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Biofuels

Upgrading Pyrolysis Oil over Ni/HZSM-5 by Cascade Reactions**

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Bio-oil, produced by fast pyrolysis or liquefaction of lignocellulosic biomass, is an aqueous, highly oxofunctionalized (but nearly sulfur-free) mixture of light-to-medium hydrocarbons containing 15–30 wt % H_2O.[1] Although it is considered to be a promising basis for second-generation energy carriers, the corrosive nature, low vapor pressure, high viscosity, and instability of bio-oil limit its direct application. Currently, bio-oil is primarily used for generating heat, but it has a heating value of below 19 MJ kg^{-1}, as compared to 42–44 MJ kg^{-1} for conventional fuel oil.[2] When it is directly burned in diesel engines, bio-oil has ignition difficulties owing to its low heating value, and the thermally unstable components leading to excessive coking.[3]

In principle, the production of high-grade transportation fuels from bio-oil is feasible; hydrogenation and hydrodeoxygenation (HDO) with sulfide catalysts such as cobalt- or nickel-doped molybdenum sulfides are currently used. However, these sulfide catalysts contaminate the products by sulfur transfer, and the removal of this sulfur from the surface of the catalysts by a reverse Mars van Krevelen mechanism causes them to eventually deactivate.[4] An alternative approach, based on zeolites, simultaneously catalyzes several reactions, including dehydration, cracking, polymerization, deoxygenation, and aromatization at temperatures between 623 and 723 K. Under these reaction conditions, oxygenates are mostly converted into aromatic molecules and carbonaceous deposits, while the yield to alkanes does not exceed 25 %.[5]

As pyrolysis oil contains high concentrations of water along with the reactive oxygen-containing compounds, it is highly beneficial to convert the aqueous mixture under mild conditions with water-tolerant catalysts. The good solubility of hydrogen in water, as exemplified by the successful conversion of polyols[6] and terpenes,[7] and the phase separation between the aqueous phase and the hydrocarbons produced, are further advantages for this approach. Previously we reported a catalytic system with dual functions, combining carbon-supported noble metal catalysts and mineral/organic acids for the aqueous-phase hydrodeoxygenation of the phenolic fraction of bio-oil at 523 K,[8a,b] achieving quantitative yields of alkanes. The combination of Raney Ni as base metal and Nafion/SiO_2 as solid acid has subsequently been shown to also be an efficient and recyclable dual-functional catalyst combination.[8c] However, the high cost and difficulty of handling of such a catalyst prohibit scale-up for large-scale continuous processes. Recently, the bifunctional (metal/acid) catalysts have also been used for efficient hydrodeoxygenation of phenols in both ionic liquids[8d] and the gas phase;[8e] notably, in the absence of water and only for individual model components. Herein, we report a new, stable, and widely applicable catalyst, zeolite HZSM-5 with a pore system containing a substantial fraction of Ni metal particles. This catalyst can quantitatively produce C_5–C_9 hydrocarbons from paraffins, naphthenes, and aromatic molecules in a cascade reaction by hydrodeoxygenation of *n*-hexane-extracted crude bio-oil in the presence of substantial concentrations of water under mild reaction conditions (523 K, 5 MPa H_2).

The crude bio-oil tested for this work is a red to black viscous liquid derived from thermal pyrolysis of pine trees (Netherlands BTG-BTL Company). The typical properties and composition of this pyrolysis oil are compiled in Table S1 of the Supporting Information. The composition of this oil can be roughly divided into water (15–30 wt %); water-soluble acetic acid, sugars, and polyols; and *n*-hexane-soluble organic molecules including phenols, ketones, aldehydes, and furans. The acetic acid, sugars, and polyols fraction can be efficiently used to generate H_2 through aqueous phase reforming (APR).[6] As lignocellulosic biomass consists of roughly 70 % cellulose and hemicellulose, and 1 mol glucose can generate 13 mol H_2 through APR, the H_2 produced by these components is sufficient for selective hydrodeoxygenation of the rest of the organic fraction to a hydrocarbon transportation fuel. With sugars and sugar derivatives remaining in the water phase, the *n*-hexane-soluble fraction of the bio-oil consisted mainly of furan and phenol, as well as ketone and aldehyde components, and accounted for approximately 40 % of the total carbon contained in the crude bio-oil, as determined by elemental analysis after solvent evaporation.

The components of *n*-hexane-extracted bio-oil mainly include C_5–C_6 substituted furans, ketones, and aldehydes derived from the deconstruction of cellulose and hemicellulose, as well as C_6–C_9 substituted phenols derived from the deconstruction of lignin (Figure 1 a). These compounds are substituted with alcohol, ketone, and ether functional groups, which tend to react to form larger molecules.[9]

Hydrodeoxygenation of such a mixture, on Ni/HZSM-5 in a semibatch reaction for four hours at 523 K and 5 MPa H_2 with a stirring speed of 680 rpm, allowed us to quantitatively convert it to the corresponding C_5–C_9 hydrocarbons. The organic part of the liquid phase included approximately 15 % of pentane, cyclopentane, and methylcyclopentane, as well as 85 % of C_6–C_9 cyclohexane with or without methyl, ethyl, or propyl groups, along with some isomerized cycloalkanes and aromatic molecules (Figure 1 b) and methanol. Only trace

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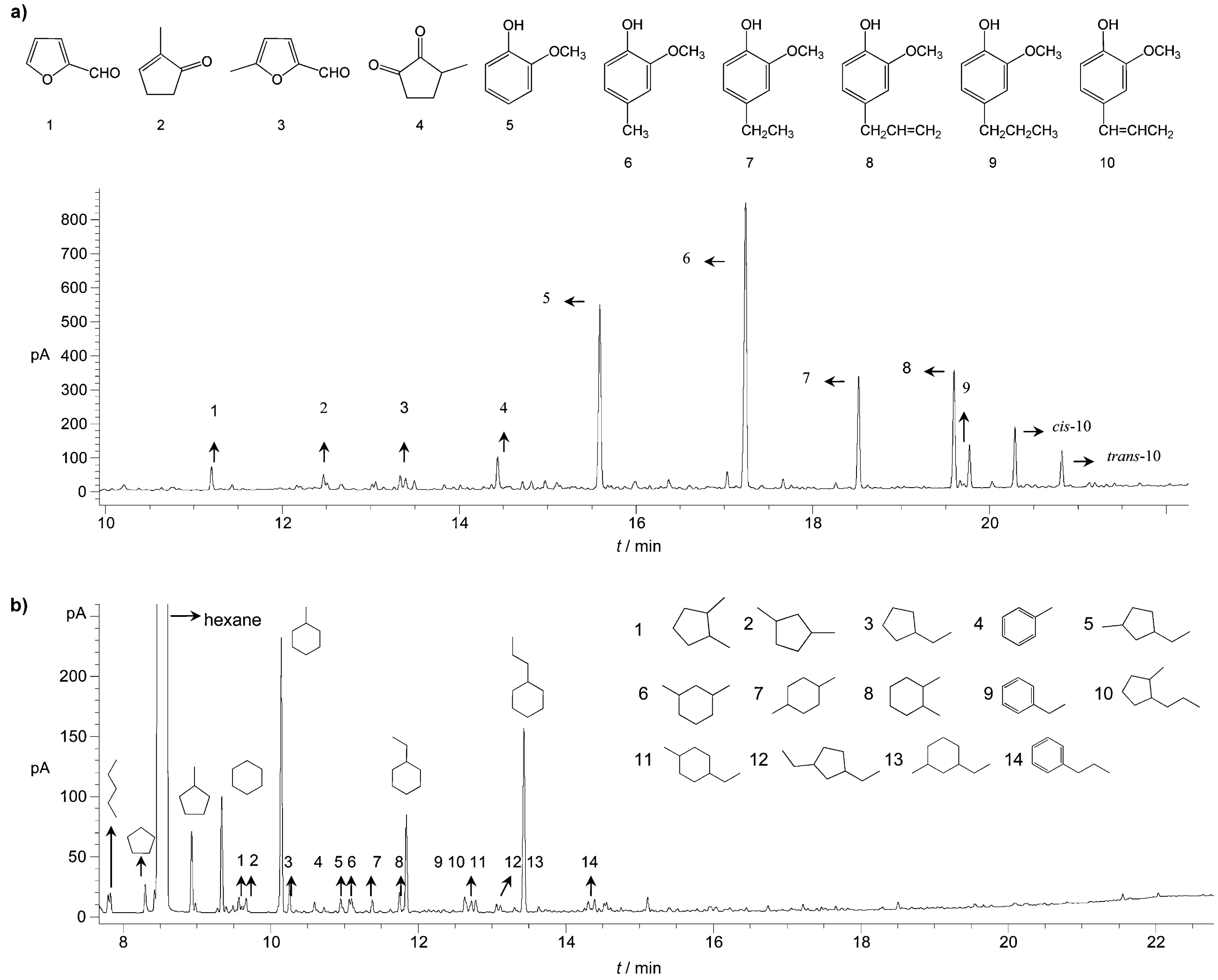


Figure 1. GC analysis of mixtures before and after upgrading. a) *n*-Hexane-extracted crude bio-oil. b) Upgraded hydrocarbon products.

amounts of CO_2 were found in the gas phase and the carbon balance in the liquid phase was better than 95%. It should also be noted that the C_5–C_9 hydrocarbon products mirrored the distribution of the corresponding components in pyrolysis oil (Figure 1a and b). Thus, we concluded that polymerization does not occur in the upgrading process. The octane numbers of the hydrocarbons produced (C_5–C_9 alkanes, cycloalkanes, and aromatics) mostly range from 80 to 120 (Supporting Information, Table S2), indicating that it is perfectly suitabile as a high-grade transportation gasoline fuel component. The water and oil phases are readily separated after reaction, allowing the produced hydrocarbons to be easily collected.

The bifunctional Ni/HZSM-5 catalyst, containing 20 wt% Ni and having a Si/Al ratio of 45 prepared by incipient wetness impregnation, shows high activity and selectivity for the hydrodeoxygenation of various C–O and C=O bonds in furans, alcohols, ketones, and phenols. The physicochemical properties of the catalyst are compiled in Figure 2 and are described in detail in the Supporting Information. Scanning electron microscopy of Ni/HZSM-5 shows corrugated zeolite particles with distinct domains of less than 1.0 μm. After Ni deposition and exchange, the pore volume (detected by N_2 sorption) decreased from 0.31 to 0.25 $cm^3 g^{-1}$ and the acid density (detected by temperature-programmed desorption of NH_3) decreased from 259 to 216 $\mu mol\, g^{-1}$. This indicates that a significant fraction of Ni is located inside the zeolite pores, providing the required proximity of metallic and acid sites for efficient hydrodeoxygenation. Analysis of this Ni fraction showed that the average Ni particle size of 24 nm as determined by transmission electron microscopy; the diameters of Ni (111) calculated from the Scherrer equation, based on the XRD patterns of Ni/HZSM-5 (22.8 nm); and the accessible fraction of Ni, determined by H_2 chemisorption (0.11); all agree perfectly. This provides sufficient hydrogenation ability for the overall reaction.

The HZSM-5 supported 20 wt% Ni catalysts were also tested in the conversion of a series of alkyl-, ketone-, or hydroxy-substituted phenols and guaiacols, as well as an alkyl-substituted syringol. This resulted in cycloalkanes (73–92%), aromatics (5.0–15%), and a fraction of methanol (0–17%),

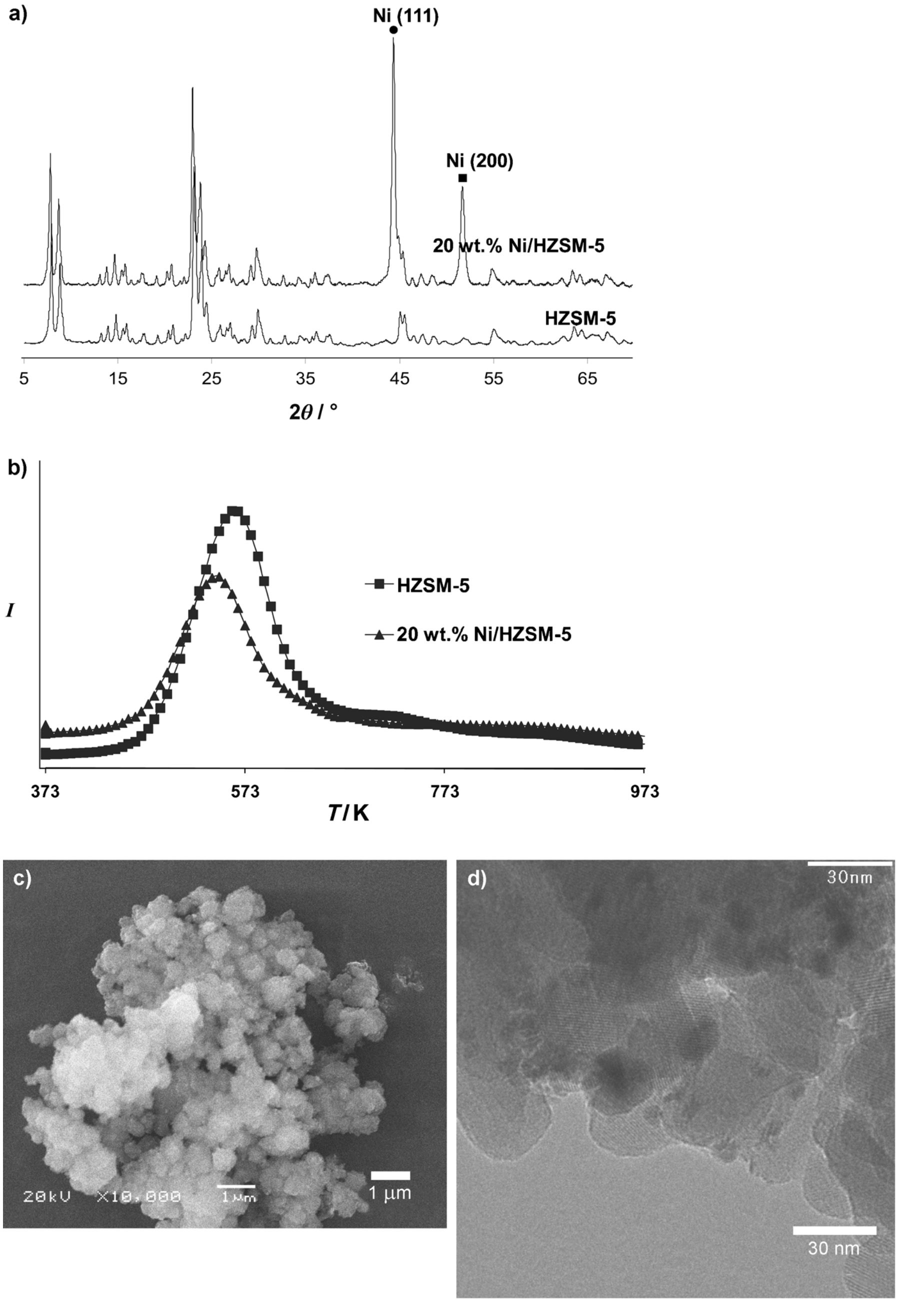


Figure 2. Characterization of HZSM-5 and Ni/HZSM-5 a) XRD. b) TPD of NH_3. c) SEM. d) TEM.

when reacted at 523 K, under 5 MPa H_2 for 2 h (Table 1). The ratio of cycloalkanes to aromatics can be altered by slightly changing the reaction parameters, such as reaction temperature, to modify the ratio of hydrogenation and dehydro-aromatization. Hydrogenation and dehydro-aromatization reactions are catalyzed by the supported Ni particles, while dehydration and hydrolysis are catalyzed by the Brønsted acid sites of HZSM-5.[8a–c] The Brønsted acidity of HZSM-5 also led to 25–60 % of cycloalkane isomers (Supporting Information, Figure S1).

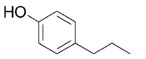
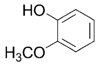
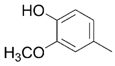
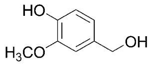
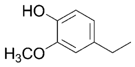
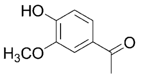
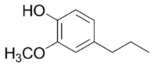
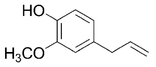
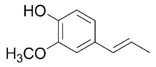
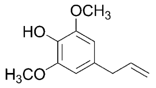
Mixtures of 4-*n*-propylphenol, 4-*n*-propylguaiacol, 4-hydroxy-3-methoxybenzyl alcohol, and 4′-hydroxy-3′-methoxyacetophenone were also successfully selectively upgraded to 90 % hydrocarbons and 10 % to methanol with quantitative conversions at 523 K after 5 h (Supporting Information, Figure S2a). Oligomerization between phenolic compounds was not observed, demonstrating that the reactive functional groups are quite stable in the selected aqueous system. Normally, phenols, aldehydes, and alcohols are quite reactive, forming hemiacetals, acetals, oligomers, and resins when exposed to acids.[3] Therefore, performing cascade reactions on Ni/HZSM-5 results in a highly integrated, atom economic process to produce hydrocarbons.

It is important to note that HZSM-5 showed a high rate of dehydration (Supporting Information, Figure S3) with turnover frequencies of approximately 1600 mol $\text{mol}_{\text{H}^+}^{-1}\,\text{h}^{-1}$, which was two orders of magnitude higher than that of H_3PO_4 (15 $\text{mol}\,\text{mol}_{\text{H}^+}^{-1}\,\text{h}^{-1}$).[7] We attribute this enhanced dehydration rate to two factors. One is related to the fact that the cyclohexanol concentration is substantial in HZSM-5, which is shown by in situ IR spectroscopy of adsorbed cyclohexanol in the gas phase (Supporting Information, Figure S4), indicating a substantial concentration of adsorbed cyclohexanol. In comparison, it was observed that cyclohexanol is hardly adsorbed at all on the other strong solid Brønsted acids tested. The second factor is that the pore size of HZSM-5 allows only the smaller alcohol monomers to reach the Brønsted acid sites of the zeolite, which rapidly shifts the alcohol monomer–oligomer equilibrium towards monomers, thus accelerating the overall dehydration rate.[10]

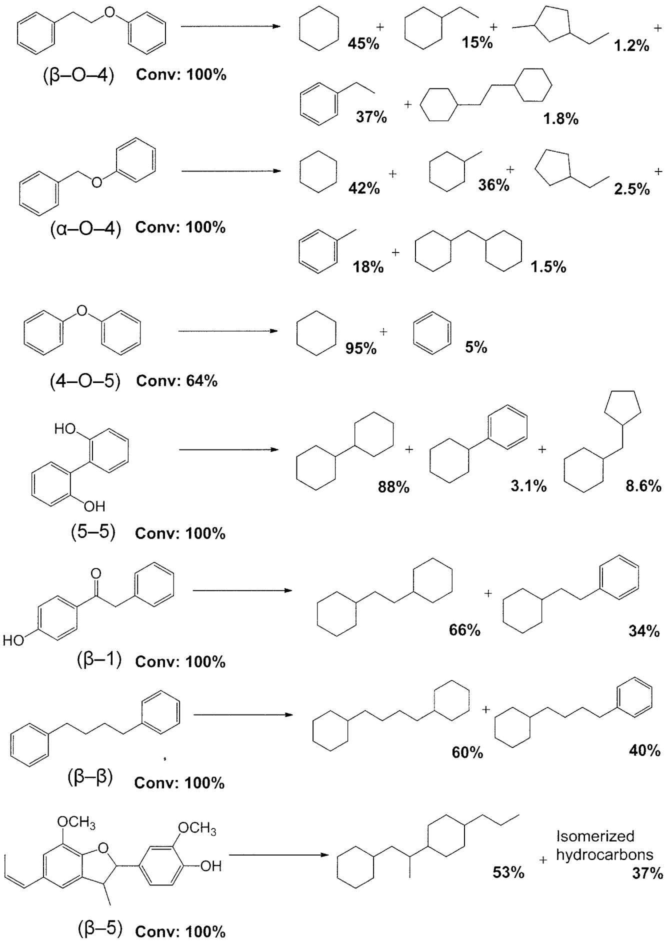
The stability of the Ni/HZSM-5 catalysts was tested by recycling the catalyst after separation, calcination, and reduction. No notable changes in activity or selectivity were observed over five cycles (Supporting Information, Figure S2b). After using the catalyst in the aqueous phase at 473 K for 80 h, leaching of Ni (monitored by atomic absorption spectroscopy) was below 5 ppm, demonstrating that the supported zeolite catalyst has high stability in water.

The Ni catalysts were also used to convert phenol dimers, which are present in large concentrations in bio-oil, because of the partial deconstruction of lignin.[11] The most representative linkages of phenolic dimers in spruce lignin are β-O-4

Table 1: Hydrodeoxygenation of phenolic monomers on Ni/HZSM-5.[a]

Phenolic reactant	Conv. [%]	Selectivity (C%) cycloalkanes	aromatics	methanol
	100	92	8.0	–
	100	74	13	13
	100	73	15	12
	99	80	9.6	10
	99	79	10	11
	100	77	12	11
	98	84	6.0	10
	100	80	11	9.0
	100	79	12	9.0
	93	78	5.0	17

[a] Reaction conditions: reactant (0.010 mol), 20 wt% Ni/HZSM-5 (0.5 g), H_2O (80 mL), 523 K, 5 MPa H_2, ambient temperature, 2 h, stirred at 680 rpm.



Scheme 1. Hydrodeoxygenation of phenolic dimers on Ni/HZSM-5. Reaction conditions: phenolic dimer (0.010 mol), 20 wt% Ni/HZSM-5 (0.5 g), H_2O (80 mL), 523 K, 5 MPa H_2, ambient temperature, 2 h, stirred at 680 rpm.

(55%), α-O-4 (8%), 5-5 (5%), 4-O-5 (5%), β-1 (15%), β-β (7%), and β-5 (10%), with both C–O–C linkages (2/3) and C–C linkages (1/3) existing. Therefore, different types of phenolic dimer model compounds were prepared (Supporting Information, Figure S3 and S4), and subsequently tested in the selected aqueous-phase process (Scheme 1).

For the C–O–C linkage, it is found that the β-O-4 and α-O-4 dimers (alkyl aryl ethers) were selectively converted over the Ni/HZSM-5 catalyst to greater than 98% yields of C_6 or C_7 hydrocarbons and less than 2% yields of C_{13} or C_{14} bicycloalkanes. Previously, thermal conversion of phenol dimers containing β-O-4 and α-O-4 bonds has always led to disordered free-radical reactions and a wide variety of by-products with less than 30% hydrocarbon selectivity and 10% conversion.[12] Conversion of α-O-4 dimer in superheated water followed both the ionic and radical mechanism pathways and also yielded a broad product distribution with phenol and many secondary recombination products.[13] In the absence of Ni, a 70% yield of recombination products, such as 2-benzylphenol, and a 30% yield of phenol were formed on acids in water under identical conditions. When Ni was added into the reaction, the product distribution was dramatically transformed into aromatics and cycloalkanes (Supporting Information, Figure S2). Recently, it has been reported that the C–O bonds in aryl ethers can be selectively hydrogenolized by a combination of ruthenium, vanadium, and nickel complexes.[14] Thus, we propose that the reaction route of β-O-4 and α-O-4 dimers proceeds through Ni-promoted hydrogenolysis to cleave the C–O bonds, followed by removal of the oxygen atoms anchored to the aromatic moieties by sequential hydrogenation and dehydration reactions.

For the conversion of the 4-O-5 dimer (diphenyl ether), benzene, and cyclohexane were formed with 64% conversion and 100% selectivity at 523 K. Hydrolysis of an aryl–aryl ether bond is very difficult, requiring drastic conditions and higher temperatures. Siskin et al. reported that even after 3 days, diphenyl ether was unreactive with aqueous solutions of 15% formic acid at 588 K and 10% phosphoric acid at 523 K.[15] It should be noted that diphenyl ether does not react when HZSM-5 alone is used as a catalyst under the reaction conditions. However, when metallic Ni and HZSM-5 were jointly applied, C–O bond cleavage of the aryl–aryl ether bond occurred, demonstrating that the bifunctional catalytic effect of the metal and the acid together is required to break down the aryl ether bonds.

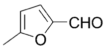
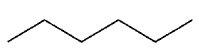
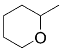
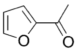
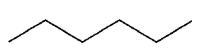
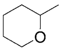
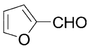
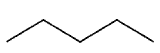
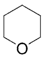
Through the sequential hydrogenation–dehydration–hydrogenation reactions, the C–C bonds in the 5-5, β-1, and β-β positions were preserved, while the oxygen-containing hydroxy or ketone functional groups were fully removed to produce C_{12}, C_{14}, and C_{16} hydrocarbons, respectively. Some aromatic products (3–40 %) were formed by the Ni catalyzed dehydroaromatization of cycloalkanes.

The β-5 linkage is a complex connection with both C–O–C and C–C bonds in an alicyclic ring containing oxygen. Under the selected conditions, the ring was selectively opened at the C–O bonds over bifunctional sites. The oxygen-containing groups in this reaction were then removed by the subsequent hydrodeoxygenation steps. Thus, a 90 % yield of C_{18} hydrocarbons (including of 37 % isomerized C_{18} hydrocarbons) and a 10 % yield of methanol were obtained (Figure 2 and Supporting Information, Figure S1).

The furan-like compounds in bio-oil are derived from the depolymerization of cellulose and hemicellulose. Cellulose and hemicellulose are pyrolyzed to C_5 or C_6 sugar units, and then these C_5 or C_6 sugars are gradually converted into C_5 or C_6 ketone-, aldehyde-, and alcohol-substituted furans through a series of dehydration, hydrolysis, and hydrogen transfer reactions (Supporting Information, Figures S7 and S8).

A typical product of cellulose pyrolysis, C_6 5-methylfurfural (MFF), was converted into 84 % *n*-hexane and 16 % 2-methyltetrahydropyran over the Ni/HZSM-5 catalyst in water at 523 K under 5 MPa H_2 for 2 h (Table 2, and Supporting Information, Figure S1). Dumesic et al.[16] reported that hydrogenation, but not ring opening, was the primary reaction for the furan ring on metal–acid bifunctional sites. Therefore, we propose that the reaction pathway for MFF hydrodeoxygenation proceeds through the hydrogenation of the furan ring, followed by hydrolysis of the C_5 ring, and subsequent alcohol dehydration/hydrogenation to form the straight-chain alkane.

Table 2: Hydrodeoxygenation of furan-like compounds on Ni/HZSM-5.[a]

Model compound	Conv. [%]	Selectivity (C %)			
	100		(84 %),		(16 %).
	100		(73 %),		(27 %).
	100		(64 %),		(36 %).

[a] Reaction conditions: reactant (0.010 mol), 20 wt % Ni/HZSM-5 (0.5 g), H_2O (80 mL), 523 K, 5 MPa H_2, ambient temperature, 2 h, stirred at 680 rpm.

The three OH groups from MFF hydrogenation and hydrolysis lie on the C_1, C_2, and C_5 positions. Thus, the most stable product, methyl-substituted C_6 tetrahydropyran, is preferentially formed by intermolecular dehydration. Once such a C_6 ring is formed, it is difficult to open by hydrolysis owing to the high conformational and tensional stability of the C_6 ring. Therefore, the parallel reactions of dehydration to form 2-methyltetrahydropyran and hydrodeoxygenation to form the alkane are competing, ultimately producing 84 % alkane and 16 % 2-methyltetrahydropyran. The conversion of the C_6 isomer, methyl 2-furyl ketone (MFK), led to a 73 % yield of *n*-hexane and a 27 % yield of 2-methyltetrahydropyran. Based on the same principle, a C_5 furfural, derived from hemicellulose pyrolysis, underwent hydrodeoxygenation/hydrolysis to give *n*-pentane in a 64 % yield and tetrahydropyran in a 36 % yield (Table 2).

Overall, the described aqueous-phase upgrading of the crude bio-oil components through the use of Ni/HZSM-5 is an efficient, sustainable, and economical bifunctional process. Under mild reaction conditions, Ni/HZSM-5 suitably hydrodeoxygenates all major components of the aromatic fraction of pyrolysis bio-oil (substituted furans, mono-phenols, and diphenols), through a hydrogenation–hydrolysis–dehydration–dehydroaromatization cascade. The resulting O-, S-, and N-free gasoline-range hydrocarbons produced contain less than 10 % of C_5–C_6 paraffins and more than 90 % of C_5–C_9 naphthenes and C_6–C_9 aromatic molecules, which allows direct blending into the gasoline pool. Because water is used as the solvent for this process, hydrocarbon products are easily collected by phase separation. The solid catalyst is highly hydrothermally stable and does not deactivate over a significant number of reaction cycles, showing that the process has great potential to be at the core of new technology for sustainable transportation fuels.

Experimental Section

The Ni/HZSM-5 catalyst was synthesized by the incipient impregnation method. A typical experiment procedure for hydrodeoxygenation of extracted bio-oil was carried out as follows: the crude bio-oil (200 mL) was extracted by *n*-hexane (6 × 40 mL), and then the organic layer was concentrated in vacuo (170 mbar) at ambient temperature. The weight fraction of *n*-hexane-soluble organic compounds was determined after solvent evaporation (20 wt % with 70 % C content). The extracted carbon content C % = (extracted weight fraction × C content)/[(1−water fraction) × C content] × 100 %.

The extracted organics derived from bio-oil (10 mL) were then loaded into a stainless steel Parr autoclave (Series 4848, 300 mL) with distilled water (80 mL) and Ni/HZSM-5 (20 wt %, 2.0 g, Si/Al = 45) at 523 K. The reaction mixture was then placed under 5 MPa H_2 at ambient temperature for 4 h, with a stirring speed of 680 rpm. After reaction, the organic layer and aqueous layer were separated and analyzed by GC (Shimadzu 2010, flame ionization detector) on a capillary column (HP-5; 30 m × 250 μm) and by GC-MS (Shimadzu QP 2010S). The gas phase was analyzed by a GC (HP 6890) equipped with a capillary column (Plot Q; 30 m × 250 μm) and a thermal conductivity detector (TCD). Hydrogen (99 %) and trace amounts of CO_2 and methanol were found in the gas phase, so in this work only the changes in the liquid phase were considered. The calculations of conversion and selectivity were performed on a carbon mole basis. Conversion = (changes in raw material/total amount of raw phenolic compounds) × 100 %. Selectivity = (C atoms in each product/total C atoms in the products) × 100 %. The carbon balance in the liquid phase is up to 94 ± 3 %.

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