Applied Energy 229 (2018) 314–325

Contents lists available at ScienceDirect

Applied Energy

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

Stepwise pyrolysis of mixed plastics and paper for separation of oxygenated and hydrocarbon condensates

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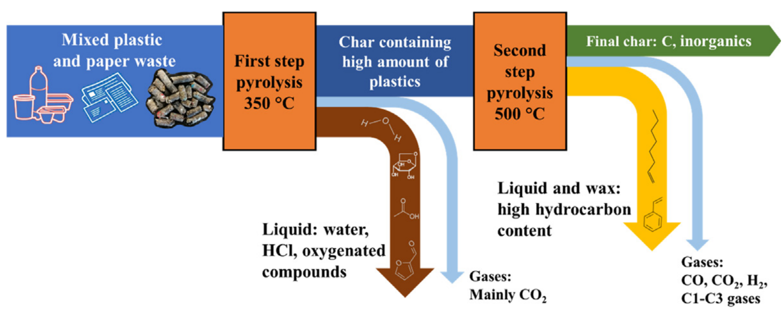
HIGHLIGHTS

- Stepwise pyrolysis at 350 and 500 °C can separate products into two fractions.
- First step liquid product was acidic and had high amounts of oxygenated compounds.
- Products from the second step had high hydrocarbon contents and low acidity.
- Interaction between cellulose and plastics during stepwise pyrolysis was observed.
- Test on real wastes and discussion of scaling-up possibilities were presented.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Cellulose
Plastics
Paper reject
Stepwise pyrolysis
Oxygenated products
Hydrocarbons

ABSTRACT

Mixed plastics and papers are two of the main fractions in municipal solid waste which is a critical environmental issue today. Recovering energy and chemicals from this waste stream by pyrolysis is one of the favorable options to achieve a circular economy. While pyrolysis products from plastics are mainly hydrocarbons, pyrolysis products from paper/biomass are highly oxygenated. The different nature of the two pyrolysis products results in different treatments and applications as well as economic values. Therefore, separation of these two products by multi-step pyrolysis based on their different decomposition temperatures could be beneficial for downstream processes to recover materials, chemicals and/or energy. In this work, stepwise pyrolysis of mixed plastics and paper waste was performed in a batch type fixed bed reactor using two different pyrolysis temperatures. Neat plastic materials (polystyrene, polyethylene) and cellulose mixtures were used as starting materials. Then, the same conditions were applied to a mixed plastics and paper residue stream derived from paper recycling process. The condensable products were analyzed by GC/MS. It was found that pyrolysis temperatures during the first and second step of 350 and 500 °C resulted in a better separation of the oxygenated and hydrocarbon condensates than when a lower pyrolysis temperature (300 °C) was used in the first step. The products from the first step were derived from cellulose with some heavy fraction of styrene oligomers, while the products from the second step were mainly hydrocarbons derived from polystyrene and polyethylene. This thus shows that stepwise pyrolysis can separate the products from these materials, although with some degree of overlapping products. Indications of interaction between PS and cellulose during stepwise pyrolysis were observed including an increase in char yield, a decrease in liquid yield from the first temperature step and changes in liquid composition, compared to stepwise pyrolysis of the two materials separately. A longer vapor residence time in the second step was found to help reducing the amount of wax derived from polyethylene. Results from stepwise

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https://doi.org/10.1016/j.apenergy.2018.08.006
Received 21 May 2018; Received in revised form 21 July 2018; Accepted 2 August 2018
0306-2619/

pyrolysis of a real waste showed that oxygenated and acidic products were concentrated in the liquid from the first step, while the product from the second step contained a high portion of hydrocarbons and had a low acid number.

1. Introduction

It is undeniable that municipal solid waste (MSW) has globally become an urgent threat to the environment. Although recycling is highly encouraged, it requires sorting and high purity of the materials to be recycled. Moreover, some plastics can only be recycled for a few cycles before their properties are compromised [1]. Therefore, a considerable amount of waste cannot be recycled, and other technical solutions should be proposed for the end-of-life materials. Currently, only less than 30% of plastics waste in the EU is recycled, while the rest is disposed of in landfill sites or is incinerated which is not sustainable [2]. Investigation in waste pyrolysis could give a clue to a more sustainable solution for the end-of-life materials.

Pyrolysis is a thermochemical conversion process in the absence of added oxygen or other oxidizers at a relatively low temperature as compared to incineration temperatures. This process can be used to recover materials and energy in the form of chemicals and fuels. While pyrolysis of waste has been a continuous effort for many decades, not many efforts have completely succeeded in recovering fuels and materials from waste feedstock by this method [3,4]. This is due to the complexity and heterogeneity of the feedstocks that causes the liquid products obtained to be mixed, acidic and highly oxygenated.

Mixed plastics and paper are the two main fractions of MSW as they are primary constituents of packaging. While cellulose is the main component of paper and cloths, there are many types of plastics. The most abundant plastics in MSW are polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), and polyvinyl chloride (PVC). While the first three plastics consist of only carbon and hydrogen, PET and PVC consist also of heteroatoms, i.e., oxygen and chlorine. While PET is usually recycled, most of the PVC remains as a part of MSW.

The different thermal decomposition behaviors and products of paper/cellulose compared to plastics are due to their chemical structures and bond-breaking mechanisms. Pyrolysis of paper/cellulose gives a biooil which contains highly acidic and unstable oxygenated compounds, e.g., anhydrosugars, furans, aldehydes, carboxylic acids. This currently limits its direct usage only to combustion in specific burners [5] or modified diesel engines [6]. Extensive research on biooil upgrading using different catalysts is ongoing but has not yet been fully accomplished. On the other hand, pyrolysis of mixed plastics produces mainly hydrocarbons with a quality comparable to commercial diesel oil [7]. Thus, it could be easily upgraded and fed into an existing oil-refinery plant to recover petrochemicals for new plastics/materials production. It could therefore be beneficial to separate the products which derive from each feedstock already in the pyrolysis process.

Stepwise pyrolysis is defined as a pyrolysis process with more than one temperature step, where the products from each temperature step are collected separately. The inspiration to investigate this process arises from many observations on the properties of the two main feedstocks which are as follows: (1) Cellulose thermally decomposes at around 300–400 °C, while plastics decompose at higher temperature (380–500 °C) [8–10]. Fig. 1 illustrates these thermal decomposition temperature ranges. (2) Oxygenated and hydrocarbon condensates generated from paper/cellulose and plastics pyrolysis have different values and applications. (3) Although some observations indicate synergistic effects between the pyrolysis products of plastics (PE, PP, PS) and biomass in the presence of catalysts [11–13] or with pre-treatment of the biomass [14], which could improve the overall quality of the liquids obtained, the interactions between the products of the two material types are limited when no catalyst or special treatment of the feedstock is applied [15,16]. Moreover, a recent study indicates that the catalytic activity of a HZSM-5 catalyst was lower when cellulose and

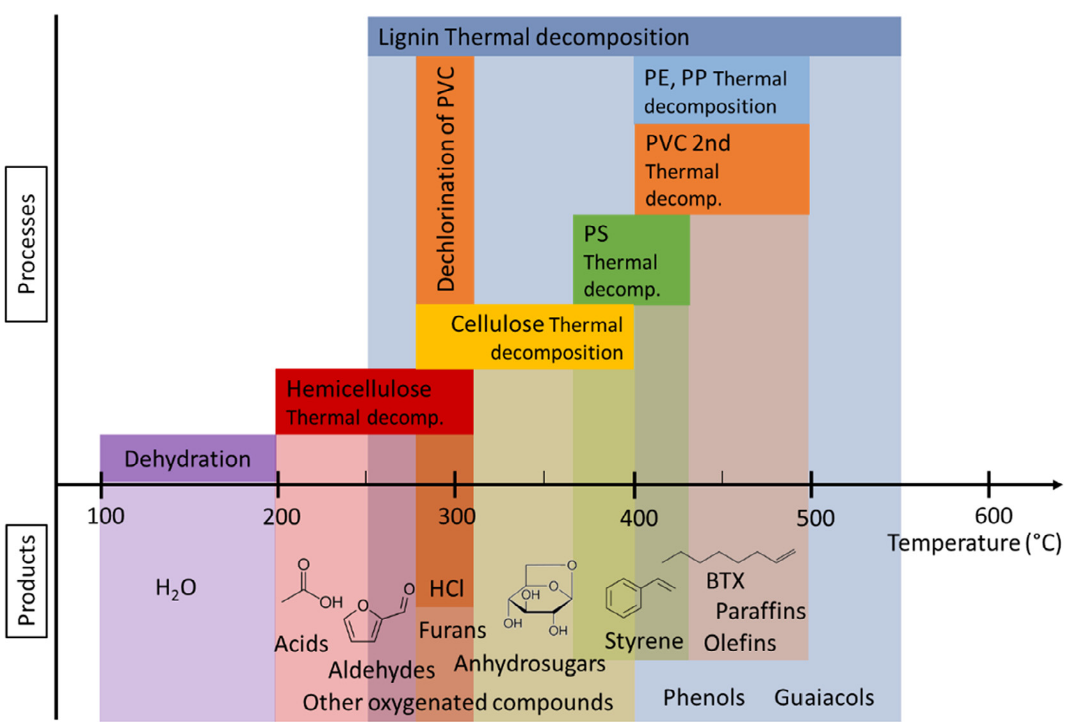

Fig. 1. Thermal decomposition of different materials as a function of temperature, and their products [8–10,46].