaturated hydrocarbons (e.g., alkenes, dienes and acetylenes for energy applications or acetylenes for recovery of alkenes) is required. The purpose of this study was to investigate the selective decomposition of unsaturated hydrocarbons with simultaneous dechlorination of non-condensable pyrolysis gas using a catalytic sorbent containing nickel oxide loaded on calcium carbonate support. Herein, the effects of temperature, initial HCl content in pyrolysis gas and calcium support on the decomposition of hydrocarbons and HCl removal were studied.

2. Materials and methods

2.1. Materials

Virgin polymers were used to simulate mixed plastic waste containing 0.75 g (40%) low density polyethylene (LDPE) from PTT Global Chemical Public Co. Ltd. (Thailand), 0.75 g (40%) polypropylene (PP) from Sinopec (China), 0.18 g (10%) polystyrene (PS) from Formosa Plastics Corp. (Taiwan) and 0.18 g (10%) polyvinyl chloride (PVC) from Hop Fu Plastics Ltd. (China). The prepared plastic mixture was denoted as LDPE-PP-PS-PVC. A mixture of LDPE, PP and PS (0.75 g, 0.75 g and 0.18 g, respectively) denoted as LDPE-PP-PS was used as a reference to investigate the influence of PVC on the catalytic decomposition of hydrocarbons. Proximate and ultimate analyses of the virgin plastics and mixtures are shown in Table S1.

The catalytic sorbent was prepared using calcium carbonate and nickel (II) nitrate hexahydrate. 5 g of nickel (II) nitrate hexahydrate (97% pure, Sigma-Aldrich) was dissolved in 100 mL of anhydrous ethanol (99.5% pure, Sigma-Aldrich) and then 19 g of calcium carbonate (99% pure, Hayashi Pure Chemical Ind. Ltd., Japan) was added to the solution. The suspension was thoroughly mixed and the solvent was evaporated in a rotary evaporator Hei-Vap Precision (Heidolph Instruments) at 50 °C under 100 mbar vacuum. The material was dried overnight in an oven at 55 °C and then calcined in air at 750 °C for 3 h (heating rate 2 °C min^{-1}). The calcined material with Ni loading 5% by mass was sieved to collect particles with sizes 63–212 μm, and is denoted as Ni-Ca. The BET surface area of Ni-Ca determined by N_2 adsorption isotherm was 2.3 $m^2 g^{-1}$. To prepare the support without nickel, calcium carbonate was calcined and sieved using the same procedure. The support material containing only calcium compounds is denoted as Ca.

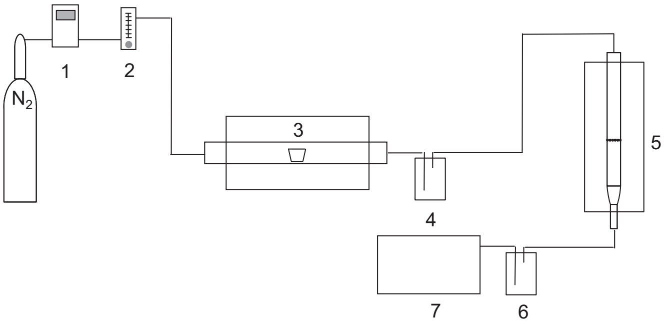

Fig. 1. Experimental setup: 1 – N_2 mass flow meter with totalizer, 2 – N_2 rotameter, 3 – horizontal reactor for plastic pyrolysis, 4 – condenser, 5 – vertical reactor for decomposition of hydrocarbons, 6 – HCl trap and 7 – gas sampling bag.

2.2. Experimental procedure

The experiments were conducted in a setup comprising of two reactors (Fig. 1). The horizontal quartz reactor (i.d. 53 mm) was used for pyrolysis of plastic mixture, while the vertical quartz reactor (i.d. 17 mm) was used for catalytic decomposition of non-condensable pyrolysis gas and HCl removal. For pyrolysis, a plastic mixture (1.86 g of LDPE-PP-PS-PVC or 1.68 g of LDPE-PP-PS) was placed in a crucible and then inserted in the middle of the horizontal quartz reactor. A known mass of catalytic sorbent was loaded into the vertical reactor, which had a fritted disc in the middle with 50–90 μm openings to support the catalytic sorbent bed. The flow of N_2 (carrier gas) was adjusted to 100 mL min^{-1} and the catalytic sorbent in the vertical reactor was heated at 15 °C min^{-1} to 500, 600 or 700 °C. Once the desired temperature was reached, the plastics in the horizontal reactor were heated at 10 °C min^{-1} to 600 °C and pyrolyzed for 0.5 h. To ensure separation of condensable oils, the generated gas from the pyrolysis reactor passed through a condenser at ambient temperature (23 °C) before entering the vertical reactor. The total HCl content in the pyrolysis gas was 43 mg. To study the HCl effect, a second condenser was installed between the reactors decreasing the HCl content to 13 mg. To quantify the HCl content, approximately 200 mL of NaOH (0.025 M) was used in the HCl trap installed downstream the vertical reactor (Fig. 1). The content of captured HCl was measured by ion chromatography (Dionex ICS-1100, Thermo Scientific).

The gas from the vertical reactor was collected in a gas bag. The collection of gas started when the temperature in the pyrolysis reactor with loaded plastics reached 100 °C and finished after 30 min of isothermal heating at 600 °C. The total N_2 volume collected during each run was quantified by a mass flow meter with totalizer (GFM17, Aalborg, USA) installed before the horizontal reactor. The collected gas was analyzed using a calibrated gas chromatograph equipped with a flame ionization detector for 21 C_1–C_5 hydrocarbon species and two thermal conductivity detectors for N_2, O_2, CO, CO_2, and H_2 analysis (7890B model, Agilent Technologies Inc.). The volumes of gas components containing in the non-condensable pyrolysis gas were calculated based on the concentrations determined by the gas chromatograph and a known volume of N_2 carrier gas measured by the mass flow meter with totalizer.

To calculate the amounts of hydrocarbons decomposed during the catalytic treatment, experiments without catalytic sorbent were carried out at 500, 600 or 700 °C. The percent of decomposed hydrocarbons (alkanes, alkenes, alkynes and dienes) was calculated by the volumes of hydrocarbons recovered with and without catalytic treatment of non-condensable pyrolysis gas in the vertical reactor at the same temperature. All experiments were triplicated and the data are presented as averages of three runs with calculated uncertainties (standard deviations). Error analysis was carried out using Gaussian error propagation.