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Quantitative Study of Straw Bio-oil Hydrodeoxygenation over a Sulfided NiMo Catalyst

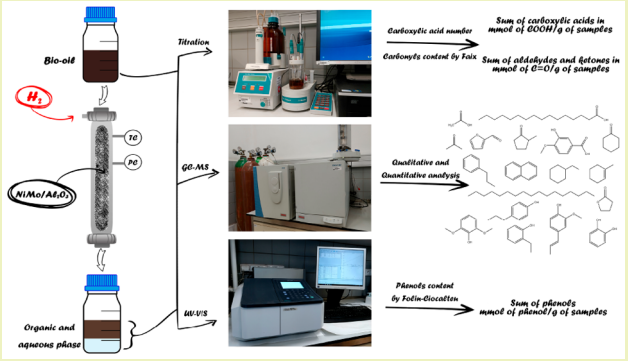
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Supporting Information

ABSTRACT: Bio-oil upgrading through its hydrodeoxygenation (HDO) using sulfided catalysts has attracted significant attention because of its potential to provide advanced biofuels. Although many studies have been undertaken, a detailed understanding of the changes in the chemical composition on the molecular level that would allow the better design of catalysts for bio-oil upgrading is still insufficient. Therefore, we have subjected straw bio-oil and products obtained from its hydrotreatment over a broad range of experimental conditions to a detailed quantitative chemical analysis. Most of the volatile compounds were quantified by GC-MS. Among them, 115 compounds were quantified directly (i.e., using the appropriate standards) and more than 100 indirectly (i.e., based on their structural similarity with corresponding standards). Moreover, the total concentrations of carboxylic acids, carbonyls and phenols were quantified by the carboxylic acid number (CAN), Faix, and Folin−Ciocalteu methods, respectively, to obtain complementary and supporting information on the chemical composition to the GC-MS data. The detailed quantification of most volatile compounds in the feed and the products allowed us to create a reactivity order of the oxygen-containing functional groups present and to understand the origin of some of the compounds. On the basis of the results, the upgrading of straw bio-oil from ablative fast pyrolysis at 340 °C and 4 MPa seems to be optimal when evaluating the severity of the reaction conditions and hydrogen consumption, on the one hand, and the products quality, on the other hand. This provides a good starting point for further catalyst development and optimization allowing the long-term upgrading of the bio-oil for obtaining petroleum-refinery-compatible feedstock.



KEYWORDS: *Ablative flash pyrolysis, Hydrodeoxygenation, Quantitative analysis, GC-MS, Carboxylic acids, Carbonyls, Phenols*

INTRODUCTION

Fast pyrolysis is one of the simplest and most cost-effective options for the conversion of a lignocellulosic biomass into a bio-oil, achieving yields of up to 75 wt %.[1] Despite its undesirable properties (thermal lability, high acidity, high water/oxygen content),[2] the bio-oil has the potential to be used for the production of advanced biofuels. For this purpose, it is necessary to reduce the oxygen content of the bio-oil and to improve its properties in general. Despite its high operating expenditures, hydrotreatment is one of the most promising methods for bio-oil upgrading, producing higher yields of upgraded products with an acceptable quality.[3] Thus, it is desirable to optimize the bio-oil hydrotreatment process. For this purpose, a quantitative characterization of the chemical composition of the bio-oil and its upgraded products is crucial.[4]

A bio-oil is a complex mixture of hundreds to thousands of oxygenates.[5] Together with the fact that its chemical composition is strongly dependent on the original biomass,[2] this makes a detailed quantitative characterization very difficult and time-consuming. Probably, for this reason, some papers studying bio-oil hydrodeoxygenation (HDO) only focused on the characterization of the physicochemical properties of the HDO products.[6−8] To simplify the determination of the bio-oil composition, some researchers used the percentage of the total peak area obtained from GC-MS to estimate the content of the individual chemical compounds.[4,9−11] However, such an approach can be misleading due to the different response factors of the different oxygenates.

To our best knowledge, just three papers focused on the detailed quantification of the chemical changes occurring during the bio-oil HDO.[12−14] Routary et al.[12] used GC-FID and HPLC-RI to quantify oxygenates and a special GC-MS

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technique (nitric oxide ionization spectroscopy evaluation) to quantify the hydrocarbons formed. Sanna et al.[14] used GC-MS for the quantification of 28 different compounds and HPLC for the quantification of saccharides. Nevertheless, the most detailed study up to now was apparently carried out by Stankovikj et al.[13] from the National Renewable Energy Laboratory (NREL). This team developed, validated,[15] and recently published several methods for quantifying the most important chemical groups in bio-oils, such as carboxylic acids (CAN method),[16] carbonyls (Faix method),[17] and phenols (Folin−Ciocalteu method).[18] Stankovikj et al.[13] applied these methods to study the changes that occur in the nonvolatile oligomeric fractions during the bio-oil HDO. To quantify the changes in the volatile fraction, they used GC-MS. All of these works were focused on the hydrotreatment of wood bio-oil over noble metal catalysts. Because of their very high catalytic activity, the hydrogen consumption in the bio-oil HDO over these nonsulfided catalysts is higher than that over the sulfided catalysts, thereby increasing the processing costs and reducing product sustainability.[19] Moreover, the noble metals can be poisoned by the presence of even small amounts of sulfur compounds in the bio-oil,[19] which is why the well-established and robust sulfided catalysts remain the preferred choice for bio-oil HDO.[20]

Compared with noble metal catalysts, where HDO is often preceded by saturation of the aromatic rings, HDO preferably takes place over sulfided catalysts.[21] Often, only model compounds representing the typical compounds present in bio-oil have been hydrodeoxygenated over sulfided catalysts.[22] Typically, the reactivity of such compounds has been assessed individually, but their reactivity can be quite different in complex mixtures, such as bio-oils. The HDO of real bio-oils over sulfided catalysts has been studied as well[9,23,24] but with the main focus on the qualitative changes in the physicochemical properties, that is, none of the studies quantified the changes that take place in the chemical composition of bio-oils.

In our previous paper, we tested a sulfided $NiMo/Al_2O_3$ catalyst for the HDO of a straw bio-oil (as an alternative to the wood bio-oil generally used) from the ablative fast pyrolysis and analyzed the physicochemical properties of the resulting HDO products.[25] To provide a deeper understanding of the whole straw bio-oil HDO process over the sulfided catalysts, we have built upon our previous work and present what, to our best knowledge, is the first such detailed quantitative study of this process including analysis of both the aqueous and organic phases formed. Low-molecular compounds were quantified by GC-MS, 115 of them were quantified directly and the other more than 100 indirectly. The total concentrations of the carboxylic acids, carbonyls and phenols were quantified by the carboxylic acid number (CAN), Faix, and Folin−Ciocalteu methods, respectively. Thanks to the detailed analysis of the volatile compounds, we were able to consider the reactivity of the respective groups in the nonvolatile fractions of the samples. All of this allowed us to understand the complexity of the bio-oil HDO and to decide about the most favorable conditions for maximizing deoxygenation while minimizing hydrogenation of the aromatic rings. Moreover, the manuscript can serve as an overview of the HDO of oxygenates present in a real bio-oil over a sulfided catalyst. This quantitative description contributes to a better understanding of the whole process that is necessary for further advances in bio-oil hydrotreatment.

EXPERIMENTAL SECTION

Bio-oil and Hydrotreatment. Straw bio-oil was produced at Fraunhofer UMSICHT by the ablative fast pyrolysis of straw (wheat and barley, 1:1 w/w). The straw in the form of pellets was pressed onto a hot rotating disc and pyrolyzed at 550 °C with a vapor residence time of less than 1 s. After condensation at 2−5 °C, the liquid product spontaneously separated into an aqueous and organic phase (bio-oil used as feed for the hydrotreatment). More details are given in the literature by Schulzke et al.[26]

Before the hydrotreatment experiments, the bio-oil was first filtered to remove residual solids and then doped with 0.5 wt % dimethyl disulfide (Sigma-Aldrich, DMDS ≥ 99.0%) to maintain the catalyst activity as suggested by Yoshimura et al.[27] A commercial sulfided $NiMo/Al_2O_3$ catalyst (5.5 wt % of NiO and 28.3 wt % of MoO_3) and hydrogen (SIAD, 99.9 vol %) were used in the continuous fixed-bed hydrotreatment experiments. Two sets of experiments were carried out. In the first one (further labeled as $T/4$), the temperature (T) was increased from 240 to 350 °C at a constant hydrogen pressure of 4 MPa. The second experiment set was labeled as T/P; the temperature (T) and hydrogen pressure (P) varied between 300−360 °C and 2−8 MPa, respectively. Compared to our previous paper,[25] the $T/4$ experiment was repeated with a greater emphasis on the reaction conditions around 300 °C and 4 MPa, where the density of the organic phase became lower than that of water for the first time. Therefore, the temperature change step between 280−330 °C was only 10 °C.

The reaction products were labeled as follows: T/P = desired average temperature (°C)/pressure (MPa), the real average temperature in the catalyst bed and the time on stream of each reaction condition are summarized in Tables S1 and S2. The other reaction parameters were kept constant: WHSV was 1 h^{-1} (feed flow 50 $g{\cdot}h^{-1}$) and hydrogen flow rate at standard conditions was 90 $L{\cdot}h^{-1}$. The reactor configuration, catalyst activation, and other details of the hydrotreatment process are described in detail elsewhere.[25]

Analysis of the Feed and Products. The detailed description of the analytic measurement procedures for the elemental composition and water content analyses, commented on in this manuscript, was given elsewhere.[25]

GC-MS Analysis. A gas chromatograph Focus GC equipped with an autoinjector AI 3000, connected to a DSQ mass spectrometer (all Thermo-Fisher Scientific) was used for the GC-MS analyses. The instrument control, data acquisition, and processing were performed using Xcalibur 2.2 software (Thermo-Fisher Scientific). The conditions of the GC-MS analysis are given in Table 1. All samples

Table 1. Conditions of the GC-MS Analysis

parameter	description
injection	250 °C, 1 μL, split 1:20
carrier gas	helium, (5.5), 1 $mL{\cdot}min^{-1}$
temperature program	32 °C (8 min), then 5 $°C{\cdot}min^{-1}$ to 300 °C (10 min)
column	ZB-5MSi, W/Guardian, 30 m (+5 m Guardian end) × 0.25 mm × 0.25 μm
interface	280 °C
MS ionization	EI^+, 70 eV
solvent delay	3.0 min (only for analysis of acetone solutions)
data acquisition	full scan, 20−500 Da
scanning frequency	5 $scans{\cdot}s^{-1}$
analyzer	quadrupole

(~80 mg) were dissolved in about 1.7 mL of acetone (Penta, p.a.) for the GC-MS analysis. Compounds with retention lower than or equal to that of acetone were analyzed in an *n*-butanol (Penta, p.a.) solution prepared at the same concentration level. The exact weight concentration obtained was finally used for the calculation of the wt % in a real sample. Ten microliters of an internal standard stock solution was added into each sample. The internal standard solution contained 1-butoxypropan-2-ol (Sigma-Aldrich) and 2-naphthalde-

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hyde (Koch Light) dissolved in ethanol (Penta, absolute for UV spectroscopy). The concentration of each internal standard in the stock solution was 34 mg·mL^{-1}. The prepared samples were homogenized in an ultrasonic bath and filtered using a 0.45 μm syringe filter. Identification of the detected compounds was performed using a NIST 14 mass spectra library, standard compounds, or Kovats indices; only the peaks with a match factor above 700 were further quantified.

Four mixtures containing 115 standard compounds (each approximately 1 mg·mL^{-1}) were used for the direct quantification: (i) most of the oxygenates were dissolved in acetonitrile (Merck, LC grade), (ii) acids and some other oxygenates were dissolved in ethanol (Penta, absolute for UV spectroscopy) to avoid coelution with the compounds present in the first mixture, (iii) low-boiling-point oxygenates were dissolved in *n*-butanol (Penta, p.a.), and (iv) hydrocarbons were dissolved in *n*-hexane (Penta, 99%, p.a.). For each compound, a six-point calibration curve covering the concentrations from 25 to 1000 μg·mL^{-1} was created (measured from the lowest to the highest concentration). The quantification was performed using the Xcalibur 2.2 Quan Browser tool; all calibration curves were obtained with an R^2 value of ≥0.995 from at least 4 points. For a more precise quantification, the areas of the peaks from the selected extracted ions specific to each compound (instead of the total ion current (TIC)) were used. Usually, one up to three ions with the highest intensity specific for the compound concerned were selected. Other compounds were quantified indirectly based on the response factor of the most structurally similar compounds,[28] using eqs 1 and 2. The list of standards, suppliers, purity, ions for quantification, relevant oxygenates group, and other quantified compounds are given in Tables S3−S6. The primary results of the quantification expressed in μg·mL^{-1} were recalculated to wt %. For a better comparison between the product samples and the feed, the cumulative changes in wt % for each compound were calculated as the wt % of a compound divided by the yield of the relevant product, that is, as the yield of the compound. To compare between the GC-MS results and the results obtained from other applied methods (see below), the yield of each compound (cumulative wt %) was recalculated to mmol·g^{-1} using the molecular weight of relevant compound and further multiplied by the number of relevant oxygen functional groups for CAN and Faix methods.

$$C_i = A_{m/z}(i)/k(i) \times k(\mathrm{STD})/A_{m/z}(\mathrm{STD}) \times C_{\mathrm{STD}} \quad (1)$$

where C = concentration, A = peak area, k = ratio of ions area, i = similar compound to STD, and STD = standard compound.

$$k(i) = \frac{A_{m/z}(i)}{A_{\mathrm{TIC}}(i)} \quad (2)$$

where k (i) is the ratio of the area of ions for the quantification and total TIC area, determined from the NIST library.

Carboxylic Acid Number. The carboxylic acid number (CAN) was determined by a 716 DMS Titrino instrument (Metrohm AG) equipped with LabX titration software using a titration method described in detail elsewhere.[16] The electrode system consisted of combined glass, silver chloride and platinum electrodes (Metrohm AG). The sample (0.2−3.0 g, the amount used increased with its decreasing acidity) was titrated by a 0.1 M solution of tetrabutylammonium hydroxide (86854 Sigma-Aldrich) dissolved in a 10:1 V/V mixture of isopropyl alcohol and methanol (Penta, p.a.) standardized by a known amount of potassium hydrogen phthalate (Sigma-Aldrich). A 0.4 M solution of tetraethylammonium bromide (Sigma-Aldrich, 98%) dissolved in ethylene glycol (Penta) was used as an electrolyte in the silver chloride electrode and isopropanol (Penta, p.a.) was used as a sample solvent. Each sample (feed or HDO product) was analyzed in triplicate.

Carbonyls Content by Faix. The total carbonyls content was determined by the Faix method based on the oximation of the carbonyl group and further by the reverse titration of the released HCl, described in detail elsewhere.[17] The sample (0.2 g for the feed, up to 1.0 g for the best, that is, the most deoxygenated product 360/8) was weighed into an 8 mL vial. Then, (i) 1 mL of dimethyl sulfoxide (DMSO; Penta, p.a.), (ii) 2 mL of hydroxylamine hydrochloride (NH_2OH·HCl, Sigma-Aldrich, ≥99.9995%) solution (0.3 M in 80% ethanol), and (iii) 2 mL of triethanolamine (TEA, Sigma-Aldrich, ≥ 99.0%) solution (0.5 M in ethanol) were added in the given order. The vial was tightly closed and placed into a preheated bath (80 °C), where it was stirred for 2 h to complete the reaction. In addition, each sample group included three blank samples (consisting of a mixture of the DMSO, NH_2OH·HCl, and TEA solutions). After it was cooled down to ambient temperature, the sample was quantitatively transferred into a titration vessel using distilled water and ethanol to create an 80% ethanol solution and titrated. Each sample (feed or HDO product) was prepared, oximated, and analyzed in triplicate.

Phenols by Folin−Ciocalteu. The total content of the phenols was measured by the Folin−Ciocalteu method optimized for bio-oils.[18] The bio-oil and products were dissolved in ethanol (Penta, absolute for UV spectroscopy) to obtain samples with a concentration of ∼500 mg·L^{-1}. The sample was homogenized in an ultrasound bath and then 20 μL of this solution was weighed into a 1 cm path-length polystyrene cuvette. Then, 1.58 mL of distilled water and 100 μL of the Folin−Ciocalteu reagent (Sigma-Aldrich, 2 N) were added, and the content of the cuvette was properly mixed. After ∼5 min, 300 μL of a 20% aqueous solution of sodium carbonate was added in to the cuvette. The mixture was again properly mixed and allowed to develop the color for 2 h at ambient temperature. Gallic acid (Sigma-Aldrich, 97.5−102.5%) was used as a calibration standard to create a four-point calibration curve between the concentrations of 50 and 500 mg·L^{-1}. The absorbance of all the samples was measured after a final homogenization against a blank (20 μL of ethanol instead of a sample) at 765 nm using a UV-1800 spectrophotometer (Shimadzu, Japan). The average of three measurements was recalculated to mmol of phenols per gram assuming phenol as the surrogate structure[29] to allow a direct comparison with the GC-MS results.

RESULTS AND DISCUSSION

Physicochemical Properties. The physicochemical properties of the organic phases were discussed in our previous paper.[25] Regarding the aqueous phase (AP), only the elemental composition and water content were measured. We found that the AP contained 8.7 and 7.3 wt % of carbon for the mildest reaction conditions of 240 °C at 4 MPa and 300 °C at 2 MPa, respectively. The carbon content gradually decreased with the increasing severity of the reaction conditions (and, thus, the lower content of the polar oxygenates in the reaction system) to 2.4 and 1.0 wt % for the most severe conditions tested, that is, 350 °C at 4 MPa and 360 °C at 8 MPa, respectively (Tables S1 and S2). The carbon content in the AP evidence the presence of organics in the aqueous phase, which consequently contained between 85 to 98 wt % of water only (Tables S1 and S2).

GC-MS Analysis. First, the temperature program of the GC-MS analysis was optimized to obtain the optimum separation of all the samples. Then, two internal standards, which did not coelute with any peak in all of the samples, were selected. The first one (1-butoxypropan-2-ol) eluted in the first quarter of the chromatogram (retention time 16.45 min) was used for the quantification of all the compounds with the retention time (RT) of up to 24.50 min. The second one (2-naphthaldehyde RT 33.50 min) was used for the quantification of all the compounds with the RT of 24.51 min and higher. In total, 115 compounds were quantified directly and almost 140 other ones indirectly; most of them were present in the product organic phase and in the feed. Only some compounds were unique for the product aqueous phase, such as cyclohexanediols.

The feed (being the least homogeneous sample) was used, after homogenization, to prepare five samples for further analysis. Each of them was analyzed three times using the same calibration curve. We found that for the most of the oxygenates

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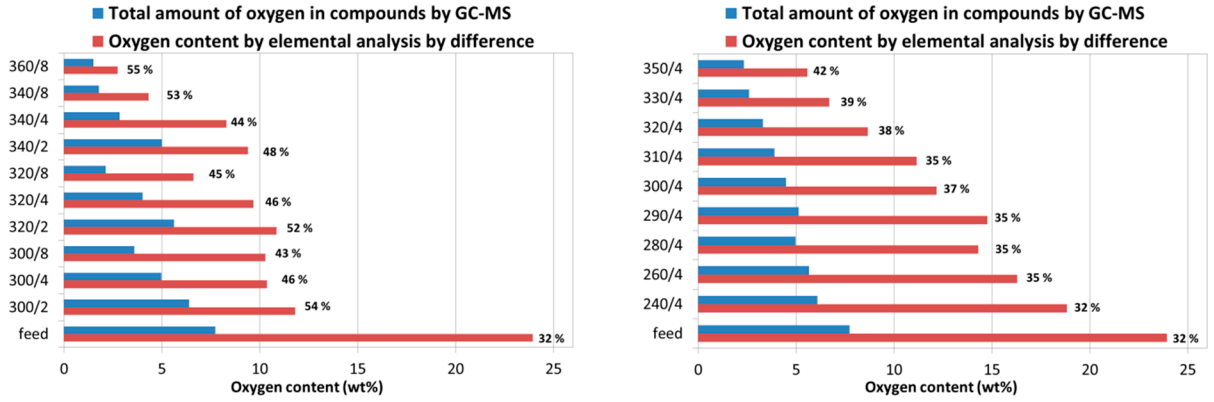


Figure 1. Total amount of oxygen in oxygenates determined by GC-MS vs the total amount of oxygen determined by elemental analysis in organic phase of bio-oil and products. The number on the right side of the red column is the share of the blue/red column.

in the standard mixtures (Tables S3−S5), the calibration curve was very stable with an R^2 value significantly higher than 0.995, and the relative standard deviation (RSD) was up to 5% for the 15 results obtained for each compound in the feed, see Table S7. There were only a few compounds with an RSD between 5−6%, such as pentan-3-one, 2,6-dimethylphenol, 2-propylphenol, 2,4,5-trimethylphenol, and 2,3-dimethylphenol (Table S7). The slightly higher RSD for these compounds was mainly caused by their low concentrations in the feed (below 0.1 wt %). For 2-ethyl-4-methylphenol, *cis*-methylisoeugenol, and 3-/4-propylphenol, the RSD was higher than 6% (Table S7), and this was caused by even lower concentrations of these compounds (below 0.05 wt %). The only compounds with a poorly stable calibration curve (RSD above 6%) were carboxylic acids (vanillic, isovanillic, palmitic, and stearic), pyrocatechol, and levoglucosan (Table S7); all of these compounds had tailing peaks. Excluding pyrocatechol, the higher RSD was probably caused also by high boiling points of these compounds leading to their discrimination in the injector.

Quantification of Oxygenates in the Aqueous Phase by GC-MS. As mentioned in previous section, the aqueous phase contained less than 9 wt % of carbon. We were only able to quantify 44 different oxygenates in the aqueous phases (APs) in total. They included predominantly low-molecular-weight alcohols, ketones, and acids up to valeric acid with acetic acid amounting to at least 40% of all the organic compounds present. All quantified compounds and their calculated amounts are given in Tables S8 and S9. The directly quantified compounds constituted more than 80% from all the quantified compounds in the AP. Except for the mentioned compounds, benzenediols, phenols, and lactones were present in the AP. The quantified compounds accounted from 50 wt % up to almost 90 wt % of the total carbon content determined by elemental analysis in the APs (Tables S8 and S9). We observed very low oxidation stability of the APs except those from the 340/8 and 360/8 products, which contained a very low amount of organic matter. After the removal of the APs from the samples and enabling access to the air, solid dark particles were formed after a few days, see Figure S1. This implies that most of the unidentified carbon was probably constituted by unstable compounds probably of saccharides or lignin origin that were soluble in water and not detectable by GC-MS.

Quantification of Oxygenates in the Organic Phase by GC-MS. We were able to identify and determine 32% of the volatile oxygenates in the feed. For the best, that is, the most deoxygenated product (360/8), it was more than 50 wt % (Tables S10 and S11). The total amount of oxygen (determined by elemental analysis by difference) in the *T*/*P* experiment sharply decreased to one-half compared to the feed already in the 300/2 product. This step change was definitely caused by the removal of water from the product by the separation of the HDO products into an aqueous and organic phase. Another reason could be the decomposition of the high-boiling pyrolytic lignin molecules and the subsequent deoxygenation of the aldehyde and aliphatic hydroxyl groups. An increase in pressure at 300 and 320 °C led to a gradual decrease in the ratio of volatile oxygenate compounds (Figure 1). As the decrease in volatile fractions was sharper than the decrease in the total oxygen content in the whole sample, we think (based on GC-MS chromatogram) that this difference was caused by the occurrence of many intermediates volatile products that were not identified and, thus, quantified due to coelution and/or unavailability of the spectra in the MS library. The decomposition of the pyrolytic lignin molecules further increased at 340 °C and 8 MPa, and thus, the share of oxygen in the volatile compounds (mainly with propyl substituent) has again increased (Figure 1). In the course of all the subsequent reactions (Figure S2), the main product of this decomposition, 4-propylphenol, reached its maximum content at 350 °C and 4 MPa (Figure 2G). Unfortunately, the results from *T*/*P* and *T*/4 experiments at the same reaction conditions (300 and 320 °C at 4 MPa) are not directly comparable. It is a consequence of a significant difference in the time-on-stream (Tables S1 and S2) and, hence, the different extent of the catalyst deactivation.

The total amount of the compounds quantified in the organic phases by GC-MS varied between 23 and 38 wt % (Tables S10 and S11). The highest amount of the compounds was determined as expected (based on the significant decrease in the MCR) in the sample prepared at 360 °C and 8 MPa (i.e., 360/8). The total fraction of the sample that was identified can be obtained by adding the water content in the relevant sample to the total concentration of all the organic compounds identified and quantified by GC-MS. For example, 48.4 wt % of the feed was determined in detail (Table S10). A change in temperature as well as in the pressure only had a minimal influence on the share of the quantified compounds in the volatile fractions, the only exceptions were the conditions ≥340 °C at 8 MPa (Table S11), caused by the increase in the extent of the pyrolytic lignin decomposition as was discussed above.

Nonquantified compounds formed approximately 5% of total TIC peak area of feed, to less than 15% in the case of the HDO products. This slightly higher abundance of the nonquantified

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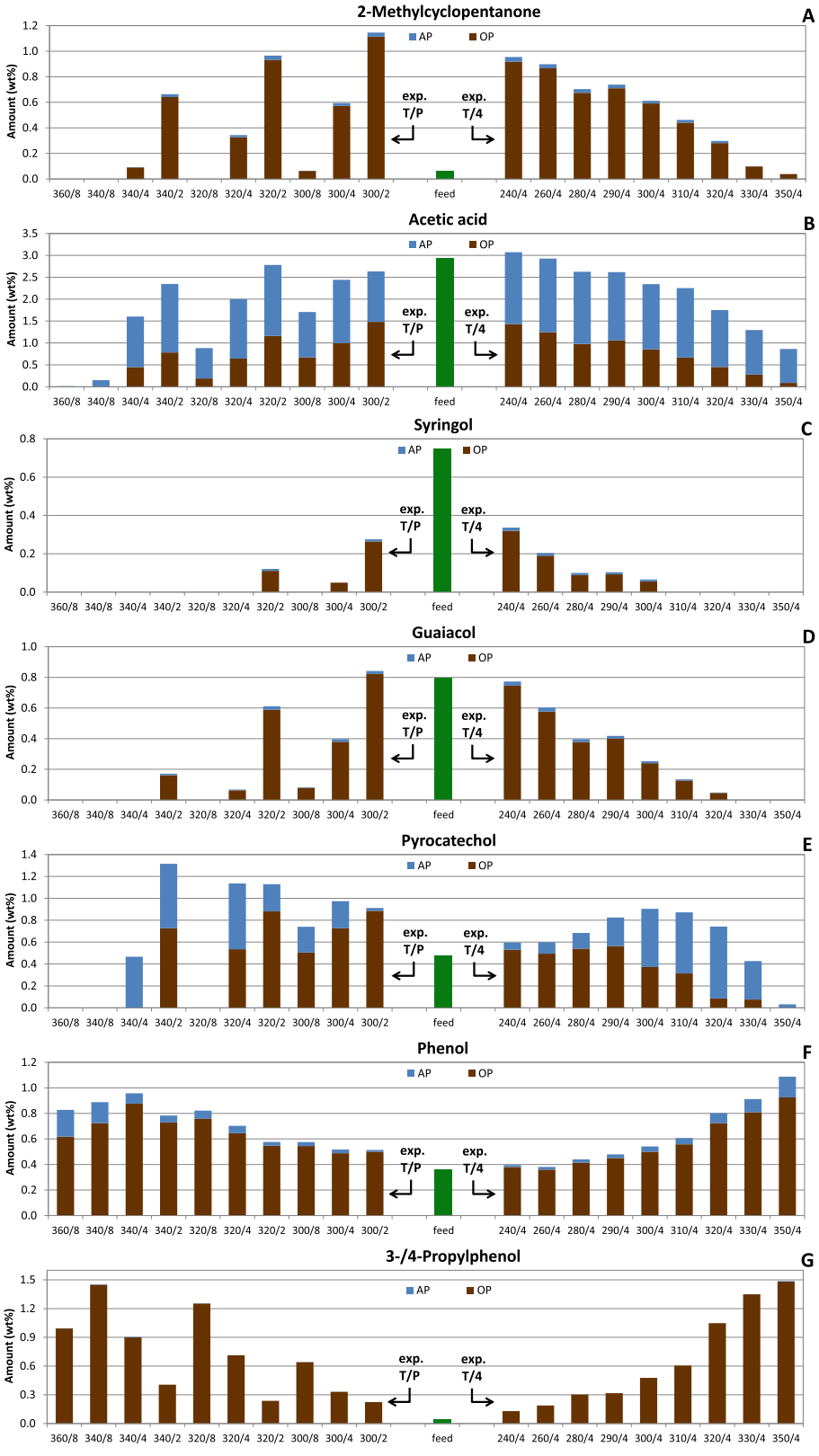


Figure 2. Cumulative changes in wt % of the compounds representing each group of oxygenates and their distributions between the aqueous and organic phase.

compounds was due to several reasons: (i) the increase in the number of compounds with a very low concentration that could not be identified with sufficient precision (and thus quantified); (ii) the increase in the peak coelution and then impossible identification; and (iii) more compounds with high-boiling-point that could not be identified and quantified were also present. Nonetheless, the majority of the volatile compounds was reliably identified and thus quantified.

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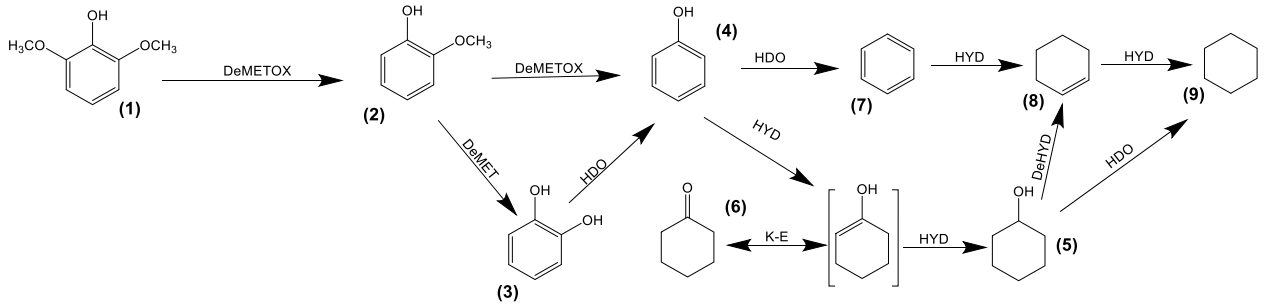


Figure 3. Reaction scheme of the nonalkyl monocyclic compounds. Compounds: (1) syringol; (2) guaiacol; (3) pyrocatechol; (4) phenol; (5) cyclohexanol; (6) cyclohexanone; (7) benzene; (8) cyclohexene; (9) cyclohexane. Reactions: HYD, hydrogenation; DeMEOX, demethoxylation; DeMET, demethylation; HDO, hydrodeoxygenation; K-E, ketone/enol isomerization.

Distribution of the Selected Compounds between the Organic and Aqueous Phase. During the bio-oil hydrotreatment, the single-phase bio-oil separated into an organic and aqueous phase as a result of the changes in its polarity. Consequently, some of the oxygenates were present in both the organic and aqueous phases which makes rigorous quantification of these compounds challenging. Significant elution into the aqueous phases was observed particularly for acids and benzenediols (Figure 2B and E) and at elevated reaction temperatures (>320 °C) for phenol also (Figure 2 F). The elution of these compounds into the aqueous phase was favored by the increased hydrotreatment severity that resulted in the decreasing of the organic phase polarity. The elution of other compounds into the aqueous phase was very limited (Figure 2). As expected, the presence and the increasing length of the alkyl chain in the phenolic compounds decreased their solubility in the aqueous phase. Thus, 3-/4-propylphenol was present in the aqueous phase in a very small concentration only at the most severe hydrotreatment conditions, that is, when the least polar organic phase product was obtained (Figure 2G, Tables S8 and S9). These findings are supported by the solubility of these compounds in water (Table S12). These results also show the necessity of analyzing both the aqueous and organic phases to obtain the complete information about the products formed. This can be demonstrated on pyrocatechol and acetic acid. Without the aqueous phase analysis, one would erroneously concluded that pyrocatechol and acetic acid were completely removed already from the reaction mixture at 340 °C and 4 MPa and 340 °C and 8 MPa, respectively. However, under these conditions, the unconverted pyrocatechol and acetic acid were present exclusively in the aqueous phase (Figure 2B and E).

For 2-methylcyclopentanone, as a ketone with the highest concentration in the HDO products, only very low elution into the aqueous phase was observed. More interestingly, its concentration increased dramatically in the products, particularly those obtained at the mildest reaction conditions, that is, at 300/2 and 240/4 (Figure 2A). On the basis of the detailed quantitative GC-MS analysis, we suggest that 2-methylcyclopentanone was created, in addition to hydrogenation of 2-methylcyclopent-2-enone (0.30 wt % in the feed) as also reported by Gunawan et al.,[30] by partial deoxygenation of 3-methylcyclopenta-1,2-dione (0.60 wt % in the feed).

Deoxygenation of Typical Oxygenates Groups. In this section, we will discuss the reactivity of all the typical oxygenate groups present in the bio-oils. We start with compounds created predominantly by the pyrolysis of cellulose and hemicellulose. Then, we will describe the reactivity of the typical aromatic compounds produced by lignin pyrolysis. We focused on nonalkylated ones and those with a propyl substituent. For those two groups, the reaction schemes were created.

The most reactive oxygenates were aldehydes that completely disappeared under both mildest conditions tested, see Tables S13 and S14. These results are in line with those presented by Elliott[31] for sulfided catalyst. On the contrary, we observed a lower reactivity of the ketones and alcohols that were completely removed only at 320 °C and 8 MPa, and at 340 °C and 8 MPa, respectively, compared to the temperatures below 200 °C reported by Elliott.[31] The main reason was probably their formation from other compounds (by consecutive reactions) and higher space velocity (1 h^{-1}) than usually used for the bio-oil hydrotreatment (~0.3 h^{-1}),[32] which did not allow their complete deoxygenation. The starting temperature of the reactivity of acetic acid in our experiments was close to that reported by Elliott[31] for acids in general (>260 °C vs ca. 290 °C). Only at 240 °C and 4 MPa, we observed a little bit higher concentration of acetic acid in the reaction system (Figure 2 B), which was caused probably by its creation from other compounds by consecutive reactions. Butyric acid was the only quantified acid for which we observed the significant increase in concentration in the products (Tables S7 and S15). The significant creation of butyric acid during hydrotreatment (the deoxygenation exceeds creation at 300 °C and 4 MPa for the first time) is in line with the results published by Chaiwat et al.[33] Although, the deoxygenation (conversion) of carboxylic acids started at temperatures below 300 °C, it was completely finished only at the conditions of 360 °C and 8 MPa, as obvious better from Figure 2 B, mainly due to the distribution of acids between the aqueous and organic phase. The reactivity of esters and lactones was slightly higher than that of acids (Tables S13 and S14), which is in accordance with the conclusions of Laurent and Delmon.[34]

However, dihydrobenzofuran completely disappeared from the reaction mixture already at the mildest conditions tested; furfurals and acetylfuran were removed at 240 °C and 4 MPa and at 290 °C and 4 MPa, respectively (Tables S7 and S15). Moreover, 2-methylfuran and 2,5-dimethylfuran were completely removed from the reaction mixture only at the conditions of 360 °C and 8 MPa (the only detected furans since acetyl furan was removed, see the content of furans in Tables S13 and S14). The presence of these furans at these conditions was probably caused because of the steric hindrance of furanic oxygen by the methyl group. Alternatively, these furans could be formed by the decomposition of the pyrolytic lignin macromolecules, where the furanic units could be present.[35] On the basis of the similar increasing trend in

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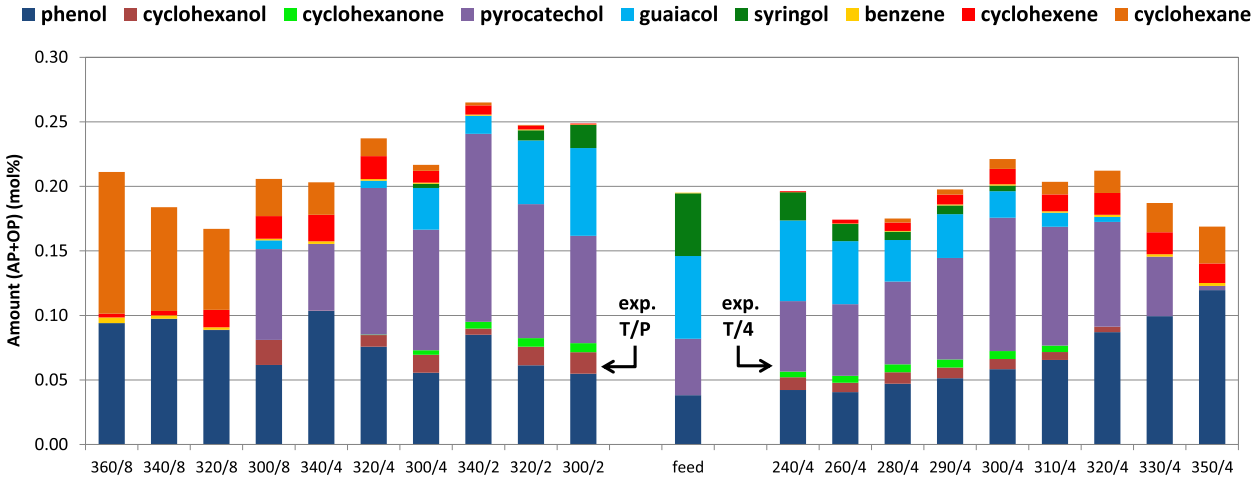


Figure 4. Cumulative changes of the nonalkyl monocyclic compounds in the feed and all products.

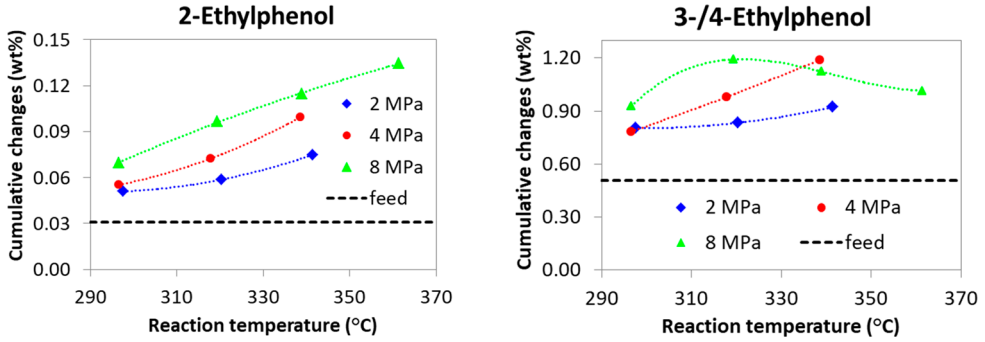


Figure 5. Content of 2-ethylphenol and 3-/4-ethylphenol in the feed and all the organic phases of products from the *T*/*P* experiment.

content of furans and monohydroxybenzenes during the increasing pressure at 300 °C (Table S14), we think that the formation of furans from the pyrolytic lignin could be possible.

The reaction scheme of the nonalkyl monocyclic compounds is shown in Figure 3. The yields of these compounds in the feed and all the products are shown in Figure 4 as the sum for the whole group of the related reaction products in molar % to allow a good comparison between the different compounds. The observed fluctuation in the content of the nonalkyl monocyclic compounds (Figure 4) can be attributed to the measurement errors and the necessary recalculations. This indicates that these compounds were formed neither by pyrolytic lignin decomposition that occurred nor by the dealkylation of alkyl monocyclic compounds.

Syringol started to deoxygenate at the mildest condition tested. On the basis of Figure 4, we can propose several reaction routes for syringol (Figure 3): (i) both methoxy groups were removed to create phenol (the concentration of guaiacol did not rise), (ii) only one methoxy group was removed and approximately the same amount of created guaiacol was deoxygenated through demethoxylation, or (iii) one methoxy group was demethoxylated and the other one was demethylated to create pyrocatechol, whose concentration increased up to the condition of 300 °C and 4 MPa and 340 °C and 2 MPa, respectively (Figure 2 E). When both methoxy groups were removed, phenol was formed and underwent further hydrogenation to yield some intermediate products such as cyclohexanone and cyclohexanol (Figure 3). These intermediates were completely removed from the reaction mixture for the *T*/4 experiment at temperatures 320 °C and for *T*/*P* experiment at all temperatures at a pressure of 8 MPa (Figure 4). It is obvious that also small amount of phenolic hydroxyl group (probably due the subsequent demethoxylation of methoxy phenols) was already deoxygenated to benzene, cyclohexane, and cyclohexene at both mildest conditions (Figure 4, Tables S16 and S17).

Assuming that guaiacol was first formed by the demethoxylation of syringol, then its demethoxylation rate was higher than that of syringol at 260 °C and 4 MPa, and 320 °C and 2 MPa, respectively, since its yield did not increase (Figure 2 D). Although benzene-di/triols were quantified with a larger measurement error (as already explained), it is obvious from the GC-MS results that their deoxygenation rate was lower than their rate of formation by guaiacol demethylation up to 300 °C at 4 MPa and for 340 °C at 2 MPa (Tables S13 and S14 and Figure 2 E).

Monohydroxylbenzenes were the least reactive compounds. Their rate of deoxygenation exceeded their rate of formation (by demethoxylation of methoxy phenols and pyrolytic lignin decomposition) at 360 °C and 8 MPa only. These results are also in line with those presented by Elliott.[31]

The presence of the alkyl chain in the ortho position of phenols could reduce the accessibility of the hydroxyl group to the catalyst active site, as was discussed by Gevert et al.[36] Therefore, compounds, such as *o*-cresol, 2-propylphenol, and 2-ethylphenol, were not deoxygenated significantly at 340 and 360 °C and 8 MPa. The concentration of 2-ethylphenol even continued to rise, which could be attributed to its significant presence and formation from pyrolytic lignin, alternatively, 2-

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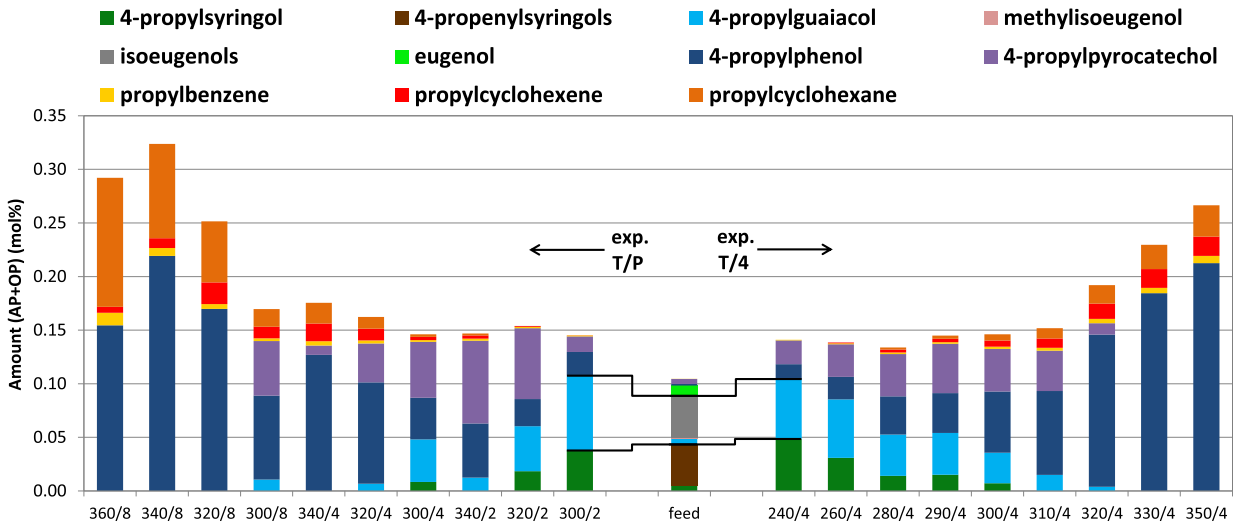


Figure 6. Cumulative changes of the compounds with one ring substituted with propyl chain (propyl monocyclic compounds); the black lines separate the compounds that were transformed to 4-propylguaiacol (gray and light blue row) and 4-propylsyringol (brown and dark green row) through hydrogenation of the double bound in the propyl substituent.

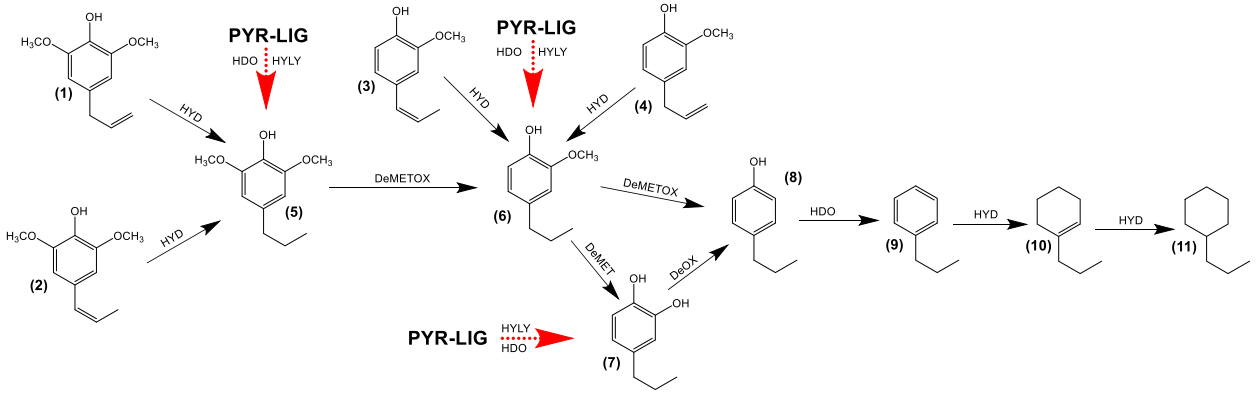


Figure 7. Reaction scheme of the propyl monocyclic compounds: (1) 4-allyl-syringol, (2) 4-(1-propenyl)syringol, (3) isoeugenol, (4) eugenol, (5) 4-propylsyringol, (6) 4-propylguaiacol, (7) 4-propylpyrocatechol, (8) 4-propylphenol, (9) propylbenzene, (10) 1-propylcyclohexene, (11) propylcyclohexane. Reactions: HYD, hydrogenation; DeMEOX, demethoxylation; DeMET, demethylation; HDO, hydrodeoxygenation; HYLY, hydrogenolysis. The compounds whose concentration is affected by the decomposition (hydrolysis) of pyrolytic lignin followed by subsequent deoxygenation of aldehydes and free hydroxyl groups are marked by red arrows.

ethylphenol could be created from benzofuran[37] possibly released from pyrolytic lignin, see Figure 5 and Table S15.

In contrast to nonalkylated monocyclic compounds, whose overall concentration was virtually constant in the range of the tested experimental conditions, the concentration of the propyl monocyclic compounds, as well as other alkylated phenols clearly increased with the increasing severity of the hydrotreatment. The increase can be attributed to the decomposition of pyrolytic lignin as indicated in Figure 7.

The hydrogenation of the double bonds in the alkyl substituents on the aromatic ring already took place at the mildest reaction conditions of both the experiments, which resulted in the complete hydrogenation of eugenol and isoeugenols to 4-propylguaiacol. The yield of 4-propylguaiacol in the product was higher than the sum of the molar yields of all the propenylguaiacols (Figure 6). This can be explained by the partial decomposition of the pyrolytic lignin molecule, where 4-propyl(enyl)guaiacols could be present, at the mildest condition of both the experiments, as assumed in previous section. For the condition of 300 °C and 2 MPa, the increase in 4-propylguaiacol could be caused by the partial demethoxylation of 4-propylsyringol. Methoxyeugenol and 4-propenylsyringols were hydrogenated to 4-propylsyringol, whose concentration slightly increased at 240 °C and 4 MPa probably because of the formation of 4-propylsyringol from pyrolytic lignin. But at 300 °C and 2 MPa, 4-propylsyringol was already partially deoxygenated to 4-propylguaiacol or to 4-propylpyrocatechol, 4-propylphenol or even completely to propylbenzene, propylcyclohexene, or propylcyclohexane (Figure 7). The same reactivity of a double bound conjugated to an aromatic ring was observed in case of 4-vinylguaiacol that was fully hydrogenated to 4-ethylguaiacol under both the mildest conditions, see Tables S7 and S15. All the aromatic oxygenates with an alkyl substituent could in principle be pyrolytic lignin decomposition products as shown in Figure 7.

The concentration of 4-propylphenol increased six times and ten times compared to the feed and products 240/4 and 300/2, respectively (Figure 2 G). At these products, the sum of all propyl monocyclic compounds increased by one-third which is further confirmation of the suggested pyrolytic lignin decomposition. Until the conditions of 310 °C at 4 MPa, the total content of propyl monocyclic compounds was almost

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Table 2. Reactivity of the Compounds during the Bio-oil Hydrodeoxygenation over the Sulfided NiMo Catalyst

Decreasing reactivity ↓	Group of compounds	Rate of removing exceeds rate of formation* (°C/MPa)	Complete disappearance from reaction mixture* (°C/MPa)
	Aldehydes	ND	<240/4; <300/2
	Syringols	<240/4; <300/2	340/2; 310/4
	Guaiacols	240/4; 320/2	330/4; 320/8
	Benzenediols	310/4	320/8
	Esters/Lactones	<240/4; <300/2	350/4; 340/8
	Ketones	<240/4; <300/2	340/8
	Alcohols	<240/4; <300/2	360/8
	Furans	<240/4; <300/2	360/8
	Carboxylic acids	260/4	360/8
	Mono-hydroxy-benzenes	360/8	ND

*The mildest conditions when the one of these two states was reached. The table was created based on the cumulative sum of each group. The individual compounds could have slightly different reactivity, and hence, different temperature when a change in their concentration is observed.

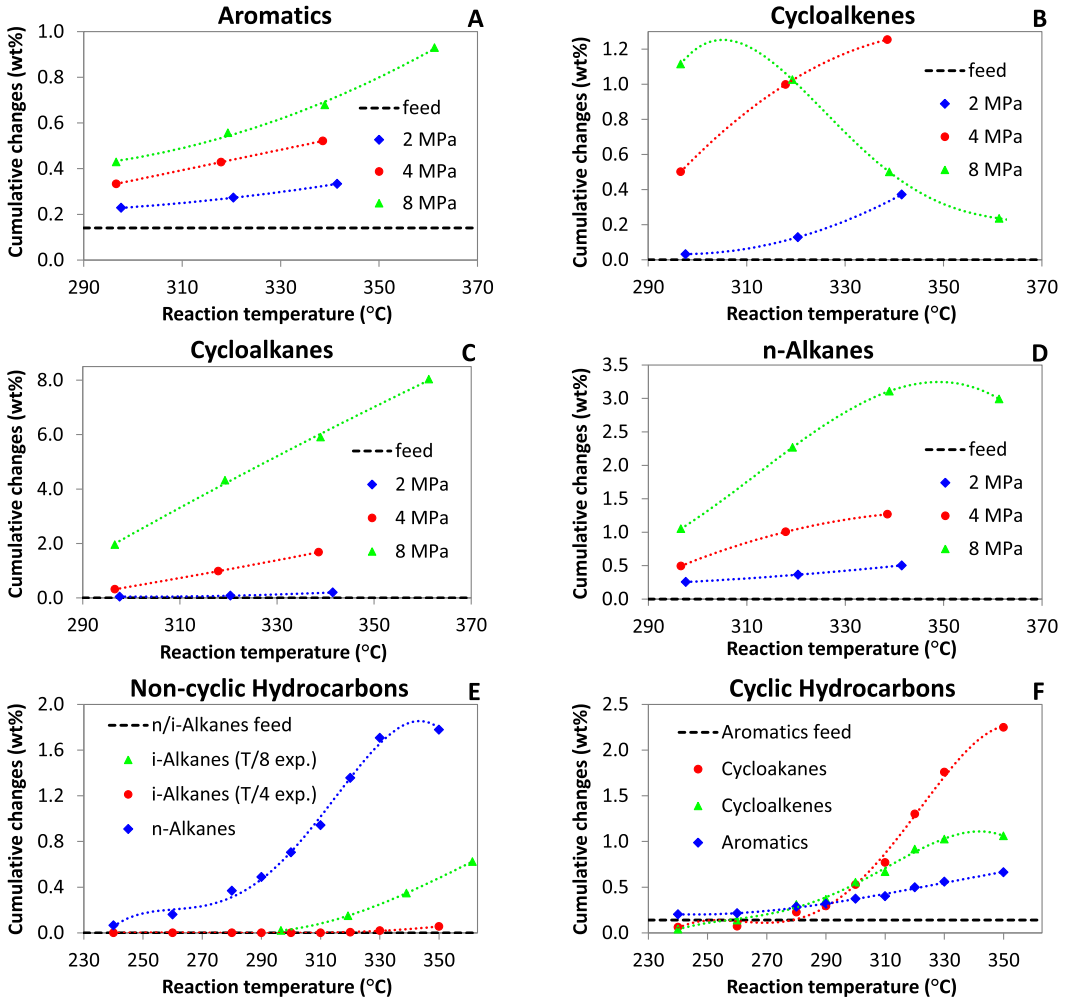


Figure 8. Cumulative changes in wt % by hydrocarbon groups A–D for the T/P and E–F for the T/4 experiment. *i*-Alkanes represent the sum of C5–C9 *i*-alkanes.

constant (Figure 6). Above 310 °C at 4 MPa, the concentration of propyl monocyclic compounds increased dramatically (Figure 6), most likely due to the further decomposition of pyrolytic lignin. The reactivity of the propyl monocyclic compounds was almost the same as that of the nonalkylated monocyclic ones. The only noteworthy difference was that no significant concentration of intermediates products, such as 4-propylcyclohexanol or 4-propylcyclohexanone, was observed. This could be attributed to the significant creation of the propyl monocyclic compounds from pyrolytic lignin and, thus, their short residence time in the reactor.

On the basis of the overall yields of the individual chemical groups over the studied range of experimental conditions (Tables S13 and S14), the order of apparent reactivity of the compounds present in the bio-oil during its hydrodeoxygenation over the sulfided catalyst at WHSV of 1 h^{-1} was established and is reported in Table 2. As the conclusions are drawn based on the bio-oil hydrotreatment, competitive adsorption or

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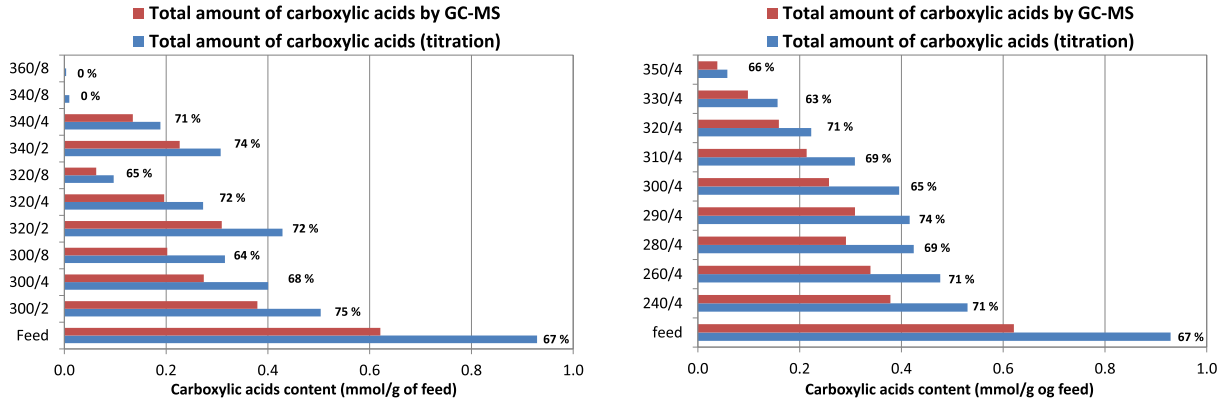


Figure 9. Amount of carboxylic acids in the organic phase (GC-MS vs CAN). The number on the right side of the blue row is the ratio of the red/blue row.

mutual inhibition effects may play a significant role in these observations.

The Quantification of Hydrocarbons by GC-MS. Only the aromatic compounds like benzene, toluene, xylenes, and naphthalene were found above the limit of quantification (LOQ) in the feed (crude bio-oil). However, their total concentration was only 0.14 wt % (Table S13). The content of all the detected hydrocarbons (except cycloalkenes in the experiments at 8 MPa) increased significantly with the hydrotreatment severity.

Compared to the double bound in alkyl substituent of phenolics, such as eugenols present in bio-oil, cycloalkenes (created by the consecutives reactions of phenolics deoxygenation) were observed even in the hydrotreatment product prepared at 360 °C and 8 MPa (Figure 8 B). The content of cycloalkenes (as sum) significantly decreased first at 340 °C and 8 MPa. According to us the main reason for the presence of cycloalkenes even at 360 °C and 8 MPa was just their creation during bio-oil hydrotreatment and not sufficient time for their hydrogenation at the used space velocity (1 h^{-1}) as they are products of consecutive reactions formed most likely at the end of the catalyst bed. Most of the detected alkylated cycloalkenes had an alkyl substituent in the position one and thus steric hindrance by the alkyl group could contribute to the lower reactivity of the double bond. Compared to 1-alkylcycloalkenes, the content of cyclohexene and 3-methylcyclohexene (i.e., compounds with not sterically hindered double bound) started to decrease at milder conditions (Table S15). There is no doubt regarding the cycloalkenes identification as it was based on the known retention time of the standards (in addition to the standards we used also 1-ethylcyclohexene), on their mass spectrum and Kovats indices.

Complete bio-oil hydrodeoxygenation to hydrocarbons could be reached by multiple step hydrotreatment, but this process is cost unattractive as it consumes too much hydrogen. The hydrogen cost constitutes up to 85% of the total bio-oil upgrading cost.[38] From the hydrogen consumption and thus sustainability point of view, it is advantageous to deoxygenate phenolic compounds in bio-oil without saturation of the aromatic rings. However, already at 320 °C and 8 MPa, a significant increase in the saturation of the aromatic ring was observed (Figure 8C). Consequently, the combination of maximal deoxygenation and minimal saturation of aromatic rings is fulfilled at conditions 340 °C and 4 MPa (Figures 1 and 8).

The yield of *n*-alkanes reached a maximum at 340 °C and 8 MPa; *n*-alkanes with an odd number of carbon atoms predominated. C15 and C17 *n*-alkanes were formed predominantly from C16 and C18 fatty acids through decarbonylation and decarboxylation reactions. On the basis of the cumulative molar yields of the possible sources of these *n*-alkanes, it is obvious that only 55% or 21% of acids and ketones were converted to C15−16 and C17−18 *n*-alkanes, respectively (Tables S18 and S19). The rest of the acids contributed to the creation of higher *n*-alkanes, by used GC-MS conditions, visible up to the n-C32 hydrocarbon. Complete deoxygenation of the acids and relevant ket-2-ones was achieved at 330 °C and 4 MPa and 320 °C and 8 MPa, respectively (Tables S7 and S15). In contrast, the *n*-alkane contents did not yet reach their maximum under these conditions (Tables S16 and S17). It is, therefore, obvious that these *n*-alkanes must also be produced from other sources than the corresponding fatty acids and ket-2-ones, probably by the cracking of longer the *n*-alkanes. The changes in the nonvolatile high-molecular-weight compounds during hydrodeoxygenation at molecular level will be studied in future work. Further, we observed that *n*-alkanes started to crack and isomerize at 360 °C and 8 MPa. The isomerization and cracking were confirmed by an increase in the concentration of the hydrocarbons in the distillation range of gasoline (Figure 8E, Tables S16 and S17). Among the C6−C12 *n*-alkanes whose content increased in the samples with the increasing severity (Tables S16 and S17), compounds with six carbons in the molecule were those mostly formed by cracking (the content of *n*-hexane in the best product 360/8 was 1.09 wt %).

Carboxylic Acid Number (CAN) in the Organic Liquid Phase. Carboxylic acids belong to the most problematic substances in bio-oils because of their corrosiveness and lower reactivity in HDO. Hence, it is also important to quantify acids in the nonvolatile bio-oil fractions in addition to the volatile fraction, where mainly acetic acid is present. We found that the concentration of carboxylic acids was below the LOQ in the products obtained at 340 and 360 °C and 8 MPa, although low acid number values were determined (~3.7 and 0.4 mg KOH·g^{-1} respectively[25]). On the basis of the evaluation of the titration curve profile, we are convinced that acids are not present in the organic phase under these conditions. The measured titration curves resemble those of phenols as a strong equivalence point is missing. We also did not detect any carbonyl group by IR in the sample 360/8, so the carboxylic acid content could be expected to be close to zero as measured

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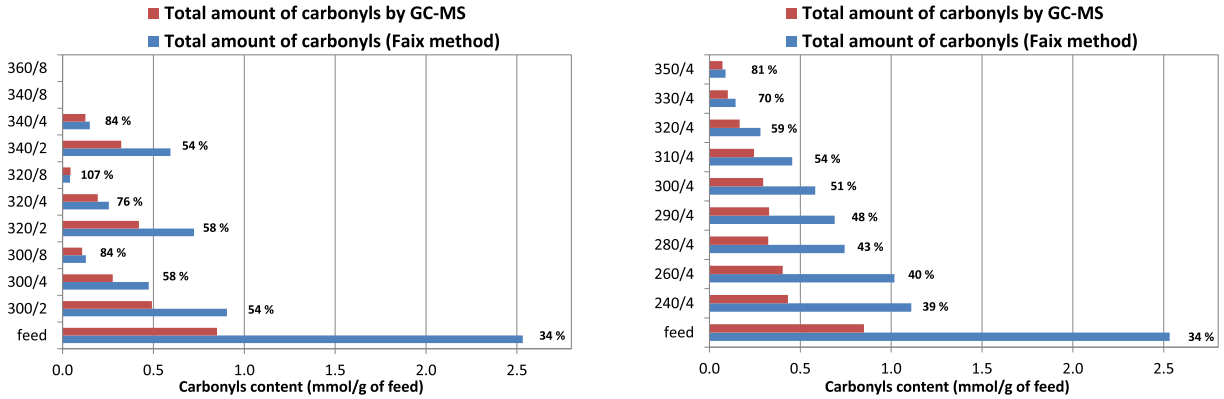


Figure 10. Amount of carbonyls in the organic phase (GC-MS vs Faix method). The number on the right side of the blue row is the ratio of the red/blue row.

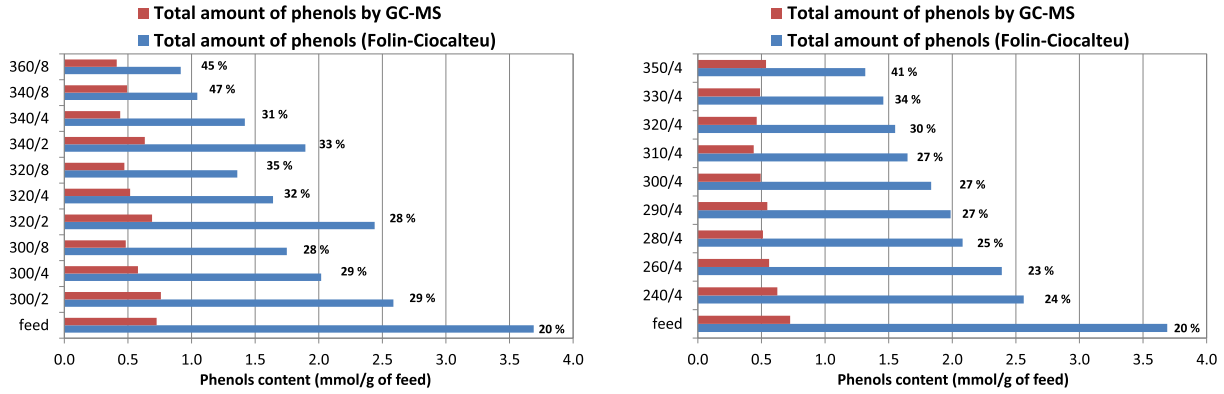


Figure 11. Amount of phenols in the organic phase (GC-MS vs Folin−Ciocalteu method). The number on the right side of the blue row is the ratio of the red/blue row.

by the CAN method. For a more precise measurement, we would need to increase the sample amount for CAN analysis that would exceed the total amount of the hydrotreated product sample. The GC-MS detectable acids were already removed from the organic phase at 340 °C and 8 MPa, where the acids were also below the limit of detection (LOD) of the CAN method.

A significant decrease in CAN (by almost 50%), between the feed on the one hand and the 300/2 and 240/4 products on the other, was probably caused by the elution of carboxylic acids (mainly acetic acid) into the aqueous phase (Figure 2 B). Thanks to the detailed GC-MS analysis, we quantified more than 64% of all the acids present, assuming that the CAN method reliably detected all the acids present. If the C6−C13 acids appeared in the samples (mainly in the feed) they were probably present in very small concentrations below the LOQ, probably even below the LOD. So, based on the assumption that we quantified almost all the volatile acids, the other undetected acid groups were probably present in high-molecular-weight compounds, for example in the pyrolytic lignin molecules. The presence of carboxylic groups in pyrolytic lignin was published by Stankovikj et al.[29]

We found the ratio of C2 + C3 versus C16 + C18 acids was almost constant for all the products (Tables S7 and S15), which implies that the reactivity of the low- and high-molecular-weight carboxylic acid was probably almost the same. This conclusion is further supported by the almost constant ratio of the volatile acids vs CAN for the feed and all the products (being in the range 65−75%, see Figure 9). Because of the low reactivity of the acids, it is necessary to optimize the catalyst composition and type of support, not only in terms of its resistance to acids, but also for its selectivity for the removal of acids.

Carbonyls in the Organic Liquid Phase by the Faix Method. Carbonyl compounds, especially aldehydes, are among the most reactive compounds and cause the low thermo-oxidative stability of bio-oils.[39] The determination of the content of the carbonyl compounds in both the volatile and nonvolatile fractions of the bio-oils and its HDO products is, therefore, important information. All the detected aldehydes were already removed under the mildest conditions of 300 °C and 2 MPa and 240 °C and 4 MPa. Thus, the carbonyl compounds detected by the Faix method were predominantly ketones and high-molecular-weight pyrolytic lignin compounds not detectable by GC-MS containing both aldehyde and ketone groups. All further conclusions are based on the assumption that all carbonyl compounds are oximated quantitatively.

The sharp drop in the carbonyl content in nonvolatile fractions (GC-MS not detectable) between the feed and the 300/2 product (Figure 10), points to a significant content of carbonyls, especially aldehydes, in the pyrolytic lignin molecules. The presence of the aldehyde groups in pyrolytic lignin could be expected based on the research of Patil et al.[40] The results also showed that the number of the carbonyl groups in the nonvolatile fractions was higher than that of the carboxyl groups (higher ratio in Figure 9). Compared to the carboxylic acids, the nonvolatile carbonyls were removed more easily than the volatile carbonyls, which could be attributed to the higher

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presence and reactivity of aldehydes in the pyrolytic lignin molecules compared to both the low- and high-molecular-weight ketones. Therefore, the ratio of the carbonyls quantified by GC-MS vs the total carbonyls rose (Figure 10). At 320 °C and 8 MPa, all the high-boiling carbonyls were removed. Because of this, the sum of all the carbonyls quantified by GC-MS was almost equal to the results of the Faix method (ratio of 107%). A ratio higher than 100% was probably caused due to the measurement error of these methods.

Total Content of Phenols in the Organic Liquid Phase by the Folin−Ciocalteu Method. Phenolics are in general among the least reactive oxygenates present in the bio-oils as known from literature.[31] On the other hand, 1,3-di-, 1,3,4-tri-, and 1,2,3-tri-hydroxybenzenes were identified together with aldehydes as the most reactive compounds contributing to the aging of the bio-oils during storage.[39]

The small decrease in the total phenolic content (Figure 11) was probably caused by the deoxygenation of di- and trihydroxyl benzenes to phenols. Because, as known from literature,[18] monohydroxybenzenes provide method about 2/3 of absorbance in the Folin−Ciocalteu (FC) compared to the gallic acid (trihydroxybenzoic acid) used for the calibration. Moreover, the presence of the alkyl chain in phenolics further reduces the absorbance to one-third of the Gallic acid absorbance.[18] For this reason, it is obvious that the results from the FC method are not able to give us an absolute number and it is problematic to draw other conclusions, than those already drawn in the previous sections. Nevertheless, the FC method was found as a good indicator of the antioxidant capacity of the bio-oil as a whole.[41] We plan to provide a more detailed comparison of the response of the wider range of the phenolic compounds in the FC method, typically present in bio-oils and the HDO bio-oils, in a dedicated study in the future.

CONCLUSIONS

We presented the first detailed quantitative study mapping the fate of the individual key oxygenates during the one-stage hydrotreatment of straw bio-oil over a sulfided catalyst in a wide range of reaction conditions. Using a complex analysis of the aqueous and organic phases based on the combination of GC-MS analysis with functional-group-specific analytical methods (i.e., carboxylic acids, carbonyls and phenols determined by the carboxylic acid number, Faix, and Folin−Ciocalteu methods, respectively), we obtained a comprehensive understanding of the formation and/or consumption of oxygenates and hydrocarbons as a function of the reaction conditions used. Among the tested reaction conditions, one-stage bio-oil upgrading at 340 °C and 4 MPa is to be preferred, as there was no significant saturation of the aromatic ring while a majority of the oxygenates was removed. Thus, a sustainable product with minimum hydrogen consumption suitable for the subsequent coprocessing with petroleum fractions in a refinery was obtained. Moreover, the biobased aromatics are very desired components of the gasoline and jet-fuel blending pools The results will allow further optimization of the sulfided NiMo catalyst to ensure the more efficient removal of carboxylic acids and, thus, additional enhancement of its stability during long-term bio-oil hydrotreatment.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b06860.

Properties of the aqueous phases, overview of standards used for GC-MS quantitative analysis, results for all directly quantified compounds by GC-MS in the products organic and aqueous phase, solubility of chosen compounds, volatile oxygenates group analysis, cumulative changes in C15 + C16 and C17 + C18 alkyl chain molecules, scheme of the decomposition of possible pyrolytic lignin molecule, and photo of aqueous phase aging (PDF)

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Notes

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ABBREVIATIONS

AP	aqueous phase
CAN	carboxylic acid number
FC	Folin−Ciocalteu
HDO	hydrodeoxygenation
LOD	limit of detection
LOQ	limit of quantification
MCR	micro Conradson carbonization residue
RSD	relative standard deviation
TIC	total ion current

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