In situ upgrading of whole biomass to biofuel precursors with low average molecular weight and acidity by the use of zeolite mixture†

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The pyrolysis of whole biomass—pine wood and bark—with mordenite (M), beta (b) and Y zeolites has been examined at 600 °C. The GPC results indicated that the pyrolysis oils upgraded by Y and b zeolites have a very low average molecular weight range (70 – 170 g mol^{-1}). Several NMR methods have been employed to characterize the whole portion of pyrolysis products. After the use of these two zeolites (Y and b), the two main products from the pyrolysis of cellulose—levoglucosan and HMF—were eliminated; this indicates a significant deoxygenation process. When a mixture of zeolites (Y and M) was used, the upgraded pyrolysis oil exhibited advantages provided by both zeolites; this pyrolysis oil represents a biofuel precursor that has a very low average molecular weight and a relatively low acidity. This study opens up a new way to upgrade pyrolysis oils by employing mixtures of different functional zeolites to produce biofuel/biochemical precursors from whole biomass.

Introduction

The increasing total world energy consumption[1] and the growing concerns of CO_2 emissions from petroleum have reinvigorated interest in renewable energy sources, including biomass.[2,3] As an abundant wood species in the southeastern United States, loblolly pine (*Pinus taeda*) has been used in various industries.[4] Harvesting of loblolly pine provides significant amounts of residues (*e.g.*, limbs, stumps, dead trees, and tops) and bark, which represent a potential source of biofuels and bio-based chemicals.[5] Pyrolysis is an efficient way to utilize these residues for bio-fuels and bio-based chemicals. However, the produced liquid products (pyrolysis oil) always have some challenging properties, including considerably higher molecular weight, oxygen content, acidity, and viscosity, than petroleum fuels.[6,7] Therefore, the upgrading processes for pyrolysis oil have to be accomplished before their further application as fuel.

Traditional upgrading processes, including hydrogenation (HYD), hydrodeoxygenation (HDO), and selective ring opening (SRO), are necessary to convert oxygenated biomass derived intermediates (biofuel precursors) to drop-in biofuels. However, the pyrolysis oils typically contain hundreds of compounds, many of which cannot be upgraded by the traditional HYD, HDO, and SRO techniques. High molecular weight, oxygen content and high acidity are the major barriers for the further upgrading processes of pyrolysis oils. Therefore, one-step thermochemical conversion (*in situ* upgrading) of biomass to low average molecular weight liquid products with low acidity and oxygen content, which could be used as an ideal biofuel precursor, appears to be very attractive.

As a promising type of additives, zeolites could provide *in situ* improved properties of pyrolysis oils during the thermal treatment. For example, Huber's groups investigated the applications of ZSM-5 zeolites to upgrade biomass pyrolysis products into aromatics and olefins.[8,9] Uzun *et al.* and Zhang *et al.* investigated the catalytic pyrolysis process for corn stalks by employing ZSM-5 and Y zeolites.[10,11] Decreased oxygen content and improved higher heating value (HHV) of upgraded pyrolysis oil were observed. The production of aromatics also has been shown to increase with the use of Y zeolite. Pattiya *et al.* studied the influence of various zeolites on the pyrolysis processing of cassava rhizome.[12,13] The use of Criterion-534, Al-MSU-F, and ZSM-5 additives was found to improve the formation of aromatic hydrocarbons and phenols. An increased amount of acetic acid has been reported with most of the tested zeolites in Pattiya's study. Catalytic pyrolysis of poplar by ZSM-5 zeolite also has been reported by Agblevor *et al.* and Fabbri *et al.*[14,15] The upgraded liquid products exhibited reduced viscosity and

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contained abundant phenolics, but minor carbohydrate decomposition products. In addition, the content of polycyclic aromatic hydrocarbons (PAH) increased dramatically after employing ZSM-5 zeolite. Zhao et al. and Williams et al. studied the pyrolysis process for rice husks with the use of ZSM-5 zeolite.[16,17] Instead of water, CO and CO_2 were the major deoxygenation byproducts at higher catalyst temperatures (>500 °C). The upgrading of various other bio-oils from maple,[18] bamboos,[19] empty palm fruit bunches,[20] oak,[21] beech[22,23] and pine[24,25] have also been examined with different zeolites in recent years.

Ben and Ragauskas[26] investigated the influence of five different zeolites on the properties of lignin pyrolysis oil. The BEA (b) and FAU (Y) zeolites were shown to significantly improve the cleavage of ether and methoxy-aromatic bonds and produce the upgraded pyrolysis oil with low average molecular weight. Furthermore, the acidity of the upgraded pyrolysis oils was found to be decreased after the use of MOR (M), FER (F), and MFI (Z) zeolites, which may be due to the efficient decomposition of carboxyl groups; this made the resulting upgraded pyrolysis oils more suitable for their usage as fuels. Compared to the biomass components, the whole lignocellulosic biomass is more difficult to be upgraded, which is more meaningful and important for its use as the feedstock to produce fuels and chemicals.

The general goal of this study is to upgrade whole biomass (pine wood and bark) to low average molecular weight liquid products with low acidity in one step by employing a mixture of zeolites. Only about 55% of pyrolysis oils has been reported to be detected by GC and HPLC. In addition, the similar polarity and molecular weight of the components in the pyrolysis oil cause barriers for chromatography separation and subsequent MS characterization.[7] Therefore, finding alternative analytical methods, capable of characterization of all pyrolysis products, is an active research area. In particular, the use of NMR techniques to characterize pyrolysis oils is a rapidly growing field of study.[27–32] The use of HSQC-NMR (heteronuclear multiple quantum correlation-nuclear magnetic resonance) could provide a detailed analysis for the whole portion of bio-oils. Another powerful method, ^{31}P NMR, could provide quantitative results for various hydroxyl groups present in the pyrolysis products. Most importantly, this method could indicate the content of carboxylic acid. It has been indicated that, as one of the challenging properties of pyrolysis oils, the acidity is caused mainly (60–70%) by carboxylic acids.[33] In this study, very detailed characterizations of pyrolysis products were accomplished by GPC, ^{31}P NMR, and HSQC. The fate of all the major pyrolysis components is discussed to facilitate future upgrading pathways.

Materials and methods

All the reagents used in this study were used as received, and purchased commercially from Sigma-Aldrich (St. Louis, MO) and VWR International. Zeolites (CBV 720, CBV 21A and CP814E) were purchased from Zeolyst, Inc. Loblolly pine bark and wood were provided by a research plot in Macon, GA.[4] The wood samples were refined by a Wiley mill (0.13 cm screen), and then ball milled before drying in a high vacuum oven at 50 °C for 48 h. The biomass samples were stored at ~0 °C until further experiments.

Table 1 SiO_2/Al_2O_3 mole ratio, framework, pore size and code name of each zeolite used in this work[26,34]

	CP814E	CBV 720	CBV 21A
SiO_2/Al_2O_3 mole ratio	25	30	20
Framework	BEA	FAU	MOR
Code name	b	Y	M
Pore size (Å)	6.6 × 6.7; 5.6 × 5.6	7.4 × 7.4	6.5 × 7.0; 2.6 × 5.7

Preparation of pyrolysis samples

Different types of (CBV 720, CBV 21A and CP814E) zeolites were employed as the *in situ* additives in this study. All the zeolite samples were pre-activated in a furnace at 500 °C under N_2 for 6 h. All the pyrolysis samples were prepared by mixing ball milled biomass with active zeolites at a ratio of 1 : 1 (wt : wt) under nitrogen at room temperature. Table 1 shows the basic information of each zeolite used in this study.

Process and equipment of pyrolysis

The pyrolysis equipment and process have been reported in the previous study.[27] Briefly, the pyrolysis system has been shown in Fig. S1.† The heating rate (~3 °C s^{-1}) was monitored by a K-type thermocouple, which was immersed in the sample powder during the pyrolysis process. Normally, two immiscible phases in the liquid pyrolysis products have been denoted as heavy (organic and bottom phase) and light (aqueous and top phase) oils. The yield for solid product, char, was gravimetrically measured, and the gas products were determined by mass difference.

Characterization of heavy oils by GPC

The weight average molecular weight (M_w) and number average molecular weight (M_n) of the heavy oils were determined by GPC analysis following a reported method.[27] Briefly, 1 mg mL^{-1} of the pyrolysis oil samples was dissolved in tetrahydrofuran (THF). A Polymer Standards Service (PSS) Security 1200 system powered by an Agilent HPLC vacuum degasser, refractive index (RI) analyzer, UV detector (270 nm), and isocratic pump was employed for GPC measurement. THF was used as the mobile phase (1.0 mL min^{-1}) in four Waters Styragel columns (HR0.5, HR2, HR4, and HR6). M_w and M_n were calibrated against a series of polystyrene standards (7210, 4430, 1390, and 580 Da), dioctyl-phthalate, 2,2′-dihydroxy-4,4′-dimethoxyl-benzophenone, 2-phenyl-hydroquinone, phenol and acetone.

Characterization of pyrolysis products by NMR

Characterization of whole portion of pyrolysis products by HSQC-NMR. The detailed parameters for HSQC-NMR have been reported in a previous study.[28] In general, a solution of 100.0 mg/450 mL pyrolysis oil (both heavy and light oils combined)/DMSO-d_6 has been examined by "hsqcetgpsi.2", which is a standard Bruker pulse sequence. HSQC-NMR data were processed by the default template in MestReNova v7.1.0.

Characterization of pyrolysis products by ^{31}P-NMR. The method for quantitative ^{31}P-NMR measurement of pyrolysis oils has been reported in the literature.[27] Typically, the reaction of 10.0 mg of heavy oil with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) was conducted in a pyridine/$CDCl_3$ (1.6 : 1 v/v) solution. Chromium acetylacetonate was used as a relaxation agent, and endo-N-hydroxy-5-norbornene-2,3-dicarboximide was employed as the internal standard.

Results and discussion

The b and Y types of zeolite have been reported[26] to have the ability to upgrade lignin to low average molecular weight products in a one-step pyrolysis process. In addition, the M type of zeolite could perform better decarboxylation process for the pyrolysis of lignin. In this study, these three types of zeolites have been employed to improve the properties of whole biomass pyrolysis oils. The catalytic abilities of a mixture of Y and M types of zeolite were also examined. The yields from pyrolyzing pine wood and bark at 600 °C with these different zeolites are shown in Table 2, which indicates that the yields of light oil, char and gas increase after employing the zeolites. In contrast, the yield of heavy oil decreased after the use of zeolites. Compared to the pine bark, the yield of light oil increased more insignificantly for pine wood. The differences between the pyrolysis of two biomasses with zeolites may be due to the differences of carbohydrate content in pine wood (68.5%) and pine bark (51.0%),[4] which may exhibit different upgrading outcomes compared to those obtained from lignin and tannin.

GPC characterization of pyrolysis oils

The weight and number average molecular weights (M_w and M_n) for the upgraded pyrolysis oils are shown in Table 3. The results indicate that the weight average molecular weight decreased by 44–68% after using b and Y zeolites. The pyrolysis oils upgraded by these two zeolites have a molecular weight profile at a very low range (~80–120 g mol^{-1}). The GC-MS results (Table S1†) show that, after employing b and Y zeolites, there are considerably fewer guaiacols and catechols but more phenols in the upgraded pyrolysis oils, which indicates that a deoxygenation process has occurred. Y and b zeolites have been reported[26] to have the ability to reduce the molecular weight of lignin pyrolysis oils due to the improved cleavages of ether bonds, methoxy groups and hydroxyl groups, whereas M zeolites could perform a better decarboxylation compared to Y and b zeolites. Therefore, ideally, by employing a mixture of these two zeolites, the upgraded pyrolysis oil could exhibit advantages provided by both zeolites, which will represent a biofuel precursor with improved properties—low average molecular weight, oxygen content and acidity—for biofuel. The GPC results prove that, after using a mixture of Y and M zeolites, the molecular weight also decreased to a very low range. Furthermore, the pour point (the lowest temperature at which the liquid becomes semi solid and loses its flow characteristics) for pyrolysis oils produced from pine bark and Y zeolite upgraded pyrolysis oils were examined and the results are shown in Fig. S3 and S4.† For pine bark pyrolysis oil, the pour point is 24 °C, which is considerably higher than the normal fuels. Very interestingly, for the Y zeolite upgraded pyrolysis oil, not only the molecular weight decreased to a very low range, but the pour point also decreased to −21 °C, which is close to the pour point of diesel (−23 °C).[35] A lifetime study for the use of zeolites has also been examined. The results (Fig. S5 and S6†) show that the zeolites are almost intact after three times usage when an appropriate recovery procedure was applied.

Upgraded pine bark pyrolysis oils

To understand the detailed chemical structure of the components in upgraded pyrolysis oils, HSQC-NMR analysis of the upgraded pine bark pyrolysis oils using zeolites was examined and is shown in Fig. 1a–d. HSQC-NMR results show that the use of zeolites during pyrolysis yields a pyrolysis oil that contains some polyaromatic hydrocarbons (PAH). Compared to the Y zeolite upgraded pyrolysis oil, there are relatively more PAH in the b zeolite upgraded pyrolysis oil, which is similar to upgraded lignin pyrolysis oil[26,36] and could be evidence that the lignin component in the whole biomass should have the major

Table 2 Yields of heavy oil, light oil, gas, and char for the pyrolysis of pine wood and bark at 600 °C for 10 min with 1.0/1.0 ($W_{additive}/W_{biomass}$) ratio of zeolites as additives. The results are shown as wt%

	Light oil	Heavy oil	Char	Gas
Pine bark (PB)	20.2	30.7	34.6	14.5
PB + Y	21.6	16.1	42.0	20.3
PB + b	21.1	16.1	41.5	21.3
Pine wood (PW)	21.9	35.1	26.7	16.3
PW + Y	29.6	17.7	33.0	19.7
PW + M	29.4	24.5	27.1	19.0
PW + (Y + M)[a]	30.4	20.9	30.1	18.6

[a] A mixture of Y + M zeolites has a wt/wt ¼ 1/1.

Table 3 Weight average (M_w) and number average (M_n) molecular weight distribution of pyrolysis oils produced by the pyrolysis of pine bark (PB) and wood (PW) and pyrolysis at 600 °C for 10 min with 1.0/1.0 ($W_{additive}/W_{biomass}$) ratio of zeolites (Y, b, M, and mixture of Y and M) as additives

	M_w (g mol^{-1})	M_n (g mol^{-1})		M_w (g mol^{-1})	M_n (g mol^{-1})
PB	447	170	PW	293	119
PB + Y	145	72	PW + Y	164	76
PB + b	160	87	PW + M	208	129
			PW + (Y + M)[a]	169	91

[a] A mixture of Y + M zeolites has a wt/wt ¼ 1/1.

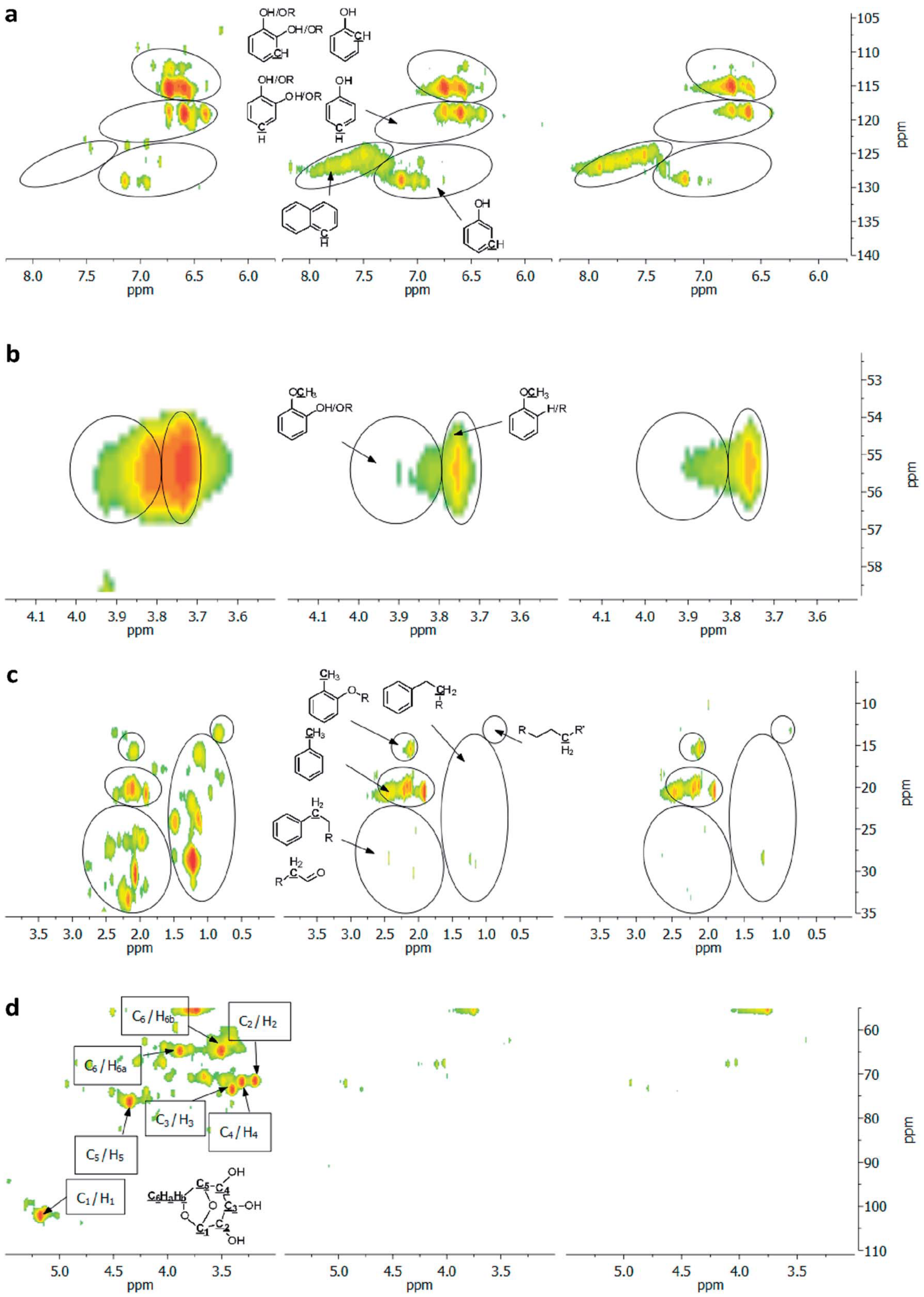

Fig. 1 (a) Aromatic C – H bonds in the HSQC-NMR spectra for the pyrolysis oils produced from PB, PB + Y and PB + b (from left to right). (b) Methoxy groups in the HSQC-NMR spectra for the pyrolysis oils produced from PB, PB + Y and PB + b (from left to right). (c) Aliphatic C – H bonds in the HSQC-NMR spectra for the pyrolysis oils produced from PB, PB + Y and PB + b (from left to right). (d) HSQC-NMR spectra and assignments for each C – H bond in the levoglucosan present in pyrolysis oils produced from PB, PB + Y and PB + b (from left to right).

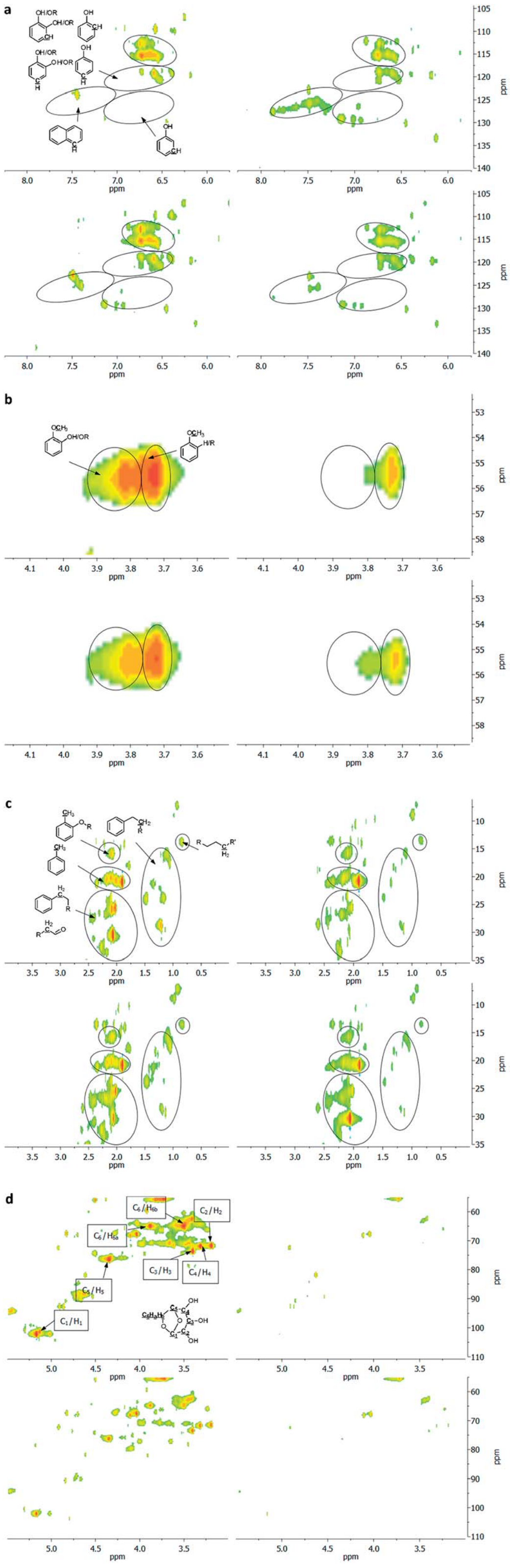

Fig. 2 (a) Aromatic C–H bonds in the HSQC-NMR spectra for the pyrolysis oils produced from PW, PW + Y, PW + M and PW + (Y + M) (from top left to bottom right). (b) Methoxy groups in the HSQC-NMR spectra for the pyrolysis oils produced from PW, PW + Y, PW + M and PW + (Y + M) (from top left to bottom right). (c) Aliphatic C–H bonds in the HSQC-NMR spectra for the pyrolysis oils produced from PW, PW + Y, PW + M and PW + (Y + M) (from top left to bottom right). (d) HSQC-NMR spectra and assignments for each C–H bond in the levoglucosan present in pyrolysis oils produced from PW, PW + Y, PW + M and PW + (Y + M) (from top left to bottom right).

responsibility for the formation of PAH. The upgraded pyrolysis oils have considerably less spectral overlap, which indicates that there are more similar and simple components in the upgraded pyrolysis oil. The original methoxy groups, which have ether bond or hydroxyl group in the ortho position, have been nearly completely decomposed after the use of b and Y zeolites during the pyrolysis. The limited amount of the remaining rearranged methoxy groups, which have no ether bond or hydroxyl group in the ortho position, in the upgraded pyrolysis oils suggests that the zeolites prefer to decompose the original methoxy group and this may be due to the fact that the hydroxyl groups in the ortho position facilitate such cleavage.[5,28] After employing zeolites, there are relatively more methyl-aromatic bonds in pyrolysis oil, which may be due to the improved decomposition of its precursor—methoxy groups; however, the cleavage of normal aliphatic C–C bonds has been improved by Y and b types of zeolite. Most interestingly, after the use of a zeolite, the main product from the pyrolysis of cellulose—levoglucosan—has been completely eliminated. In addition, another representative component—hydroxymethylfurfural (HMF)—produced from the thermal treatment of cellulose has also been completely decomposed. Huber's group[34] examined the shape selectivity of various zeolites on the properties of glucose pyrolysis products. The thermal decomposition of glucose to aromatics has been reported to be affected by the pore size of the zeolite catalysts. Using small pore-size zeolites (3.9–4.3 Å), the thermal conversion of glucose could not produce aromatics. However, employing the medium pore-size (5.2–5.9 Å) zeolites produced significant amounts of aromatic products. When large pore-size (6.6–7.4 Å) zeolites were used, lower aromatics, higher coke, and reduced oxygenated species were observed. Their conclusions about the influences of the pore size of zeolites on the pyrolysis products support the observations obtained in this study.

Upgraded pine wood pyrolysis oils

Pyrolysis oils always have higher molecular weight, acidity, oxygen content, and viscosity than the normal petroleum fuels.[7] The acidity, which is mainly derived from carboxylic acid, of pyrolysis oil has been reported to have significant impact on stability.[30,33] In this study, ^{31}P NMR was employed to examine the acidity and other hydroxyl groups in pyrolysis oils. The results, which are shown in Fig. S2,† indicate that, except for carboxylic acid, the Y type of zeolite could produce improved upgrading results (improved dehydration of aliphatic hydroxyl groups and cleavage of methoxy groups and ether bonds) compared to M zeolite. Nevertheless, the use of M zeolite could minimize the content of carboxylic acid by ∼70%, which dramatically decreases the acidity of the pyrolysis oil. Most interestingly, the upgraded pyrolysis oil obtained using the

Table 4 Dimensions of major pyrolysis components produced from pine wood and bark and lignin upgraded pyrolysis oil by employing Y zeolites [a]

Resource	Compound	x (Å)	y (Å)	z (Å)
Pine bark and pine wood pyrolysis oil	Phenol, 3-methyl- [b]	8.73	7.36	4.17
	Phenol, 2-methoxy- [b]	9.48	8.10	4.20
	Phenol, 3,5-dimethyl-	8.87	8.18	4.29
	Phenol, 2-methoxy-4-methyl- [b]	9.27	7.91	4.20
	1,2-Benzenediol [b]	7.36	7.33	3.40
	Hydroxymethylfurfural	9.20	6.76	4.71
	1,2-Benzenediol, 3-methyl- [b]	8.89	8.01	4.16
	Phenol, 4-ethyl-2-methoxy- [b]	10.70	8.05	4.20
	1,2-Benzenediol, 4-methyl- [b]	8.76	7.70	4.17
	3-Allyl-6-methoxyphenol	12.35	7.67	5.48
	1,3-Benzenediol, 4-ethyl-	10.29	7.53	4.17
	Vanillin [b]	10.19	7.33	4.19
	Isoeugenol	11.24	8.35	4.19
	Levoglucosan	8.66	8.12	5.58
	Homovanillic acid	11.48	7.66	5.41
	4-Hydroxy-2-methoxycinnamaldehyde	11.76	9.45	4.20
	2-Methoxy-4-vinylphenol	10.52	8.07	4.19
Y Zeolite upgraded lignin pyrolysis oil [c]	Phenol [b]	8.10	6.73	3.40
	Phenol, 2-methyl- [b]	8.14	7.43	4.17
	Phenol, 2,6-dimethyl-	9.17	8.01	4.18
	Phenol, 2,4-dimethyl-	9.03	7.56	4.17
	Naphthalene [b]	9.17	7.39	3.40
	Phenol, 3,4-dimethyl-	9.02	7.88	4.16
	Naphthalene, 1-methyl- [b]	9.61	8.10	4.17
	Naphthalene, 1,4-dimethyl-	9.54	9.25	4.17

[a] Molecular dimension computation accomplished by Gaussian 03 software and conducted using the default optimization algorithm at B3LYP/6-31+G* level. The van der Waals radii of the hydrogen (1.2 Å), oxygen (1.52 Å) and carbon (1.70 Å) were then corrected for the calculation of dimensions. [b] Data reported in the literature.[37] [c] The GC-MS data have been reported in our previous study.

mixture of these two zeolites exhibits the advantages provided by both zeolites.

HSQC-NMR spectra for the upgraded pine wood pyrolysis oils after the use of zeolites were also obtained, and are shown in Fig. 2a–d. The results show that, compared to the Y zeolite, M zeolite has only limited effects on the methoxy groups. However, the mixture of Y and M zeolites could produce upgrading results comparable to Y zeolite for the cleavage of methoxy groups. A similar phenomenon was also found for HMF and levoglucosan; although Y zeolite exhibits superior capability for the upgrading, the mixture of 1/1 (wt/wt) Y and M zeolites could provide ability similar to Y zeolite. In addition, using both Y and M zeolites, the two major pyrolysis products from cellulose were further decomposed; this is consistent with the ^{31}P NMR result that the aliphatic OH decreased up to 60% after the use of zeolites, indicating a significant deoxygenation process.

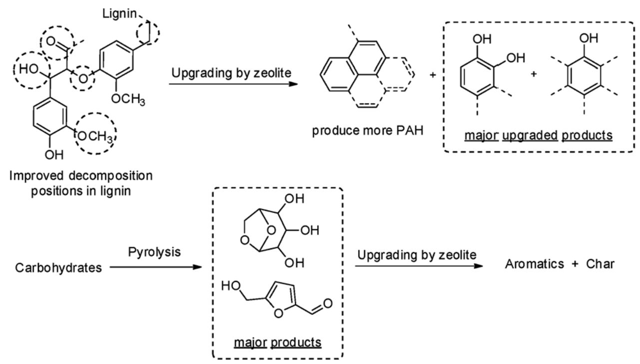

Fig. 3 Upgrading pathways for lignin and carbohydrates in the whole biomass by employing zeolites as additives during the pyrolysis process.

Possible improved decomposition pathways

To explain the possible reason that Y zeolite could provide a relatively superior upgrading result, shape selectivity has been considered. Table 4 lists the dimensions of some major components present in the pyrolysis oils. It has been found that, compared to the M zeolite, Y zeolite has a larger and a three-dimensional channel, which could allow most of the pyrolysis components to pass through and perform a better upgrading process. For ZSM-5, mordenite (M), beta (β), and Y zeolites, it has been reported that the zeolite pore structure could be enlarged by 2.5–3.4 Å at high temperatures (such as 650 °C).[37] Therefore, all the major components in the pine wood and pine bark upgraded pyrolysis oil are able to enter the pores of Y zeolite and perform a more effective conversion. A summary of major upgrading pathways for major components in the whole biomass—lignin and cellulose—using zeolites as additives during the pyrolysis process has been shown in Fig. 3.

Conclusions

After the use of Y and b zeolites, the M_w for upgraded pine wood and bark pyrolysis oils decreased by 44–68%, and they have a low average molecular weight in the range of 80–120 g mol^{-1}. A mixture of two types (Y and M) of zeolite was also studied; the upgraded pyrolysis oil exhibited advantages provided by both zeolites. This study opens up a new way to upgrade pyrolysis oils by employing mixtures of different functional zeolites to produce pyrolysis oils that have low average molecular weight and acidity.

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Notes and references

1 A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick Jr, J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer and T. Tschaplinski, Science, 2006, 311, 484–489.
2 K. David and A. J. Ragauskas, Energy Environ. Sci., 2010, 3, 1182–1190.
3 P. Sannigrahi, A. J. Ragauskas and G. A. Tuskan, Biofuels, Bioprod. Biorefin., 2010, 4, 209–226.
4 F. Huang, P. M. Singh and A. J. Ragauskas, J. Agric. Food Chem., 2011, 59, 12910–12916.
5 H. Pakdel, C. Amen-Chen and C. Roy, Can. J. Chem. Eng., 1997, 75, 121–126.
6 W. Mu, H. Ben, A. Ragauskas and Y. Deng, BioEnergy Res., 2013, 1–22, DOI: 10.1007/s12155-013-9314-7.
7 D. Mohan, C. U. Pittman and P. H. Steele, Energy Fuels, 2006, 20, 848–889.
8 T. R. Carlson, Y.-T. Cheng, J. Jae and G. W. Huber, Energy Environ. Sci., 2011, 4, 145.
9 T. R. Carlson, G. A. Tompsett, W. C. Conner and G. W. Huber, Top. Catal., 2009, 52, 241–252.
10 H. Zhang, R. Xiao, H. Huang and G. Xiao, Bioresour. Technol., 2009, 100, 1428–1434.
11 B. B. Uzun and N. Sarioğlu, Fuel Process. Technol., 2009, 90, 705–716.
12 A. Pattiya, J. O. Titiloye and A. V. Bridgwater, Fuel, 2010, 89, 244–253.
13 A. Pattiya, J. Titiloye and A. Bridgwater, J. Anal. Appl. Pyrolysis, 2008, 81, 72–79.
14 F. A. Agblevor, S. Beis, O. Mante and N. Abdoulmoumine, Ind. Eng. Chem. Res., 2010, 49, 3533–3538.
15 D. Fabbri, A. Adamiano and C. Torri, Anal. Bioanal. Chem., 2010, 397, 309–317.
16 Y. Zhao, L. Deng, B. Liao, Y. Fu and Q.-X. Guo, Energy Fuels, 2010, 24, 5735–5740.
17 P. T. Williams and N. Nugranad, Energy, 2000, 25, 493–513.
18 J. D. Adjaye and N. N. Bakhshi, Fuel Process. Technol., 1995, 45, 161–183.
19 W. Y. Qi, C. W. Hu, G. Y. Li, L. H. Guo, Y. Yang, J. Luo, X. Miao and Y. Du, Green Chem., 2006, 8, 183.
20 M. Misson, R. Haron, M. F. Kamaroddin and N. A. Amin, Bioresour. Technol., 2009, 100, 2867–2873.
21 S. Vitolo, M. Seggiani, P. Frediani, G. Ambrosini and L. Politi, Fuel, 1999, 78, 1147–1159.
22 E. F. Iliopoulou, E. V. Antonakou, S. A. Karakoulia, I. A. Vasalos, A. A. Lappas and K. S. Triantafyllidis, Chem. Eng. J., 2007, 134, 51–57.
23 S. Stephanidis, C. Nitsos, K. Kalogiannis, E. F. Iliopoulou, A. A. Lappas and K. S. Triantafyllidis, Catal. Today, 2011, 167, 37–45.
24 B. Valle, A. G. Gayubo, A. S. T. Aguayo, M. Olazar and J. Bilbao, Energy Fuels, 2010, 24, 2060–2070.
25 A. Atutxa, R. Aguado, A. G. Gayubo, M. Olazar and J. Bilbao, Energy Fuels, 2005, 19, 765–774.
26 H. Ben and A. J. Ragauskas, RSC Adv., 2012, 2, 12892–12898.
27 H. Ben and A. J. Ragauskas, Energy Fuels, 2011, 25, 2322–2332.
28 H. Ben and A. J. Ragauskas, Energy Fuels, 2011, 25, 5791–5801.
29 H. Ben and A. J. Ragauskas, Green Chem., 2012, 14, 72–76.
30 H. Ben and A. J. Ragauskas, ChemSusChem, 2012, 5, 1687–1693.
31 F. Huang, S. Pan, Y. Pu, H. Ben and A. J. Ragauskas, RSC Adv., 2014, 4, 17743–17747.
32 K. David, H. Ben, J. Muzzy, C. Feik, K. Iisa and A. Ragauskas, Biofuels, 2012, 3, 123–128.
33 A. Oasmaa, D. C. Elliott and J. Korhonen, Energy Fuels, 2010, 24, 6548–6554.
34 J. Jae, G. A. Tompsett, A. J. Foster, K. D. Hammond, S. M. Auerbach, R. F. Lobo and G. W. Huber, J. Catal., 2011, 279, 257–268.
35 H. Joshi, B. R. Moser, J. Toler, W. F. Smith and T. Walker, Biomass Bioenergy, 2011, 35, 3262–3266.
36 H. Ben and A. J. Ragauskas, ACS Sustainable Chem. Eng., 2013, 1, 316–324.
37 Y. Yu, X. Li, L. Su, Y. Zhang, Y. Wang and H. Zhang, Appl. Catal., A, 2012, 447–448, 115–123.