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Origin of carbon in aromatic and olefin products derived from HZSM-5 catalyzed co-pyrolysis of cellulose and plastics via isotopic labeling

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ABSTRACT

Catalytic pyrolysis over HZSM-5 is an effective method for the conversion of biomass to aromatic hydrocarbons, albeit with low yield and short catalyst lifetimes. Addition of co-reactants rich in carbon and hydrogen can enhance yield and possibly increase catalyst lifetimes by reducing coke formation. Particularly, the catalytic co-pyrolysis of plastic and biomass has been shown to enhance conversion to aromatic hydrocarbons, and also offers a method for productive disposal of waste agricultural plastics. In an effort to determine the origin of the carbon (plastic or biomass) in the products from this catalytic co-pyrolysis, mixtures of uniformly labeled ^{13}C cellulose and non-labeled plastic including polyethylene terephthalate, polypropylene, high density polyethylene, low density polyethylene and polystyrene were subjected to catalytic fast pyrolysis (CFP) at 650 °C in the presence of HZSM-5. A micro pyrolyzer coupled with GC/MS (py-GC/MS) advised product distributions and mass spectral data was used to determine the distribution of biogenic carbon and plastic derived carbon in the products. The results demonstrate that aromatic hydrocarbon products formed from the CFP of mixtures of cellulose and plastic are composed mostly of molecules containing carbon of mixed origin. Data on the distribution of $^{13}C_x\,^{12}C_y$ from the products followed in this study show that polyolefin mixtures with cellulose favor the formation of alkyl benzenes that incorporate carbon from both sources. Utilization of aromatic polymers (polystyrene or polyethylene terephthalate) is more selective for formation of naphthalenes with carbon derived from both products. The distribution of various$^{13}C_x\,^{12}C_y$ products is used to suggest active mechanisms that result in the formation of the observed products.

1. Introduction

Pyrolysis, which is the thermal processing of material in the absence of oxygen can reduce waste by weight and volume and produce gases, solids and liquids which can be used as fuel or feedstock for chemical conversion [1]. The liquids produced from the pyrolysis of lignocellulosic biomass, called pyrolysis oil or bio-oil, are potential intermediates for production of drop-in renewable advanced hydrocarbon biofuels. However, incompatibility with hydrocarbons and instability resulting from a high concentration of reactive oxygenated components has limited the utility of pyrolysis oil to date. Much research has been done on catalytic fast pyrolysis (CFP), in an effort to produce deoxygenated pyrolysis liquids with more favorable properties. HZSM-5 which can produce aromatic hydrocarbons from biomass has been the most studied catalyst for this process [2–9] but is plagued by short catalysts lifetimes and low carbon efficiencies. These problems are associated with the low H/C ratio of biomass; dehydrogenation and dehydration reactions catalyzed by HZSM-5 further reduce the hydrogen content, leading to coke formation. It is possible that incorporation of carbon and hydrogen rich co-reactants into the CFP process with biomass could help mitigate these problems; such a material could be waste agricultural plastics.

Farmers rely on plastics to increase crop yields, reduce the use of herbicides and pesticides as well as to conserve water [10]. Approximately two million tons of agricultural plastics are used annually worldwide [11] and an estimated 521 million pounds of agricultural plastics are used in the U.S. per year alone [3]. Utilization of waste plastics in this manner could have the added benefit of alleviating a major waste disposal problem for farmers in a meaningful way. Current methods for disposing of agricultural plastic waste include on farm incineration, burial or disposal in landfills [12]. Unfortunately, efforts toward the recycling of agricultural plastic waste [13–15] encounter many barriers which lead to increased costs for processing recycled plastics [16]. While incineration can produce usable energy it also releases toxins [17–19]. However,

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pyrolysis produces fewer toxins due to the absence of oxygen and furthermore pyrolysis processes can handle mixed plastic waste with as much as 20% dirt or soil containments [20].

Pyrolysis of plastics has been conducted in the presence of catalysts to increase the production of desirable hydrocarbons for fuel [21–24] and catalytic co-pyrolysis of plastics and biomass or its constituents have been shown to increase aromatic product yields [25–28]. Plastic, catalyst and temperature were varied in experiments of the catalytic co-pyrolysis of pine sawdust and plastics [28]. The catalyst with the best performance was LOSA-1, which is made up of mostly ZSM-5, and doubled the petrochemical yields in these experiments [28]. Initial studies on the catalytic co-pyrolysis of low density polyethylene (LDPE) and cellulose in the presence of ZSM-5 gave increased aromatic carbon yields and reduced coke/char formation [25]. Cellulose was further investigated along with lignin and pine wood in combination with various plastics in catalytic co-pyrolysis and a synergy was found between cellulose and LDPE for petrochemical production and a reduction in coke formation [27]. An increase in aromatic products was found when comparing the co-fed CFP product yields to the additive yields of the CFP of the cellulose or biomass and plastics alone. In particular, combinations with polyethylene (PE) exhibited increases in alkylbenzenes [26]. It has been suggested that the formation of a hydrocarbon pool increases the conversion of oxygenates to aromatics [25,26]. The mechanisms thought to be involved in the catalytic conversion of cellulose through the formation of the hydrocarbon pool have been illustrated previously in the literature [29]. However, the results from these studies [25–28] do not indicate the amount of cellulose and plastic derived carbon that is contained in the products. An effective method for gaining insight on the mixing of reactants to form the products of pyrolysis involves the use of isotopically labeled reactants [30–32]. In this study the catalytic co-pyrolysis of ^{13}C labeled cellulose with several different plastics including polyethylene terephthalate (PET), polypropylene (PP), high density polyethylene (HDPE), LDPE and polystyrene (PS) were compared. Using mass spectral data from py-GC/MS experiments, the ratios of plastic and cellulose derived carbon that produced the condensable aromatic hydrocarbons such as benzene, toluene, ethylbenzene, *p*-xylene, *o*-xylene, naphthalene and 2-methylnaphthalene via CFP were determined. Also, the formation of non-condensable pyrolysis products including carbon monoxide, carbon dioxide, methane, ethylene, ethane, propylene, propane and butane were studied. Experiments were conducted using an identical non-labeled cellulose to serve as a calibration of the mass spectra data. The information was used to suggest active reaction mechanisms for each combination that lead to the yield and selectivity enhancements observed.

2. Experimental

2.1. Materials

Polyethylene terephthalate (PET), granular was purchased from Sigma-Aldrich and was milled using a Thomas Wiley ® Mini Mill with a delivery unit size of 0.85 mm, U.S. Std. no. 20. Polypropylene (PP), amorphous (avg. *Mw* ~14,000; avg. *Mn* ~ 3700 GPC vs. polyethylene stds.) was purchased from Sigma-Aldrich and was pliable at room temperature. A pellet was pressed flat using a spatula and then strips of PP were cut using scissors. The PP strips were then cut into smaller pieces (~1–2 mm) using scissors. High density polyethylene (HDPE) (melt index 2.2 g/10 min (190 °C/2.16 kg)), low density polyethylene (LDPE) (melt index 25 g/10 min (190 °C/2.16 kg)) and polystyrene (PS) (avg. *Mw* ~ 192,000) were purchased from Sigma-Aldrich and were milled using a Wiley Mill No. 1 (Arthur H. Thomas Co., Philadelphia, PA, U.S.A.) with a mesh size of 0.5 mm. Uniformly labeled ^{13}C cellulose high DP (97 atom% ^{13}C) from *Zea mays* (^{13}C cellulose) as well as the identical non-labeled cellulose high DP (1.2 atom% ^{13}C) from *Z. mays* (NL cellulose) were purchased from Iso*Life*. Zeolite NH_4ZSM5 powder (CBV 2314) was purchased from Zeolyst International and was converted to HZSM-5 by heating the powder to 650 °C overnight. The HZSM-5 was heated to over 100 °C for at least 2 h to remove water prior to using in experiments. The Si/Al ratio of the HZSM-5 was 23.

2.2. Pyrolysis

Pyrolysis experiments were conducted using a Frontier Lab Double-Shot micro pyrolyzer PY-2020iD equipped with the Frontier Lab Auto-Shot Sampler AS-1020E coupled to a gas chromatograph, Shimadzu GC-2010 [33–35]. Pyrolysis products were detected using a Shimadzu GCMS-QP2010S mass spectrometer (MS). For these experiments, the micro pyrolyzer was set to an interface temperature of 325 °C and a furnace temperature of 650 °C. Mixtures of ^{13}C cellulose or NL cellulose (0.250 mg) with plastic (1.3:1 cellulose (^{13}C):plastic (^{12}C)) and HZSM-5 (7.5 mg) were added to a stainless steel sample cup (Disposable eco-cup LF purchased from Frontier Laboratories). The sample is constructed by first placing the plastic in the sample cup followed by the biomass and then finally the catalyst on top. The sample is not initially mixed and is placed in the Auto-Shot Sampler. The sample is gravity fed into the inert atmosphere of the pre-heated pyrolysis furnace (650 °C), where the sample is subjected to pyrolysis conditions for 18 s. The helium carrier gas is also used to purge air in the sample prior to pyrolysis and to convey the pyrolysis gas through the pyrolysis reactor, a quartz tube, then to the GC–MS. GC analyses for the condensable gas products were performed on a RTX-1701 60 m × 0.25 mm, 0.25 m film thickness GC fused silica capillary column. The oven was programmed to hold at 45 °C for 4 min and ramped at 3 °C/min to 280 °C, after which it was held at this temperature for 20 min. The injector temperature was kept at 250 °C with the injector split ratio set to 90:1 and the helium flow rate was maintained at 1 mL/min. MS detection was carried out under electron impact (EI) ionization conditions in full scan from *m*/*z* 35–500 with a threshold at 20. GC analysis was performed using a fused silica capillary column, CP-PoraBOND Q, 25 m × 0.25 mm (Varian, Palo Alto, CA) with the following program: 3 min at 35 °C then ramped at 5 °C/min up to 150 °C followed by 10 °C/min up to 250 °C and held for 45 min for a total run time of 81 min. MS detection was carried out under electron impact (EI) ionization conditions in full scan from *m*/*z* 14–350 with a threshold at 1000.

2.3. Quantification

CFP experiments CFP of ^{13}C cellulose with plastics were performed in triplicate and the mass table data for a particular product was utilized to quantify the amount of ^{13}C from ^{13}C cellulose and ^{12}C from plastic in each of the products analyzed. For the determination of yields, experiments with an identical NL cellulose were performed in triplicate and the weight percent (wt%) yields were quantified with calibration curves produced using internal standards of the condensable gas products toluene, ethylbenzene, *p*-xylene, *o*-xylene, naphthalene and 2-methylnaphthalene. The gas yields were quantified with calibration curves produced using a standard gas mixture comprising CO, CO_2, CH_4, C_2H_4,C_2H_6, C_3H_6, C_3H_8, and C_4H_{10} in helium (custom-mixed by Scott Specialty Gases, Plumsteadville, PA). The carbon yields, determined from wt% yields, are presented as averages and were calculated as previously described [26]. Determinations of distribution of ^{13}C and ^{12}C carbon in each product were done using mass