

Kinetics of synergistic effects in co-pyrolysis of biomass with plastic wastes

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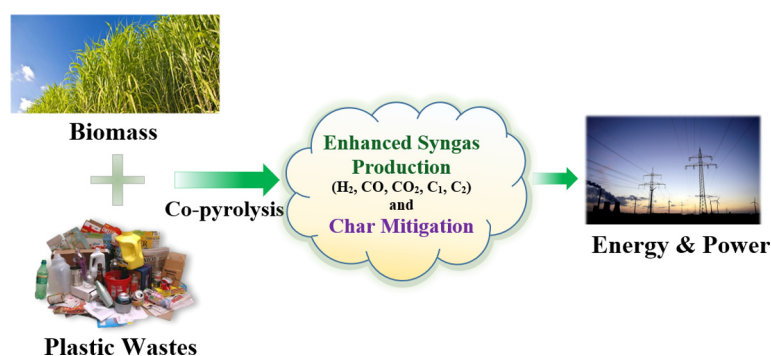
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HIGHLIGHTS

- Examined co-pyrolysis of polypropylene, polyester and polycarbonate with biomass.
- Co-pyrolysis synergistically lowered char yield in TGA.
- Distributed activation energy model was used to convert DTG to E_a based evaluation.
- Polyester and polypropylene synergy proposed to be via physical interaction.
- Polycarbonate proposed to chemically interact with biomass lowering E_a .

GRAPHICAL ABSTRACT



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ABSTRACT

Co-pyrolysis of pinewood and different kinds of plastic wastes in different mass fractions using polypropylene (PP), polyethylene terephthalate (PETE), and polycarbonate (BPC) were investigated. The results compared with the pyrolysis of individual components revealed non-additive synergistic effects from co-pyrolysis. Differential thermography (DTG) results showed enhanced decomposition peaks of biomass along with longer evolution of syngas and decreased peak of plastic polymers using BPC or PETE. Char residue was non-additively reduced by some 5% (dry wt. basis) using PP and BPC, and by 2–3% using PETE when pyrolyzed with biomass. This suggests increased carbon conversion efficiency and volatiles yield during co-pyrolysis compared to individual component pyrolysis. First order distributed activation energy modeling (DAEM) with 5 pseudo-components revealed that the synergistic effects of biomass with PP or PETE were mainly due to physical nature of the polymers as observed from increased activation energy bandwidth of biomass decomposition. BPC and pinewood mixtures showed an overlap in their activation energy distribution between 100 and 150 kJ/mol. This overlap caused the set of reaction with similar energetics to mutually interact chemically and enhance the composite mixture pyrolysis. Activation energy of BPC in the presence of pinewood was reduced by some 50 kJ/mol compared to individually examined polymer decomposition. The observed quantitative synergistic kinetics results in co-pyrolysis of biomass-plastic wastes mixtures as compared to individual component pyrolysis provide vital information towards the development of feed-flexible, clean pyrolysis and gasification system for efficient fuels production.

1. Introduction

Continuously increasing energy demands due to growing population

and enhanced lifestyles means sole dependence on fossil fuels alone are not sustainable as these resources are limited and also cause anthropogenic global warming [1]. Increase in solid wastes generation, a

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result of growing population and enhancing lifestyle, provide carbon negative or neutral hydrocarbon energy resources that can be converted to energy to help address issues on both energy needs and waste disposal. Of the total plastic resin produced in the USA, 85% (50 million tons) is from thermoplastic polymer production and 15% from thermoset polymer production [2]. Major thermoplastics includes polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS) and others such as polyethylene terephthalate (PETE), and nylons. The thermosets include polyurethanes, epoxy and other thermosets. Plastics are used mostly in packaging. Approximately, municipal solid wastes contribute to 33 million tons of plastic wastes generation and collection. Plastic in the municipal solid waste is only about 13%. 75% of that plastic waste generated end up in landfills. The rest is either recycled or combusted for energy recovery [3]. These plastic wastes are rapidly filling up landfills since they are not biodegradable. They possess heterogeneity, which lead to low degree of recycling value, low economic value, and pose challenges in their separation from the other waste stream. Estimating in terms of energy units, assuming waste plastic heating value to be that of PETE, 2.8 quads of energy equivalent is being dumped to landfills. This means significant portion of fossil fuel energy, such as, natural gas and naphtha, used for synthetic polymer production, are dumped to landfills as plastic wastes. This causes unsustainable imbalance in the production-disposal cycle considering continuously increasing plastic demands. This can be circumvented if these landfill-destined plastic wastes (no net economic value in recycling) can be converted to energy or fuels or to some intermediates such as syngas for their use in chemicals and petrochemicals. Due to the ease in generation and short carbon cycle, biomass and other lignocellulosic wastes (such as agricultural wastes, paper wastes and yard wastes) are sustainable and also carbon neutral/negative sources which along with plastic wastes can be converted to sustainable clean syngas energy [4].

Thermochemical conversion techniques such as pyrolysis and gasification can provide an ideal pathway for fuels production from the biomass and plastic wastes. They involve thermal decomposition of solid carbonaceous materials to form gases with medium to high heating value. Depending on the temperatures chosen, the gaseous products (also referred to as syngas) that evolve include H_2 , CO, CO_2 , CH_4 , C_2H_6 and trace amounts of other higher series of hydrocarbons. Kinetics of biomass decomposition was examined using thermogravimetric analysis (TGA) and pathways using micro-pyrolyzer. The decomposition products were analyzed using mass spectroscopy (TGA-MS), Fourier-transform infrared spectroscopy (FTIR), gas-chromatography (TGA-GC or TGA-GC/MS) [4–6]. Syngas or liquid yields obtained using fixed bed, and fluidized bed or lab scale semi batch reactors provided quantify the product syngas yield for different feedstocks and operational conditions [7–9].

In-situ FTIR studies of lignocellulosic wastes revealed that at initial temperatures between 473 and 673 K, the peaks of O–H, C–OH, C–H, and C=O increased, but as the temperature increased, C=O and C–H decreased to form CO and CO_2 , while C–C decreased to form CH_4 and C–H decomposed to form H_2 [3–8]. In the case of plastic wastes, the composition of product yield depends significantly on the monomeric structure of these plastics – straight chains yielded H_2 and hydrocarbons [10], while aromatic and C–O–C linked polymers yielded CO, CO_2 and char so that aromatics were involved in decarboxylation, dehydration along with rearrangement reactions. Molecular pathway modeled for decomposition of different types of plastics is given [11].

Interest in co-pyrolysis and co-gasification of different types of biomass and plastic wastes has increased due to common availability of these feedstocks in wastes. Co-pyrolysis of cellulose and polypropylene showed activation energy reduction and revealed lowered char yield from co-pyrolysis compared to individual pyrolysis. This was attributed to H-abstraction in polypropylene leading to radical formation from cellulose and OH from cellulose reacting with polypropylene oligomer radicals to form long chain alcohols along with biomass char catalyzed

propylene pyrolysis [12–14]. Synergistic effects resulting in non-additive increase in syngas and H_2 yields were also observed from co-gasification of pinewood with different types of plastics including polyethylene, polypropylene, PETE, polycarbonate [15–17]. Enhanced syngas and hydrogen yields from steam gasification and bio-oil yields from fast pyrolysis of biomass-plastic blends were demonstrated in fluidized bed and fixed bed reactors [18–26]. Investigations into the influence of synergistic effects of co-pyrolysis on the pathway, the kinetics of conversion and products evolution along with intermediates speciation are essential to further our knowledge on understanding the exclusive pyrolysis of biomass (lignocellulose) and plastic materials.

TGA conversion of lignocellulosic materials was modeled by different types of models, of which, distributed activation energy model (DAEM) stands out due to its ability to consider the effect of varying activation energy distribution, depending on the types of bonds present in the feedstock [4,27,28]. While DAEM is a parallel reactions model, other models which consider an aggregate of sequential and parallel degradation pathways such as Broido-Schafizadeh scheme, were also investigated in the literature [29]. A comparison of different reaction pathway models and fitting using genetic optimization algorithm, using cellulose was discussed in Ref. [29]. A derivation of DAEM (formulation given in Section 2) is used in this paper to represent the contribution of individual components in both naturally mixed materials of only lignocellulose materials and also artificial blends of biomass-plastic mixtures. This will help provide quantitative differences in gasification of individual components compared to biomass-plastic blends [30]. This has motivated us to use DAEM for all mixtures but with a higher number of pseudo-components.

This paper examines kinetics of co-pyrolysis of biomass and plastic wastes using different types of plastics. Pinewood was chosen here as the lignocellulosic biomass material. Recycled polymer pellets of black polycarbonate (BPC), polyethylene terephthalate (PETE), and polypropylene (PP) were chosen for the plastics since they vary in their monomeric O/C content, energy content, and the linking bonds. While BPC and PETE contain aromatic content, they vary in the polymer linkage but PP is significantly different from these two as it has no aromatic content and the polymeric linkage is between C–C bonds. Investigations were carried out using TGA to understand the influence of heating rates, composition of plastics in the mixture on the activation energy, reaction rates and contributions of individual components. The goal was to help assist in determining the importance of blending biomass with plastics in terms of the enhanced carbon conversion, volatiles yield, and increased reaction rate which are important for the development of energy efficient large scale, feedstock flexible pyrolysis and gasification reactors for continuous operation irrespective of the feedstock composition. These studies are aimed at fostering energy sustainability in the energy future from increased use of waste plastics and municipal solid wastes.

2. Methods and materials

2.1. Experimental method and materials

Exclusive and co-pyrolysis of pinewood with BPC, PETE and PP was examined using TGA (TA Instruments SDT Q600) with horizontal balance, which was equipped for simultaneous thermogravimetric analysis and differential scanning calorimetry (TGA-DSC). See Fig. S1, for schematic of the equipment. For all the investigations 10 mg of sample was used. The sample was dried at isothermal conditions of 383 K for 10 min in the TGA before ramping to higher temperatures. Chemically pure argon at 100 sccm flowrate was used as the purge gas for all the experiments. Experiments were conducted in an alumina pan, wherein a thin layer of the sample was laid for even reaction kinetics. In all the experiments, different blends of biomass and plastic mixtures were heated from 383 K to 1273 K at constant heating rates of 10 K min^{-1} . In order to understand the influence of ramp rate, pyrolysis of individual

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