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H-ZSM5 Catalyzed Co-Pyrolysis of Biomass and Plastics

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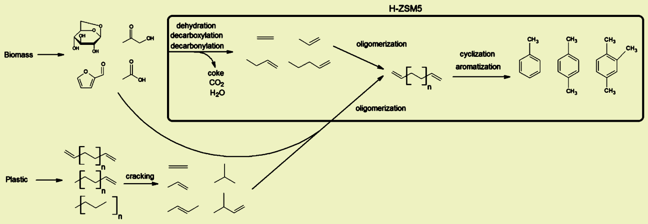

ABSTRACT: This study aims to address two important problems vital to agriculture: disposal of agricultural plastics and production of drop-in fuels from biomass via co-pyrolysis of both feedstocks. Mixtures of biomass (switchgrass, cellulose, xylan, and lignin) and plastic (polyethylene terephthalate (PET), polypropylene (PP), high density polyethylene (HDPE), low density polyethylene (LDPE), and polystyrene (PS)) were subjected to catalytic fast pyrolysis (CFP) at 650 °C in the presence of H-ZSM5. A micro-pyrolyzer coupled with GC/MS (py-GC/MS) was utilized to evaluate desired mixes and product distribution. Yields of the aromatic compounds typically observed as catalytic pyrolysis products including toluene, ethylbenzene, *p*-xylene, *o*-xylene, naphthalene, and 2-methylnaphthalene and their sum were tracked. The carbon yield of products from CFP of mixtures of biomass and plastic were compared with that of biomass alone, plastic alone, and the calculated arithmetic sum of yield values expected if there was no chemical interaction between the two feedstocks. The latter provides insights as to whether a synergetic effect occurred that enhanced the selectivity to aromatics of the blend or just the additive sum of the individual products. It was found that in several cases conversion enhancement occurred for the mixture, with the aliphatic polymers (PE and PP) and PET generally providing the biggest increase in total aromatic yields. Changes in selectivity for the production of individual aromatic compounds were also observed in the blends compared with the biomass or plastics alone.

KEYWORDS: *Catalytic fast pyrolysis, Agriculture, Olefin, Aromatic, Biomass*

■ INTRODUCTION

Fast pyrolysis, the rapid heating of organic material in the absence of oxygen, is one of the most efficient methods available for production of liquids from lignocellulosic biomass. These liquids called pyrolysis oil or bio-oil are potential intermediates for production of drop-in renewable hydrocarbon fuels. 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. The zeolite H-ZSM5, known to produce aromatic hydrocarbons from biomass, has been the most studied catalyst for this process;[1−8] however, it is plagued by short catalysts lifetimes and low carbon efficiencies. It is possible that incorporation of carbon- and hydrogen-rich co-reactants into the catalytic pyrolysis process using H-ZSM5 with biomass could help mitigate these problems. One source of C and H could be agricultural plastics. Utilization of plastics in this manner could have the added benefit of alleviating a major waste disposal problem for farmers.

Today, farmers rely on plastics to improve the conditions and production of their crops. Various agricultural uses include plastic mulch films, hay bale covers, silage "ag-bags", and containers for agricultural chemicals. The use of plastics in agriculture has many benefits including increased crop yields and less reliance on herbicides and pesticides, as well as improved conservation of water.[9] It has been reported that approximately two million tons of agricultural plastics are used annually worldwide,[10] and a comprehensive national study found that an estimated 521 million pounds of agricultural plastics are used per year in the United States alone.[11] The large amount of agricultural plastics being used inevitably leads to large amounts of agricultural plastic waste. Current methods for disposing of agricultural plastic waste include on-farm incineration, burial, or disposal in landfills.[11] Increased environmental and air quality concerns have led to initiatives that encourage recycling.[12−14] Unfortunately, recycling of agricultural plastic waste encounters many barriers including the separation and cleaning of plastics with various compositions prior to reprocessing, which leads to an increased cost for processing recycled plastics versus virgin resin.[15] Another method for dealing with agricultural plastic waste is its utilization as solid fuel in specially designed incineration apparatus or modified kilns and boilers for the production of steam, heat, or electricity.[16] Incineration or the burning of material in the presence of oxygen may produce energy, but it can lead to the release of toxic compounds such as SO_2, NO_x, dioxins, and furans into the atmosphere.[17,18] Pyrolysis can reduce waste by weight and volume and produce gases, solids, and liquids that can be used as fuel or feedstock for chemical conversion.[19] Another advantage of waste plastic pyrolysis is

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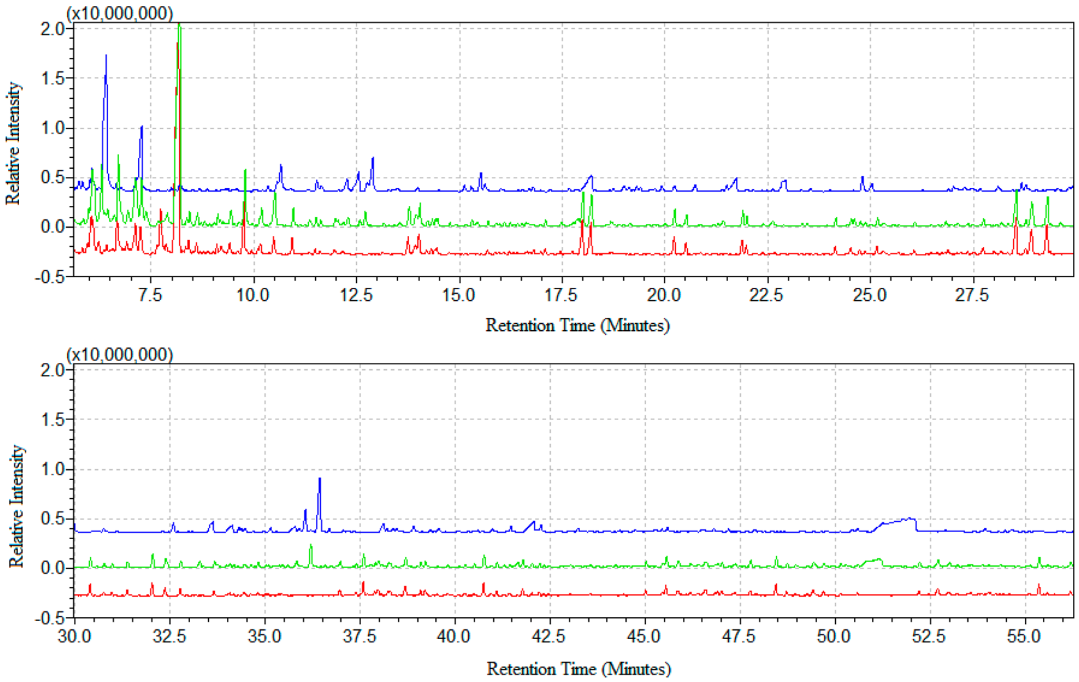


Figure 1. Chromatograms of the noncatalytic fast pyrolysis of switchgrass (blue), polypropylene (red), and their mixture (green).

that plastics with as much as 20% dirt/soil as well as various plastic mixtures can be processed by pyrolysis making sorting or washing the plastics prior to pyrolysis unnecessary.[20] Pyrolysis of plastics is not new[21−24] and has been conducted in the presence of catalysts to increase the production of desirable hydrocarbons for fuel. A common problem in biomass catalytic fast pyrolysis is coke formation that deactivates the catalyst.[25] However, experiments conducted on the CFP of cellulose and low density polyethylene (LDPE) mixtures found that there was reduced coke formation as well as an increase in the amount of desirable aromatic products when cellulose and LDPE were subjected to CFP versus the CFP of cellulose or LDPE alone.[25] This study aims to determine if a similar increase in aromatic products will be observed for the CFP of biomass (switchgrass, cellulose, xylan, and lignin) and various other plastics (polyethylene terephthalate, polypropylene, high density polyethylene, low density polyethylene, and polystyrene) by subjecting the individual reagents and their mixtures to CFP in the presence of a heterogeneous catalyst, H-ZSM5.

■ EXPERIMENTAL SECTION

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 #20. Polypropylene (PP), amorphous (avg. M_w ~14,000; avg. Mn~3,700 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 2.2g/10 min (190 °C/2.16 kg), low density polyethylene (LDPE) (melt index 25g/10 min (190 °C/2.16 kg), and polystyrene (PS) (avg. M_w ~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. Cellulose powder, ~20 μm, and xylan, from Beechwood (≥90%), were purchased from Sigma-Aldrich. Switchgrass was obtained from the McDonnell farm in East Greenville, Pennsylvania. Lignin was purchased from Granit Research and Development SA. Zeolite ammonium ZSM-5 powder (CBV 2314) was purchased from Zeolyst International and was converted to H-ZSM5 by heating the powder to 650 °C overnight. The H-ZSM5 was heated to over 100 °C for at least 2 h to remove water prior to using in experiments. Samples were placed in deactivated stainless steel cups (disposable eco-cup LF) purchased from Frontier Laboratories.

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. 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. For the catalytic fast pyrolysis (CFP) reactions of plastic or biomass with H-ZSM5, approximately 0.500 mg of plastic or biomass was placed in a stainless steel cup followed by the addition of approximately 7.500 mg of H-ZSM5. For experiments of the CFP of mixtures of plastic and biomass with H-ZSM5, approximately 0.250 mg of the plastic was placed in a stainless steel cup, followed by approximately 0.250 mg of biomass, and then followed by the addition of approximately 7.500 mg of H-ZSM5. The sample was constructed by first placing the plastic in the sample cup followed by the biomass and then finally the catalyst on top. A 15:1 catalyst to organic matter ratio was utilized in these experiments to ensure the complete conversion of the starting materials to the hydrocarbon products. The sample is not initially mixed but placed in the auto-shot sampler and is gravity fed into the inert atmosphere of the preheated pyrolysis furnace (650 °C), where it is subjected to pyrolysis conditions for 18 s. Helium carrier gas used for the GC is also used to purge air in the sample prior to pyrolysis and to convey the pyrolysis gas product through the pyrolysis reactor, a quartz tube, and then to the GC−MS. GC analyses were performed on a RTX-1701 60 m × 0.25 mm GC fused silica capillary column, 0.25 μm film thickness. The oven was programmed to hold at 45 °C for 4 min and was 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 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. For the CFP of plastics and biomass, the experiments were performed in triplicate, and the absolute yields were quantified with calibration curves produced using internal standards of toluene, ethylbenzene, *p*-xylene, *o*-xylene, naphthalene, and 2-methylnaphthalene. The absolute yields were

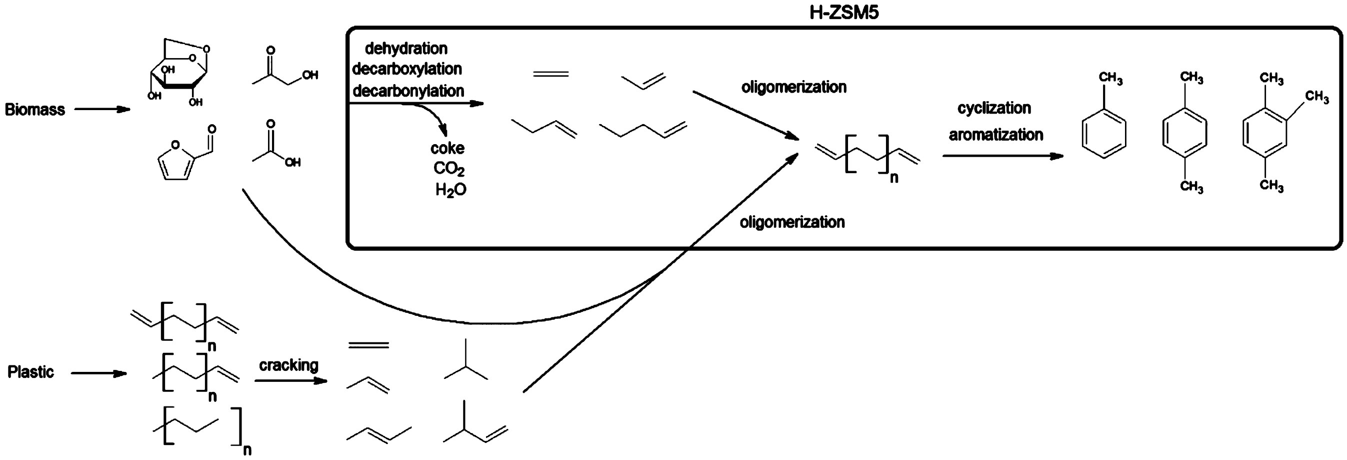


Figure 2. Suggested reaction pathways for the breakdown of biomass and plastic and the formation of aromatic compounds.

utilized to calculate the carbon yields (%) and are presented as averages of triplicate runs.

The carbon yield ($\mathrm{CY}_{\mathrm{Pr}}$) of a particular product was determined using the following relationships

$$\mathrm{CY}_{\mathrm{Pr}} = (\mathrm{CM}_{\mathrm{Pr}}/\mathrm{CM}_{\mathrm{M}}) \times 100 \tag{1}$$

where $\mathrm{CM}_{\mathrm{Pr}}$ is the carbon mass of the product (i.e., individual hydrocarbon compound) and CM_{M} is the carbon mass of the starting material mixtures. The carbon mass of the product ($\mathrm{CM}_{\mathrm{Pr}}$) was calculated by the following equation

$$\mathrm{CM}_{\mathrm{Pr}} = (M_{\mathrm{M}}) \times (Y_{\mathrm{Pr}}) \times (\%C_{\mathrm{Pr}}) \tag{2}$$

where M_{M} is the total mass of the mixture of biomass and plastic, Y_{Pr} is the mass yield of the product as given by the py-GC/MS, and $\%C_{\mathrm{Pr}}$ is the percent carbon in the product.

The carbon mass of the starting material mixture (CM_{M}) was determined as follows

$$\mathrm{CM}_{\mathrm{M}} = [(M_{\mathrm{Bio}}) \times (\%C_{\mathrm{Bio}})] + [(M_{\mathrm{Pl}}) \times (\%C_{\mathrm{Pl}})] \tag{3}$$

where M_{Bio} is the mass of biomass, $\%C_{\mathrm{Bio}}$ is the percent carbon of the biomass and the M_{Pl} and $\%C_{\mathrm{Pl}}$ are the mass and the percent carbon of the plastic.

The percent carbon of each product or starting material ($\%C_{\mathrm{Pr}}$, $\%C_{\mathrm{bio}}$, $\%C_{\mathrm{Pl}}$) was defined by elemental analysis, intrinsic for pure materials (hydrocarbon products, plastics, and cellulose) and experimentally measured for heterogeneous material (switchgrass, xylan, and lignin).

To determine the expected carbon yield value ($\mathrm{CY}_{\mathrm{EV}}$) for a particular product from the catalytic pyrolysis of the mixture of plastic and biomass the following equation is utilized

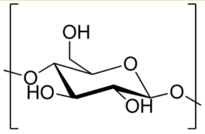
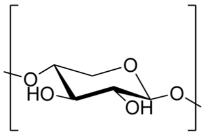
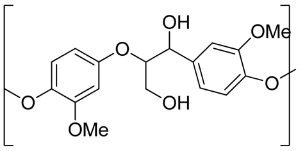
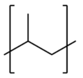
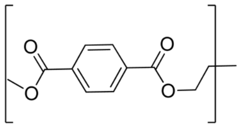
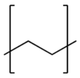
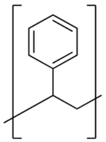
$$\begin{aligned}\mathrm{CY}_{\mathrm{EV}} = {} & [(\mathrm{CY}_{\mathrm{PrBio}}) \times ((\%C_{\mathrm{Bio}})/(\%C_{\mathrm{Bio}} + \%C_{\mathrm{Pl}}))] \\ & + [(\mathrm{CY}_{\mathrm{PrPl}}) \times ((\%C_{\mathrm{Pl}})/(\%C_{\mathrm{Bio}} + \%C_{\mathrm{Pl}}))]\end{aligned} \tag{4}$$

where $\mathrm{CY}_{\mathrm{PrBio}}$ represents the carbon yield from the product of the catalytic fast pyrolysis of biomass, and $\mathrm{CY}_{\mathrm{PrPl}}$ is the carbon yield of the same product of the catalytic fast pyrolysis of plastic.

■ RESULTS AND DISCUSSION

To begin the investigation of the effect of the presence of plastics on biomass fast pyrolysis, the noncatalytic pyrolysis of switchgrass, various plastics, and a 1:1 mixture of the two was first performed using the py-GC/MS. As expected, each of these components separately results in very different product compositions. Without the presence of H-ZSM5, switchgrass decomposes into a mixture of oxygenated hydrocarbons, a result of the breakdown of the cellulose, hemicellulose, and lignin of which it is composed, while PP decomposes into a mixture of saturated alkanes, a result of its long hydrocarbon chain structure. Comparison of chromatograms produced from the noncatalytic pyrolysis of switchgrass, plastic, and a mixture of switchgrass and plastic revealed that the product peaks found in the chromatograms are just arithmetic sums of the product peaks found in the pyrograms of the switchgrass or plastic alone. There was no observation of new product formation or a large change in the relative yields of any products resulting from either the biomass or the plastic. Figure 1 demonstrates a specific example of the chromatograms from the non-CFP of

Table 1. Empirical Formulas and Structures of Biomass Components and Plastics on a C_6 Basis

Compound	Empirical Formula	Structure
Cellulose	$C_6H_{10}O_5$	
Switchgrass	$C_6H_{10.31}O_{4.03}$	
Xylan[a]	$C_6H_{9.6}O_{4.8}$	
Lignin[a]	$C_6H_{6.55}$ $O_{1.97}$	
PP	C_6H_{12}	
PET	$C_6H_{4.8}O_{2.4}$	
PE	C_6H_{12}	
PS	C_6H_6	

[a]Xylan and lignin are irregular polymers; sample structure is given.

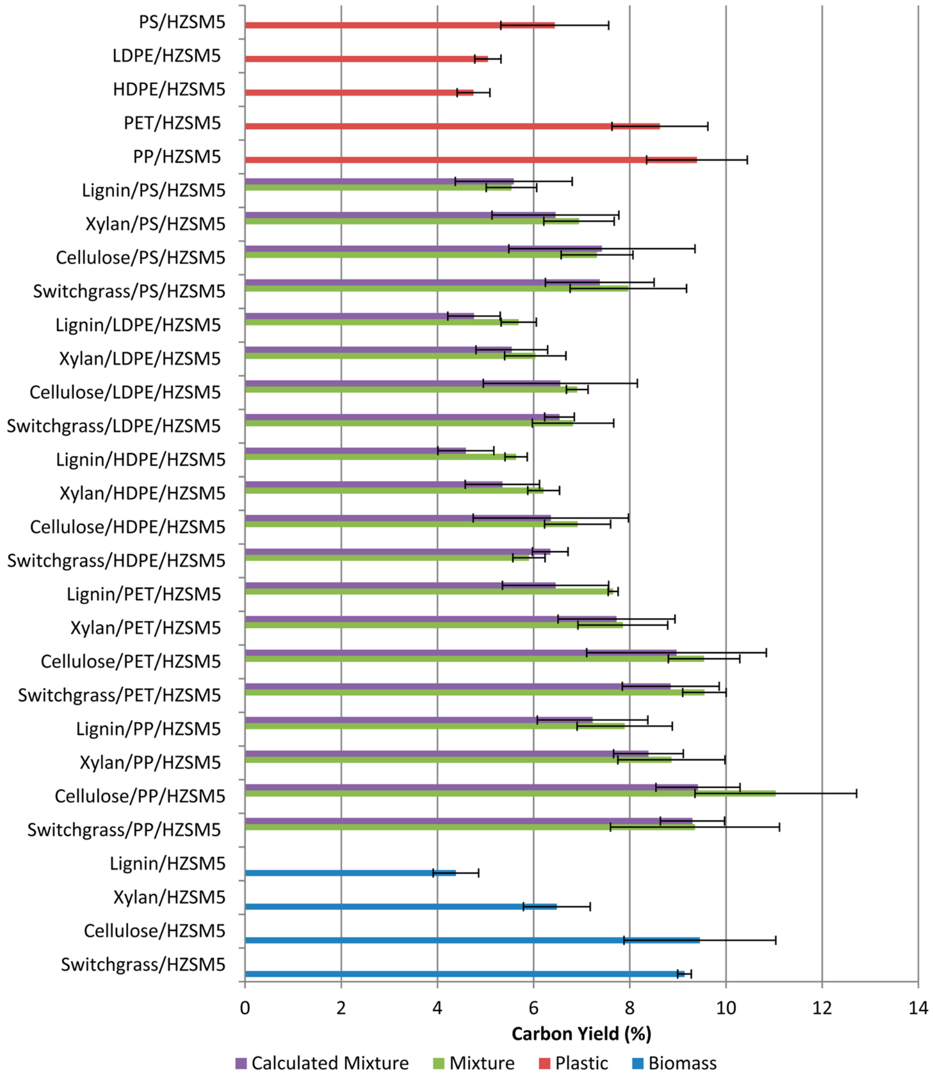


Figure 3. Carbon yield of the total of six aromatic compounds (toluene, ethyl benzene, *o*- and *p*-xylene, naphthalene, and 2-methylnaphthalene) from the catalytic fast pyrolysis (CFP) of biomass, plastic, their mixtures, and the calculated averages.

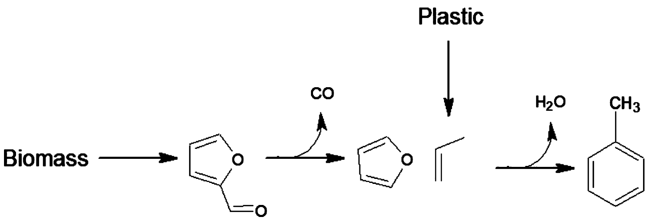


Figure 4. Reaction scheme of biomass pyrolysis product and plastic pyrolysis product participating in a Diels–Alder type reaction to form an aromatic product.[37]

switchgrass, PP, and a mixture of switchgrass and PP. The result suggests that the mixing of biomass and plastic would have a positive effect on the properties of the bio-oil product in terms of higher C/O and H/C ratios and energy contents when compared to the product of biomass alone, as has been reported by others.[26−29] However, this is only an effect of the presence of the hydrocarbon products from the plastic and not a result of any change in the chemical pathways of thermal decomposition or level of production of compounds directly from the biomass. Conversion of biomass derived oxygenates into deoxygenated products also does not occur as a result of the presence of the plastic coreactant alone.

Catalytic pyrolysis of biomass over H-ZSM5 has been extensively shown to convert the biomass derived oxygenates into aromatic hydrocarbons and is a method available to produce deoxygenated pyrolysis liquids. H-ZSM5, a shape-selective acid catalyst, acts to initiate conversion of the oxygenates through carbocation formation,[30] leading to olefins that aromatize in the presence of the catalyst. Because of the chemical diversity of the functional groups found in the biomass-derived vapors encountering the H-ZSM5 catalyst, many different mechanisms are initiated including decarboxylation, decarbonylation, dehydration, and dehydrogenation.[31] The latter two lead to loss of hydrogen from the biomass, and because biomass is already hydrogen deficient, the pathway leads to coke formation. This coke formation represents a loss of carbon that needs to be converted to liquids; therefore, catalytic pyrolysis, despite its potential for producing deoxygenated pyrolysis liquids, is still a low-efficiency process.[32] In the presence of H-ZSM5, pyrolysis of plastics has shown to be active in converting aliphatic hydrocarbons to aromatics through a similar mechanism of olefin formation followed by aromatization. However, coke formation has been shown to be

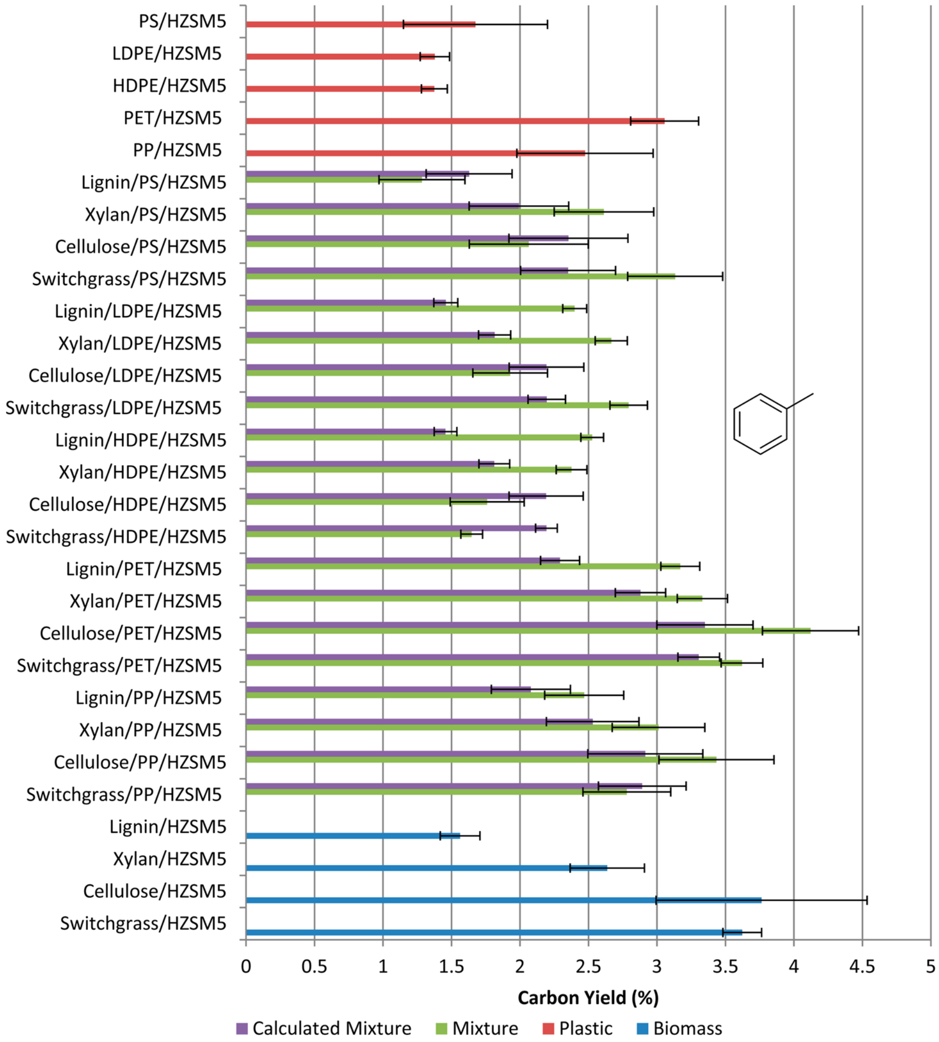


Figure 5. Carbon yield of toluene from the catalytic fast pyrolysis of biomass and plastic blends.

less of a problem in the latter case because unlike biomass there is more hydrogen available to support the formation of liquid range products. A general scheme illustrating the conversion of biomass or plastic to aromatic products in the presence of H-ZSM5, as described previously, is presented in Figure 2. For the purpose of the analysis, we present in Table 1 the chemical formulas of the biomass, plastics, and their components for the feedstock materials that we employ in this study on a C_6 basis. As illustrated in Figure 2, much of the hydrogen contained in the biomass and its components is bound to oxygen in hydroxyl groups but not to the carbon and is therefore effectively unavailable for hydrocarbon formation because it is easily removed as water, meaning the empirical formulas underestimate the relevant H/C ratios. The H/C ratio is simply the ratio of hydrogen to carbon in a structure; it does not give any information on connectivity especially if other atoms, such as oxygen, are present. For the plastics, however, the hydrogen content in its entirety is bound to carbon. Because of the intersecting mechanisms to aromatics formation, one can readily hypothesize that the presence of hydrogen-rich plastics could potentially lead to greater aromatic conversion efficiency from the biomass due to the increase in the formation of hydrocarbons from the interaction of olefins made available from the breakdown of plastic and oxygenated compounds from the breakdown of biomass. By this pathway, coke, CO_2, and H_2O formation would then decrease leading to increased aromatic product yields.

The total yields of the six aromatic hydrocarbons quantified, i.e., toluene, ethylbenzene, *p*-xylene, *o*-xylene, naphthalene, and 2-methylnapthalene, are presented in Figure 3. Toluene, ethylbenzene, and xylenes are major precusors in the production of various materials utilized in the pharmaceutical, food, automobile, polymer, and textile industries and are important components in gasoline.[33] Naphthalene is utilized in the production of insecticides, resins, dyes, and tanning agents, as well as other chemicals.[34] In most cases, biomass-plastic blend yields of these aromatics were increased compared with the pyrolysis of only the biomass constituents in the presence of H-ZSM5. Furthermore, in several cases, the yield was greater than the expected combined yield where no chemical interaction between the intermediates occurred between the two materials (estimated as the average of the yield of the biomass component and the plastic). The biomass−plastic mixtures that were most effective for producing aromatics in greater quantities than the expected yield of the simple combination consisted of those with polyethylene (PE), PP, or PET in their mixture. Generally, there were no observable differences in trends between HDPE and LDPE biomass blends in H-ZSM5, suggesting that the degree of branching in PE did not have a large effect on its catalytic pyrolysis behavior. Blends

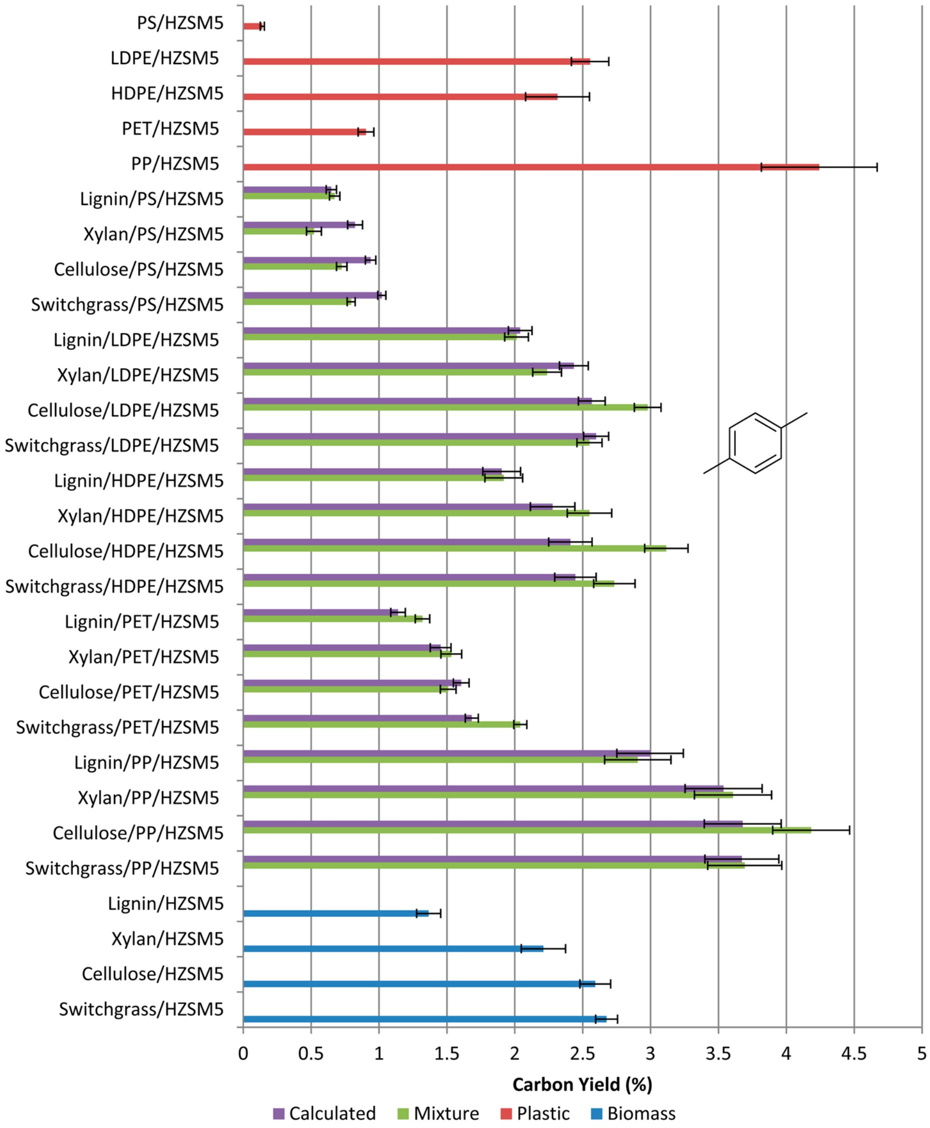


Figure 6. Carbon yield of *p*-xylene from the catalytic fast pyrolysis of biomass and plastic blends.

including PS, a highly aromatic polymer, showed minimal enhancement of the aromatics yield. This observation is consistent with our hypothesized mechanism because the breakdown of the aromatic structure does not increase the olefin pool required to produce additional aromatics from the biomass portion of the blend. Focusing on the biomass, it is evident that of the blends studied, the combination of cellulose−PP, lignin−PE, and lignin−PET produced the largest increase over the calculated combined yield of aromatic hydrocarbons. In general, lignin was the biomass component whose conversion to aromatic hydrocarbons via CFP was most benefitted by the presence of the plastics. Despite containing aromatic rings as part of the structure, lignin is known to be less productive than cellulose for production of aromatic hydrocarbons via CFP over H-ZSM5.[35] This is because its primary pyrolysis products, mainly phenolics, have low reactivity and high tendency for absorption onto H-ZSM5.[36] The results of the catalytic fast pyrolysis of lignin alone in this study were consistent with these previous observations, with lignin producing less total aromatics than the CFP of cellulose or switchgrass alone. Interestingly, when PE is subjected to pyrolysis in the presence of the heterogeneous catalyst H-ZSM5, fewer aromatics are produced compared to the other plastics. Yet, the CFP of the mixtures of lignin−HDPE and lignin−LDPE produced some of the greatest increases in aromatics compared to the average of their individual components.

Cellulose and xylan conversion to aromatic hydrocarbons in the presence of H-ZSM5 was also increased by the presence of polyethylene and polypropylene. The breakdown of cellulose and xylan are more capable of contributing olefins to the pool than lignin, but the highly oxygenated structure and low hydrogen availability force this mechanism to be carbon inefficient and therefore leads to coke production. As observed, the inclusion of hydrogen-rich PP and PE increases yields of aromatics in carbohydrate (cellulose and xylan) blends and is consistent with the hypothesized mechanism. In a previous study, Li et al.[25] observed an increase in the aromatic yield when cellulose and LDPE were subjected to CFP in the presence of H-ZSM5. They attributed this to the hydrocarbon pool mechanism, where the oxygenated compounds react with the hydrocarbon pool to ultimately form aromatic compounds.[26] This mechanism has been illustrated previously in the literature.[31] In recent literature, Diels−Alder reactions have

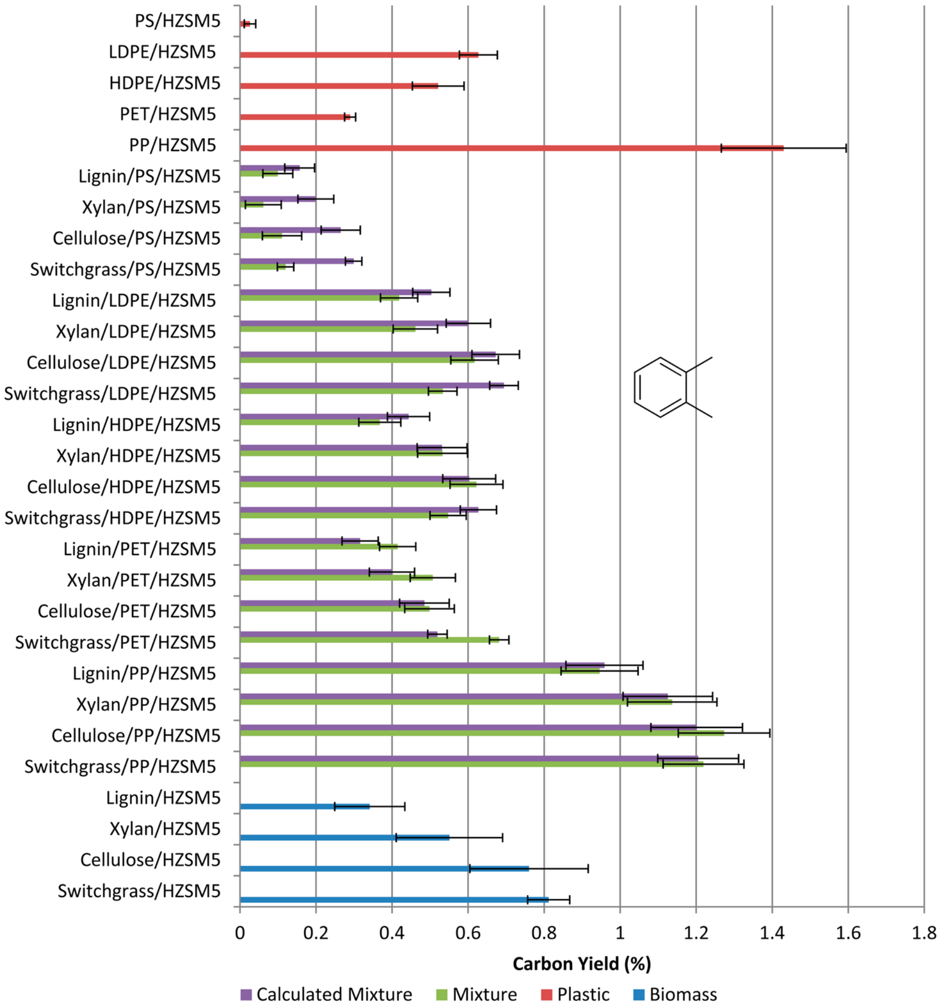


Figure 7. Carbon yield of *o*-xylene from the catalytic fast pyrolysis of biomass and plastic blends.

been suggested as the mechanism that leads to an increase in the selectivity of aromatics produced under CFP[37] (Figure 4). The reaction of furans, produced from the pyrolysis of biomass,[37] with olefins, such as those produced from the thermal degradation of polyethylene,[38] react in a Diels–Alder type reaction to produce the corresponding aromatic compounds with increased selectivity.[37] This pathway provides insights into the results obtained in this study. This explains, as described below, how the CFP of mixtures that enhance the yield of toluene, ethylbenzene, and the total aromatic product yields all contained PE.

Although the total aromatics produced from mixtures of biomass and plastic generally increased compared with the predicted yields for catalytic fast pyrolysis in the presence of H-ZSM5 (Figure 3), the increases were not evenly distributed across the individual compounds produced. Individual product contribution to the increase vary as some compounds had an overall increase in yield where as others produced the same amount as the expected value or less (Figure 5–10). It would be expected that the presence of the various plastics would alter the selectivity to individual compounds. The aromatic hydrocarbons with the greatest carbon yields from the CFP of these blends are toluene and *p*-xylene. Among the plastics, the toluene yield from pyrolysis in the presence of H-ZSM5 was greatest for PP and PET. Lignin, whose conversion to aromatics was most improved to total aromatics by the presence of plastic, showed a similar increase with respect to toluene yield when it was co-pyrolyzed with HDPE and LDPE. The aliphatic polymers (PP and PE) actually showed little change or a slight decrease in yield of xylenes from lignin (Figures 6 and 7), suggesting that the intermediate olefin pool resulting from this blend consists of a higher concentration of intermediates whose combination produces C_7 toluene and fewer intermediates for the production of the C_8 xylene.

When the biomass is cellulose, PE blends actually yield less toluene than would be predicted for the non-interacting blend. However, these blends show increases over the predicted values of the blends for *p*-xylene and ethylbenzene. This indicates that the change in selectivity in the conversion to aromatics for cellulose in the presence of the PE is the opposite of what is observed for lignin. The cellulose–PET blend does result in a significant increase in toluene yield. While the CFP of cellulose or switchgrass individually produced the greatest amount of toluene among the biomass constituents, mixtures containing lignin or xylan produced enough toluene to surpass the expected value by the largest margin, particularly in CFP combinations with PE. All of the biomass mixtures containing PET gave a significant increase in the production of toluene compared to the corresponding calculated average.

On the observation of the yields of ethylbenzene produced by the mixtures (Figure 8), it is evident that all of the mixtures containing PS and PE produce more ethylbenzene than the

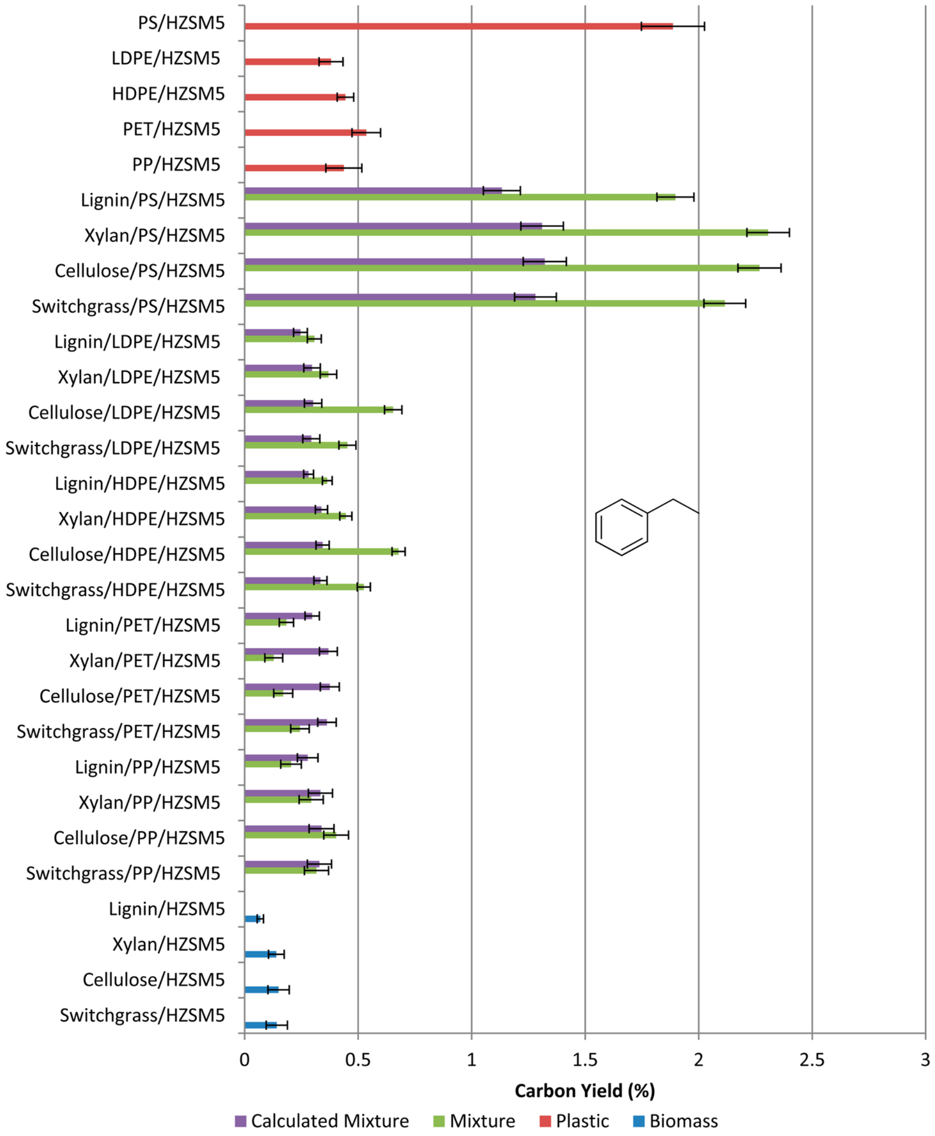


Figure 8. Carbon yield of ethylbenzene from the catalytic fast pyrolysis of biomass and plastic blends.

expected values, whereas the mixtures of PET and biomass produce significantly less ethylbenzene than expected. Conversely, the yield of 2-methylnaphthalene is significantly reduced for combinations of PS and biomass. Mixtures of switchgrass, xylan, and lignin containing PP did not increase the production of ethylbezene but did produce significantly greater amounts than produced by the mixtures with PET. For no other aromatic product is such a decrease in yield observed for mixtures of biomass and PET, which gives an indication that the presence of PET shifts the mechanism away from ethylbenzene production in particular. While PET is aromatic in nature, it is also highly oxygenated, and the pathway to the formation of ethylbenzene may not be able to overcome these structural barriers. On the contrary, in the case of *o*-xylene, mixtures of lignin, xylan, and switchgrass with PET are able to produce *o*-xylene in an amount greater than the expected value. While most mixtures containing PE and PP produce more *o*-xylene overall, they do not increase the yield of *o*-xylene further than the expected amount due to simple blending.

Two ring aromatics, naphthalenes, were also produced from the fast pyrolysis of the biomass and plastics over H-ZSM5. The CFP of PS and PET alone produce the greatest amount of naphthalene, followed by the CFP of PP. The CFP of PE produces the least amount of naphthalene (Figure 9). The trend regarding the yield of naphthalene among the plastics is present among the mixtures, with mixtures containing PS and PET producing the most naphthalene, followed by mixtures containing PP. Among the biomass constituents, the CFP of lignin, cellulose, and switchgrass produce similar yields with the CFP of xylan producing the least amount of naphthalene. This trend can be seen within each group of plastic and biomass mixtures, where the least amount of naphthalene will be produced by the plastic−xylan mixture within a group of a single plastic and its biomass blends, and similar amounts of naphthalene are produced by the plastic mixtures with lignin, cellulose, and switchgrass within the same group. This illustrates the effectiveness of the plastic−biomass interaction on the yield of naphthalene for the CFP of these mixtures. Mixtures containing PE produce less naphthalene than the expected value, suggesting that the presence of PE suppresses the formation of naphthalene from biomass. Conversely, mixtures that contain PP and PET generally enhanced the production of naphthalene. Similar trends were observed for 2-methylnaphthalene (Figure 10).

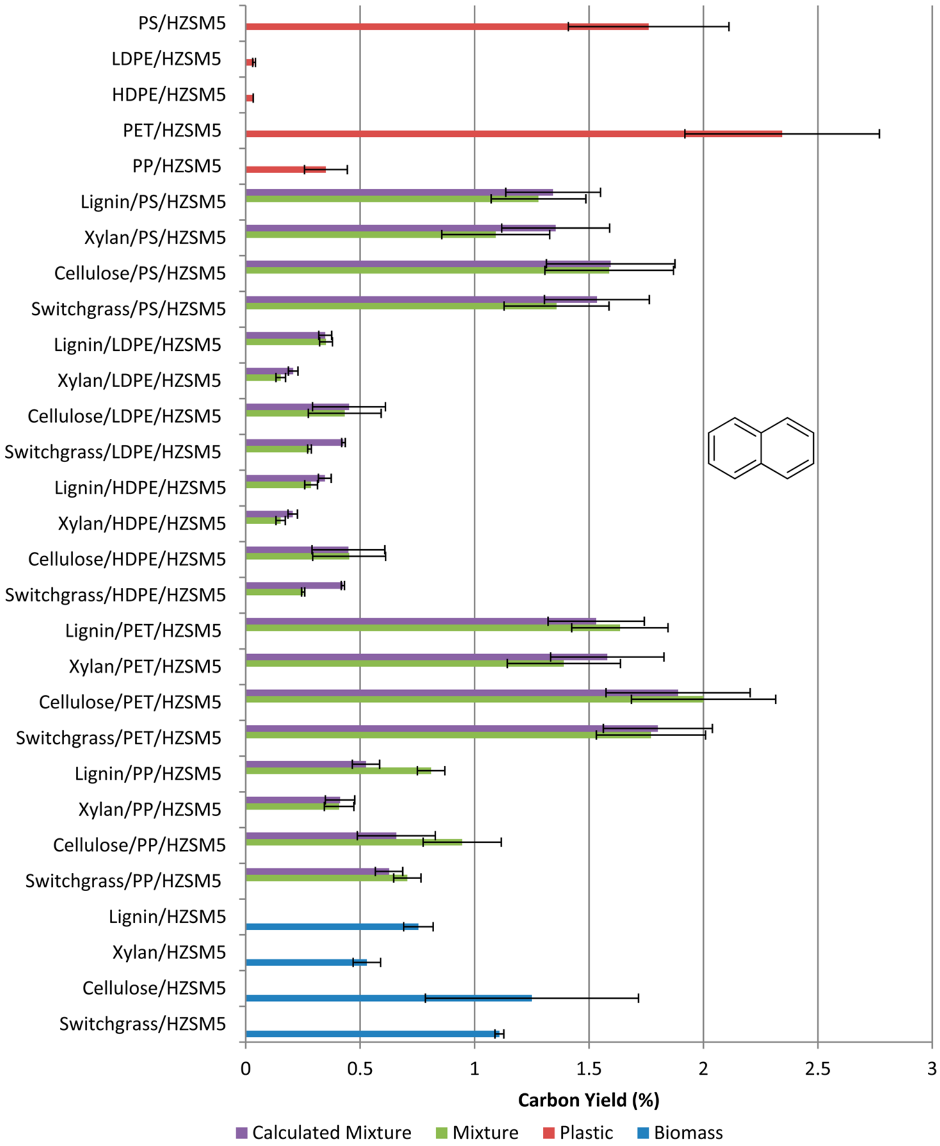


Figure 9. Carbon yield of naphthalene from the catalytic fast pyrolysis of biomass and plastic blends.

It is important to note that the carbon yield of total aromatics was between 4% and 10% for the catalytic fast pyrolysis of biomass, plastic, or their mixtures and is low compared to similar studies.[2,25] This can be attributed to the large amount of catalyst used in this study and the short reaction time (18s) used. While the excess amount of catalyst is effective method for the complete conversion of the biomass and plastic to the aromatic hydrocarbons, the short reaction time used may not allow full desorption of these products from the catalyst. This leads to reduced amounts making it to the GC column and therefore lower measured yields. Additionally, water, which is a byproduct from the catalytic pyrolysis of biomass (Figure 2) and the proposed Diels−Alder mechanism (Figure 4), can lead to the conversion of furans to diketones that can dimerize and oligomerize[39] reducing the yield of the aromatic products. Future studies will focus on coke formation and deactivation of the catalyst under the same experimental conditions.

■ CONCLUSION

The py-GC/MS data suggest that generally there is an increase in the production of total aromatic compounds when mixtures of biomass and plastic are subjected to catalytic fast pyrolysis (CFP) in the presence of H-ZSM5 compared to that of the biomass or plastic alone under the same conditions. Among the plastics studied PE, PP, and PET had more instances where they were produced in greater amounts compared to the expected values. While many of the blends produced more aromatic hydrocarbons than the calculated average from the CFP of the biomass or plastic alone, some did not, indicating that the effect is more complex than a simple arithmetic sum of the individual stand-alone products. In the case where yield enhancement occurred, the reason for some of the enhanced aromatic product formation, particularly toluene, xylenes, and ethylbenzene, can be explained by the Diels−Alder type of reaction mechanism where oxygenated products, such as furans derived from biomass, react with olefins derived from plastics increasing the production of aromatics. While it is clear from the py-GC/MS experiments that certain combinations of plastic−biomass blends favor the production of particular aromatic products in the presence of H-ZSM5, analysis of liquid samples from such blends produced in a larger scale pyrolysis reactor will be needed to provide more insights into

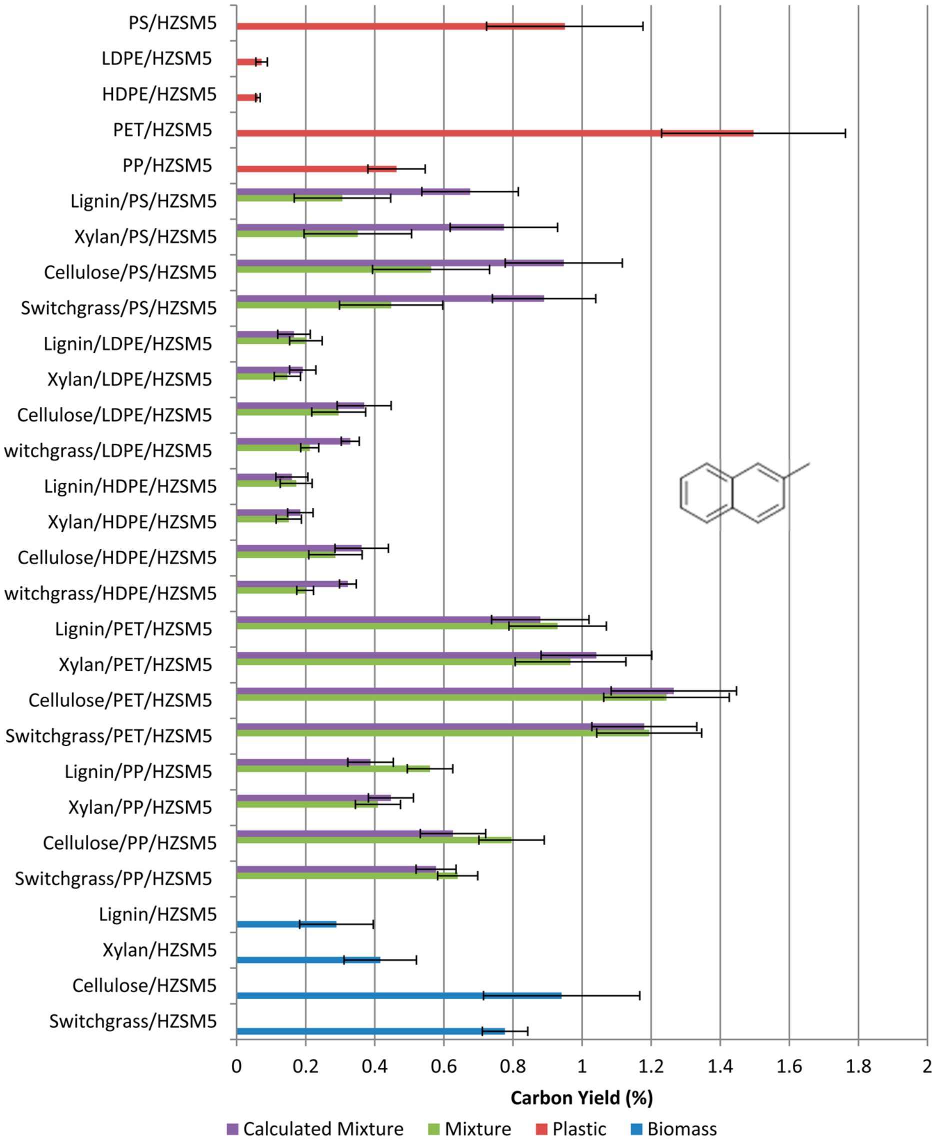


Figure 10. Carbon yield of 2-methylnaphthalene from the catalytic fast pyrolysis of biomass and plastic blends.

these complex relationships. It is expected that the analysis provided herein will adequately advise such future experiments.

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Notes

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