



Production of biofuel precursor chemicals from the mixture of cellulose and polyvinylchloride in polar aprotic solvent



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ABSTRACT

Polyvinylchloride (PVC) is the major halogen source in municipal solid waste (MSW) and its recycling is problematic. PVC can not only cause various environmental problems by releasing halogens, but also negatively impact other MSW compositions during waste to energy conversion. For instance, co-pyrolysis of biomass with PVC increases solid residue and promotes the formation of CO and CO₂ from cellulose. Herein, we report an approach to dehydrochlorinate PVC while simultaneously enhancing the production of valuable chemicals from cellulose. Specifically, cellulose and PVC were co-converted in tetrahydrofuran (THF). It was found that co-conversion of cellulose with PVC significantly increased liquid yield from cellulose and shortened the conversion time compared to converting cellulose alone. Levoglucosan was the major product from cellulose and its highest yield of 40% was achieved with 2.5 wt% of PVC at 335 °C after only 8 min of reaction. We have shown that the in-situ generated HCl derived from PVC decomposition serves as acid catalyst to enhance glycosidic bond cleavage in cellulose. Moreover, using a THF/water co-solvent could further enhance the conversion rate and increased liquid yield to a maximum of 92.55%. Pyrolysis of the solid residue did not release chlorinated organics, suggesting that PVC was fully dechlorinated in THF. The present study may be applied to convert PVC-containing, cellulose rich MSW for higher valued products in environmentally friendly approach.

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1. Introduction

Municipal solid wastes (MSW) are end-life materials consisting of both organic and synthetic polymers, generated from industrial, commercial, and residential sectors (Langholtz et al., 2016). In 2012 alone, over 1.3 billion tons of MSW was produced worldwide and its number continues to increase (Gardner, 2013). Although waste recycling has been actively promoted for years, the majority of MSW still ends up in landfills (EPA, 2015). Waste landfilling presents both environmental and economic challenges. Improper waste disposal could cause groundwater and air pollution, and increase greenhouse gas emission (Kumar and Sharma, 2014). Transporting bulky wastes to remote landfilling sites also creates an economic burden. Alternatively, Waste-to-Energy (WTE) strategies, such as combustion, gasification, and pyrolysis not only reduce the landfilled MSW, but also promote energy recirculation for sustainability. However, WTE is still under development and facing various challenges, which include poor product quality, pollutant formation, and reactor operability (Al-Salem et al., 2009; Hopewell et al., 2009; Shent et al., 1999). These difficulties are

mostly attributed to the heterogeneity of MSW compositions (Ma et al., 2010). For instance, halogens present in MSW can cause serious environmental issues during waste conversion (Valavanidis et al., 2008). Polyvinyl chloride (PVC) is known as the major halogen source in MSW and it is widely used in packaging, piping, wrappings, bottles, and containers. Compared to other major plastic wastes, PVC can easily decompose at low temperatures to release hydrogen chloride (HCl) and other chlorinated organics (Sadat-Shojai and Bakhshandeh, 2011; Yu et al., 2016). Evaporated HCl may promote clogging and corrosion in reactors, and act as a chlorine source for dioxin formation if combusted (Indrawan et al., 2011; Katami et al., 2002). In addition, chlorinated organics can cause serious environmental hazards. Since traditional recycling of PVC from a complex mixture of MSW is difficult (Braun, 2002), dechlorination of PVC containing wastes has been studied. It has been shown that co-pyrolyzing PVC and organic waste materials could reduce HCl emission compared to pyrolyzing PVC alone (Kuramochi et al., 2008; Zhou et al., 2015). However, the remaining Cl atoms end up in the solid residue or liquid product as organic chlorides. The chloride contaminated tar, pyrolysis-oil, and char can cause significant problems in their handling and subsequent applications. Recently, hydrothermal treatment has been proposed to be an effective method to dehydrochlorinate PVC (Yu et al., 2016). Since HCl is solubilized in water, Shen (2016) suggested that the

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solid residue produced from hydrothermal co-conversion of PVC and lignin has potential application as a clean solid fuel. However, their study also showed that hydrothermal dehydrochlorination is less effective if PVC was co-converted with other organic components, such as cellulose or xylan. PVC not only causes environmental concern due to halogen release, but also negatively affects decomposition of other MSW compositions when co-converted. [Zhou et al. \(2015\)](#) found that pyrolysis of biomass with PVC increased char yield and the formation of CO and CO₂. During catalytic gasification, the presence of PVC reduced tar cracking efficiency and accelerated catalyst poisoning ([Huang et al., 2016](#)). It was also reported that PVC-derived intermediates increase char yield during co-pyrolysis of PVC and other plastic wastes ([Yu et al., 2016](#)).

In the present study, a solvent-based co-conversion of cellulose and PVC was investigated. While the focus of the previously mentioned research dealt with PVC containing wastes for dechlorination, the present study aims to take the advantage of PVC dechlorination to enhance cellulose conversion to valuable chemicals. Cellulose is one of the major MSW fractions because nearly 60% of MSW is cellulose-rich organic wastes, such as paper products, yard trimmings, food wastes, and textiles. Cellulose is also known as the most important biorefinery feedstock for biofuels and chemicals ([Agirrezabal-Telleria et al., 2014](#); [Cai et al., 2013](#); [Cao et al., 2015](#); [He et al., 2017](#)). For example, cellulose-derived glucose or levoglucosan (LG) can be fermented into ethanol and other advanced biofuels. Furfural and 5-hydroxymethylfurfural (HMF), also produced from cellulose, are useful building block chemicals for further upgrading ([Agirrezabal-Telleria et al., 2014](#); [Lange et al., 2012](#)). In this study, cellulose and PVC were co-converted in the polar aprotic solvent tetrahydrofuran (THF). Unlike water or alcohols, polar aprotic solvents do not donate hydrogen. In recent studies, various polar-protic solvents have shown promise in their ability to solubilize cellulose or cellulosic biomass with high efficiencies ([Cai et al., 2013](#); [Cao et al., 2015](#); [Ghosh et al., 2016](#); [Luterbacher et al., 2014](#)). For example, [Luterbacher et al. \(2014\)](#) produced a high yield of soluble carbohydrates from corn stover using γ -Valerolactone as the solvent. [Cao et al. \(2015\)](#) produced high yields of levoglucosenone (LGO) by converting cellulose in THF. [Cai et al. \(2013\)](#) produced furfural, HMF and levulinic acid by converting pine wood in a mixture of THF and water. [Bai et al. \(2014\)](#) converted switchgrass in 1,4-dioxane to produce C₅ and C₆ sugar monomers. More recently, [Ghosh et al. \(2016\)](#) converted cellulose in seven different types of polar aprotic solvents at supercritical states and obtained 72–98% yield of soluble products.

While cellulose and PVC were co-converted in THF in this study, the main goal was to test a hypothesis that HCl generated from PVC dechlorination in-situ could act as acid catalyst to promote cellulose conversion. If this hypothesis is correct, there is a potential to positively utilize PVC to obtain valuable chemicals from cellulosic wastes among MSW for both energy and environmental sustainability. Among the common polar aprotic solvents, THF was chosen for this proof-of-concept study due to its easy accessibility, low boiling point and biomass-derivable nature ([Gallo et al., 2013](#)). In the present study, the fractions of PVC in cellulose were kept low to better represent the content of PVC compared to the content of cellulosic wastes in real-world MSW. While the plastic wastes account for 12.9% of total MSW ([EPA, 2015](#)), 10% of the plastics is PVC ([PlasticsEurope](#)). Thus, PVC fraction in entire MSW is below 2%, much lower than cellulosic organic wastes.

2. Materials and method

2.1. Materials

Cellulose with an average particle size of 50 μm was purchased from Sigma-Aldrich. HPLC grade THF with 0.025% butylated

hydroxytoluene as a stabilizer was purchased from Fisher Chemical. PVC powder was obtained from the Shanghai Yangli Mechanical and Electrical Technology Co., Ltd, China. LG (99.9%) and cellobiosan (98.7%) were purchased from Carbosynth Ltd, UK, furfural (99%), HMF (99%) and cellobiose (99.2%) were from Sigma-Aldrich, and glucose (99%) and cellobiose (99.5%) were from Fisher Scientific.

2.2. Conversion in solvent

The solvent conversion experiments were conducted in 316-stainless-steel Swagelok reactors consisting of two 3/8 in. plugs and a 3/8 in. port connector. The total volume of the reactor was 2 ml. For each experiment, 20 mg of cellulose and 0.25, 0.5 or 0.75 mg of PVC (corresponding to 1.25, 2.5 and 3.75 wt% of cellulose) were added to the reactors along with 1.2 ml of solvent. In the case of PVC conversion alone, 10 mg of PVC was loaded and reacted at 310 °C. The solvent was either THF or a 90v/10v mixture of THF and deionized water. The sealed reactors were then shaken for 15 min to enhance the mixing of the solids in the solvent. An industrial fluidized sand bed was used to supply heat for the reaction. Prior to the tests, the temperature inside the reactor was measured by inserting a thermocouple to the reactor filled with THF. It usually took less than a minute for the solvent to reach the designated temperatures. Once the temperature reached the preset temperatures, the reactors were dropped into the fluidized sand for heating. After the desired reaction time was reached, the reactor was quickly taken out of the bed and immediately quenched in a room temperature water bath. The reaction times were counted from when the reactors entered the fluidized bed until they were dropped in the water.

The liquid/solid suspension inside the cooled reactor was first extracted with a syringe. The solid residue was then separated from the liquid using a 0.45 μm glass filter. The solid residue was dried at room temperature overnight before it was weighted. To determine the amount of gas products, the reactor was weighted both before and after the reactor cap was loosened to release the trapped gases. In the present study, the gas yield was negligible in all the tested cases. Thus, the product yields were determined using equations given below:

$$\text{Solid yield \%} = \frac{\text{solid residue mass}}{\text{cellulose mass}}$$

$$\text{Liquid yield} = 100\% - \text{solid yield \%}$$

2.3. Product characterization

An Agilent 7890B Gas Chromatograph (GC) equipped with Mass Spectrometer (MS) and Flame Ionization Detector (FID) with two ZB-1701 (60 m \times 250 μm \times 0.25 μm) capillary columns was used to analyze the liquid products. Initially the GC oven temperature was held at 40 °C for 3 min, and then heated to 280 °C at a ramp of 4 °C/min. Finally, the oven was held at this temperature for additional 4 min. In the GC, helium was the carrier gas with the column flow rate of 1 ml/min, and the split ratio of 20:1 at the GC inlet. The composition of the liquid products was identified with MS and quantified by FID. The compounds were quantified based on calibration curves of the authentic chemicals. For each compound, a five-point calibration was performed to achieve the regression coefficient higher than 0.99.

The liquid products were also analyzed using a Dionex 3000 Ultimate series high performance liquid chromatography (HPLC) system. A Thermo Scientific HyperREZ carbohydrate column was used for separation using water as the eluent. The flow rate of water was 3 ml/min, and the column temperature was 85 °C. The

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