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Low Molecular Weight Biobased Aromatics from Pyrolysis Liquids Using Zeolites: Yield Improvements by Using Pyrolysis Oil Fractions

Dian S. Santosa, Leon Rohrbach, Hans Heeres, Robbie H. Venderbosch, Andre Heeres, and Hero J. Heeres*
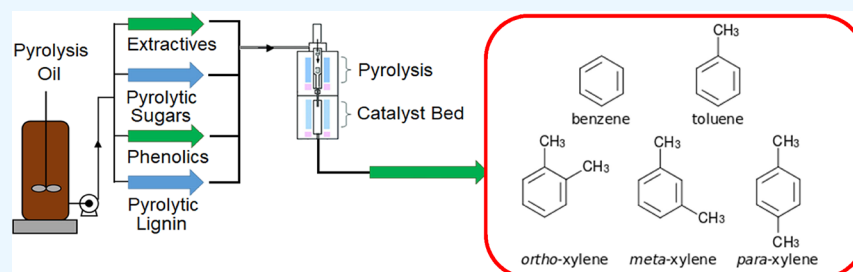
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ABSTRACT: Pyrolysis liquids from lignocellulosic biomass have the potential to be used as a feed for aromatics such as benzene, toluene, and xylenes (BTX) using catalytic upgrading with zeolites. We here report an experimental study on the conversion of various pyrolysis oil fractions to determine the most suitable one for BTX synthesis. For this purpose, the pyrolysis liquid was fractionated using several extraction/distillation steps to give four fractions with different chemical compositions. The fractions were analyzed in detail using nuclear magnetic resonance spectroscopy, elemental analysis, gas chromatography−mass spectroscopy, thermogravimetric analysis, Karl−Fischer titration, and gel permeation chromatography. Catalytic pyrolysis experiments were carried out using a tandem microreactor with H-ZSM-5 (23) as the catalyst. The highest BTX yield of 24% (on a carbon and dry basis) was obtained using the fractions enriched in phenolics, whereas all others gave far lower yields (4.4−9%, on a carbon and dry basis). Correlations were established between the chemical composition of the feed fraction and the BTX yield. These findings support the concept of a pyrolysis biorefinery, where the pyrolysis liquid is separated into well-defined fractions before further dedicated catalytic conversions to biobased chemicals and biofuels using tailored catalysts.

1. INTRODUCTION

Fast pyrolysis of lignocellulosic biomass is an efficient thermochemical process to liquefy this type of biomass in yields up to 70 wt %.[1] The process has been implemented at a commercial scale by among others BTG bioliquids.[2,3] Pyrolysis oil is not a typical crude fossil oil and for instance, has a high oxygen and water content, and is known to be thermally labile, leading to phase separation and coke formation upon heating.[4] However, it has the potential to serve as a feed for a pyrolysis oil biorefinery, in analogy with crude oil in an oil refinery, providing biofuels and biobased chemicals (Figure 1).

Due to its thermal instability, the initial separation step by distillation for crude oil is not feasible. An attractive alternative is a phase separation to obtain an aqueous fraction and a pyrolytic lignin fraction,[5,6] which can either be further separated in dedicated fractions or used as such for chemical conversions to biofuels or biobased chemicals.

The objective of the current study was to explore the potential of pyrolysis oil fractions obtained by a dedicated fractionation scheme to produce biobased aromatics. Aromatic compounds such as benzene, toluene, and xylenes, colloquially referred to as BTX, are important base chemicals and are produced in a million tons per year globally. Typically, these are intermediates for, among others, the production of monomers for plastic production (e.g., polyesters, polyamides, polyurethanes). There is a strong incentive to green up BTX production, among others, to produce plastics from renewable resources.

A vast body of literature is available on the conversion of pyrolysis liquids obtained from lignocellulosic biomass to hydrocarbons. Typically, acidic zeolites like H-ZSM-5, MCM-42 and H−Y, and metal-promoted ones are used as the catalysts.[7−10] This is undoubtedly due to the presence of both weak and strong acid sites required for hydrolysis and aromatization reactions in combination with their specific internal pore structure allowing for shape selectivity.[7−11]
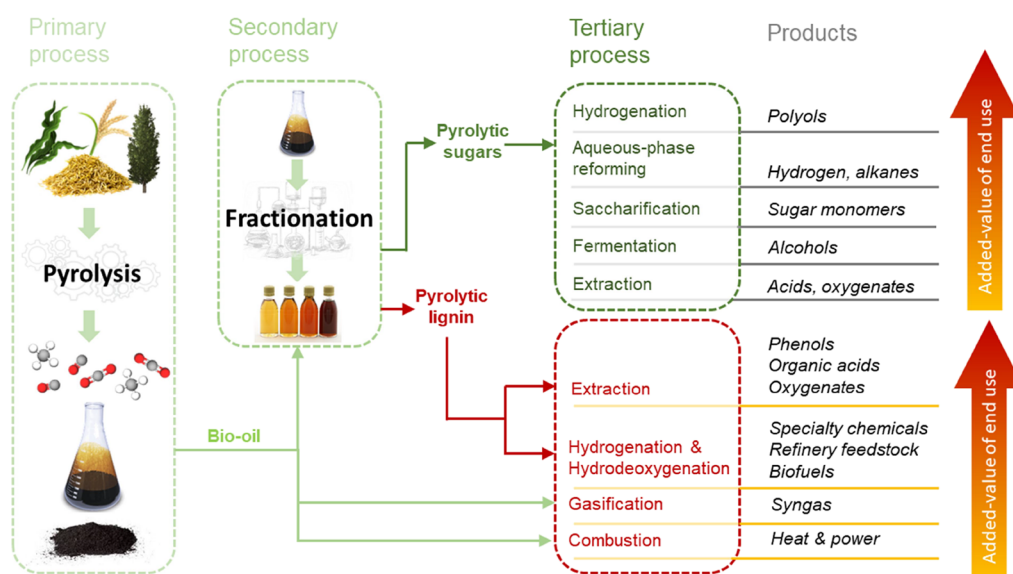
Figure 1. Pyrolysis oil biorefinery. Reprinted with permission from Figueirêdo, M. B.; Hita, I.; Deuss, P. J.; Venderbosch, R. H.; Heeres, H. J. Pyrolytic Lignin: A Promising Biorefinery Feedstock for the Production of Fuels and Valuable Chemicals. Green Chemistry 2022, 24 (12), 4680−4702. Copyright 2022, Royal Society of Chemistry.

Besides various hydrocarbons such as lower olefins, alkanes, and mono- and polyaromatics, significant amounts of char, gaseous compounds, and water are formed, limiting the hydrocarbon yields. In addition, catalyst deactivation and operational issues due to the deposition of coke have been observed. Typically, the incentive is to upgrade/deoxygenate the pyrolysis oil to a hydrocarbon biofuel or a stabilized intermediate for further processing (e.g., fluid catalytic cracking, FCC) and less attention is given specifically for BTX production, which is the prime objective of this study. When considering the available literature on the catalytic conversion of biomass-derived pyrolysis oils, the highest aromatics yield obtained so far is about 25 wt %[12] using maple wood pyrolysis oil and H-ZSM-5 (56) as the catalyst.

The experimental studies were typically performed in small-scale lab equipment (batch or continuous).[8−10,13−16] A proper quantitative comparison of the literature data when considering BTX yield is difficult as (i) the type and scale of the experimental setups vary considerably,[12,13,17] (ii) the basis for BTX yield calculations is not consistent (mol or wt % basis, wet or dry basis, organics, or organics in water, GC yields on area%),[8,10,17] and (iii) the use of the term aromatics.[9,13,17] In some cases, it is total aromatics (mono- and multiple rings), only BTX, or even in some cases including phenols. However, it is evident that the type of catalyst, process conditions, and the pyrolysis oil feed have a significant effect on the BTX yields.[8−10,13−16,18]

Exploratory catalyst studies have focused on acidic zeolites and modifications thereof. For instance, Bilbao and coworkers studied the performance of 3 zeolites (HY, H-ZSM-5, and H-Beta) for the catalytic pyrolysis of pine sawdust-derived pyrolysis liquid in a simulated riser reactor at a small lab scale (injection of 0.11 g pyrolysis liquid).[13] The highest aromatics yield (C6−C11 fraction) was 5.5 wt % using the H−Y zeolite. Valle et al. reported higher aromatics yields (up to 16%) for pyrolysis liquids obtained from pine sawdust using HY and H-ZSM-5.[18] Li and co-workers performed catalytic studies using bio-oil tar in combination with 3 different zeolites (H-ZSM-5, HY, and MCM-41).[14] The best result regarding BTX yield was

25.1 wt % using H-ZSM-5 at a temperature of 400 °C.[14] In a follow-up paper of this group, the pyrolysis oil as such was used as the feed using the same setup and catalysts. An aromatics carbon yield of 36% was obtained (including phenols) using H-ZSM-5 at 500 °C, which is lower than obtained using the bio-oil tar.[10] Adjaye et al. reported experimental studies with 5 different types of zeolites.[12] The organic product was shown to contain up to 27.9 wt % of total hydrocarbons when using H-ZSM-5 as the catalyst. The highest aromatics yield based on pyrolysis oil intake (wet) was 25.3 wt % (370 °C, WHSV 3.6 h^{-1}).[12]

Zeolites with metal promoters have also been used. Chaihad et al. reported the catalytic upgrading of pyrolysis oil from dried sunflower stalks using Cu-impregnated H-ZSM-5 (24) at 500 °C and reported a yield of aromatics of around 75% peak area.[9] Palizdar et al. investigated the use of Fe- and Zn-promoted hierarchical MFI zeolite for upgrading the pyrolysis oil obtained from beechwood to an FCC feed. At the prevailing conditions, the main products are phenolics and not hydrocarbons.[15]

Some groups have investigated the effect of different types of pyrolysis liquids on BTX yields, either from different biomass feeds or from upgraded pyrolysis liquids. The latter specifically entails liquids obtained by catalytic hydrotreatment. Here, the pyrolysis liquid is treated with hydrogen in combination with a heterogeneous metal-based catalyst to (partially) deoxygenate the sample. This is known to improve the product properties of the pyrolysis liquids significantly and has for example a positive effect on storage stability.[19] For instance, Politi and co-workers investigated the upgrading of 3 different types of wood pyrolysis oil (Canadian oak, mixture of Canadian oak and Swedish pine and pine) using two versions of ZSM-5 and HY in a continuous downflow operated fixed bed micro reactor at different WHSV's and temperatures between 410 and 490 °C.[20] The highest organic liquid yield for the best catalyst in the series (H-ZSM-5 (50)) was 18.1 wt % on a wet pyrolysis oil intake basis (25.9 wt % on a dry basis). The total aromatics yield (17 individual components, a.o. BTX, naphthalenes, and

anthracenes) was 92.8% based on GC peak areas. The liquid yields for the 3 pyrolysis oils were very similar.

Zhang/Huber et al. investigated the catalytic conversion of (treated) pyrolysis oils (obtained from pine and white oak) using H-ZSM-5 as the catalyst in a downflow fixed-bed reactor.[21] The best results were obtained using a low-temperature hydrotreated pyrolysis liquid as the feed, giving aromatics in a 23.36 C% yield. The untreated pyrolysis oil from white oak gave a far lower aromatic yield (9.81 C%). For the water-soluble fraction of this pyrolysis oil, the aromatic yield was lower and reported to be 8.19 C%. Here, the aromatics fraction includes, besides BTX ethylbenzene, styrene, indene, and naphthalene, although these were present in amounts below 1 C%.

Besides studies on real pyrolysis oils, literature is available on the catalytic pyrolysis of model components and mixtures of model components using acidic zeolites to determine the potential precursors for hydrocarbon/aromatics formation and to assess the main coke-forming ones.[16,22−25] These include studies with main component classes present in pyrolysis oils, such as alcohols, aldehydes, acids, and phenols. Examples include research from Gayubo et al.,[22,23] Asadieraghi et al.,[24] and Guvenc et al.[25] Gayubo et al.[22] tested the conversion of various alcohols and phenols using H-ZSM-5. It was shown that alcohols dehydrate rapidly to the corresponding olefins, and these are subsequently converted into C4+ paraffins and aromatics at elevated temperatures. Aromatics though, are formed in very low amounts. Phenol is not very reactive under the prevailing conditions (atmospheric pressure and temperatures between 200 and 450 °C) and produces only small amounts of light olefins. In a second paper,[23] similar experiments were carried out using representative aldehydes, ketones, and acids. In addition, Gayubo et al. also studied the reactivity of mixtures of acetone, acetic acid, acetaldehyde, phenol, 2-butanol, and methanol in combination with H-ZSM-5.[26] Initially, high amounts of light olefins and, to a lesser extent, aromatics and C4+ paraffins were obtained, though the formation rate is significantly reduced after extended time on stream due to catalyst deactivation by severe coke formation. Guvenc et al.[25] performed studies on the catalytic conversion of a mixture of model compounds (hydroxypropanol/furfural/formic acid) in combination with ethanol with different H-ZSM-5 alumina-supported metal catalysts. The main product at the prevailing conditions was olefins, and particular attention was given to the extent of coke formation and reaction pathways toward coke. Zhang/Huber et al. also investigated the catalytic conversion of model oxygenates (methanol, glycerol, glucose, sorbitol, tetrahydrofuran) beside (treated) pyrolysis oils (from pine and white oak) using H-ZSM-5 as the catalyst.[21] Data analyses using the H/C_{eff} concept showed that feeds with a low H/C_{eff} ratio give a higher amount of coke while feedstocks with an H/C_{eff} ratio higher than 0.6 only give trace amounts of coke. Furthermore, a correlation between the H/C_{eff} ratio and the BTX yields was established.

Studies on the catalytic conversion of pyrolysis oil fractions are available, although still limited. Such fractions may be obtained by physical separation schemes or by using phase-separated pyrolysis oil. The latter may occur spontaneously upon storage of the oil and an aqueous sugar phase, and a pyrolytic lignin phase are formed. Gayubo et al. performed experiments using the aqueous phase of a pyrolysis oil using H-ZSM-5 as the catalyst.[27] Hydrocarbons were formed in significant amounts and consist of aromatics, olefins, and paraffins. At 500 °C and a w8 hly space velocity (WHSV) of 4.2, the initial yield of aromatics was 22%, though it dropped rapidly by catalyst deactivation.

Mukarakate et al.[28] investigated the catalytic conversion of an aqueous phase of pyrolysis oil with H-ZSM-5 as the catalyst. The carbon yield for BTX was 25% at the initial stage of the reaction (10−20 min, 500 °C, 1 atm, WHSV of 1 h$^{−1}$) and dropped to 12.1% after 40 min, showing that catalyst deactivation occurs to a significant extent.

Here, we report a systematic study on the use of 4 pyrolysis oil fractions as a feed for specifically BTX synthesis. As such, our interest is not in the conversion of pyrolysis oils to fuels or fuel components or a range of aromatics, as in most of the literature reported so far, but specifically on BTX. The results will be compared with the BTX yields obtained for the pyrolysis oil feed.

The main objective was to identify which of the fractions of pyrolysis oil is most suitable for BTX formation. This knowledge will guide further research into the development of efficient pyrolysis oil biorefineries. The pyrolysis oil, as well as the individual fractions, were characterized in detail, pyrolyzed using a benchmark H-ZSM-5 (23) catalyst in a tandem microreactor, and the BTX yields were correlated with relevant characteristics of the various fractions.

The novelty of the current study is (i) the use of four different fractions of a representative pyrolysis oil obtained by a novel fractionation scheme (operated at pilot scale) instead of model components, mixtures of model components, or the aqueous fraction of a pyrolysis oil and (ii) the use of these fractions to specifically obtain BTX (and not a hydrocarbon biofuel). With this information, the valorization of the various fractions of the pyrolysis oil biorefinery scheme can be optimized by applying tailored catalytic conversions.

2. EXPERIMENTAL SECTION

2.1. Materials. The pyrolysis oil (obtained from pine wood) and fractions thereof were obtained from Biomass Technology Group (BTG BV, Enschede, The Netherlands). Details about their preparation are given below, and relevant compositional data are provided in Section 3. The ZSM-5 (23) catalyst with a Si/Al ratio of 23 was obtained from Zeolyst International in its ammonia form and was converted to H-ZSM-5 (23) by calcination at 600 °C for 8 h. This catalyst is the benchmark catalyst for catalytic pyrolysis studies on lignocellulosic biomass in our group.[29,31] The sample was subsequently pressed, crushed, and sieved. The fraction with particle sizes between 212 and 425 μm was used for the experiments. Catalyst characterization details are given in the Supporting Information (Table S1). Tetrahydrofuran (THF) and DMSO-d_6 were purchased from Sigma-Aldrich, benzene from VWR, toluene from Biosolve, both m-xylene and o-xylene from ABCR GmbH, and n-hexane from Macron Fine Chemicals. Both the Hydranal Titrant 5 reagent and Hydranal methanol solvent were obtained from Honeywell. All chemicals were used as received.

2.2. Fractionation of the Pyrolysis Oil. The pyrolysis oil was separated using a fractionation process, as given in Figure 2. Initially, an organic solvent extraction is performed to remove the extractive fraction, which contains waxes, fatty acids, and protein extracted from the biomass (∼1−2 wt % of pyrolysis oil). Subsequently, the extractives-free pyrolysis liquid is further separated by liquid−liquid extraction with an aqueous solvent to obtain a diluted pyrolytic sugar stream
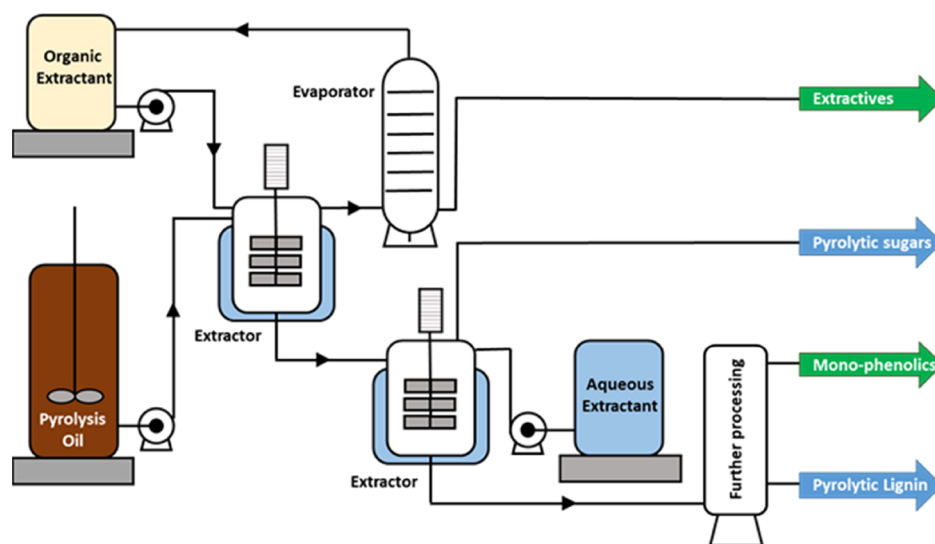
Figure 2. Fractionation scheme for pyrolysis liquids to obtain the fractions used in this study. Reprinted with permission from Heeres, H.; Leijenhorst, E.; Ongena, R.; Beld, L. V. Thermal-Chemical Fractionation of Lignocellulosic Biomass. In European Biomass Conference and Exhibition Proceedings; Lisbon, Portugal, 2019. 10.5281/zenodo.3337616. Copyright 2019, corresponding author (H. Heeres).

derived from the cellulose and hemicellulose (~70−75 wt % of pyrolysis oil) and a pyrolytic lignin stream derived from the lignin (~25−30 wt % of pyrolysis oil). The diluted pyrolytic sugar stream is further processed to obtain a product composed of syrup (~40−45 wt %) and ~30−35 wt % of a watery fraction containing a.o. organic acids. The lignin is produced as a highly viscous liquid and is further processed to yield a solid (~72 wt % of the lignin). During the processing of the pyrolytic lignin, a fraction called "mono-phenolics" is obtained as a byproduct (~28 wt % on a wet basis, ~12 wt % on a dry basis of the lignin).[30]

2.3. Catalytic Pyrolysis Experiments. The catalytic pyrolysis experiments were performed using a high-pressure tandem microreactor (Frontier Laboratories Rx-3050TR) attached on top of a GC (HP 6890A)-MSD (HP 5973) equipped with a Restek Rxi-5Sil Column (30 m × 0.25 mm × 0.25 μm). The vapor from the microreactor is passed through a cryotrap and a splitter and then analyzed using MS and FID detectors.

The tandem micro reactor consists of a pyrolysis reactor followed by a second reactor loaded with a quartz liner filled with either 80 mg of ZSM-5 catalyst to act as an ex situ catalyst or silicon carbide for calibration experiments using pure components, refer to Figure 3 for a schematic representation of

Figure 3. Schematic representation of the tandem microreactor unit used in this study.

the unit. The sample (approximately 1 mg) is loaded into a stainless-steel cup. It is injected into the pyrolysis reactor, which is set at a temperature of 500 °C. The pyrolysis vapor is transported to the second catalytic reactor (550 °C) using He as the carrier gas (54 mL/min). These temperature settings were selected based on previous catalytic pyrolysis studies performed in our group using glycerol[31] and lignin[29] and catalytic pyrolysis experiments using the aqueous fractions of pyrolysis liquids (see introduction, refs 28 and 29). Subsequently, the vapor is collected in a cryotrap set to −180 °C for one min and then transferred to the GC for analysis. The oven temperature profile was as follows: initial temperature of 40 °C, initial temperature ramp of 10 °C/min for 14 min, followed by a heating rate of 30 °C/min for 4 min, and finally isothermal at 300 °C for 7 min. Experiments were carried out in triplicate to determine the reproducibility of the results, and the average values were given.

The quantification of the individual amounts of BTX was done based on the FID peak area in combination with calibration curves for the individual components. For this purpose, calibration stock solutions were prepared using a predetermined amount of benzene, toluene, and xylenes in *n*-hexane. The stock solutions were diluted to five different concentrations to prepare a five-point calibration line. For the calibration experiment, 1 μL of the stock solution was injected. The catalyst in the catalytic reactor was replaced with a liner containing silicon carbide to avoid conversion of the standards while maintaining identical flow and pressure conditions as for the catalytic experiments. The oven temperature for a calibration experiment was increased from 40 to 140 °C at a rate of 10 °C/min.

2.4. Characterization. GPC analyses were performed using an Agilent HPLC 1100 with a refractive index detector attached to a PLGel 3 μm MIXED-E column set. A liquid sample (about 50 mg) was dissolved in THF (4 mL) and two drops of toluene as a retention marker. The sample was filtered using a 0.2 μm PTFE filter before injection. The system was calibrated using polystyrene samples of known molecular weight.
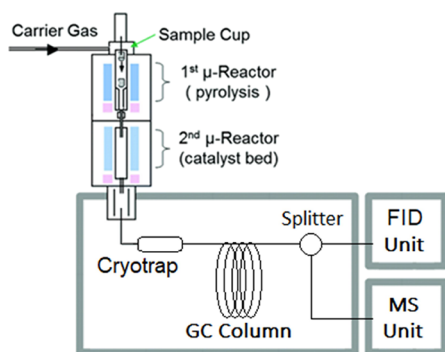
TGA analyses were performed by using a PerkinElmer TGA4000 analyzer. About 2 mg of a sample was placed into a TGA cup and then loaded into the device with an N_2 atmosphere and an initial temperature of 30 °C. The temperature was increased by 10 °C/min and held at 100 °C for 5 min to ensure complete removal of water from the sample. Afterward, the sample was further heated to 500 °C at a rate of 25 °C/min and held for 1 min, simulating the conditions used in the tandem microreactor.

The water content of the samples was determined using Karl Fischer titrations using a procedure as reported by Yin et al.[32]

GC analyses involved the dissolution of the sample (approximately 50 mg) in THF (450 mg). The sample was filtered using a 0.45 μm PTFE filter before analyses. The actual analyses were performed using an Agilent GC 1100 series instrument using He as the carrier gas (flow rate of 40 mL/min). The following oven temperature was applied: 40 °C for 5 min, followed by a temperature ramp of 3 °C/min to 250 °C. The column used in the GC unit was an Rx1−5Sil column from Restek USA with the following specifications: 30 m length, 0.25 mm inner diameter, 10 μm film thickness.

Elemental analyses (C, H, N, and S) of the pyrolysis oil fractions were performed using a Euro EA elemental analyzer with acetanilide as standard. Each sample was analyzed in duplicate, and the average value is given. The oxygen content was not determined through elemental analysis but was calculated as the difference.

2.5. Definitions. The BTX yields are on a carbon basis and given as:

$$BTX\ yield\ (mol\%) = \frac{mol\ of\ carbon\ in\ BTX}{mol\ of\ carbon\ in\ the\ feed} \times 100 \tag{1}$$

The selectivity for the individual BTX components (B, T, and the xylene isomers) is given by eq 2

$$Selectivity\ for\ an\ individual\ BTX\ component\ (wt\%)$$
$$= \frac{weight\ of\ individual\ BTX\ component\ (g)}{total\ BTX\ formed\ (g)} \times 100 \tag{2}$$

The effective hydrogen to carbon molar ratio (H/C_{eff}) of a fraction was calculated using eq 3.

$$H/C_{eff} = \frac{H - (2 \times O)}{C} \tag{3}$$

where H, C, and O are on a mole basis and calculated using the elemental composition of the fraction.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Relevant Properties of the Pyrolysis Liquid and Fractions Thereof. The pyrolysis oil sample and its fractions, obtained by a fractionation scheme given in Figure 2, were characterized using several analytical techniques (elemental composition, water content, GPC, and GC−MS), and an overview of the data is given in Table 1.

The elemental composition of the fractions differs considerably, with C contents between 21 and 78 wt %. However, this is partly due to the wide range of water contents (<0.1−18.9%), which makes the comparison cumbersome. To mitigate this, the elemental data in the form of a van Krevelen plot (H/C and O/C molar ratios) on a dry basis was prepared and is given in Figure 4.

Table 1. Relevant Properties of Samples and BTX Yield after Catalytic Pyrolysis Using H-ZSM-5 (23)

| sample name | elemental composition (wt %)[a] | | | | water content (%) | elemental molar ratio[b] | | | GPC | | | BTX yield (wt% on wet feed)[a] | | | | | total BTX yield (wt % on dry basis) | total BTX yield (carbon % on dry basis) |
	C	H	N	O		H/C	O/C	H/C eff.	Mn (g/mol)	Mw (g/mol)	D[c]	benzene	toluene	m,p-xylene	o-xylene	total BTX[a]		
pyrolytic lignin	70.7	6.39	0.5	22.41	<0.1	1.08	0.24	0.61	420	1100	2.5	1.2	2.1	0.79	0.29	4.4	4.4	7.6
pyrolytic sugar	43.98	7.08	0.16	48.79	18.85	1.36	0.55	0.27	240	340	1.5	1.2	1.8	0.64	0.25	3.9	4.8	4.4
phenols	69.47	7.99	0	22.55	3.55	1.31	0.21	0.89	110	120	1.1	6.7	9.5	3.8	1.3	21	22	24.0
extractives	78.6	9.75	0	11.65	0.47	1.48	0.11	1.27	250	350	1.4	1.8	3.2	1.6	0.5	7.1	7.1	9.0
pyrolysis oil	47.84	7.38	0.3	44.44	22.18	1.23	0.39	0.46	280	460	1.6	1.6	2.2	0.59	0.2	4.6	5.9	5.3

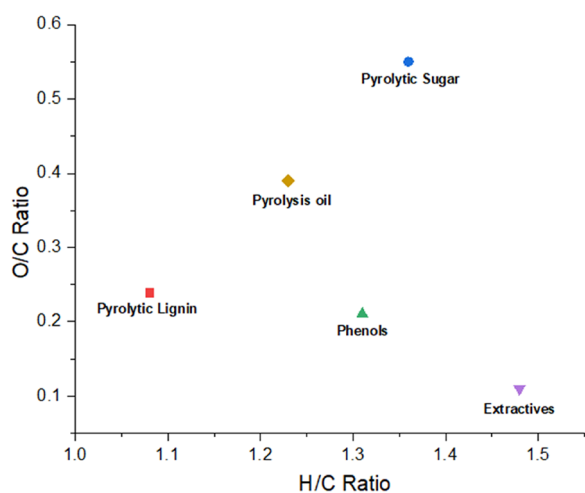[a]Wet basis. [b]Dry basis. [c]Dispersity defined as M_w/M_n.

Figure 4. van Krevelen diagram of the samples (dry basis).

The elemental compositions of the pyrolysis oil and fractions on a dry basis differ considerably. The pyrolytic sugar fraction has the highest O/C ratio due to the presence of oxygen-rich sugars and sugar-derived fragments, whereas the extractives show the lowest O/C ratio. The latter may be rationalized when considering that this fraction is rich in molecules with long hydrocarbon chains (vide infra). As expected, this also leads to a high H/C ratio for this fraction. The pyrolytic lignin fraction has the lowest H/C ratio due to the presence of high levels of aromatic rings in its structure which have a relatively low H/C ratio (vide infra).

The molecular composition of the fractions was determined using GC−MS/FID (to identify and quantify low molecular weight compounds) and GPC. The latter provides useful information on the higher molecular weight fragments in the fractions and as such is complementary to GC analyses. Representative GPC chromatograms are shown in Figure 5 for
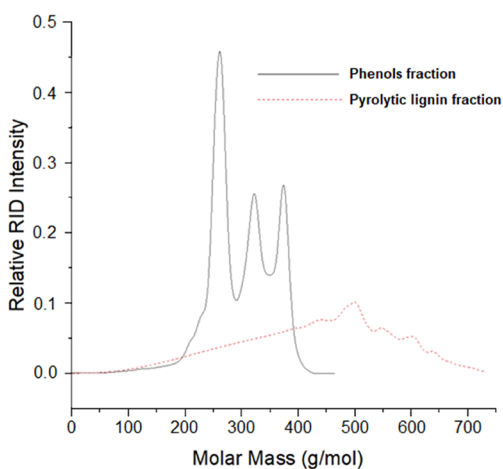

Figure 5. Representative GPC chromatograms of two fractions (phenols and the pyrolytic lignin fraction).

the phenols fraction and the pyrolytic lignin fraction. The M_w values vary between 120 and 1200, showing that the molecular weights of the fractions are relatively low. As expected, based on the fractionation scheme, the molecular weight of the phenol fraction is the lowest. However, the absolute molecular weight values should be considered with caution, as

quantification is difficult due to the absence of good calibration standards.

The type and amount of the low molecular weight components in each fraction differ considerably, see Table 2 for details. The phenolic fractions contain considerable amounts of substituted phenols, such as alkylated and methoxylated phenols, with different substitution patterns, all arising from the lignin in the biomass feed. In addition, some low molecular weight sugar-derived molecules are also present (e.g., furfural). The pyrolytic lignin sample shows only a very limited amount of identifiable low molecular weight components. This is in line with GPC and literature data, showing that most of the components are not GC-detectable and implying that the pyrolytic lignin fraction consists of oligomeric compounds.[33]

As expected, the extractives fraction contains larger organic acids like 1-phenanthrenecarboxylic acid derivatives and 6-octadecenoic acid, (Z)-, which are known extractives from woody biomass.[34]

3.2. Catalytic Pyrolysis Experiments. The catalytic pyrolysis experiments of pyrolysis oil and the 4 fractions derived thereof were performed in a tandem microreactor (TMR) consisting of a pyrolysis/vaporization section (500 °C) and an aromatization section containing the H-ZSM-5 zeolite (550 °C). Temperature levels are based on previous catalytic biomass pyrolysis studies from He et al.,[34] Ibarra et al.,[13] and Bi et al.[14] The products were analyzed and quantified using a GC instrument equipped with an FID detector for quantification and an MS detector for the identification of products. Experiments with each fraction were at least performed in triplicate, and the average value is given. Details including (relative) standard deviations are provided in the Supporting Information (Table S2). A representative FID chromatogram of a catalytic pyrolysis experiment using the dry pyrolytic sugar fraction is provided in Figure 6. Besides the desired BTX components, gases (C2−C3) and higher aromatics were detected. The latter include substituted naphthalenes, such as 1- and 2-methylnaphthalene.

The yields of the desired BTX components were quantified, and the results are given in Figure 7. The BTX yield for experiments with the pyrolysis oil as such was 5.3% on a dry carbon basis. These values are within the range of literature data for the catalytic conversion of pyrolysis oils obtained from lignocellulosic biomass to hydrocarbons using H-ZSM-5, see the Introduction section.

The BTX yields for the fractions differ considerably. The highest BTX yield of up to 24 C% (dry basis) was obtained by using the phenolic fractions. The lowest yield was found for the sugar fraction, 4.4 C% (dry basis). The experimentally observed highest yield for the phenolic fraction (24 C%) is surprising. The main components in this fraction are monomeric substituted phenols like alkylated and methoxylated phenols, the main ones being 2-methoxyphenol (guaiacol) and 2-methoxy-4-methyl phenol (Table 2). Catalytic pyrolysis experiments using these 2 substrates have been reported in the literature. The BTX yields for guaiacol using H-ZSM-5 are rather conflicting and range between low values (2.0 C% at 500 °C and 6.4 C% at 600 °C in a fixed-bed reactor)[35] and 22.4 C% (600 °C, fixed bed reactor).[36] A recent study by our group using the same TMR setup, catalyst H-ZSM-5, and experimental conditions (500 °C for pyrolysis, 550 °C for catalytic aromatization) as in this study gave 11.8 C % of BTX for guaiacol and 14.9 wt % for 4-methylguaicol.

Table 2. Major Chemical Components of Each Fraction by GC−MS Analysis (Area %)

| | GC Peak Area % | | | |
component	pyrolytic lignin	pyrolytic sugar	phenols	extractives
2-propanone, 1-hydroxy-		2.3		
furfural			3.4	
styrene			0.9	
2-cyclopenten-1-one, 2-methyl-			1.0	
phenol			0.6	
2-cyclopenten-1-one, 2-hydroxy-3-methyl-		1.6		
benzene, 1-methoxy-3-methyl-			1.1	
benzene, 1-methyl-4-(1-methylethyl)-			1.0	
phenol, 2-methoxy-		1.1	7.3	
phenol, 2-methyl-			0.6	
2,5-dimethylanisole			2.1	
phenol, 2-methoxy-4-methyl-	0.8	1.0	6.8	
phenol, 4-ethyl-2-methoxy-			1.8	
vanillin		0.9		
ethanone, 1-(4-hydroxy-3-methoxyphenyl)-		0.6		
phenol, 2-methoxy-4-(1-propenyl)-	1.1			1.1
levoglucosan		1.9		
D-allose		0.9		
4-hydroxy-2-methoxycinnamaldehyde		0.6		
6-octadecenoic acid, (Z)-				2.1
1-phenanthrenecarboxylic acid, 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-, [1R-(1.alpha.,4a.beta.,10a.alpha.)]-				10.8
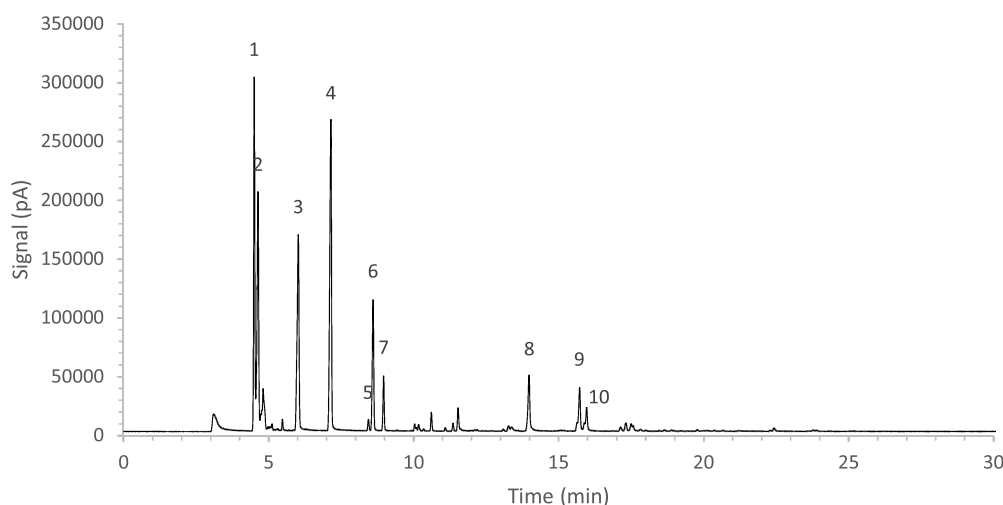
Figure 6. Products of the catalytic pyrolysis of the pyrolytic sugar fraction. (1: C2 gases, 2: C3 gases, 3: benzene, 4: toluene, 5: ethylbenzene, 6: p-/m-xylene, 7: o-xylene, 8: naphthalene, 9: 2-methylnaphthalene, 10: 1-methylnaphthalene).

These values are considerably lower than experimentally found for the phenolics fraction. However, it should be noted that the phenolics fraction also contains significant amounts of sugar-derived compounds like furfural (Table 2). The catalytic pyrolysis of furfural with HZSM-5 has been reported in the literature (500 °C), to give a 15.7 carbon% yield of aromatics, of which about 90% is BTX.[37] The presence of furfural thus cannot fully explain the high yields for the phenolic fraction, though it gives a partial explanation. It is also possible that synergic effects between the various components play a role, lead to improved yields, and should be accounted for.

The BTX for the pyrolytic sugar fraction (4.4 C% on a dry basis) was slightly lower than for the original pyrolysis oil (5.3 C% on a dry basis). The sugar fraction mainly consists of monomeric sugar derivatives (among others levoglucosan

(LG)) and oligomeric sugars like cellobiosan (vide supra). Model component studies of the catalytic pyrolysis of LG using H-ZSM-5 are limited. Recently, Bridgwater published catalytic pyrolysis experiments using LG in a Pyroprobe setup (500−600 °C) with H-ZSM-5 as the catalyst.[38] Aromatics were indeed detected, but unfortunately, GC area percentages instead of absolute BTX values were reported. Igtisamova et al.[39] reported studies on the catalytic pyrolysis of cellulose, cellobiose, and glucose using H-ZSM-5 (30) at 600 °C. The BTX yield for all three model components was about 13 C%. Huber and co-workers[40] reported 16.5 C% of BTX for the catalytic pyrolysis of cellulose using H-ZSM-5 as the catalyst at 600 °C. Thus, we can conclude that the experimentally observed carbon yield for the pyrolytic sugar fraction is lower than expected based on literature data for individual
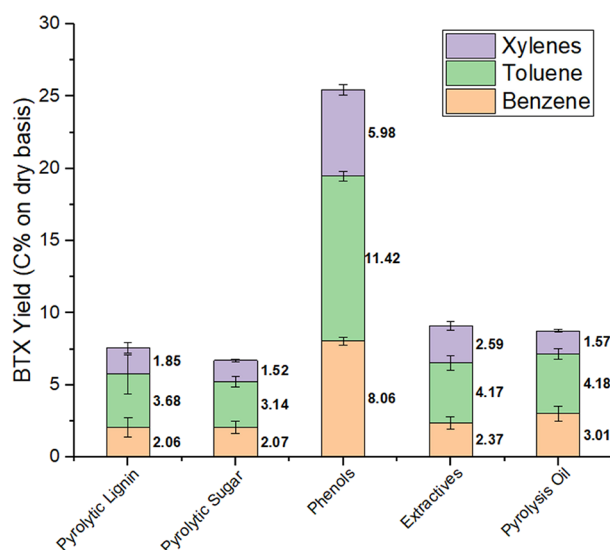
Figure 7. BTX yield for the various pyrolysis oil fractions (carbon % on a dry basis).

Figure 8. Selectivity of the individual components in the BTX fraction.

components present in this fraction. This may imply that other components present in the fraction may have a negative effect on catalyst performance, e.g., due to rapid deactivation by coke formation. However, proper comparison is hampered as the experimental conditions and set-ups differ considerably in the literature and may strongly affect BTX yields.

For the extractives, a BTX yield of 9.0 C% on a dry basis was found. This fraction contains mainly long-chain organic acids (Table 2). Catalytic pyrolysis of long-chain fatty acids like oleic acid has been reported by our group using an H-ZSM-5 type catalyst in a fixed bed reactor at 550 °C and a WHSV of 1 h^{-1}.[31,41] The highest BTX yield was 22.7 C% yield, although it dropped considerably on extended times on stream due to catalyst deactivation. The yield is much higher than that found in this study for the extractives fraction. This may be rationalized by considering that the main organic acid identified is actually a 1-phenanthrene acid derivative. Model catalytic pyrolysis studies have not been reported with this component, though it may be anticipated that due to its multiple-ring structure, it may be prone to coking and thus give relatively low BTX yields.

Possible synergistic effects were evaluated by comparing the BTX yields for the original pyrolysis oil with the sum of the BTX yields of each fraction (Table 1) taking into account the relative amount of each fraction (see Section 2). Based on these calculations, we conclude that the BTX yield for the pyrolysis oil is slightly higher than the combined yield of the fractions. As such, it appears that fractionation does not lead to overall higher BTX yields. However, it should be realized that the main objective of this study is not to assess possible synergistic effects but to give the highest possible value to pyrolysis liquids by achieving high overall carbon yields to valuable products using the biorefinery approach; see Figure 1 for details. Apparently, when aiming for high BTX yields, it is advantageous to use the phenolics fraction instead of either one of the other fractions or the pyrolysis liquid as such. The other fractions can then be used for tailored catalytic transformations aiming for the highest carbon conversions and product value. Possibilities are conversion of the sugar fraction to biobased chemicals like glucose, 5-hydroxymethyl-furfural, or levulinic acid, and conversion of the pyrolytic lignin

fraction to advanced materials (e.g., resins) or a catalytic hydrotreatment to obtain biofuels.

The selectivity of the individual components in the BTX fraction is given in Figure 8. The main component is toluene,
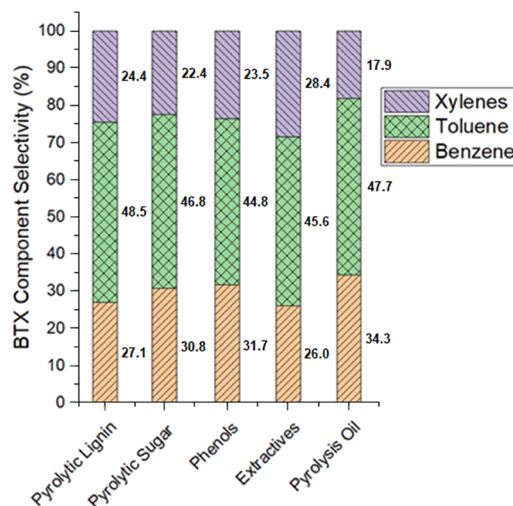
with a selectivity between 44.8 and 48.5%. Benzene is the least abundant, with a selectivity between 26.0 and 34.3%. As such, we can conclude that the selectivity depends on the fraction used, although the effect is not dramatic. Literature data on the selectivity of the individual components in the BTX fraction are scarce. Huber et al. reported data for the catalytic pyrolysis using H-ZSM-5 for pyrolysis oil obtained from white oak in a flow reactor and found that it is a function of the time on stream and varies between 15 and 20% for benzene, 35−45% for toluene, and 20−30% for xylenes. For the pine pyrolysis liquid used in our study, the benzene selectivity is higher (34.2%), whereas the xylenes are slightly lower (17.9%). These differences are likely due to the scale of the experimentation. In flow-type set-ups, the benzene selectivity is often lower than in small-scale TMR-type devices as used in our study due to condensation issues of the rather volatile benzene in flow set-ups.

3.3. Composition: BTX Yield Relations. We have attempted to correlate the BTX yields for the various fractions with the relevant properties of the fractions (water content, molecular weight, etc.). However, no clear correlations could be detected; see the Supporting Information (Figures S5−S7) for several relevant graphs between BTX yield and properties. Huber found a good correlation between the H/C$_{eff}$ ratio and aromatics yields for several model components and real (treated) pyrolysis oils.[21] The aromatic carbon yields increased from about 10 to 20% when the H/C$_{eff}$ ratio was increased from 0 to 1.25 and then leveled off between 1.25 and 2.0. A plot of the H/C$_{eff}$ ratio and BTX yield for our data set is given in Figure 9. It shows a clear optimum in BTX yields versus the H/C$_{eff}$ for the phenols fraction. However, when considering this point as an outlier (vide infra), the BTX yield for the other feeds shows a progressive increase at higher H/C$_{eff}$ ratios, in line with the findings of Huber.[21]

To explain the high BTX yield for the phenolics fraction, it appears that besides the H/C$_{eff}$ ratio, other factors play a role, and one of these is likely the molecular weight of the fractions.
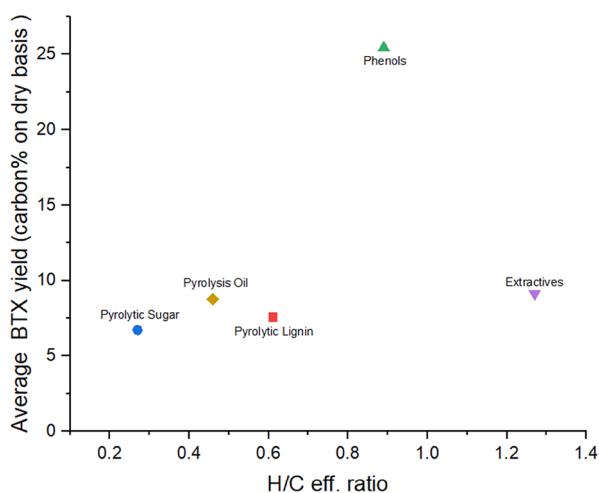
Figure 9. Correlation between the H/C$_{eff}$ ratio and BTX yield (carbon-based and on a dry feed basis).

The molecular weight of the phenol fraction is by far the lowest of all (Table 1). It is well possible that the amount of vapor generated by the phenol fraction in the pyrolysis step is much higher than that for the others, and that this has a positive effect on the BTX yield in the subsequent aromatization step. Studies with lignin model components are in progress to substantiate this statement.

4. CONCLUSIONS

We have shown that particularly, the phenolic fraction of a fractionated pyrolysis oil is suitable for BTX generation by catalytic pyrolysis using an acidic zeolite. With this fraction, a BTX yield of 24 C% (on a dry basis) is attainable, which is a factor of 5 higher than for the original pyrolysis liquid and also substantially higher than the sugar and pyrolytic lignin fraction. Most likely, the low molecular weight of this specific fraction results in a higher amount of organics in the vaporous phase during pyrolysis, thereby increasing the BTX yields. This finding supports the concept of a pyrolysis oil biorefinery, where each specific fraction is converted using tailored (catalytic) technology to maximize its value.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c03831.

> Catalyst characterization details, overview of BTX yields from catalytic pyrolysis of the fractions, and GC-FID spectra of the pyrolysis oil fractions (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Hero J. Heeres − *Green Chemical Reaction Engineering, Engineering and Technology Institute Groningen, University of Groningen, 9747 AG Groningen, The Netherlands;* ⓘ orcid.org/0000-0002-1249-543X; Email: h.j.heeres@rug.nl

Authors

Dian S. Santosa − *Green Chemical Reaction Engineering, Engineering and Technology Institute Groningen, University of Groningen, 9747 AG Groningen, The Netherlands*

Leon Rohrbach − *Green Chemical Reaction Engineering, Engineering and Technology Institute Groningen, University of Groningen, 9747 AG Groningen, The Netherlands*

Hans Heeres − *BTG Biomass Technology Group B.V., 7545 PN Enschede, The Netherlands*

Robbie H. Venderbosch − *BTG Biomass Technology Group B.V., 7545 PN Enschede, The Netherlands*

Andre Heeres − *Hanze University of Applied Sciences, 9747 AS Groningen, The Netherlands*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.4c03831

Notes

The authors declare no competing financial interest.

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