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SolvX: Solvothermal conversion of mixed waste plastics in supercritical toluene in presence of Pd/C catalyst

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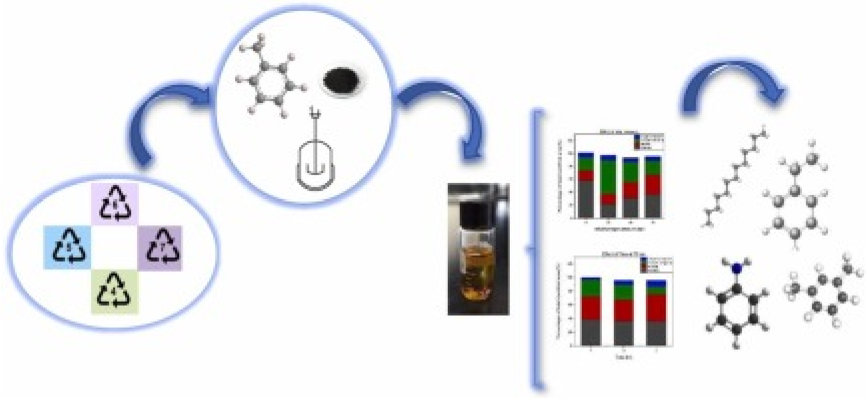
Abstract

As the world's ability to cope with the fast-rising output of disposable plastic products is limited, plastic pollution has emerged as one of the most important environmental challenges. Catalytic solvothermal conversion (SolvX) could potentially utilize mixed waste plastics (MWPs) for sustainable fuels and chemical production. In this study, the effect of SolvX reaction time (1 – 5 h), Pd/C catalyst loading (0 – 10 wt%), and hydrogen loading (0–75 bar) on MWPs were investigated using supercritical toluene as solvent at temperature 350 °C. Four major waste plastics including low-density polyethylene (#4), polypropylene (#5), polystyrene (#6), and polyurethane (#7) were used as feedstock for this study. Along with SolvX conversion, the liquid products (crude oils) were characterized for elemental composition changes using ultimate analysis, boiling point distribution via thermogravimetric analysis, functional groups alteration using Fourier transform infrared spectroscopy, and product identification via gas chromatography-mass spectrometry. The results showed that the addition of catalyst and hydrogen have positive effects on the SolvX conversion. According to the elemental analysis, the SolvX crude oils' higher heating values (HHV) range from 32 to 38 MJ/Kg. The range of boiling points demonstrates that Pd/C increases the formation of lighter hydrocarbons. Additionally, a proposed catalytic SolvX reaction mechanism shows that the aromaticity raised with the increment of residence time and Pd/C enhances hydrodenitrogenation and deoxygenation at higher hydrogen loading.

Graphical Abstract



Synopsis: Mixed plastic wastes could be solvothermally converted to valuable fuels and chemicals.

Introduction

According to the latest data from the Guardian report, the U.S. produced 42 million metric tons of plastic waste in 2021 [1]. While about 8.6% of plastic waste was recycled and about 15.6% was combusted for energy, the rest of them was landfilled [2]. Looking closer into the recycled portion of the plastics, it is predominantly recycled #1 (polyethylene terephthalate) and #2 (high density polyethylene) of plastics [2]. In fact, these are the only plastics that are separated relatively easily and because of the thermoplastic nature of the plastics, they can be melted and regenerated. On the other hand, higher recycle types like #4 - #7 (e.g., low-density polyethylene, polypropylene, polystyrene, and polyurethane, respectively) are difficult to separate mechanically and some are thermosets rather than thermoplastics; therefore, most of them are either landfilled or incinerated [3]. Although these technologies have partially succeeded in recycling plastic, they also have highlighted significant flaws in the actual application procedure [4]. Landfill technology consumes a lot of space, has a long processing time, and has a low waste disposal capacity [5]. Plastic incineration is a low-level disposal process that generates hazardous compounds that could harm the environment [6]. Therefore, recycling mixed waste plastics (MWPs) has become a serious liability for the environment. On the flip side of the coin, MWPs are consistent, low-cost, and stable feedstock with high carbon and high hydrogen contents. With an appropriate conversion technology, these high carbon and hydrogen of the MWPs can be converted to valuable fuels and chemicals [7], [8], [9], [10], [11].

Among various waste plastic conversion technologies, SolvX conversion using sub-and supercritical fluids is an emerging one. The goal of utilizing sub and supercritical solvents is to provide a mild reaction environment but with enhanced mass and heat transfer [12]. Till date, various types of solvents have been tested for SolvX. One of the most common solvents is water in its sub and supercritical forms. This technology is widely known as hydrothermal liquefaction (HTL). HTL has been an attractive technology primarily for wet feedstocks (e.g., food waste [13], sewage sludge [14], agricultural residues [15]), which converts wet wastes to liquid biocrude. In fact, co-HTL with plastics [16] or even HTL of plastics [17] have been reported in the literature. For example, Seshasayee and Savage [18] studied the possibility of energy dense oils from four type of plastics (PP, PS, PC, and PET at temperatures 350–450 °C (sub and supercritical water) for 0.5–1 h in a batch reactor. They revealed that the oil from PP and PS has a higher heating value (44–45 MJ/kg), which is equivalent to gasoline. Nevertheless, even at sub-or supercritical water temperatures, plastics are less reactive[19]. Furthermore, HTL frequently leads to carbon loss in aqueous phase and gaseous phase. Moreover, the HTL process liquid must be treated properly before being released into the environment [20]. Beside water, other oxygenated solvents like methanol and acetone were used in SolvX for depolymerization of polyethylene [21]. The results showed that these oxygenated solvents are more effective than water to depolymerize polyethylene[22]. In comparison to HTL, SolvX has two key advantages: Organic solvents like toluene often have low critical temperatures and critical pressures, resulting in reactions at lower operating conditions; and solvent regeneration and reuse require less energy. But some solvents are toxic or combustible, which can pollute the environment [23], [24]. Iwaya et al. [25]used benzyl alcohol (BZA) and diethyleneglycol monomethylethter to depolymerize unsaturated polyester (UP) at temperatures 463–623 K (subcritical state) for 1–8 h in a batch reactor. They found that the depolymerization of UP grew as the catalyst/solvent molar ratio raised and it was improved in the presence of K_3PO_4 catalyst in subcritical BZA. However, a recent study has revealed that the oxygen content of the solvents may be undesirable for a wide range of fuel-based applications [26]. The solvent is often a reactant that dissolves the reaction products, blocking or delaying higher order reactions [27]. In fact, utilizing oxygenated solvents increases the risk of oxygen impurity of crude oil, while increasing the expense of the process, which needs either separation or a market that can accept crude oil with oxygen [24]. For example, to produce appropriate fuels for transportation through biomass liquefaction, one criterion is to remove oxygen from biooil using chemical processes such as, decarboxylation, and hydrodeoxygenation[26].

On the other hand, non-oxygenated solvents may be utilized for solvothermal conversion (SolvX) of MWPs. Our research group has recently investigated the degradation of three type of plastics (polyurethane, polypropylene, and polystyrene) in toluene as a non-oxygenated solvent at sub-and supercritical conditions [24]. Nonpolar solvent, toluene, has a lower critical point in comparison to water. Nonpolar fraction of degraded plastics were dissolved easily in toluene, made the product separation easier [24]. Although toluene is flammable, we have studied preliminary process safety proposing inherently safer design and recommending preventive and mitigative safeguards for supercritical toluene process [20]. Regardless, SolvX products still had significant amount of oxygen, most likely derived from plastic itself [24]. Liquid fuels like gasoline, kerosene, diesel, etc. have low tolerance for oxygen. In the industry, oxygen content in the crude oil is often reduced using deoxygenation using hydrogen gas and heterogeneous catalysts. This well-known technique eliminates oxygen from crude oil while also improving its stability by transforming aldehydes and unsaturated compounds into more durable chemicals[28]. It is crucial to use the appropriate heterogeneous catalysts in this process to hydrodeoxygenate the oxygen-rich crudes. These catalysts should preferably be active, effectively remove oxygen from crude oil with a high yield, and not form coke. In general, NiMo and CoMo have been used as appropriate catalysts in most investigations [29]. Furthermore, noble metal catalysts such as Ru/C, Pt/C, and Pd/C have been evaluated and demonstrated to provide greater yields than conventional hydrodeoxygenation catalysts [30], [31]. Noble metal catalysts have emerged as a crucial part of contemporary synthetic chemistry, finding use in everything from bench-scale research to large-scale manufacturing [32]. The recovery of noble metal catalysts from used catalysts should be an ecologically benign, cost-effective, small-scale procedure. Less polluting methods have been developed in the last 20 years, including non-cyanide leaching, smelting in a furnace, mild leaching, and physical separation pre-treatment [33], [34], [35].

Although noble metal catalysts like Pd/C in hydrogen atmosphere have been reported to upgrade crude oil into a refined product, literature has yet to report catalytic SolvX of MWPs in presence of hydrogen. To fill this gap, in this work, a comprehensive investigation was performed into catalytic SolvX of #4-#7 mixed plastics using supercritical toluene as a non-oxygenated solvent with Pd/C catalyst in hydrogen atmosphere. Moreover, the effects of residence time, hydrogen loading, and catalyst loading on the conversion, composition, and quality of the SolvX product in supercritical conditions were studied. Finally, a SolvX reaction mechanism is proposed based on gas chromatography mass spectroscopy data of the SolvX crude oils. The novelty of current work in comparison to our recent work[24] is using Pd/C catalyst as well as hydrogen in solvothermal liquefaction of mixed plastic. The limitation of this work in industrial scale could be the high price of Pd/C catalyst as well as the safety risk of using hydrogen because it is an extremely flammable gas that, if not handled properly, can result in explosions.

Section snippets

Materials

Polypropylene (PP), low density polyethylene (LDPE), polystyrene (PS), and polyurethane (PU) were obtained from commercially available sources. To make the mixed plastic feedstock, all four types of plastic were manually mixed in a weight ratio of 1/4 each, which is mentioned in Table 1. The SolvX solvent (toluene) was bought from Fisher Scientific company. Furthermore, 5 wt%

Pd/C, type 490 was purchased from Alfa Aesar (Haverhill, MA). These types of plastic (LDPE: #4, Propylene: #5,...

SolvX Conversion and Elemental Analysis of SolvX crude oils

Table 2 shows the SolvX conversion of mixed plastics at various SolvX process conditions. The SolvX conversion is defined as the unrecovered percentage fraction of solid MWP through SolvX. Along with the solid and liquid SolvX products, the trials produced a minor quantity of gases and volatile compounds. It can be seen from Table 2, with an increase in reaction time, SolvX conversion rises; however, the increment of SolvX conversion is minimal after 3 h. This could be due to the promotion of...

Conclusions

Catalytic solvothermal conversion (SolvX) of mixed waste plastics were conducted using supercritical toluene at 350 °C in presence of Pd/C catalyst with hydrogen loading. The effects of different operating conditions on SolvX crude oils were studied. The main finding of this work are as follows:

- The result showed that the longer reaction periods tend to increase depolymerization of plastics....

- The addition of Pd/C catalyst and hydrogen resulted in a decrease in O/C and an increase in H/C and HHV....

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CRediT authorship contribution statement

Soudeh Banivaheb: Conceptualization, Data curation, Formal analysis, Writing – original draft, Writing – review & editing. **Vahab Ghalandari:** Formal Analysis, Writing – original draft, Writing – review & editing. **Hunter Smith:** Formal Analysis, Writing – original draft. **M. Toufiq Reza:** Funding acquisition, Conceptualization, Writing – review & editing, Project administration....

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper....

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[1] These authors contributed equally and share the first authorship.

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