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PAPER

Catalytic upgrading of bio-oil using 1-octene and 1-butanol over sulfonic acid resin catalysts

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Raw bio-oil from fast pyrolysis of biomass must be refined before it can be used as a transportation fuel, a petroleum refinery feed or for many other fuel uses. Raw bio-oil was upgraded with the neat model olefin, 1-octene, and with 1-octene/1-butanol mixtures over sulfonic acid resin catalysts from 80 to 150 °C in order to simultaneously lower water content and acidity and to increase hydrophobicity and heating value. Phase separation and coke formation were key factors limiting the reaction rate during upgrading with neat 1-octene, although octanols were formed by 1-octene hydration along with small amounts of octyl acetates and ethers. GC-MS analysis confirmed that olefin hydration, carboxylic acid esterification, acetal formation from aldehydes and ketones and O- and C-alkylations of phenolic compounds occurred simultaneously during upgrading with 1-octene/1-butanol mixtures. Addition of 1-butanol increased olefin conversion dramatically by reducing mass transfer restraints and serving as a cosolvent or emulsifying agent. It also reacted with carboxylic acids and aldehydes/ketones to form esters and acetals, respectively, while also serving to stabilize bio-oil during heating. 1-Butanol addition also protected the catalysts, increasing catalyst lifetime and reducing or eliminating coking. Upgrading sharply increased ester content and decreased the amounts of levoglucosan, polyhydric alcohols and organic acids. Upgrading lowered acidity (pH value rise from 2.5 to >3.0), removed the unpleasant odor and increased hydrocarbon solubility. Water content decreased from 37.2% to <7.5% dramatically and calorific value increased from 12.6 MJ kg^{-1} to about 30.0 MJ kg^{-1}.

1. Introduction

Biomass is a carbon-neutral renewable energy resource. It is relatively cheap and available in large quantities.[1] Lignocellulosic biomass from plants is the most abundant form of biomass and does not directly compete with human food uses and animal feed stocks.[2] Fast pyrolysis of lignocellulosic biomass can yield 60–75% liquid bio-oil, with the potential to produce biofuels or valued chemicals.[2,3] However, the crude bio-oil must be upgraded or blended to be used as transportation fuels in engines because of its low heating values, high corrosiveness, thermal instability and immiscibility with crude-oil-based fuels. These problems are due to the presence of large amounts of water, organic acids, phenols, aldehydes, anhydrosugars, furan derivatives, *etc.*[4,5]

Currently, the most actively pursued approaches for bio-oil upgrading are hydrodeoxygenation (HDO), zeolite upgrading and steam-reforming.[6,7] However, these methods need temperatures from 300 to 800 °C where coke and tar formation is fast and results in catalyst deactivation and reactor clogging.[3,8] HDO can remove most of the oxygen but it requires high pressures and, most importantly, huge quantities of hydrogen to remove the 35–50% oxygen, typically present in bio-oil.[6,7] An alternative approach is partial bio-oil refining to combustible and stable oxygen-containing organic fuels where oxygen is not fully removed. This allows more or all of the bio-oil's original caloric value to remain in the product. For example, upgrading by mixing and reacting bio-oil with alcohols can convert reactive organic acids and aldehydes to esters and acetals, respectively, further improving the product properties significantly but these reactions produce water.[9–15] The use of excess alcohol and water removal is required to drive both of these equilibrium reactions. Reactive adsorption and reactive distilling have been applied for this purpose.[16–19]

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A neglected approach is the addition of -OH functions across olefins, taught in every first year organic chemistry course (*e.g.* acid-catalyzed olefin hydration). Upgrading by acid-catalyzed addition of carboxylic acids, phenolic hydroxyls, alcohols and water across olefins could form less hydrophilic, higher fuel value products without generating water. Olefin hydration would remove or reduce water rather than generate it as in esterification with alcohols. Indeed, we demonstrated that bio-oil model compound mixtures reacted with olefins.[20,21] The feasibility of simultaneously adding water, carboxylic acids, alcohols, phenols and water across olefins was demonstrated.[20,21] This will be an extremely complex system requiring extensive process development in order to apply olefinations to raw bio-oil. However, under acid-catalyzed conditions, olefins can react individually and simultaneously with carboxylic acids, water, phenol and alcohols at low temperatures (60–125 °C), opening the possibility for bio-oil upgrading process development.[20,21] Key challenges to solve include phase separation, reaction kinetics and catalyst deactivation.

In this paper, raw bio-oil was upgraded by reaction with the model olefin, 1-octene, and with 1-octene/1-butanol co-solvent mixtures over sulfonic acid resin catalysts at temperatures between 80 and 150 °C. Combined upgrading with 1-octene/1-butanol was particularly promising. The commercial sulfonic acid resin, Dowex50WX2 was employed as the heterogeneous acid catalyst and Amberlyst70, Amberlyst15 and Nafion NR50 were used for comparison. Dowex50WX2 was previously demonstrated to be a more water-tolerant catalyst than Amberlyst15.[21] Amberlyst70 is a new macroporous chlorinated styrene/divinylbenzene resin catalyst with a high thermal stability which is well suited for olefin hydration, esterification and aromatic alkylation processes.[22] 1-Octene was selected because its C8 chain length is representative of the naphtha range olefins and its boiling point (bp. 121–122 °C) facilitated its use in laboratory glassware at low pressures.[23] However, in general, any olefin (C3 to higher olefins) or their mixtures can be used. 1-Butanol was selected as both a reactant and cosolvent. 1-Butanol has been targeted as a future biofuel by Dupont and British Petroleum *via* cellulose conversion from genetically modified organisms.[24] Its high heating value, higher solubility in hydrocarbons and lower hydrophilicity are advantages over ethanol. Ethanol, 2-propanol, iso-butanol and *tert*-butanol were used for comparison.

2. Experimental

2.1 Chemicals

All the chemicals were used without further purification unless otherwise noted. Four commercial cation-exchange resins, Dowex50WX2, Amberlyst70, Amberlyst15 and Nafion NR50 were purchased from Sigma–Aldrich. All the three catalysts were dried at 105 °C for 3 h before use. The physical properties of the catalytic resins are listed in Table 1.

2.2 Bio-oil production and characterization

Crude bio-oil was obtained by fast pyrolysis of pine chips at 450 °C in an auger-fed reactor, at Mississippi State University. The specific operating conditions have been reported.[25] The water content of this bio-oil was 37.2 wt%. The water content of samples was determined by Karl–Fisher titration (ASTM D1744) using a Cole–Parmer model C-25800-10 titration apparatus. Bio-oil pH values were determined in water using a method similar to those used for wood or soil. Bio-oil (1.00 g) was stirred with water (50 ml). The pH of the water was recorded using a calibrated pH meter model pH 11 (Cole–Parmer Instrument Co.). GC-MS analysis (Shimadzu QP2010S) was conducted to analyze the bio-oil composition using *n*-dodecane as the internal standard. The caloric value was measured as the higher heating value (HHV). Heating values (MJ kg^{-1}) and elemental analyses were determined by Hazen Research, Inc., Golden, CO. Elemental carbon, hydrogen, and nitrogen analyses of the bio-oil samples were performed by combustion in pure oxygen at 950 °C and analysis of CO_2, H_2O, NO_x, N_2, and SO_x. Oxygen was determined by difference.

2.3 Bio-oil upgrading

In a typical reaction without 1-butanol addition, raw bio-oil (1.5 g), 1-octene (98%) (0.25 g), 1-dodecane (internal standard, 99.9%) (0.02 g) and catalyst (0.15 g) were placed in a glass pressure reaction vessel equipped with a magnetic stirrer and maintained for 3 h at the desired temperatures (80–150 °C) using an external oil bath. Then, the two-phase mixture was cooled to room temperature and the catalyst was removed by filtration or centrifugation. Methanol (3 ml) was added to dilute and convert the two-phase liquid into one phase for immediate GC-MS analysis. The compositions of raw bio-oil liquid products obtained from each reaction were identified by GC-MS. The percent conversion of 1-octene charged into the upgrading reactions which underwent conversion to other products was determined by the change in peak area *versus* that of the IS, 1-dodecane. This was examined *vs.* time at each reaction temperature. In the reactions where both 1-butanol and 1-octene were used, 1-butanol (0.25–0.75 g) served as a cosolvent/emulsifier to reduce phase separation and speed mass transport during the reaction. The same amounts of raw bio-oil, 1-dodecane, 1-octene and catalyst were used. Reactions were performed with other cosolvents for comparison, including ethanol, tetrahydrofuran (THF) and ethyl acetate (EA).

3. Results and discussion

3.1 Chemical composition of the raw bio-oil

Raw bio-oil, a dark brown liquid with a smoky odor, has a complex array of components. A GC-MS analysis of a portion of its contents is listed in Table 2, where area percents based on the total ion current are given. These are not proportional to the molar composition. Table 2 shows that oxygen-containing organic components of raw bio-oil involve many classes of compounds such as anhydro-sugars, carboxylic acids, alcohols, phenols, aldehydes, ketones, esters and furans. The most abundant organic component in raw bio-oil was levoglucosan (1,6-anhydro-β-D-glucopyranose). Its peak area is about 45%, the largest percentage of the oxygenated organic components present. This broad peak may also contain some related anhydro-monosaccharides. Levoglucosan is generated from the decomposition of cellulose to glucose, followed by

Table 1 Properties of the acid catalysts

Physical property	Dowex50WX2	Amberlyst70	Amberlyst15-dry	Nafion NR50
Matrix	Styrene-divinylbenzene copolymers (gel type)	Halogenated styrene-divinylbenzene copolymers (macroreticular)	Styrene-divinylbenzene copolymers (macroreticular)	Perfluorinated polymer (gel type or microporous)
Matrix active group	Sulfonic acid	Sulfonic acid	Sulfonic acid	Sulfonic acid
Shape	Bead	Bead	Bead	Pellets
Size (mesh)	50–100	25–30	16–50	7–9
Water retention capacity (%)	74–82	53–59	1.6	2
Cross-linking density (%)	2%	7–12%	20–25%	—
Temperature stability (°C)	150	190	120	220
Ion exchange capacity (meq/g)	5.0	2.55	4.7	0.81

Table 2 Selected organic oxygen-containing components of raw bio-oil[a]

Components	Area (%)	Components	Area (%)
Acids		**Alcohols**	
Glyoxylic acid	0.19	Glycerin	11.17
Formic acid	1.16	1,2,3,4-Butanetetrol	0.59
Acetic acid	8.84	2,3-Dimethylcyclohexanol	0.18
Propanoic acid	1.70	3-Methoxy-1,2,4-butanetriol,	0.03
Butanedioic acid	0.41	**Esters and acetals**	
2-Hydroxy-3-methoxy-succinic acid	0.17	2,2-Dimethoxypropane	0.1
D-Araboascorbic acid	0.20	Hexanedioic acid, monomethyl ester	0.58
Phenols		Acetic acid, 2-propyltetrahydropyran-3-yl ester	1.49
Phenol	0.59	**Furans**	
2-Methyl phenol	0.22	2,5-Dimethylfuran	0.92
3-Methyl phenol	0.37	(2-Hydroxy-1-methoxy) ethylfuran	0.18
2-Methoxyphenol	2.33	2(5H)-Furanone	0.41
2,6-Dimethyl phenol	0.26	2,3-Dihydro-2,5-dimethylfuran	0.08
2-Methoxy-4-methyl phenol	3.44	2,5-Dimethoxytetrahydrofuran	0.05
1,2-Benzenediol (catechol)	0.98	**Sugars**	
4-Ethyl-2-methoxy phenol	0.75	D-Arabinitol	0.17
2-Methoxy-5-propenyl phenol	0.73	1-Deoxy-D-arabitol	0.33
2-Methoxy-4-propyl phenol	0.15	2-Deoxy-D-galactose	0.54
1-(4-Hydroxy-3-methoxyphenyl)-2-propanone,	0.56	2,2-Dimethyl-3-heptanone	0.60
4-(3-Hydroxy-1-propenyl)-2-methoxy-phenol	0.17	3-Deoxyglucose	0.13
5-Hydroxy-6-methoxy-1-benzofuran-3(2H)-one	0.09	1,4:3,6-Dianhydro-α-D-glucopyranose	0.43
Ketones and aldehydes[b]		2,3-Anhydro-D-galactosan	0.69
3-Hydroxy-2-butanone	0.08	2,3-Anhydro-D-mannosan	0.33
1-Hydroxy-2-butanone	0.46	3,4-Anhydro-D-galactosan	1.93
4-Hydroxy-3-methyl-2-butanone	0.64	D-Allose	1.46
2-Methyl-cyclopentanone	0.14	1,6-Anhydro-β-D-glucopyranose (levoglucosan)	44.13
3-Methyl-1,2-cyclopentanedione	1.45	D-Glycero-D-*galacto*-heptose	0.35
2,2-Dimethyl-3-heptanone	0.60	D-Glycero-d-ido-heptose	0.23
4-Ethoxy-cyclohexanone	0.17	Diacetonyl-D-mannosan	0.26
4-Hydroxy-3-methoxy-benzaldehyde	0.33	**Others**	
4-Hydroxy-2-methoxycinnamaldehyde	0.20	2,3-Dihydroxy-1,4-dioxane	2.01
2,3-Methylenedioxyanisole	0.26	2-(2-Propenyl)-1,3-dioxolane	0.38
Hexanedial	0.33	Octahydro-4a(2H)-naphthalenecarboxylic acid	2.28

[a] The bio-oil was produced by fast pyrolysis in an auger-fed reactor at 450 °C from southern pine sawdust using the methanol described in reference 25. [b] No hydroxylacetaldehyde (HAD) peak was detected, but 2,3-dihydroxy-1,4-dioxane, which is the cyclic dimmer of HAD, was detected. This appears to be due to the GC-column and conditions employed.

dehydration. This compound and related sugars and anhydrosugars can readily lead to charring or coking of heterogeneous catalysts during a variety of upgrading processes. D-allose, D-mannoheptulose, 2-deoxy-D-galactose and anhydrosaccharides (anhydro-galactosan, anhydro-mannosan) generated from hemicellulose were present.

Organic acids were abundant including formic acid, acetic acid, propanoic acid, butanoic acid, butanedioic acid *etc.* Acetic acid is typically the most abundant acid in raw bio-oil, accounting for more than 8% of the peak area. Raw bio-oil contains phenol and many phenol derivatives with methyl, propenyl, ketone, and aldehyde groups attached. These phenolic compounds form by lignin decomposition and the sum of their corresponding peak areas was higher than 10%. The typical ketones include 1-hydroxy-2-butanone, 3-methyl-1,2-cyclopentanedione, 2,2-dimethyl-3-heptanone, 4-ethoxy-cyclohexanone and 2-methyl-cyclopentanone. Alcohols represented about 11% of the peak areas and included abundant 1,2,3-propanetriol with 2,3-dimethyl-cyclohexanol and 1,2,3,4-butaneteraol also observed. Furan derivatives with good fuel properties such as 3,4-dimethyl-2,5-dihydrofuran, 2,5-dimethylfuran, 2,5-dimethoxytetrahydrofuran, 2-hydroxy-1-methoxy-ethylfuran and 2(5H)-furanone were also detected. The esters contained in raw bio-oil included hexanedioic acid's

monomethyl ester and 2-propyltetrahydropyran-3-yl acetate. Some other compounds contained in raw bio-oil include 2-(2-propenyl)-1,3-dioxolane, 2,2-dimethoxypropane and 2,3-dihydroxy-1,4-dioxane. This last compound is the cyclic dimmer hemiacetal of hydroxyacetaldehyde.

This complex oxygenated bio-oil mixture rapidly cokes petroleum refining catalysts so it can't be blended into crude oil entering refinery processes to make gasoline or diesel fuels (cracking, hydrocracking *etc.*). This suggests that demonstrating detailed reaction routes within the upgrading progress will be difficult. Partial upgrading of this complex raw bio-oil to oxygen-containing fuels requires that organic acids, phenolic compounds, aldehydes, polyols and water should be converted to acceptable fuel molecules. The acidity must be reduced and both the heating value and the thermal instability increased.

3.2 Bio-oil upgrading with neat 1-octene

Reactions of raw bio-oil with neat 1-octene were carried out for 3 h at temperatures between 60 and 120 °C with magnetic stirring. These were all two liquid phase reactions over the heterogeneous resin (third phase) catalyst, because highly polar, hydrophilic raw bio-oil is almost immiscible with 1-octene. This phase separation severely limits mass transfer in the reactions. The conversions of 1-octene increase with increasing time and temperature, reaching 25% at 120 °C in 3 h (1.5 g raw bio-oil; 0.25 g 1-octene). Fig. 1 shows 1-octene consumption *vs.* time at each temperature.

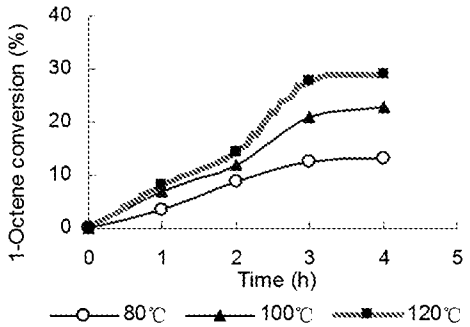

Fig. 1 1-Octene consumption *vs.* time at 80, 100 and 120 °C.

Fig. 2 compares the GC-MS chromatograms of raw bio-oil (**black**) and bio-oil (**blue**) upgraded with neat 1-octene at 120 °C for 3 h. Large differences in the chemical compositions of the raw bio-oil *versus* the neat 1-octene-treated bio-oils were not observed except for the detection of unreacted 1-octene. Small amounts of octanols (2-octanol and 3-octanol) from water addition were observed. The octanols content increase as temperature is increased, indicating the reaction of 1-octene slowly consumes water (see Fig. 3). 1-Octene also isomerizes slowly, producing 2-, 3- and 4-octene, but no octene oligomers (C16, C24···) or fragmented olefins (olefins cleaved from 1-octene or C16 and higher oligomers) were detected. Similar results were found previously in model reactions of 1-octene with water, phenol, acetic acid and methanol.[20,21]

Products from O- or C-octylation of phenolic derivatives were not definitively observed in the complex upgraded products. Individual phenolic bio-oil derivatives are present in low

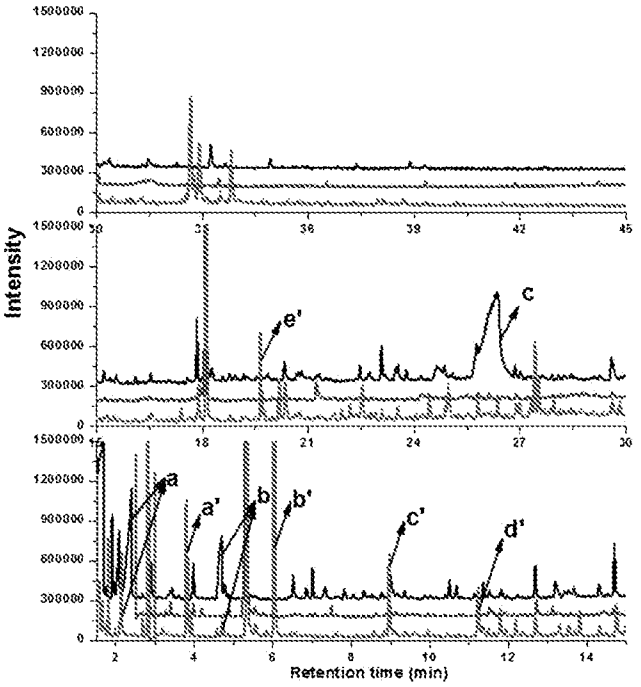

Fig. 2 Comparison of the GC-MS chromatograms of raw bio-oil, bio-oil upgraded with neat 1-octene and 1-octene/1-butanol at 120 °C after 3 h.

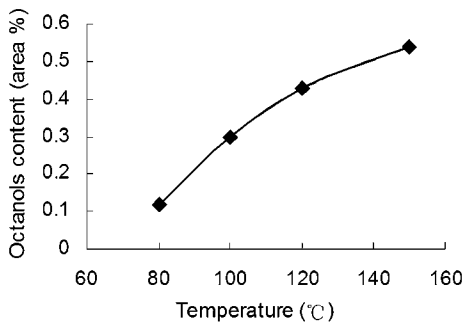

Fig. 3 Octanols content of bio-oil upgraded with 1-octene/1-butanol after 3 h at 80, 100, 120 and 150 °C.

concentrations in raw bio-oil, so their partial conversion to O- or C-octylates would be hard to detect. High temperature accelerates the aging of bio-oil. At 80 °C, slow char/coke formation occurred. This char is likely generated mostly from the levoglucosan, thermally unstable aldehydes/ketones and lignin-derived oligomers.[9] The content of these components in the bio-oil decreased from about 50% to 25% of the GC area% in 3 h.

3.3 Upgrading bio-oil with 1-octene and 1-butanol

Phase separation and progressive catalyst deactivation were the major problems hindering the acid-catalyzed reaction of 1-octene with bio-oil. A solvent which would completely dissolve the organic bio-oil components and 1-octene into one liquid phase should speed reaction rates by removing mass transfer restraints. This should enhance 1-octene/hydroxyl-containing compound contact at the catalyst, raising upgrading efficiency. 1-Butanol, which can be made from lignocellulosic biomass, is a target molecule to replace ethanol in gasoline according to BP

Inc. and DuPont,[24] 1-Butanol can dissolve both organic hydroxyl compounds and olefins.[24,26]

Previously, we demonstrated that 1-butanol addition improved conversion of 1-octene in model reactions of phenol/water/1-octene over heterogeneous acid catalysts.[21] O- and C-octylated phenol and octyl alcohols were produced. Furthermore, 1-butanol addition protected the catalyst against decomposition in these reactions. Therefore, 1-butanol was employed here as both a cosolvent and as an upgrading reagent. This alcohol can react with carboxylic acids to give butyl esters and with aldehydes/ketones to form acetals. 1-Butanol can also be transformed into dibutyl ether *via* acid-catalyzed S_N2 substitutions. Reactions of raw bio-oil with 1-octene and 1-butanol are described next. Depending on the amount of 1-butanol added, one phase reactions can be achieved or emulsified/semiemulsified systems allowing rapid mass transport can be generated.

3.3.1. Composition changes in bio-oil reacted with 1-octene/1-butanol. A GC-MS chromatogram of bio-oil after it was upgraded with a mixture of 1-octene/1-butanol (1.5g/0.25g/0.5g) at 120 °C for 3 h over Dowex50WX2 is presented in Fig. 2 (**red**). Many obvious peak changes occurred *versus* the GC-MS chromatogram of raw bio-oil. For example, peaks a, b and c, represent acetic acid, 1,2,3-propanetriol and levoglucosan, three of the most abundant compounds in this raw bio-oil, respectively. After the upgrading reaction, the respective relative intensity of these peaks decreased by 82%, 96% and 99%. Butyl acetate (peak b′) represents the most abundant component in upgraded bio-oil except for residual 1-butanol and 1-octene. Other major new peaks generated include a′, c′, d′ and e′, representing butyl formate, butyl propionate, butyl hydroxyl acetate and the butyl ester of levulinic acid, respectively.

A GC-MS analysis of this upgraded bio-oil is shown in Table 3. After upgrading, most of the organic acids (formic acid, acetic acid, propanoic acid, butanoic acid, butanedioic acid *etc.*) were converted into butyl or octyl esters *via* esterification with 1-butanol and octanols (product of 1-octene plus water) and by carboxylic acid additions across 1-octene. As many as 30 of these esters were formed, accounting for more than 25% of the total corresponding peak area. This total exceeds that of either residual 1-butanol (15.22%) or 1-octene (22.45%). Typical esters formed from 1-butanol included butyl formate, butyl acetate, butyl propionates, butyl levulinate, butyl hydroxyacetate, monobutyl ester of butanedioic acid, butyl 2-hydroxypropanoate, and dibutyl butanedioate. 2-Octanol and 3-octanol were formed by hydration of 1-octene and 2-octene, respectively. Four octene isomers were observed after the reactions, including 1-, 2-, 3-, and 4-octene, but no oligomeric or fragmented olefins from octenes were detected. A variety of isomeric octyl esters were formed from the isomeric octenes and octanols, including octyl acetates, octyl propionates and octyl butanoates. 2,2-Dimethoxypropane was detected in both raw bio-oil and in a diminished concentration in upgraded bio-oil. 2,2-Dimethoxypropane originates from acetone and methanol, either from small amounts added to the bio-oil directly after its pyrolysis vapors have been condensed from wood flour pyrolysis (for stabilization) or from the methanol which is used as the solvent for GC-MS analysis. Other acetals detected in this upgraded bio-oil included formaldehyde, acetaldehyde dibutyl acetal and 1,1-dibutoxy-2-propanone. These were generated from acetal-forming equilibria with formaldehyde, acetaldehyde and methylglyoxal, respectively, with 1-butanol.

Phenolic compounds present in raw bio-oil, such as phenol, 2-methylphenol, 2-methoxyphenol, 2-methoxy-4-methyl phenol, *etc.*, were detected in diminished amounts in upgraded bio-oil. Furthermore, the phenolic derivatives 1,2-benzenediol, 2-methoxy-5-propenyl phenol, 4-hydroxy-3-methoxybenaldehyde (vanillin) present in raw bio-oil could not be detected in upgraded bio-oil. Small quantities of various octyl-substituted phenols were detected, suggesting that phenolic O- and C-alkylation reactions with the isomeric octenes had taken place. Absolute structural identification of these compounds, however, was not possible since their authentic standards were not available.

Although small amounts of 2(5H)-furanone, 5-propyl-2(3H)-dihydrofuranone and 2,3-dihydro-2,5-dimethylfuran were found in upgraded bio-oil, both the number and content of these furan derivatives decreased after upgrading treatment. The drop in concentration or elimination of several active phenol and furan derivatives will increase stability and hydrocarbon blending ability of the upgraded bio-oil. The amounts of hydroxy butanones, 2-methyl-cyclopentanone and 2,2-dimethyl-3-heptanone decreased in the upgraded bio-oil. Some ketones such as 3-methyl-1,2-cyclopentanedione, 4-ethoxycyclohexanone and 4-hydroxy-3-methyl-2-butanone, which exist in raw bio-oil, totally disappeared after upgrading. Some new ketones appeared including 2-cyclopenten-1-one, 2-hydroxy-1-methylcyclopenten-3-one, and 2-allyl-2-methyl-1,3-cyclopentanedione *etc.* Levoglucosan's concentration decreased dramatically during upgrading from more than 40 area% to less than 0.5%. This was accompanied by formation of some amounts of galactopyranose methyl glycoside, methyl-beta-D-glucopyranoside and methyl glucose ether and, probably, their butyl analogs.

It is also interesting that the polyhydric alcohols content decreased dramatically. Glycerin, a major component of this raw bio-oil, and 1,2,3,4-butanetetraol concentrations drop from a combined area percent of 12% before treatment to only 0.41% after upgrading. This would lower the viscosity and hydrophilicity of the product. Traces of 1-butoxyethanol and butoxyacetic acid were also detected in the upgraded bio-oil. These form from reactions of 1-butanol with acetaldehyde and hydroxyacetic acid, respectively.

In contrast to upgrading treatments using only 1-octene, no charring or coking of the bio-oil was detected in the upgrading treatments with 1-octene/1-butanol, even at 120 °C.

The presence of 1-butanol inhibits bio-oil ageing over the entire temperature range to 120 °C and prevents catalyst deactivation by coking. Both dilution of char formers and their reaction to generate other less fouling compounds occur. Examples of coke or polymer-forming compounds include glyoxylic acid, acetaldehyde, levoglucosan, hydroxymethylfurfural and monosaccharides.

It is apparent that hydration of olefins, esterifications of organic acids, acetalations of aldehydes and ketones and O- and C-alkylations of phenolic compounds occur to varying extents simultaneously during 1-octene/1-butanol upgrading. The amounts of esters sharply increased, while the amounts

Table 3 Selected organic oxygen-containing components of bio-oil upgraded with 1-octene/1-butanol at 120 °C for 3 h[a]

Components	Area (%)	Components	Area (%)
Acids		**Esters**	
Glyoxylic acid	0.20	*n*-Butyl formate	3.65
Acetic acid	1.57	*n*-Butyl acetate	11.34
Propanoic acid	0.11	*n*-Butyl propanoate	1.89
4-Pentenoic acid	0.09	*n*-Butyl butanoate	0.94
Butoxyacetic acid	0.02	*n*-Butyl-2-hydroxypropanoate	0.35
2-Pentenoic acid	0.08	*n*-Butyl hydroxyacetate	1.28
Phenols		*n*-Butyl pentanoate	0.44
Phenol	0.17	*n*-Butyl hexanoate	0.13
2-Methylphenol	0.07	*n*-Butyl levulinate	1.91
3-Methylphenol	0.22	Octyl acetates	1.12
2-Methoxyphenol	0.65	*n*-Butyl acetoacetate	0.25
2,6-Dimethylphenol	0.10	Octyl propenoates	0.37
1-Ethyl-3-hydroxybenzene	0.06	Octyl butanoates	1.07
2-Methoxy-4-methyl phenol	0.71	Octyl pentanoates	0.46
1-(4-Hydroxy-3-methoxyphenyl)-ethanone	0.54	*n*-Butyl butanedioate	0.59
1-(4-Hydroxy-3-methoxyphenyl)2-propanone	0.26	2,2-Dimethyl-3-hexanol acetate	1.71
Octyl derivatives of phenol and substituted phenol phenols	1.14	Dibutyl butanedioate	1.1
Ketones and aldehydes		Dibutyl pentanedioate	0.38
5-Methoxy-2-pentanone	0.05	Octyl acetoacetate	0.29
1-Hydroxy-2-butanone	0.02	Cyclopentyl-2,2-dimethylpropioate	1.71
2-Cyclopenten-1-one	0.12	**Acetals**	
2-Methylcyclopentanone	0.07	2,2-Dimethoxypropane	0.29
2-Hydroxy-1-methylcyclopenten-3-one	0.54	2,2-Dimethoxybutane	0.17
2,2-Dimethyl-3-heptanone	0.03	Formaldehyde dibutyl acetal	0.50
3-Ethyl-2-hydroxy-2-cyclopenten-1-one	0.06	Acetaldehyde dibutyl acetal	0.11
2-Allyl-2-methyl-1,3-cyclopentanedione	0.10	1,1-dibutoxyacetone	1.15
Alcohols		Iso-Valeraldehyde propyleneglycol acetal	0.16
1-Butanol	15.13	**Furans**	
Glycerin	0.39	2,3-dihydro-2,5-dimethylfuran	0.04
1,2,4-Butanetriol	0.03	2(5H)-Furanone	0.11
3-Cyclopentene-1,2-diol	0.11	Dihydro-5-propyl-2(3H)-Furanone	0.08
1,2,3,4-Butanetetrol	0.02	1-(2-Furyl)-1,2-butanediol	0.27
2-Octanol	0.15	**Others**	
3-Octanol	0.23	2,3-Dihydroxy-1,4-dioxane	0.06
2,2-Dimethyl-3-hexanol	0.11	Toluene	0.30
Sugars		Octahydro-4a(2H)-naphthalenecarboxylic acid	2.30
2-Deoxy-D-arabinose	0.17	2-*n*-Butoxyethanol	0.09
1,5-Anhydro-D-talitol	0.90	2-Ethyldecahydronaphthalene	0.10
1,5-Anhydro-D-mannitol	0.27	1-Dodecane	12.91
1,6-Anhydro-β-D-glucopyranose	0.24	1-Octene	18.88
α-D-Galactopyranose methyl glycoside	3.76	4-Octene	0.19
Methyl-β-D-glucopyranoside	2.02	3-Octene	0.10
α-Methyl D-glucose ether	1.68	2-Octene	0.02

[a] The bio-oil/1-octene/1-butanol weight ratio used was 1.5 : 0.25 : 0.5.

of levoglucosan, other anhydro-sugars, monosaccharides, carboxylic acids and polyhydric alcohols decreased. This showed that 1-octene/1-butanol upgrading is promising.

3.3.2 Phase and temperature effects in 1-octene/1-butanol bio-oil upgrading. 1-Butanol addition plays a major role in solving the phase separation problem. Before the reaction, many bio-oil components and 1-ocetene become a single liquid phase with a small portion of an emulsion-like liquid forming that can be observed in the resulting fluid. Sufficient 1-butanol addition gives a single phase. The relative weights of 1-butanol, 1-octene and bio-oil determine the exact nature of both the initial and after reaction fluids. Table 4 shows the effect of using different ratios on the fluids' phase nature and on the conversions of 1-octene and 1-butanol. Even when ratios are used where two phases are present, 1-butanol causes more 1-octene to reside in the bio-oil rich phase and visa versa. Thus, mass transfer limitations are reduced. For example, using 0.25 g of 1-butanol with 0.25 g 1-octene and 1.5 g raw bio-oil still gave two liquid phases, but the conversion of 1-octene increased and 29.2 weight of 1-butanol reacted (Table 4). Increasing the 1-butanol to 0.5 g greatly increases conversions of both 1-octene and 1-butanol. Surprisingly, the 1-octene conversion sharply dropped when the amount of 1-butanol was raised to 0.75 g where the reaction mixture became almost clear. We don't understand the dependence of rates on these changes, but an olefin-rich, more hydrophobic region may exist inside the tiny droplets present in the reactions with 0.25 g of 1-butanol. Rapid mass transfer in and out of these phases can occur.

The resin acid catalyst activities may depend upon the polarity or hydrophilicity of the phase where 1-octene and bio-oil components react. High 1-octene conversions were again observed when 0.75 g 1-butanol *versus* 0.6 g 1-octene and 1.5 g raw bio-oil was used. A similar emulsion-like liquid was initially

Table 4 Effect of reactant mass ratios on the on conversions of both 1-octetne and 1-butanol[a]

Mass (g)			Conversion (%)		Phase state	
Bio-oil	1-Octene	1-Butanol	1-Octene	1-Butanol	Before reaction	After reaction
1.5	0.25	0	24.7	—	Two	Two, charring
1.5	0.25	0.25	27.9	29.2	Two	Two
1.5	0.25	0.5	**69.2**	**89.8**	Emulsion-like	One
1.5	0.25	0.75	27.5	78.9	One	one
1.5	0.5	0.5	15.2	52.3	Two	Two
1.5	0.75	0.5	13.2	39.4	Two	Two
1.5	0.60	0.75	50.8	80.3	Emulsion-like	One

[a] Reaction conditions: Dowex50WX2, 5wt% of raw bio-oil; 120 °C; 3 h.

formed, but a single liquid phase was present after the reaction. Obviously, the amount of 1-butanol and the weight ratio of 1-butanol *versus* 1-octene for a specific amount of raw bio-oil affected the "droplet" or micelle size and phase compositions. This, in turn, led to the varying rates. When the amount of 1-butanol was held constant (0.5 g), the conversion of 1-butanol decreased as the amount of 1-octene was raised and the amount of 1-octene which reacted increased. The dilution of 1-butanol by this increase in 1-octene and the competitive reactions from octanols generated from 1-octene all have effects in this complex system.

1-Octene and 1-butanol conversions increased from 28.1% to 83.2% and 69.2% to 89.8% respectively, when the reaction temperature was raised from 80 °C to 120 °C (see Fig. 4). These reactions used a bio-oil/1-butanol/1-octene ratio of 1.5/0.5/0.25. However, at 150 °C, 1-butanol conversion dropped to 82.7% while 1-octene conversion increased slightly to 70.1%. While the boiling points of the both 1-octene (bp. 121.3 °C) and 1-butanol (bp. 117.7 °C) are lower than 150 °C, these reactions were run in closed reaction vessels, so vapors could not escape. The higher temperature dependence of 1-octene conversion at this specific set of conditions suggests that more 1-butanol is consumed earlier in the reaction. No obvious charring or coking occurred even at 150 °C. However, some darkening of the initial yellow color of Dowex50WX2 catalyst may indicate that some decomposition of this catalyst occurred. Amberlyst70, which has higher thermal stability (190 °C), exhibited no changes. To achieve good 1-octene and 1-butanol conversions at 1 atm. pressure, 120 °C was selected as the optimum operating temperature.

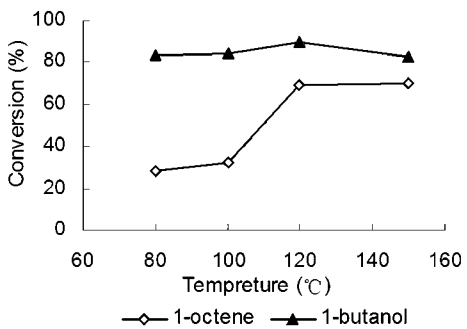

Fig. 4 Effects of reaction temperature on conversions of 1-octene and 1-butanol in 3h.

Fig. 5 shows the plots of conversions of 1-octene and 1-butanol *versus* time at 120 °C over Dowex50WX2. 1-Octene was 40–50% consumed in 1 h and >65% consumed in 3 h. Beyond 3 h 1-octene conversion increased slowly. Similar trends were found in 1-butanol conversion. Thus, a 3 h reaction time was selected for batch reactions.

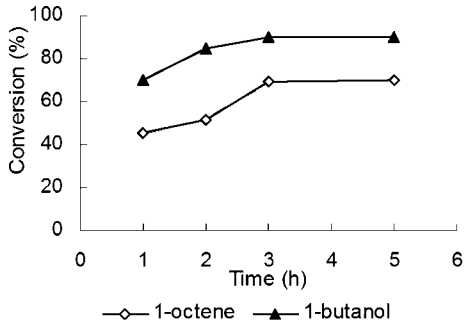

Fig. 5 Effects of reaction time on conversions of 1-octene and 1-butanol over Dowex50WX2 at 120 °C.

Fig. 6 shows the conversions of both 1-octene and 1-butanol at 120 °C after 3 h with four different catalysts. Dowex50WX2 gave the highest conversions of both 1-octene and 1-butanol along with a pale yellow to deep yellow color change. Serious decomposition of Amberlyst15 occurred as the catalyst bead fragments after reaction. Clearly, the swellable 2%, divinylbenzene Dowex50WX2, withstands the reaction conditions better than the macroreticular, 20–25% divinylbenzene content, fragile Amberlyst15. Swelling of the Dowex50WX2 and Amberlyst70 resins in the reaction medium is crucial for diffusion to the internal sulfonic acid sites. Swelling volumes increase with a decrease in the cross-linking percentage.[27] The Dowex50WX2 (gel type resin) does not fracture into tiny particles as Amberlyst15 (macroporous beads) is prone to do. Dowex50WX2 can not be simply poisoned at the surface. Good swelling gave good active-site accessibility to the soluble reactants. Amberlyst70, which is a new macroporous chlorinated styrene/divinylbenzene resin catalyst with a high thermal stability remained in good condition and showed a higher activity, while Nafion NR50, a sulfonated tetrafluroethylene-based fluorinated sulfonic acid copolymer, gave the lowest conversions of both 1-octene and 1-butanol.

The catalyst reusability was tested using model reactions in our previous work. Those results showed that these catalysts can be recycled in several runs while retaining a high activity.[21] When

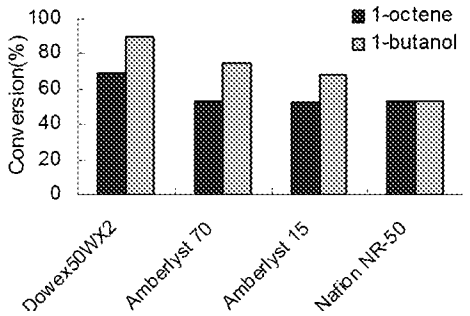

Fig. 6 Effects of different catalysts on conversions of 1-octene and 1-butanol at 120 °C in 3 h.

the reaction was run without good phase transfer occurring, catalyst deactivation took place more rapidly. When cosolvent was absent, the catalysts showed lower catalytic activities because serious aging and coking of the bio-oil blocked and inhibited diffusion of the reactants to the catalyst surface. Good catalyst swelling promotes active-site accessibility to the soluble reactants, leading to better catalytic activity. When sufficient amounts of a cosolvent, such as 1-butanol were added, the appearance and catalyst shape remained almost unchanged except for a volume expansion. Catalyst coking was effectively suppressed even at higher temperature (>120 °C). Less thermally stable catalysts, like Amberlyst15 have poor stability and undergo both fragmentation to smaller particles and desulfonation when heated with raw bio-oil and olefins. The rate of Amberlyst15 deactivation slows when 1-butanol is added, but more stable catalysts such as Amberlyst70 or Dowex50WX2 are better and may be used up to 120 °C.

Sample conversions of different olefins and alcohol co-solvents and the phase state of the compositions are shown in Table 5, both before and after the reactions. Dowex50WX2 was used as the catalyst. The conversions of cyclohexene, 1,7-octadiene or trimethylpentene were similar to those of 1-octene when used in identical upgrading reactions with 1-butanol. Also, the 1-butanol conversions were similar. Significantly, the milky-like two phase starting mixtures become a single phase by the end of the reaction. This indicates clearly that the initially charged raw bio-oil had become significantly less hydrophilic as reactions with olefin and 1-butanol proceeded. It also confirms that other olefins, such as olefin refinery cuts, should be successfully employed for upgrading. However, when the same amount (weight) of ethanol or 2-propanol were used as the alcohol co-solvent, 1-octene conversion decreased from 69.2% (that with 1-butanol) to less than 30%. After the reaction, phase separation still existed. Clearly, at a bio-oil/alcohol co-solvent weight ratio of 3 : 1, the reaction rate with 1-octene dropped because mass transfer/phase limitations were not overcome.

Both ethanol and 2-propanol are too polar to reduce phase separation as well as 1-butanol. When *tert*-butyl alcohol was used as the co-solvent, 1-octene conversion remained high (67.8%), close to the value that was found when using 1-butanol. Addition of all these alcohols inhibited coking of the catalysts to various extents. In contrast, adding the equivalent molar amount of non-reactive solvents, such as THF or dichloromethane, led to catalyst coking. Obviously, alcohols can react with ketones and aldehydes, aldo-saccharides and keto-saccharides to form acetals and esterify carboxylic acids while other non-reactive solvents could not. The water present in bio-oil could further react with anhydro-sugars at the acid catalysts during upgrading to generate their corresponding original sugar anomers. These anomers will be in equilibrium through ring-opened aldehydo or keto forms. These equilibira could permit reaction of the open chain sugars with 1-butanol to form acetals, thereby lowering the amount of sugars and anhydro-sugars as upgrading progresses.

3.4 Properties of upgraded bio-oil

Some representative properties of raw bio-oil *versus* upgraded bio-oil are summarized in Table 6. Although the appearance of upgraded bio-oil was similar to that of raw bio-oil, the odor changed noticeably from an unpleasant heavy smoke-like aroma to a banana-like fragrance. This change is due to three key transformations. First, the formation of butyl esters from the organic acids present in raw bio-oil causes a very typical sweet fruity smell that resembles bananas. The formation of large amounts of butyl acetate occurred. Secondly, the reduction in the amount of malodorous phenolic compounds like quiacol and methyl phenols has occurred, in part by O-alkylations by olefins. Third, the amounts of levoglucosan, which has a smoky aroma, decreased dramatically.

The water content of the bio-oil upgraded with 1-octene/1-butanol (bio-oil, 1.5g; 1-octene, 0.6g; 1-butanol, 0.75 g) was reduced from 37.2% to <7.5%. This decrease is due to the addition of water across 1-octene (or other olefins). Upon olefin protonation, water can rapidly react at the carbocation center forming alcohols. The reduction of water is especially

Table 5 Upgrading bio-oil over Dowex50WX2 with different alcohols and olefins at 120 °C for 3 h[a]

		Conversion (%)		Phase state	
Alcohol co-solvent	Olefin	Olefins	Alcohol	Before reaction	After reaction
1-Butanol	1-Octene	69.2	89.8	Two	One
1-Butanol	Cyclohexene	70.6	82.5	Two	One
1-Butanol	2,4,4-Trimethylpentene	65.1	83.0	Two	One
1-Butanol	1,7-Octadiene	45.4	87.8	Two	One
Iso-butanol	1-Octene	68.1	89.2	Two	One
Tert-butanol alcohol	1-Octene	67.8	88.1	Two	Two
2-Propanol	1-Octene	22.6	89.6	Two	Two
Ethanol	1-Octene	23.3	90.5	Two	Two

[a] Weight ratio, raw bio-oil : co-solvent : olefin = 1.5 : 0.5 : 0.25; Dowex50WX2, 5wt% of raw bio-oil.

Table 6 Fuel properties of raw bio-oil and bio-oil upgraded with 1-octene/1-butanol over Dowex50WX2 for 3 h

Properties	Raw Bio-oil	Bio-oil Upgraded with 1-octene/1-butanol[a]		
		80 °C	100 °C	120 °C
Water content (wt%)	37.19	6.48	6.785	7.385
HHV (MJ kg^{-1})	12.55	30.20	30.76	29.77
pH value	2.62	3.21	3.23	3.47
C (%)	32.08	61.00	60.87	61.05
H (%)	8.09	10.76	10.03	10.55
O (%)	59.71	28.16	29.06	28.18
N (%)	0.11	0.08	0.04	0.22
Addition of water	Emulsion liquid	Phase separated	Phase separated	Phase separated
[b]Mix with hexane–toluene	Two or more phases		One clear phase	

[a] Weight ratio, raw bio-oil : 1-octene : 1-butanol = 1.5 : 0.6 : 0.75; Dowex50WX2, 5 wt% of raw bio-oil; 3 h. [b] Weight ratio, hexane : toluene : bio-oil = 0.25 : 0.75 : 0.50.

noteworthy, because many of the upgrading reactions generate more water in the bio-oil. Acetal and ester formation generate a mole equivalent of water. Alcohol conversions to ethers generate water. These reactions add water to the already large amounts of water in raw bio-oils. In particular, large amounts of water were formed during esterifications in these upgrading reactions. The significant reductions in water observed *versus* time, which continued at extended reaction times and higher temperatures, suggests that 1-octene is being progressively converted to octanols. This is confirmed by the presence of octanols in the products.

The pH value of bio-oil, upgraded with 0.75 g of 1-butanol and 0.6 g of 1-octene per 1.5 of bio-oil, rose from 2.62 to 3.2–3.5, with higher pH values found with increasing reaction temperature. These values for one step batch reactions might be further raised in continuous flow reactions where, after reaction at 120 °C, subsequent further exposure to olefin could be made to take place at lower temperatures where O-alkylation of phenols is increasingly favored *versus* C-alkylation. Moreover, at these conditions, equilibria from carboxylic acids to esters becomes more favorable.

The HHV (high heating value) value of the bio-oil upgraded with a bio-oil/1-butanol/1-octene ratio of 1.5/0.75/0.6 at 120 °C after 3 h over Dowex50WX2 increased considerably from 12.6 MJ kg^{-1} to 29.8 MJ kg^{-1}. This increase is the result of the presence of 1-butanol and 1-octene and their reaction products with raw bio-oil components. The HHV values of 1-butanol (36.1 MJ kg^{-1}) and 1-octene (47.3 MJ kg^{-1}) are greater than that of raw bio-oil. *In this olefin/alcohol upgrading process, all the caloric value of the original bio-oil remains in the product.* The caloric content of the added alcohol and olefin will also be in the product. The total product's caloric value will be the sum of all the constituents and the caloric value per unit volume will be a function of the final product density. The significant advantage of this process is that no loss of caloric value occurs by loss of bio-oil carbon (*via* carbon dioxide or carbon monoxide) or bio-oil hydrogen (*via* water), as occurs during gasification processes. Furthermore, water reduction by an energy intensive distillation, which causes the loss of other bio-oil components and tar formation, or by drying agents is avoided.

The most abundant component in raw bio-oil is water. Raw bio-oil has a complex multi microphase structure and more water can be added. After some amount of water uptake, phase separations occur with water and organics in both phases (see Fig. 7a). However, addition of water into the upgraded bio-oils produced here led to two sharp phases and very little incorporation of this added water to the upgraded bio-oil (see Fig. 7b). Clearly, the upgraded products had become more hydrophobic. These upgraded liquids can be blended with bio-diesel or petroleum-based products and they are far less viscous than he starting bio-oil.

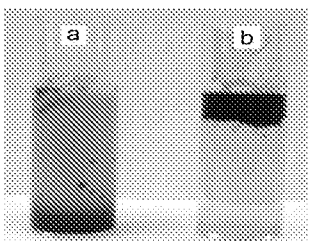

Fig. 7 Miscibility of water with raw bio-oil *versus* upgraded bio-oil.

4. Conclusions

Bio-oil obtained from the fast pyrolysis of pine chips was successfully upgraded with olefin/alcohol cosolvent mixtures. Alcohols with four carbons (1-butanol, *t*-butanol) exhibited superior cosolvent/phase compatibility abilities in this process. The reaction rates were a complex function of the phase behavior, which depends strongly on the amount of C-4 alcohol (1-butanol) present and the bio-oil/1-butanol/olefin ratio. For example, sufficient 1-butanol addition can bring most bio-oil components and 1-octnene into one liquid phase or it can give emulsion-like fluids acting as a cosolvent. In either case, mass transfer is accelerated and olefin conversion increases as enhanced 1-octene/hydroxyl-containing compound contact occurs at the catalyst. Secondly, 1-butanol or other alcohols react with carboxylic acids and aldehydes/ketones to form esters and acetals, respectively. Anhydro-sugars can react with water in the presence of the acid catalysts to reform their original pyranose or furanose sugars. The anomers of both pyranose and furanose sugars can equilibrate through small concentrations of their open chain aldehydo or keto forms and these, in turn, can form acetals from excess alcohols (1-butanol). These conversions to acetals enhance hydrophobicity

of the bio-oil's organic content, but generate water, adding to the water already present. Water unfavorably shifts the equilibria between esters and carboxylic acids and the acetal/aldehyde, ketone equilibria back towards the staring materials. *The seminal advantage of having olefins present is that olefins are hydrated to alcohols, thereby helping to lower the concentration of water.* This, in turn enhances the amounts of esters and acetals by shifting the position of equilibrium in these complex equilibria present during upgrading. For example, 1-butanol can be further converted to esters and acetals, and even to ethers in reactions with alcohol as the olefin present is hydrated to an alcohol. Pyranose and furanose forms of monosaccharides equilibrating to low concentrations of their open chain aldehydo and keto forms, can be further converted to acetals more favorably as water concentrations decrease upon olefin hydration.

After these upgrading reactions, large increases in esters are observed, while the amounts of levoglucosan, monosacchrides, polyhydric alcohols and organic acids decreased. Phenolic compounds can be both O- and C-alkylated under these conditions, accounting for their decreasing presence after upgrading. All these changes appear beneficial to bio-oil's stability. The formation of char/coke upon heating the product after upgrading or char/coke formation during the reactions is avoided. The catalyst is protected against rapid deactivation.

In contrast to the simultaneous use of the C-4 alcohols and olefins, when pine bio-oil was upgraded with neat olefins over heterogeneous sulfonic acid resin catalysts, two liquid phases remained throughout. This phase separation limited mass transport, slowing the kinetics. High temperature favored 1-octene hydration and 1-octene conversion, but accelerated the aging of bio-oil. Char/tar formation occurred when the temperature exceeded 80 °C. Large differences were not achieved in the chemical compositions of the raw and upgraded bio-oils, due to the slow kinetics.

The formation of esters, acetals and both O- and/or C-alkylated phenolic derivatives removes the unpleasant odor of bio-oil as the maloderous carboxylic acids, aldehydes and phenolics are reacted. Finally, the pH decreases and the heat values are enhanced in the upgraded bio-oil, without loss of caloric value original present in the staring raw bio-oil.

Closing statement

This upgrading process is far from being optimized. A large process development effort is needed to adjust the amounts of olefins and alcohol that will give a satisfactory upgraded product for different bio-oil feeds containing different amounts of water. Cost optimizations have not been studied. However, the general concept has been demonstrated. This upgrading process can be used to produce oxygenated fuels which can be blended with petroleum fuels or biodiesel liquids. The products are not intended as "drop in" replacements for gasoline or diesel engines. However, high oxygen content fuel someday might have application in low temperature/high compression diesel engines requiring low cetane number fuels.

Acknowledgements

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