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Synthesis of Bio-aromatics from Black Liquors Using Catalytic Pyrolysis

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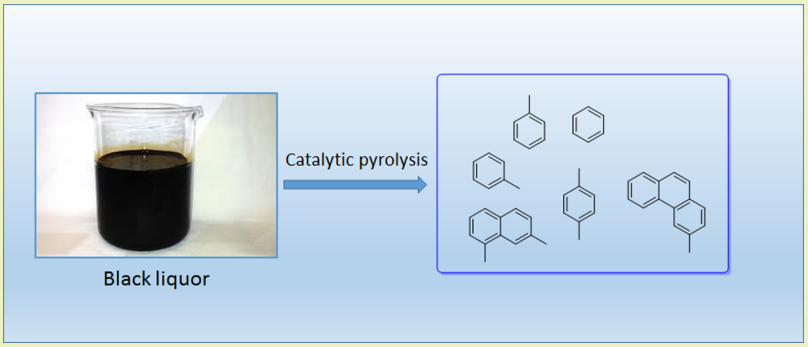

ABSTRACT: Bio-aromatics (benzene, toluene, xylenes, BTX) were prepared by the catalytic pyrolysis of six different black liquors using both in situ and ex situ approaches. A wide range of catalysts was screened and conditions were optimized in microscale reactors. Up to 7 wt % of BTX, based on the organic fraction of the black liquors, was obtained for both the in situ and ex situ pyrolysis (T = 500−600 °C) using a Ga-modified H-ZSM-5 catalyst. The in situ catalytic pyrolysis of black liquors from hardwood paper mills afforded slightly higher yields of aromatics/BTX than softwood black liquors, a trend that could be confirmed by the results obtained in the ex situ catalytic pyrolysis. An almost full deoxygenation of the lignin and carbohydrate fraction was achieved and both organic fractions were converted to a broad range of (substituted) aromatics. The zeolite catalyst used was remarkably stable and even after 100 experiments in batch mode with intermittent oxidative catalyst regeneration, the yields and selectivity toward BTX remained similar. The ex situ pyrolysis of black liquor has potential for large-scale implementation in a paper mill without disturbing the paper production process.

KEYWORDS: *black liquor, catalytic pyrolysis, aromatics*

INTRODUCTION

The growing world population and increasing welfare levels will result in a steady growing demand for materials, including plastics in the near future.[1] The foreseen reduction in fossil resource supply, in combination with the demand for more environmentally friendly processes (CO_2 reduction) make renewable biomass an attractive candidate for the preparation of plastics. Low molecular weight aromatics, such as benzene, toluene, and xylenes (BTX) are important building blocks for high-volume plastics, including several polyesters and polyurethanes, and many examples in both the open and patent literature describe the attempts to prepare BTX from biomass.[2]

Routes currently under investigation for preparation of aromatics from nonpetrochemical sources are aqueous-phase reforming,[3] conversion of syngas into aromatics,[4] dehydration, and aromatization of pyrolysis oil and alcohols with zeolites,[5,6] and for the production of *p*-xylene, a chemoenzymatic route is claimed involving the dimerization/dehydrocyclization of renewable isobutanol.[7] Furthermore, benzene and also ethylene are formed during the gasification of biomass at high temperatures (T > 850 °C) and by catalytic hydrotreatment of either biomass fractions like lignin or pyrolysis oils.[8,9]

Catalytic pyrolysis of biomass toward BTX has been recognized as an attractive technology as it is a scalable one-step procedure, most often utilizing commercially available zeolite catalysts for aromatization. Various biomass feedstreams, including lignins, have been identified for their potential to produce bio-aromatics.[10−15] However, to the best of our knowledge, no attempts have been reported for the catalytic pyrolysis of black liquor, an important and high-volume lignin-containing stream of the paper industry, toward these essential building blocks for the chemical industry.

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Black liquor is formed in the paper production by the digestion of pulpwood. In the Kraft paper process the addition of sodium hydroxide and sodium sulfide to pulpwood results in the extraction of lignins and hemicellulose from the insoluble cellulose fraction. The liquor obtained is most often concentrated toward approximately 30% water content and subsequently added to large recovery boilers for energy production and to recover the cooking chemicals from the pulping process. The black liquor produced in this Kraft paper process consists of an aqueous solution of lignin, tall oil, turpentine, (depolymerized) oxidized (hemi)cellulose fragments, and inorganic salts.[16]

Until now, most of the research programs performed on the pyrolysis of black liquor focused on the noncatalytic, thermochemical conversion for mainly energy and syngas production.[17] Bhattacharya et al. pyrolyzed black liquor solids of different sizes in a fixed bed reactor under N_2 atmosphere at different temperatures (T = 590−740 °C).[18] Improved yields of bio-oils (liquids, condensed volatiles) and gases were obtained at higher temperatures. At a reaction time of 15 min black liquor was converted to roughly 50% char, 30% liquids, and 20% gases (H_2, CH_4, CO, CO_2, H_2S). The particle size of the black liquor solids only had small effects on the product distribution. The results obtained were confirmed by studies of Demirbas.[19,20] High heating rates and rapid quenching of the volatiles obtained are beneficial for biocrude production.[21−23] The fast quenching of volatiles formed during pyrolysis avoids secondary pyrolysis toward higher molecular weight compounds. Fletcher and co-workers recently used a chemical percolation devolatilization model (CPD), originally developed for pyrolysis of coal, to predict biocrude and light gas yields from black liquor. The model includes the effect of heating rate, temperature, residence time and pressure on char, pyrolysis oil and gas formation.[24]

In general, the yield of bio-oils (condensed volatiles) from pyrolyzed black liquor solids are lower than for typical lignocellulosic biomass streams such as cellulose or lignocellulose. The high amount of alkali salts (NaOH, Na_2CO_3) are considered to slow down the formation of alcohols, phenols, hydrocarbons and aldehydes/ketones during pyrolysis and higher temperatures are needed for release. As a result side reactions and secondary pyrolysis of volatiles occur that negatively influence the formation of condensable volatiles. Addition of CaO, $CuCO_3$, and $Cu(OH)_2$ slightly increased the amount of liquids formed during pyrolysis of black liquor.[25]

To the best of our knowledge, no attempts in either the open and patent literature describe the catalytic pyrolysis of crude black liquor toward aromatics. The study described in this paper focuses on the catalytic pyrolysis of concentrated black liquors and their potential to produce bio-aromatics, including BTX. Our approach was to first screen a wide range of commercially available zeolite catalysts for their potential to convert different black liquors to aromatics in an in situ microscale unit (PTV GC-MS). In this setup the black liquor is mixed with the catalyst and subsequently pyrolyzed under an inert atmosphere. The most promising catalysts were screened in an ex situ setup using a Tandem micro-Reactor (TMR) and optimized for BTX synthesis. In an ex situ approach black liquors are first pyrolyzed toward a complex mixture of small organic molecules and subsequently catalytically aromatized in a second reaction chamber. In addition, black liquors from various sources were tested and the best one considering BTX yield was identified. Finally, irreversible catalyst deactivation by e.g. accumulation of salts present in the black liquors was tested using catalyst recycle experiments in a microreactor.

EXPERIMENTAL SECTION

Materials. Six black liquors, obtained from various sources, were tested including Eucalyptus hardwood, Soda Southern hardwood, Kraft Northern hardwood, Kraft Southern hardwood, Kraft Northern softwood and Kraft Southern softwood. Zeolite catalysts were obtained from Zeolyst International and Huntsman Everberg. For the various ZSM-5 catalysts, the number in brackets (e.g., ZSM-5 (23)) is the Si/Al ratio in the catalyst formulation as provided by the supplier. Catalysts were calcined in a Nabertherm oven (LT 9/11-p330) under static air conditions with the following temperature program: heating from room temperature to 550 °C within 8 h, then held at this temperature for 8 h before cooling down. The powder was then compacted using a mechanical hydraulic press under 7 bar pressure for 10 s, crushed, and sieved to 212−425 μm particle size before use in the PTV GC/MS or tandem micro reactor. For analysis and calibration purposes, *n*-hexane (product no. A36C11X) and toluene (product no. A22A11X) were purchased from Lab-scan (Sowińskiego, Poland). Benzene (product no. 1779) and para- and meta-xylene (product no. 108661) were obtained from Merck (Darmstadt, Germany). Ortho-xylene was provided from Baker chemicals (Deventer, The Netherlands).

Synthesis of Ga-, Mo-, and Zn-Loaded Zeolites. *Synthesis of Ga/ZSM-5 (23).* To an aqueous solution of 0.01 M $Ga(NO_3)_3$ (gallium III nitrate hydrate, 99.9%, Sigma-Aldrich) in demineralized water (200 mL, 2 mM, 511 mg) was added H-ZSM-5 (23) (2000 mg) The mixture was heated to 80 °C and stirred for 6 h. The reaction mixture was cooled to room temperature and centrifuged afterward. The precipitate obtained was dried overnight in an oven at 110 °C. Finally the solid product was calcined at 550 °C in air for 8 h. The theoretical gallium loading at full ion exchange would be 5 wt %. The exact loading was determined by ICP analysis and established at 1.47 wt % .

The zeolites Zn/ZSM-5 (23) and Mo/ZSM-5 (23) were prepared in a similar way, using respectively zinc nitrate hexahydrate (98%, Sigma-Aldrich) and ammonium heptamolybdate tetrahydrate (>99%, Merck). The metal loading was, according to ICP analysis, 4.3% for the Zn-impregnated catalyst and 0.06% for the Mo-impregnated catalyst. Ga/ZSM-5 (50) was prepared using H-ZSM-5 (50). The exact loading was determined by ICP analysis and established at 2.98 wt %.

Analysis. A literature procedure (TAPPI standard test method T-650 pm-84) was used for the determination of the organic, inorganic and water content of black liquors. A known amount (10−12 g, triplicate) of black liquor was dried in a hot air oven at 105 ± 2 °C until constant weight. The amount of water was determined by the difference in weight before and after the experiment. Subsequently, the crucible with the dried contents was placed in a muffle furnace at T = 525 ± 25 °C. Contents were allowed to burn to a constant weight. The total organic content of wet black liquor was determined by the difference in weight before and after the experiment and the remaining residue reflects the inorganic part of the black liquor. For black liquor obtained from Eucalyptus hardwood the lignin content was determined according to literature procedures. Freeze-dried samples of black liquors were obtained by first freezing the black liquors in a flash using liquid nitrogen and subsequently subliming the water using high vacuum.

Analysis of the organic products of the (catalytic) pyrolysis experiments was performed by gas chromatography (GC), using a Hewlett-Packard 5890 series equipped with a Restek Rx1−5Sil column (length 30 m, diameter 0.25 mm and film 10 μm) coupled to a mass spectrometer (MS) Hewlett-Packard 5972 series detector. The injection temperature was set to 280 °C, with a split of 50:1. The oven program started at 45 °C for 5 min, then heated up to 100 °C at a rate of 10 °C/min, then to 200 °C at a rate of 20 °C/min and finally to 300 °C at a rate of 30 °C/min and kept constant for 3 min before cooling down.

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Table 1. Relevant Properties of the Black Liquors Used in This Study

composition (wt %)	eucalyptus hardwood	soda southern hardwood	Kraft northern hardwood	Kraft southern hardwood	Kraft northern softwood	Kraft southern softwood
H_2O	28.3	26.4	33.3	30.6	31.4	34.2
organics	40.2	41.6	33.3	38.9	36.9	38.8
lignin	32.0					
(oxidized) carbohydrates	8.2					
inorganics	31.5	32	33.4	30.5	31.7	27

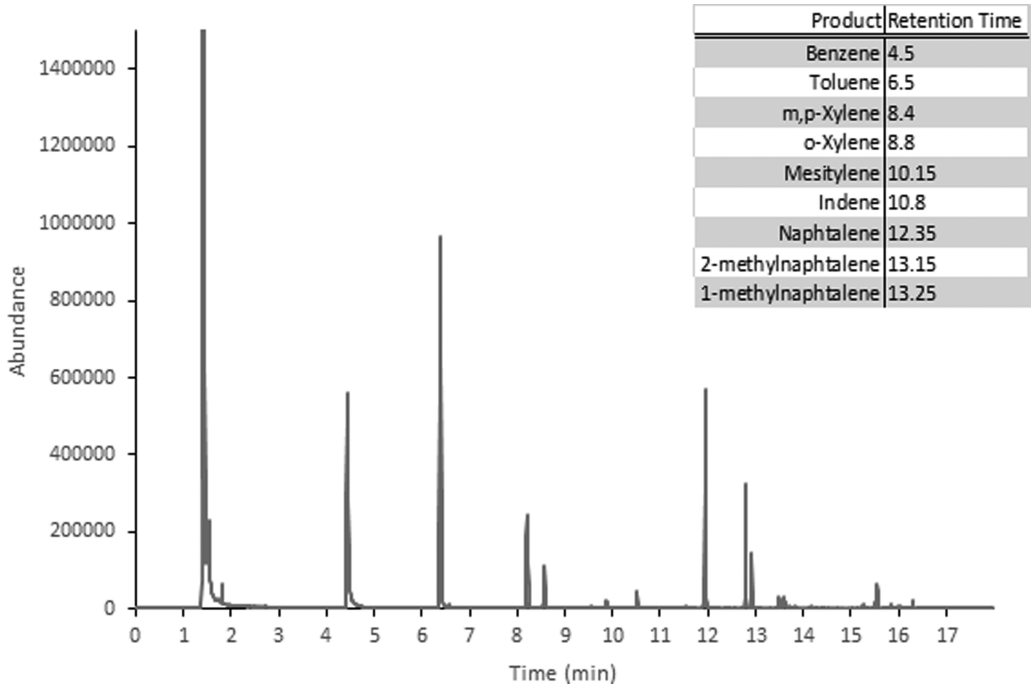

Figure 1. Typical GC for the in situ catalytic pyrolysis of black liquor.

Quantification of aromatics produced in the PTV-GC/MS and TMR was performed by means of an external calibration method using benzene, toluene, and o-, m-, *p*-xylene. Injection of calibration solutions was performed by a hot needle approach where the needle was allowed to heat up for 3−5 s in the GC-injector before the plunger was pressed. The injection temperature was set to 280 °C, the split to 50:1 and the helium flow was kept constant at 50 mL/min. Quantification of CFP (catalytic fast pyrolysis) products was done using an adjusted GC oven program, starting by maintaining an oven temperature of 40 °C for 3 min followed by heating to 300 °C with a rate of 10 °C/min. The GC inlet temperature was set to 280 °C. The peaks in GC chromatograms were interpreted by the NIST05 library of mass spectra and grouped to several product classes for brevity.

In Situ Pyrolysis (PTV-GC/MS). For the in situ pyrolysis of black liquors, a programmable temperature vaporizer was used. Catalyst and black liquor were mixed or layered and put into a DMI insert (microvial, 30 μL). The vial was subsequently inserted into a liner and supported at a fixed height by quartz wool. A continuous flow of helium (50 mL/min) was used to maintain an inert atmosphere. The temperature and pressure in the injector were controlled by an optic 2 device. A split of 1/50 was applied to furnish a 1 mL/min flow on the GC column (HP 5890 series II GC with an Agilent column VF-5MS 30 × 0.25 mm, 1 μL film thickness). The flow was led to a mass selective detector (HP 5972 series MSD). The PTV was operated at a starting temperature of 40 °C, followed by ramping at a speed of 20 °C/s until the final temperature of 600 °C was reached. The yields of BTX obtained were the average of triplicate measurements and based on the organic fraction present in the black liquors (eq 1).

$$\text{BTX yield (wt\%)} = \frac{\text{amount of BTX formed (g)}}{\text{black liquor intake (g organic fraction)}} \times 100 \quad (1)$$

Ex Situ Pyrolysis (TMR). The experiments were performed on a Tandem μ-Reactor from Frontier Lab (Rx-3050TR) equipped with a single shot sampler (PY1-1040). The temperatures of both reactors and interfaces were controlled separately, allowing different reaction conditions for the pyrolysis (first reactor) and aromatization unit (second reactor). A carrier gas inlet was connected on the top of the first reactor, providing carrier gas flow through the reactors into the GC-MS. The entire system was attached by a docking station on top of the GC-MS and connected by an injection needle through a rubber septum.

Before experiments, approximately 80 mg of a ZSM-5 catalyst was put in a quartz liner inside the second reactor. Thereafter, the system was pressurized to 150 kPa with an inert carrier gas (helium) to check for leakage. After the leak check, the pressure was set back to 50 kPa using a helium flow rate of 50 mL/min and the system was heated (reactor 1:550 °C, reactor 2:575 °C and for both interfaces: 300 °C). A stainless steel cup was filled with black liquor and attached to the sample injector, which hangs slightly above the first reactor. The system was closed and flushed for 3 min with helium gas. After flushing, the cup was dropped into the first reactor to start the pyrolysis reaction. The vapor products travel through the ZSM-5 catalyst bed before entering the GC-MS. The yields of BTX were the average of duplicate measurements and based on the organic fraction present in the black liquors (eq 1).

Catalyst Recycle/Regeneration Studies. To determine possible irreversible deactivation of the catalyst, eucalyptus black liquor was ex

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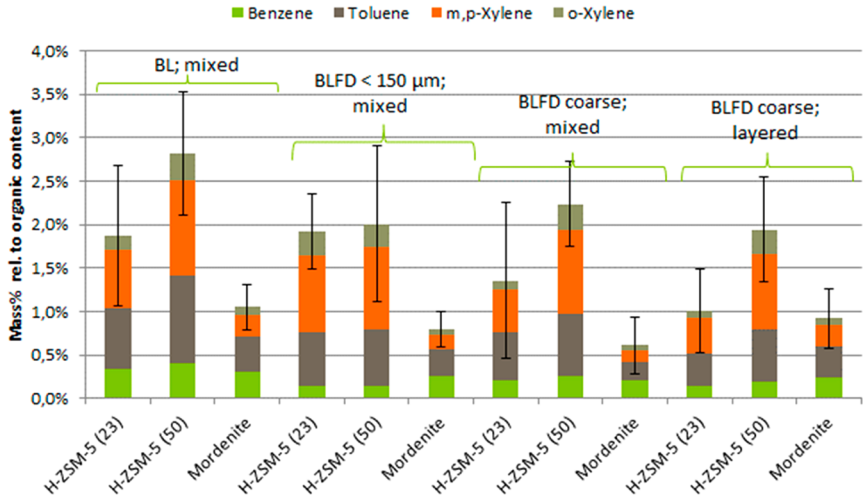

Figure 2. BTX yields for the in situ pyrolysis of black liquor originating from Eucalyptus wood as a function of the catalyst and black liquor pretreatment procedure (BL = black liquor, BLFD = freeze-dried black liquor.

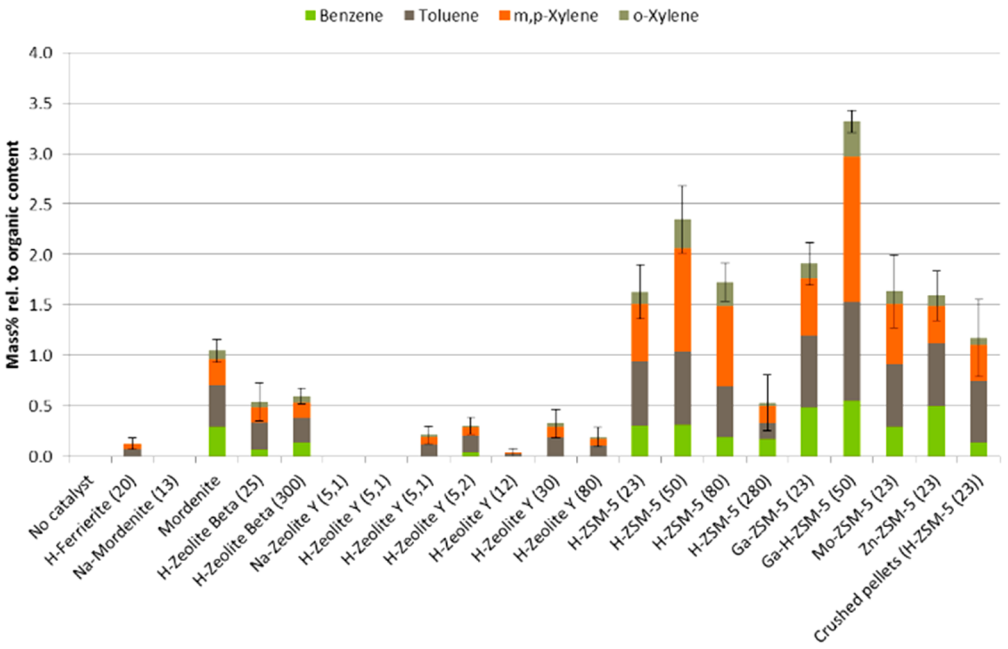

Figure 3. BTX yields for in situ catalytic pyrolysis of black liquor (eucalyptus hardwood, based upon organic content).

situ pyrolyzed in the TMR using an excess of 70 wt equivalents of a H-ZSM-5 catalyst. Fresh black liquor samples (in total 100) were pyrolyzed and aromatized with the H-ZSM-5 catalyst. Between each experiment oxygen was introduced within the system to burn off the coke formed on the catalyst.

RESULTS AND DISCUSSION

Characterization of the Black Liquors. Table 1 shows the water, inorganics and organics present in the 6 different black liquors used in this study. For eucalyptus hardwood the organic fraction is a mixture of lignins (80%) and (oxidized) (hemi)cellulose (20%). In general the water content of all black liquors used is between 26% and 35% and the organic content between 33% and 42%. Of relevance is the high amount of inorganics, which may have an effect on catalyst activity and particularly stability (due to irreversible zeolite deactivation), and even be catalysts by themselves.

In Situ Catalytic Pyrolysis of Black Liquor. *Effect of Water, Particle Size, and Distribution of the Catalyst (Homogeneous/Heterogeneous (Top-Layered)) on the Yield of BTX for In Situ Catalytic Pyrolysis of Black Liquors.* Our screening started with a black liquor originating from a Kraft process using Eucalyptus wood as the feed. Three different catalysts (H-ZSM-5 (23), H-ZSM-5 (50), and mordenite, in 20-fold weight excess on black liquor) were explored to determine the effect of water content and the particle size of the black liquor source and the distribution of the catalyst in the sample (homogeneous/heterogeneous (top-layered)) on the yield of BTX for in situ catalytic pyrolysis. To investigate the effect of water and particle size, the black liquor as received from the paper mill, freeze-dried black liquor and freeze-dried black liquor that was sieved (particle size <150 μm) before testing were used. Furthermore, two mixing procedures of catalyst-freeze-dried black liquor were tested, namely, (i) where the black liquor was homogeneously mixed with the catalyst

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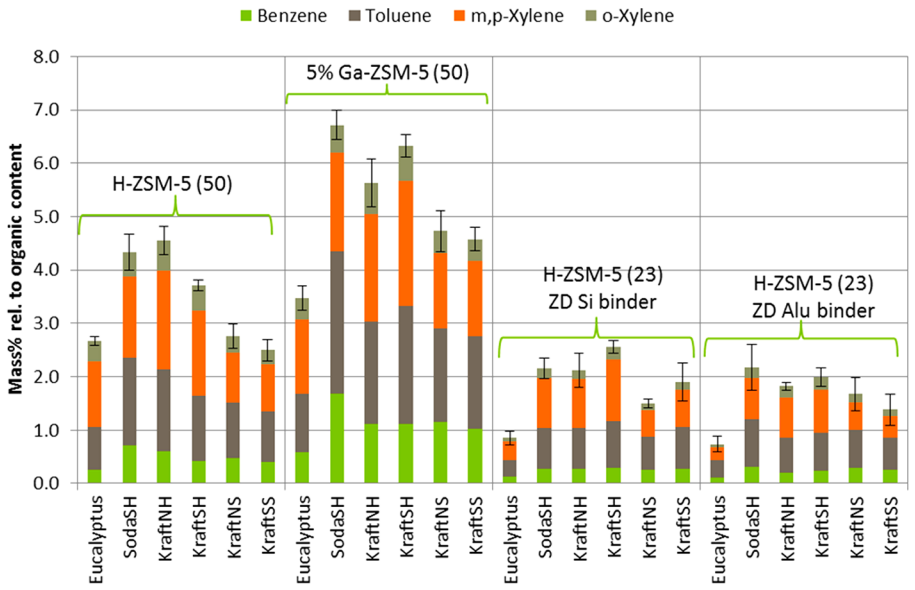

Figure 4. BTX yields for in situ catalytic pyrolysis of several black liquors

and (ii) where the catalyst was placed on top of the black liquor.

Experiments were performed in a PTV-GC/MS and a typical GC chromatogram of an experiment is shown in Figure 1. It clearly shows the formation of substituted low molecular weight aromatics, including benzene, toluene and xylenes. Besides these aromatics, it shows the presence of higher substituted polycyclic aromatics. Almost no phenols or other oxygen-containing compounds were present and the zeolite catalyst is thus clearly able to deoxygenate almost all organic vapors being formed in the pyrolysis process and to convert it to aromatics under the conditions used. Within this setup, mass balances are far from complete and not included are char formation, formation of gas phase components and higher molecular weight aromatics. The latter are insufficiently volatile and thus not detectable using gas chromatography.

The BTX yields are depicted in Figure 2 and show the yields based on the organic content of the Eucalyptus black liquor fraction used. The highest BTX yields were obtained using the H-ZSM-5 (50) catalyst whereas the yields were lowest for the mordenite catalyst. In general the selectivity for the lower molecular weight aromatics follows the trend xylenes > toluene > benzene. A broader screening of catalyst will be reported in the next paragraph.

Furthermore, it was observed, that the yields (based on the organic fraction of the black liquors) for the as received black liquors were higher compared to black liquors that were freeze-dried before pyrolysis. This is clearly illustrated when comparing the BTX yields for the best catalyst (H-ZSM-5 (50)) in the series *viz.*, 2.80% with the as received black liquor, and 1.90−2.25% for the various freeze-dried substrates. The presence of water may possibly lead to a more efficient breakdown of the biopolymers or prevents repolymerization. As such, the black liquor as received (including water) from the paper mill was used as the starting material for further studies.

In Situ Catalyst Screening Studies Using As Received Eucalyptus Black Liquor. On the basis of the initial screening experiments described in the previous section, a more extended in situ catalyst screening study was conducted using a PTV GC-MS micro reactor with ZSM-5 based catalysts and as received "wet" black liquor from Eucalyptus wood. The final temperature of the pyrolysis reactor was set at T = 550 °C, the ramping rate was at T = 20 °C/s and the catalyst/biomass ratio (C:B) was 20. Figure 3 shows the yields of BTX for the set of catalysts screened. The ZSM-5 series have highest potential for preparation of BTX. As such, the pore size of this catalyst (5.4−5.6 Å) is likely the best for aromatization of small organic fragments originating from the (oxidized) carbohydrate fraction of black liquor and for the deoxygenation of phenols, resulting from the lignin fraction, toward BTX.[26] The acidity of the catalyst seems to have an optimum for H-ZSM-5 (50), as lower yields of BTX are obtained using a more acidic (H-ZSM-5 (23) and less acidic (H-ZSM-5 (80) and H-ZSM-5 (280)) catalyst. In line with this observation is that the Na salt of some of the catalysts used were inactive.

Experiments with the metal-impregnated catalyst (Ga-ZSM-5 (50), slightly increased the yield of BTX to 3.25%. The Ga-ZSM-5 (23) afforded slightly lower yields but also in this case the yield is higher compared to the H-ZSM-5 (23) catalyst. The yields for the Zn- and Mo-ZSM-5 (23) catalysts are in line with the nonmetal impregnated zeolite and thus these metals do not seem to have a beneficial effect on BTX formation. In general the selectivity between the individual aromatics is in the order xylenes > toluene > benzene.

In Situ Catalytic Pyrolysis with Best Catalysts Using Various Black Liquors. To investigate the influence of the composition of the feedstock on BTX yield, black liquors of different sources (eucalyptus hardwood, soda southern hardwood, Kraft northern hardwood, Kraft southern hardwood, Kraft northern softwood, Kraft southern softwood) were used and screened for the in situ pyrolysis with the best catalysts H-ZSM-5 (50) and Ga-ZSM-5 (50). As commercially used zeolite catalysts are most often embedded in a matrix we also studied the results for the pyrolysis of black liquors using a commercially spray-dried catalyst containing a zeolite (H-ZSM-5) catalyst and H-ZSM-5 (23) coated on a commercial spray-dried aluminum-based binder (SD binder) for BTX formation (see Figure 4).

Highest BTX yields for most of the black liquors are observed for the Ga-ZSM-5 (50) catalyst. Depending on the

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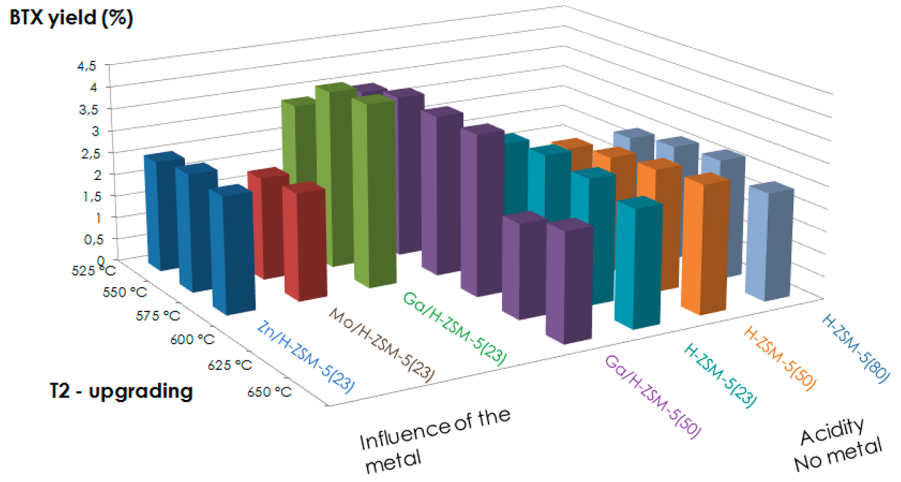

Figure 5. BTX yields for ex situ catalytic pyrolysis of black liquor (eucalyptus hardwood, based upon organic content, T_1 = 500 °C).

feedstock, the yields of BTX vary between 3.25 and 6.75%, based upon organics in the feed. The yields of BTX for Eucalyptus hardwood are slightly lower than for the other black liquors. This may be due to an aging effect as in this case the feed stock was already stored for >1 year, whereas the other sources were screened within 1 month after production in the paper mill. Furthermore, it seems that black liquors originating from hardwood paper mills give higher yields of BTX compared to black liquors from softwood paper mills for in situ catalytic pyrolysis. This finding does not match the trends observed for the in situ catalytic pyrolysis of purified lignins with H-ZSM-5 catalysts,[27−32] where softwood lignins (more guaiacyl units) results in a higher yield of aromatics than hardwood lignin (more syringyl units). It is well possible that other factors such as the composition of the black liquors (amounts of carbohydrates, inorganic salts, sulfur containing compounds, molecular weight of the lignins/carbohydrates), partly related to the feed composition and partly to the process conditions applied in the paper mill, play a role in the catalytic conversion and have a larger influence than only the guiacyl/syringyl ratio of the lignin fraction. Extended quantitative studies, beyond the scope of the current study, will be required to draw definite conclusions.

In all cases the selectivity toward the individual aromatics is almost similar and in the range benzene < toluene = xylenes, though in the case of Ga-ZSM-5 (50) the ratio of benzene is slightly increased. The yields obtained are in the range with a previous in situ pyrolysis studies for 4 different lignins as performed by Mullen et al. (5−7%). However, in this case the Al/Si ratio and thus the acidity of the ZSM-5 catalyst was not reported.[33]

Ex Situ Pyrolysis of Black Liquor. It is well-recognized that one of the main disadvantages of an in situ catalytic pyrolysis of biomass is the potential irreversible deactivation of the acidic zeolite catalyst by inorganic cations (Na^+, K^+, Ca^{2+}) present in the feed stock.[34] As black liquor, originating from a paper mill, contains high amounts sodium and potassium, this may lead to a reduction of the acidity of the zeolite catalyst by H^+/metal cation exchange, resulting in a lower conversion toward aromatics. Though this is not relevant for our experiments performed in the PTV, in which we use excess catalyst, it strongly becomes an issue if the process is scaled-up and the amount of catalyst is lowered significantly. In an ex situ process the pyrolysis is separated from the catalytic aromatization step, thereby avoiding direct contact between biomass and the catalyst. Especially using black liquors as a feed stock, the latter approach has more potential to be of commercial interest.

Ex Situ Pyrolysis in a Tandem micro-Reactor (TMR). A Tandem micro-Reactor (TMR) is especially suited to study the ex situ pyrolysis of biomass feedstocks. It consists of two independent reactors that can be fed with the biomass (reactor 1) and catalyst (reactor 2). Under an inert helium stream (51 mL/min) the organic vapors obtained during pyrolysis (heating rate = 50−70 °C/min.) are transported to the catalyst (cat: BL ratio = 70) where, depending on the catalyst and conditions used, aromatization is to occur.

In an initial study, the effect of the temperature of the pyrolysis reactor (T_1) on the BTX yield was studied. For the ex situ pyrolysis of Eucalyptus hardwood, the effect of T_1 within the range of T = 400−600 °C on the BTX yields was negligible. Wang and co-workers reported the same results for the ex situ catalytic pyrolysis of hybrid poplar toward aromatics and olefins and described this to two counteracting processes. Increasing pyrolysis temperatures favor the formation of small organic oxygen-containing fragments able to enter the pores of the zeolite catalyst whereas on the other hand higher temperatures result in an increased formation of small gas phase components and particularly carbon oxides.[35]

The effect of the temperature of the aromatization reactor (T_2) on the yield of BTX was investigated for a number of catalysts and black liquor sources. The temperature of the pyrolysis reactor (T_1) was set at 500 °C. For Eucalyptus hardwood black liquor, highest yields of BTX were obtained using Ga-impregnated H-ZSM-5 (50) and H-ZSM-5 (23) at aromatization temperatures of T = 550−600 °C (Figure 5). The yields (about 3.5%) are in line with the values observed for the in situ catalytic pyrolysis. The impregnation of the catalysts with gallium not only effects the Bronsted acidity of the catalysts but it is also known that it positively influences the deoxygenation/decarbonylation of phenols and is able to aromatize aliphatics/olefins, in our case originating from remaining carbohydrates and the aliphatic backbone of the lignin framework of black liquor.[36] For the nonimpregnated ZSM-5 analogues (23, 50, 80) the yields of BTX are almost similar (T = 600−625 °C) but at lower temperatures higher Si−Al ratio's (lower acidity) result in lower yields of BTX.

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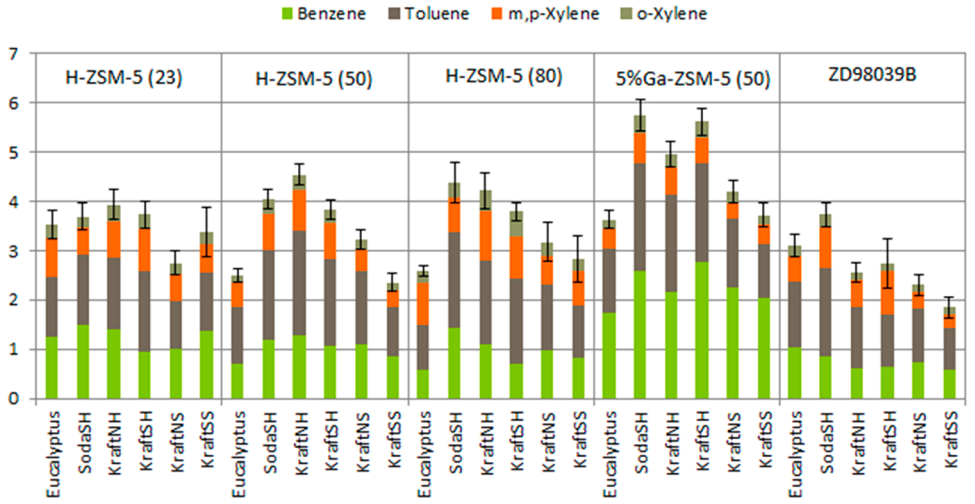

Figure 6. Influence of the black liquors feed and catalysts on the individual yields of aromatics for ex situ catalytic pyrolysis of black liquor (based upon organic content, T_1 = 500 °C, T_2 = 600 °C).

GC-MS confirms the formation of a complex mixture of substituted aromatics, including BTX. Almost no phenols or small organic acids are present and it can be concluded that almost full deoxygenation occurs under the prevailing reaction conditions.

The influence of the source of the black liquor on BTX yield is depicted in Figure 6. Highest yields of BTX were obtained for the ex situ pyrolysis of black liquor from hardwoods using a Ga-ZSM-5 (50) catalyst (T_1 = 500 °C, T_2 = 600 °C). The results obtained are slightly lower than the in situ pyrolysis but also in this case it seems that hardwood black liquors result in higher yields of BTX than softwood analogs.

The ratio between the individual aromatics is slightly dependent on the conditions and catalyst used and in general seems to be toluene > benzene > xylenes but in the case of the Ga-impregnated catalysts higher amounts of benzene are formed.

DISCUSSION

The advantage of an ex situ process is that it can more easily be integrated in a paper mill as the residual char obtained after pyrolysis can be (co)fed to the recovery boiler. In this way the inorganics present in the char phase can be recycled to the paper mill and the char may be used for energy generation. The ex situ catalytic pyrolysis thus seems applicable for implementation in paper mills without a major disturbance of the overall pulping process.

To the best of our knowledge, the catalytic pyrolysis of black liquor to BTX is not reported in the open literature. This makes it difficult to compare our results with other research in this field. Most relevant for our work are studies performed with lignin, as this is the main organic fractions in black liquor. Recently, Zhou and co-workers reported the ex situ pyrolysis of lignin over a H-ZSM-5 catalyst.[37] Though almost full deoxygenation toward aromatics was observed, the isolated yield of the bio-oil obtained was rather low (5.7 wt %, based on organics). The authors mentioned that the low yields partly originate from inefficient condensation of the low molecular weight aromatics formed. Also the amount of BTX present in the bio-oil was not determined accurately. The catalytic upgrading suffered from thermal char and also coke formation on the catalyst. In their setup, a noncatalytic pyrolysis, afforded an oxygen-rich bio-oil in a yield of 28 wt %.

The group of Prins reported the ex situ pyrolysis of pine wood with a ZSM-5 catalyst and compared the yield of liquid product formed for the ex situ pyrolysis (20.2 wt %), the in situ pyrolysis (20.6 wt %) and a noncatalytic reaction (about 38 wt %).[38] In both the in situ and ex situ pyrolysis, the liquid phase mainly consisted of a mixture of phenols and aromatics, showing that the oxygen removal is not complete. We have also compared the yields for the in and ex situ catalytic pyrolysis for various black liquor sources and the best catalyst in the series (H-ZSM-5 (50) and Ga-ZSM-5 (50), see Figures 3 and 4). The results are given in Figure 7 and show that the BTX yields for in- and ex-situ approach do not differ significantly. These findings are in line with the results from Prins et al.[38]

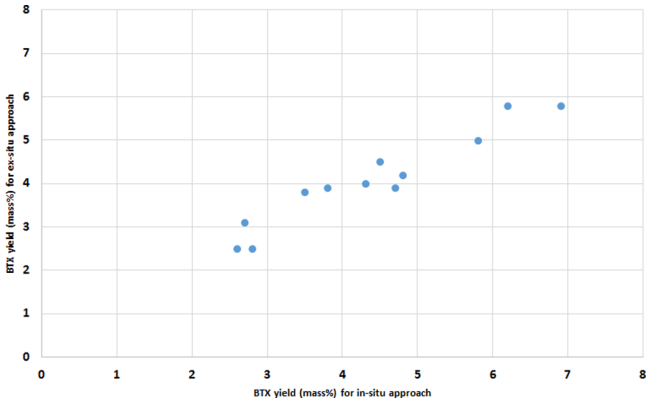

Figure 7. Comparison of the BTX yields for the in and ex situ approach using various black liquor sources and H-ZSM-5 (50) and Ga-ZSM-5 (50) as the catalyst.

Reaction Pathways. The mechanism for the conversion of the phenolics toward aromatics is still under debate. It seems likely that at first methoxy groups are cleaved by the high temperature and acidity of the catalyst. As most of the monomers of lignins consist of syringyl (S) and guaiacyl units (G) and to a lesser extent of *p*-hydroxphenyl units (H), this results in a mixture of mainly catechols/pyrogallols.[39] It is well-known that these intermediates are less stable than phenols and

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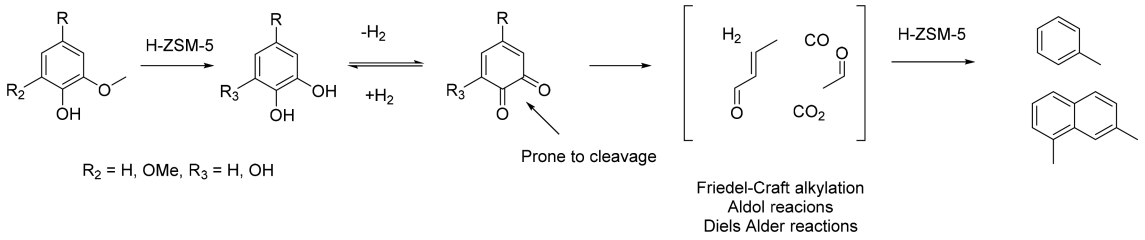

Figure 8. Proposed mechanism for the catalytic pyrolysis/aromatization of lignins.

may defragment under the harsh conditions, via the corresponding quinones, in smaller units, able to enter the pores of the zeolite catalysts where the actual aromatization takes place (see Figure 8).[40] However, this does not seem to be the end point of the reaction and further reaction with small organic fraction (Friedel Craft alkylations, Diels–Alder, aldol condensations, etc.) toward higher substituted aromatics occurs.

Catalyst Deactivation-Regeneration Studies Using H-ZSM-5 (23). The lifetime of the zeolite catalysts is one of the key parameters in the commercial exploitation of catalytic pyrolysis of black liquors. Deactivation owing to coke formation is known to be severe, though reversible as the coke can easily be removed/gasified at high temperatures in the presence of oxygen. Though the direct contact between biomass and catalyst is avoided in the ex situ pyrolysis of black liquors approach, the catalyst still might suffer from irreversible deactivation owing to the formation of aerosols in the vapor phase after the primary pyrolysis process containing some of the inorganic salts,[41] fouling and attrition. To test the irreversible deactivation of the catalyst, eucalyptus black liquor was repeatedly ex situ pyrolyzed using one catalyst batch in the TMR. Between each experiment oxygen was introduced in the system to burn off the coke formed on the catalyst, to be able to distinguish between reversible (by coke) and irreversible deactivation. After each run fresh black liquor was introduced in the pyrolysis chamber. Figure 9 shows that even after 100

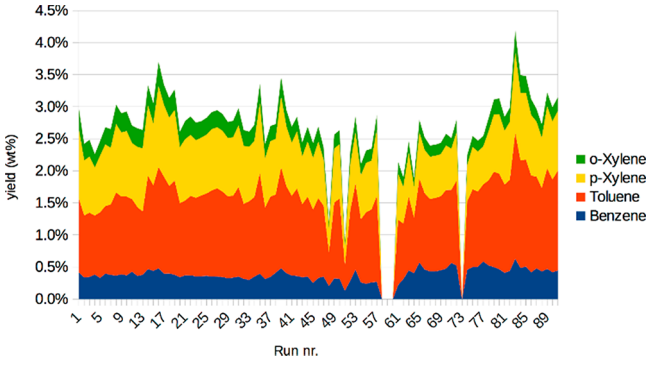

Figure 9. Catalyst stability studies (H-ZSM-5 (23)) for the ex situ pyrolysis of black liquor with intermediate oxidative catalyst regeneration.

experiments the catalyst is still active and the yield of BTX and the ratio of the individual aromatics remains similar. This preliminary experiment indicates that (i) reversible deactivation is not a major issue and the coke formed during reaction may be burned off easily and (ii) irreversible deactivation also does not occur to a significant extent. As such, entrainment of metals from the pyrolysis reactor to the aromatization reactor, for example, in the form of aerosols, seems not to be a major issue.

CONCLUSIONS

The potential for the production of green aromatics from concentrated black liquors from paper mills was screened using microscale reactors using both in situ and ex situ catalytic pyrolysis. Our screening program showed that acidic, preferably gallium impregnated, H-ZSM-5 catalysts afforded BTX in yields of about 5–7 wt % based on the organic fraction present in the black liquor. The yields were slightly dependent on the source of the black liquors and somewhat higher yields were obtained for black liquors originating from hardwood converting paper mills. No significant differences were observed in the BTX yields for the in situ and ex situ approach. However, from an industrial point of view the ex situ pyrolysis of black liquor seems preferred as this prevents catalyst deactivation by inorganics in the black liquor feed. The attractiveness of an ex situ process is supported by the observation that significant deactivation of the catalyst for the ex situ process was not observed (TMR) and after 100 experiments with intermittent oxidative regeneration to burn of the coke, the catalyst remained the same activity/selectivity.

In subsequent studies the ex situ pyrolysis of black liquor will be scaled-up to obtain higher amounts of product for full analyses and to determine the overall mass balances. This, together with further investigations regarding the stability of the catalyst during the process, should provide the information about the commercially attractiveness of the conversion of black liquor toward green aromatics.

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Notes

The authors declare no competing financial interest.

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