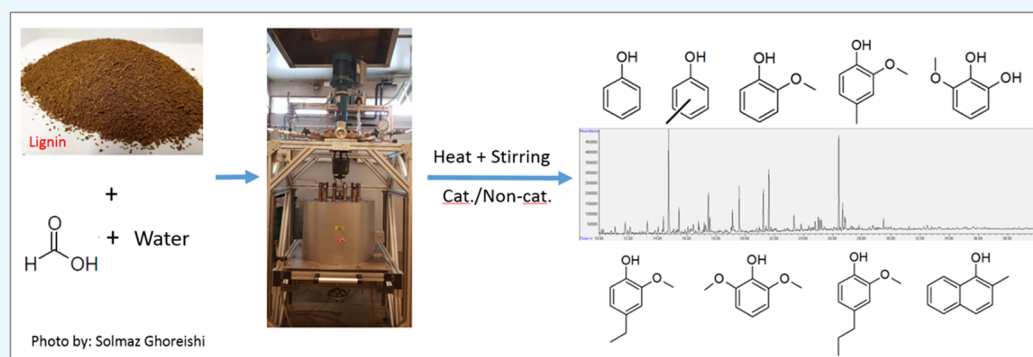


# Effect of Reaction Conditions on Catalytic and Noncatalytic Lignin Solvolysis in Water Media Investigated for a 5 L Reactor

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## Supporting Information



**ABSTRACT:** The high content of oxygen in the lignin polymer and the prevalence of phenolic functional groups make the conversion of lignin to fuels and value-added products with well-defined chemical properties challenging. The lignin-to-liquid process using a water/formic acid reaction medium has been shown to convert the lignin polymer to monomers with a molecular weight range of 300–600 Da. The bio-oil comprises a complex mixture of monomeric phenols, aromatics, and aliphatic hydrocarbons with a high H/C and low O/C ratio. This study investigates the effect of the stirring rate, level of loading, and catalyst at 305 and 350 °C in a 5 L pilot scale reactor. The oil yields are found to be highest for experiments conducted using the maximum stirring rate, maximum level of loading, and Ru/Al<sub>2</sub>O<sub>3</sub> catalyst with yields of more than 69 wt % on lignin intake. Goethite as a catalyst does not show good conversion efficiency at either reaction temperatures. The carbon recovery is highest for products produced at 305 °C. Furthermore, results from solid phase extraction on a DSC-CN solid phase show that 65–92 wt % the bio-oils can be recovered as fractions separated based on polarity.

## 1. INTRODUCTION

The production and storage of biofuels and bulk chemicals from sustainable, renewable, and naturally abundant lignocellulosic biomass has been considered to be an outstanding option as a biorefinery feedstock due to low costs and carbon neutrality.<sup>1–3</sup>

Lignocellulosic biomass is composed of three main biopolymers, cellulose (40–50 wt %), hemicellulose (15–25 wt %), and lignin (15–35 wt %).<sup>1,4</sup> In many biorefinery concepts, the carbohydrate fraction of biomass (cellulose and hemicellulose) is converted to bioethanol through the well-established lignocellulosic-to-ethanol process, leaving behind lignin as waste.<sup>1,5,6</sup> Lignin is an amorphous copolymer consisting of three main aromatic units: *p*-hydroxyphenyl (H-lignin), guaiacyl (G-lignin), and syringyl (S-lignin) units, which differ on their methoxylation degrees. The monomers are connected through different linkage patterns, depending on the biomass source and processing conditions. However, the C–O–C and C–C bonds are the most common bonding patterns in the lignin structure.<sup>7–9</sup> Since the high cost of cellulosic ethanol has limited its market, it would be essential for the overall process economy to develop an efficient and

appropriate thermochemical method/catalytic technology for conversion of waste lignin streams into fuels and chemicals such as aromatics, phenols, aromatic ethers, vanillin, etc. However, the conversion technology of lignin is still lagging behind.<sup>1–3</sup>

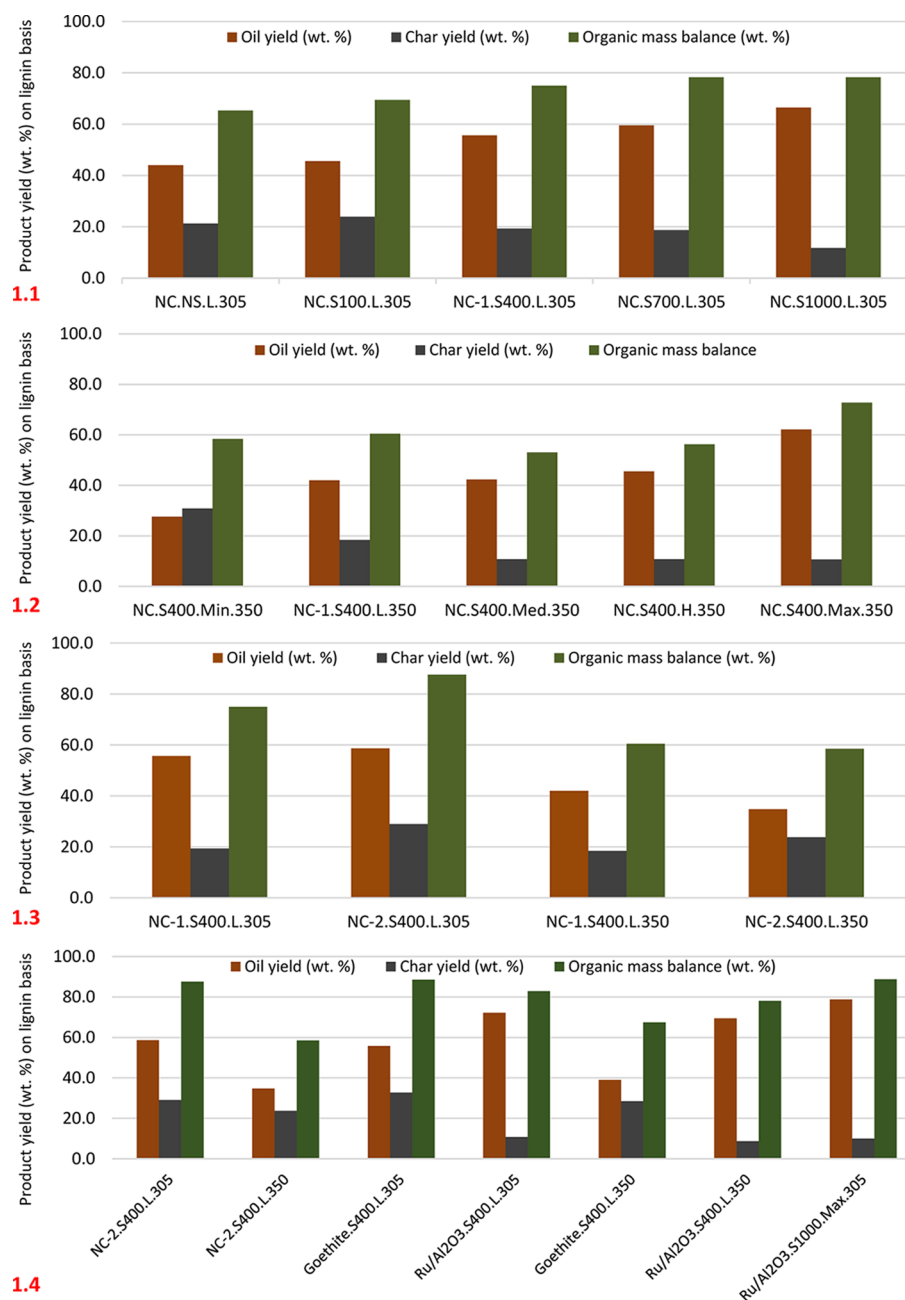
For conversion of lignin or lignin-rich residues into value-added functional materials, various thermochemical processes have been studied.<sup>10,11</sup> However, pyrolysis or catalytic pyrolysis,<sup>12–15</sup> liquefaction,<sup>16</sup> gasification,<sup>17,18</sup> solvolysis,<sup>19,20</sup> and hydrogenolysis<sup>21,22</sup> are among the most interesting concepts investigated in this respect.

In 2008, Kleinert and Barth reported a process termed Lignin-to-Liquid (LtL), a thermochemical solvolytic process that comprises simultaneous depolymerization of the lignin structures with subsequent hydrodeoxygenation of the lignin monomers in a polar solvent such as water and alcohols. Formic acid is used as a hydrogen donor, which has been proven to be more reactive than molecular hydrogen. During

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**Figure 1.** Column diagrams showing product yields and lignin mass balances as mass fractions of lignin input as a function of (1.1) different stirring rates at 305 °C, (1.2) different levels of loading in the reactor at 350 °C, (1.3) long-term storage of the feedstock at both 305 and 350 °C, and (1.4) catalyst use at both 305 and 350 °C. (For coding see Table 2.)

the LtL process, formic acid is converted in situ to molecular hydrogen and  $\text{CO}_2/\text{CO}$ .<sup>23</sup> Based on recent studies, the decomposition of formic acid and the chemical reaction between lignin and formic acid are competing reactions. Therefore, a formylation–elimination–hydrogenolysis mechanism for the formic acid-aided lignin conversion is proposed. Thus, carbon balances over 100 wt % indicate a potential carbon contribution from formic acid to the conversion products.<sup>24,25</sup>

A recent study reported by Huang et al. (2014) showed that the addition of formic acid to a water–ethanol solvent mixture has contributed to more than 90 wt % bio-oil yields from Kraft lignin even without any catalysts.<sup>26</sup> Riaz et al. (2018) reported that the combined use of supercritical ethanol and formic acid

produced high amounts of lignin-derived monomers from alkali lignin without using external catalysts and molecular hydrogen. The complete lignin conversion resulted in high aromatic monomer yields of 36.7 wt % on a dry ash-free lignin basis.<sup>27</sup>

However, the depolymerization behavior of lignin also is dependent on the structure of lignin, and thus bio-oils produced from different types of lignin are supposed to have different chemical compositions. In a recent study, Park et al. (2018) reported that the content of ether linkages in hardwood lignins was approximately three times higher than that in softwood lignins due to the presence of sinapyl alcohol units in hardwood lignins.<sup>28</sup> Furthermore, Park et al. reported that the content of ether linkages was also strongly dependent on lignin

isolation methods used where the highest bio-oil yields were obtained from hardwood lignin isolated through formosolv fractionation.<sup>28</sup> On the contrary, Hita et al. (2018) explored that enhanced monomer yields could be obtained irrespective of the ether linkage content, and a high amount of  $\beta$ -O-4 linkages was actually shown to slightly reduce monomer yields.<sup>9</sup>

Moreover, several authors have reported significantly improved yields and reduced oxygen content of bio-oils using various types of supported noble metal catalysts.<sup>29–31</sup> However, the development of cheap, sturdy, and environmentally friendly catalysts for the thermochemical conversion of low-value feedstock to value-added products is still an important issue. In a recent study from 2017, Agarwal et al. reported that 92 wt % the product from the hydrotreatment of Kraft lignin at 450 °C using a limonite catalyst is detectable by GC–GC, implying that the obtained bio-oil consists of low-molecular weight compounds.<sup>32</sup> Breunig et al. (2017) explored that Fe-based catalysts were beneficial in order to prevent the char formation in favor of higher oil yields in solvent-free hydrogenolysis of different lignin types.<sup>33</sup> Hita et al. (2018) recently explored that alumina-based noble metal catalysts, for example, Rh/Al<sub>2</sub>O<sub>3</sub>, Pd/Al<sub>2</sub>O<sub>3</sub>, Ru/Al<sub>2</sub>O<sub>3</sub>, and Pt/Al<sub>2</sub>O<sub>3</sub>, have given better results compared to carbon-supported ones, for example, Rh/C, Pd/C, Ru/C, and Pt/C in terms of lignin oil yield and composition.<sup>34</sup> In another study from 2018, Hita et al. reported that 16–29 wt % the input lignin can be converted into valuable platform chemicals through solvent-free hydrotreatment using a Fe-based limonite catalyst at 450 °C and 4 h. Sixty-seven to eighty-one percent of lignin-oil components were detectable by 2D GC–GC-FID in which low-molecular weight alkylphenolics and aromatics were the main product fractions.<sup>9</sup>

The major challenge in developing an appropriate process for lignin conversion is to obtain high amounts of good quality oils while decreasing the reaction temperature and time. The properties of good quality oil can be defined as high energy content, high stability, low viscosity, a high H/C and low O/C ratio, and a low average molecular weight. Thus, the aim of this study is

- (1) to evaluate the yield, quality, and composition of the bio-oils produced in the solvolytic conversion of lignin at a 5 L scale as a function of the following reaction parameters:
  - (i) Stirring rate: by varying the stirring rate from 0 to 1000 rpm.
  - (ii) Level of loading: by gradually increasing the reactor loading.
  - (iii) Long-term storage of the raw material: effect of two years of storage.
  - (iv) Investigation of two different catalysts, Ru/Al<sub>2</sub>O<sub>3</sub> and goethite.
- (2) to separate the volatile low molecular weight oil components from the heavier nonvolatile fraction of the bio-oil using solid phase extraction (SPE) and then identifying the individual fractionated compounds using gas chromatography–mass spectroscopy analysis.

In a previous study reported by Ghoreishi et al. (2019), the highest oil yields from the Eucalyptus lignin-rich residue were achieved at reaction temperatures up to 350 °C.<sup>35</sup> Thus, all experiments related to this study are conducted at reaction temperatures up to 350 °C. In another study reported by

Ghoreishi et al. (2019), stirred reactions (400 rpm) were shown to yield higher amounts of oils compared to nonstirred reactions (0 rpm), and in the same study, a positive correlation was observed between the level of loading in the reactor and the oil yield.<sup>36</sup> Therefore, a more detailed exploration of the effect of stirring and reactor loading on LtL solvolysis is one of the main objectives of this research paper. Goethite is an iron-based mineral with catalytic properties, which consists predominantly of  $\alpha$ -FeOOH. To the best of our knowledge, we are the first to compare a conventional noble metal catalyst with goethite as a catalyst for thermochemical conversion and to demonstrate this at a 5 L scale.

## 2. RESULTS AND DISCUSSION

**2.1. Product Yields.** The feedstock used in this study is not directly soluble in the reaction media at low temperatures, and thus the initial state of the reaction in the LtL process is a suspension of lignin particles in the liquid reaction medium. While the physical state of the reaction system at the selected temperatures is not precisely known, torque readings during the heating period indicate that lignin melts into a viscous liquid and dissolves due to increased solubility at higher temperatures. The quantitative results from all LtL-process experiments are presented in Figure 1 and Table S1.

**2.1.1. Effect of the Stirring Rate on Oil and Solid Yields.** The effect of five different stirring conditions on product yields are shown in Figure 1-1.1, which gives a comparison of oil and char yields on a lignin basis, together with the organic mass balances (in wt %) from all experiments performed in this section. Experiments shown in Figure 1-1.1 are performed at the same reaction conditions (305 °C and 2 h), while the stirring rate is changed stepwise from 0 rpm (nonstirred) to 1000 rpm.

The oil and char yields range from 44 to 67 wt % and from 12 to 24 wt % on a lignin basis, respectively. The original lignin mass recovered as oil and char lies in the range of 65–78 wt %. The unaccounted mass will comprise the gas phase and aqueous products, including water produced in the thermal decomposition reactions. For this reason, determining an accurate mass balance for all products is difficult, and the carbon recovery data presented below is more relevant for an overall evaluation of yields.

Overall, the oil yields tend to increase as a function of an increased stirring rate and are consistently much higher for experiments with a stirring rate above 400 rpm. Furthermore, char formation decreases significantly as a function of an increased stirring rate when all other reaction parameters are kept constant. The increased oil yields and decreased char yields can be attributed to better mass transfer due to more efficient stirring. For oil yields, an increase of approximately 20 wt % on a lignin basis is observed when the stirring rate is increased from 0 to 1000 rpm. In addition, the organic mass balance is also increased as a function of an increased stirring rate. Thus, to produce a high amount of oil and a low amount of char, high stirring rates are preferred.

**2.1.2. Effect of the Different Loadings in the Reactor on Oil and Solid Yields.** Product yields on lignin intake, together with the organic mass balances (wt %) are shown in Figure 1-1.2. The ratio of lignin to the reaction medium is kept constant. The only difference between experiments shown in Figure 1-1.2 is the degree of filling in the reactor, while all the other conditions are kept constant (350 °C with a stirring rate of 400 rpm and 2 h).

The oil and char yields are in the range of 28 to 62 wt % and 11 to 31 wt %, respectively, on a lignin basis. In addition, over 70 wt % the original lignin mass is directly recovered as oil and char in the maximum level-loaded experiment. The results show that increasing the loading in the reactor from a minimum to a maximum level when keeping the other reaction parameters constant gives an impressive increase in bio-oil yields. This can be due to a higher operating pressure when the reactor is loaded to a high level, see Table S1. The reactor used in this work is equipped with two stirrers above each other on the stirring rod. When the reactor is loaded at the maximum level, the contact of both stirrers with the reaction medium will result in a more efficient mixing of the reactants, improving lignin depolymerization. Since the level of loading in the reactor also influences the pressure in the reactor, an increase in the amount of the reaction medium will increase the pressure inside the reactor, which improves the efficiency of the reaction.

A maximum increase of approximately 34 wt % in the oil yield on a lignin basis is observed as a function of reactor filling from a minimum level to a maximum level. In terms of char yields, a decrease of approximately 20 wt % on a lignin basis is observed. However, no significant variation in the char yield is observed as a function of increased reactor loading from the medium to maximum level. Since an optimal lignin conversion comprises a high oil yield and a low char yield, high loading levels are preferable.

**2.1.3. Reproducibility as a Function of Long-Term Storage of the Feedstock.** In this part of the study, an experiment from each section above is duplicated to examine the effect of prolonged storage of the raw material on the reproducibility.

The quantitative results presented in Figure 1-1.3 show some variations between the duplicate experiments due to long-term storage of the feedstock. The difference in the organic mass balance between experiments performed at 305 °C is approximately 13 wt % on a lignin basis. These observations indicate that the composition of the raw material has changed during storage, which shows that results from conversion tests over time cannot be assumed to be reproducible and comparisons should be done with considerable caution.

**2.1.4. Effect of the Catalyst on Oil and Solid Yields.** The effect of two different catalysts, Ru/Al<sub>2</sub>O<sub>3</sub> and goethite, on product yields and organic mass balances is investigated for some selected reaction conditions (see Table 2) and compared with the noncatalyzed experiments performed at the same reaction conditions.

Comparison of the results obtained from noncatalyzed and catalyzed experiments at 305 °C show that the oil yield on lignin intake decreases to a small extent when using goethite as a reaction catalyst, ca. 3 wt %, and increases significantly when using Ru/Al<sub>2</sub>O<sub>3</sub>, ca. 13 wt %. For the experiments performed at 350 °C, an increase is observed for the oil yield as a function of catalyst use to a small extent by using goethite, 4 wt %, and considerably when using Ru/Al<sub>2</sub>O<sub>3</sub>, ca. 35 wt %. However, char yields increase, approximately 3–5 wt %, when using goethite as the catalyst, and decrease significantly, ca. 13–15 wt %, when using Ru/Al<sub>2</sub>O<sub>3</sub> at both reaction temperatures. Thus, the effect of Ru/Al<sub>2</sub>O<sub>3</sub> catalyst is positive at both reaction temperatures giving oil and char yields in the range of 69–72 and 9–11 wt % on a lignin basis, respectively. This positive effect can be explained by the fact that reaction

pathways and kinetics of the lignin decomposition is influenced by the catalyst.<sup>31</sup> The first step in lignin solvolysis is a fast depolymerization of the lignin structure, which is followed by competing reactions giving hydrodeoxygenation or repolymerization of the depolymerized monomers. Use of catalyst in the LtL process probably reduces the activation energy of the hydrodeoxygenation process, thereby reducing the likelihood of repolymerization of depolymerized lignin monomers.

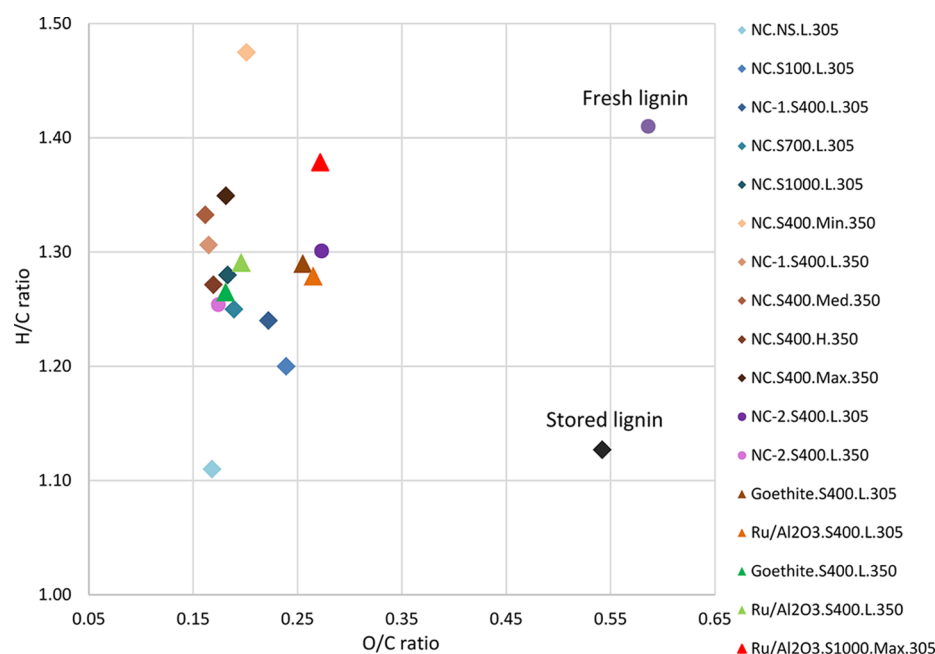
In addition, the organic mass balances do not appear to be significantly affected by the catalysts in the experiments performed at 305 °C while showing an increasing trend with catalyst use in the experiments performed at 350 °C. Nevertheless, the production of a high amount of oil and a low amount of char is the optimum result, so Ru/Al<sub>2</sub>O<sub>3</sub> is the preferred catalyst for conversion of lignin to bio-oil at the selected reaction conditions.

Furthermore, an additional experiment was performed to combine the best reaction conditions obtained in each previous section, namely, experiment Ru/Al<sub>2</sub>O<sub>3</sub>.S1000.Max.305. Results obtained from this experiment show a significant increase in the oil yield on a lignin basis compared to experiments NC.S1000.L.305, NC.S400.Max.350, and Ru/Al<sub>2</sub>O<sub>3</sub>.S400.L.305. The highest oil yield (79 wt %) and consequently the highest organic mass balance (89 wt %) is achieved in this experiment. However, the char yield does not seem to be affected by the reaction condition changes in the same degree as the oil yield.

**2.1.5. Comparison with the Published Literature.** The main purpose of this study is to find reaction conditions that are most beneficial in terms of product yield and product quality. Results presented in this study show that the bio-oil yields lie in the range of 28–83 wt % on lignin intake. These results are quite comparable with results obtained from similar conversion processes reported by other research groups. Though most of the high-yield results reported are catalyzed, Huang et al. reported in 2014 that more than 90 wt % the Kraft lignin has been converted to bio-oil using formic acid and a mixture of water/ethanol as a reaction solvent even without the use of a catalyst.<sup>26</sup> Among the noncatalyzed experiments investigated in this study, experiment NC.S1000.L.305 has given the highest bio-oil yield (approximately 67 wt % on lignin intake) using a stirring rate of 1000 rpm and low level of loading in the reactor at 305 °C. The differences between the results presented in this paper and results reported by Huang et al. are most likely due to the use of different types of raw materials, impure Eucalyptus lignin versus Kraft lignin. Quantitative comparison of the results reported in these two studies may become difficult due to the differences in procedure and reaction parameters, for example, different reaction temperatures (305/350 °C vs 200–330 °C), reaction solvents (water vs 50:50 water/ethanol mixture), stirring rates (0–1000 rpm vs 200 rpm), and reactor size (5 L vs 0.01 L). In addition, the recovery values have most probably been influenced by the use of acetone as an extracting solvent such as in the work by Huang et al. (2014) rather than the less polar ethyl acetate/THF mixture used in this study. Acetone as a solvent will incorporate a wider range of oligomeric degradation products in the depolymerized lignin fraction and consequently give higher bio-oil yields.

In 2015, Oregui-Bengoechea et al. explored that the supported noble metal catalysts have significantly improved the bio-oil yields on a lignin basis with yields up to approximately 92 wt % the input lignin using Ru/Al<sub>2</sub>O<sub>3</sub> at





**Figure 2.** Van Krevelen diagram showing H/C and O/C ratios of the LtL oils and feedstock.

340 °C and a reaction time of 6 h.<sup>31</sup> As reported here, the supported catalyst, Ru/Al<sub>2</sub>O<sub>3</sub>, also has significantly improved the bio-oil yields with the highest oil yield obtained in experiment Ru/Al<sub>2</sub>O<sub>3</sub>.S1000.Max.305. Higher reaction temperatures along with longer reaction times used by Oregui-Bengoechea et al. have most likely led to a more efficient degradation of lignin and thus have given a higher amount of lignin-derived oils.

In a study from 2018 performed by Hita et al., the Rh/Al<sub>2</sub>O<sub>3</sub> catalyst is reported as the best catalyst in terms of lignin oil yields and composition compared to other noble metal-based catalysts through solvent-free hydrotreatment of Kraft lignin at 450 °C and 4 h. The most promising result obtained was a lignin oil yield of approximately 36 wt % and 5 wt. % DCM soluble products on lignin intake, both being rich in valuable chemical compounds such as alkylphenolics, aromatics, oxygenates, and alkanes determined using GC–GC-FID.<sup>34</sup> However, Kristianto et al. (2017) reported that approximately 66 wt % of CAHL (concentrated acid hydrolysis lignin) can be converted to bio-oil using Ru/C as the catalyst in a formic acid/ethanol reaction medium.<sup>3</sup> In addition, Kristianto et al. (2017) explored that the oil yield increased as a function of an increased formic acid amount and prolonged reaction time in the presence of Ru/C, while the oxygen content of the bio-oil was shown to be reduced, substantially.<sup>3</sup> Results reported by Kristianto et al. (2017) are quite comparable with results obtained in this study from experiments performed using Ru/Al<sub>2</sub>O<sub>3</sub> (with oil yields of approximately 69, 72, and 79 wt % on a lignin basis). Additionally, the monomeric composition of the lignin oils produced in the latter study consisted mainly of phenol and its derivatives, including methyl, ethyl, and methoxy-substituted phenols, indicating the comparability of these oils.

**2.2. Elemental Analysis and Carbon Recovery.** The Van Krevelen diagram in Figure 2 displays H/C and O/C ratios of all bio-oils and the starting lignin feedstocks. The elemental composition of all oil and char samples is given in Table S2.

Figure 2 shows that the difference in hydrogen and oxygen contents between the raw materials is prominent. The higher content of hydrogen and oxygen in the fresh lignin is attributed to a higher content of carbohydrates in this feedstock. Thus, the significant decrease in the H/C ratio and the moderate reduction in the O/C ratio of the biomass after prolonged storage can be due to microbial/bacterial degradation of the carbohydrate residues that were present in the raw material.

The Van Krevelen diagram in Figure 2 also depicts a distinct reduction of oxygen content in the bio-oils relative to the starting biomasses, confirming the occurrence of deoxygenation during the LtL process. Although the H/C ratio of the bio-oils produced from stored lignin seems to have increased to some extent due to bulk hydrogenation of the starting feedstock, this does not seem to have occurred when using fresh lignin since the H/C ratio of the bio-oils have been reduced slightly relative to the starting material. The lower H/C ratio of the bio-oils compared to the fresh lignin can be caused by the elimination of hydrogen as an aqueous product, that is, water, methanol, short-chain organic acids, and furfural from the degraded carbohydrate residues. During the Lignin-to-Liquid process, hydrogen can both be added and removed. The thermal decomposition of formic acid gives highly reactive in situ hydrogen, which is responsible for conversion of lignin constituents into hydrogen-rich, oxygen-depleted products. Nevertheless, hydrogen can also be removed as an aqueous product by cleaving hydroxyl groups from the lignin structure. Since the carbon content of the bio-oils (66.77–75.41 wt %) produced in this work has increased compared to the carbon content of the starting raw materials (50.12–52.29 wt %), it is unlikely that hydrogen that is bound to carbon has been removed as an alcohol and/or aldehyde during the conversion process. In addition, as given in Table S2, the content of oxygen is reduced from, for example, 39.14 and 37.72 wt % in the raw material to a range of 16.07–24.39 wt % in the lignin-derived oils, and thus much of the mass loss will be due to loss of oxygen. The H/C value is in the range of 1.11–1.47, suggesting that aromatic rings can be predominant.

Table 1. Carbon Balance Data from LtL-Process Experiments<sup>a</sup>

experiment	carbon added as lignin (g)	carbon content in bio-oil (g)	carbon content in char (g)	carbon sum from products (g)	total carbon balance (wt %)
NC.NS.L.305	95.8	63.4	22.3	85.7	89.4
NC.S100.L.305	95.8	61.0	28.1	89.1	92.9
NC-1.S400.L.305	95.8	75.1	20.8	95.9	100.1
NC.S700.L.305	95.8	83.2	19.2	102.4	106.9
NC.S1000.L.305	95.8	93.4	10.3	103.7	108.2
NC.S400.Min.350	71.9	28.3	30.9	59.2	82.3
NC-1.S400.L.350	95.8	60.0	23.6	83.6	87.2
NC.S400.Med.350	119.8	75.5	14.7	90.2	75.3
NC.S400.H.350	143.8	97.0	16.0	113.0	78.6
NC.S400.Max.350	167.7	152.0	17.5	169.5	101.1
NC-2.S400.L.305	100.0	75.3	27.0	102.3	102.3
NC-2.S400.L.350	100.0	49.1	27.1	76.2	76.2
Goethite.S400.L.305	100.0	72.8	31.3	104.1	104.1
Ru/Al <sub>2</sub> O <sub>3</sub> .S400.L.305	100.0	93.5	7.6	101.1	101.1
Goethite.S400.L.350	100.0	54.8	31.7	86.5	86.5
Ru/Al <sub>2</sub> O <sub>3</sub> .S400.L.350	100.0	95.8	5.1	100.9	100.9
Ru/Al <sub>2</sub> O <sub>3</sub> .S1000.Max.305	175.0	176.1	10.9	187.0	106.9

<sup>a</sup>All calculations are carried out on an ash-free basis.

In addition, a trend of reduction in the O/C ratio is observed as a function of increased reaction temperature when all other reaction parameters are kept constant. Comparison of experiment NC-1.S400.L.305 with experiment NC-1.S400.L.350 shows a reduction in the O/C ratio and an increase in the H/C ratio indicating that the lignin structure degradation is more intense at higher temperatures. However, the same trend is not common when comparing experiment NC-2.S400.L.305 with experiment NC-2.S400.L.350 where both H/C and O/C ratios have decreased as a function of the reaction temperature increase.

A general observation is that the O/C value of the bio-oils does not seem to be influenced by the variations in reactor loading, while the H/C values appear to be more affected. However, variation in the H/C ratio does not follow a specific trend with the highest H/C ratio obtained in experiment NC.S400.Min.350. In the case of experiments performed under different stirring conditions, the H/C ratio of the oils has shown an increasing trend as a function of an increased stirring rate with the lowest H/C ratio for oil produced in experiment NC.NS.L.305, while the O/C ratio shows an increasing trend from experiment NC.NS.L.305 to experiment NC.S100.L.305 and then a trend of reduction.

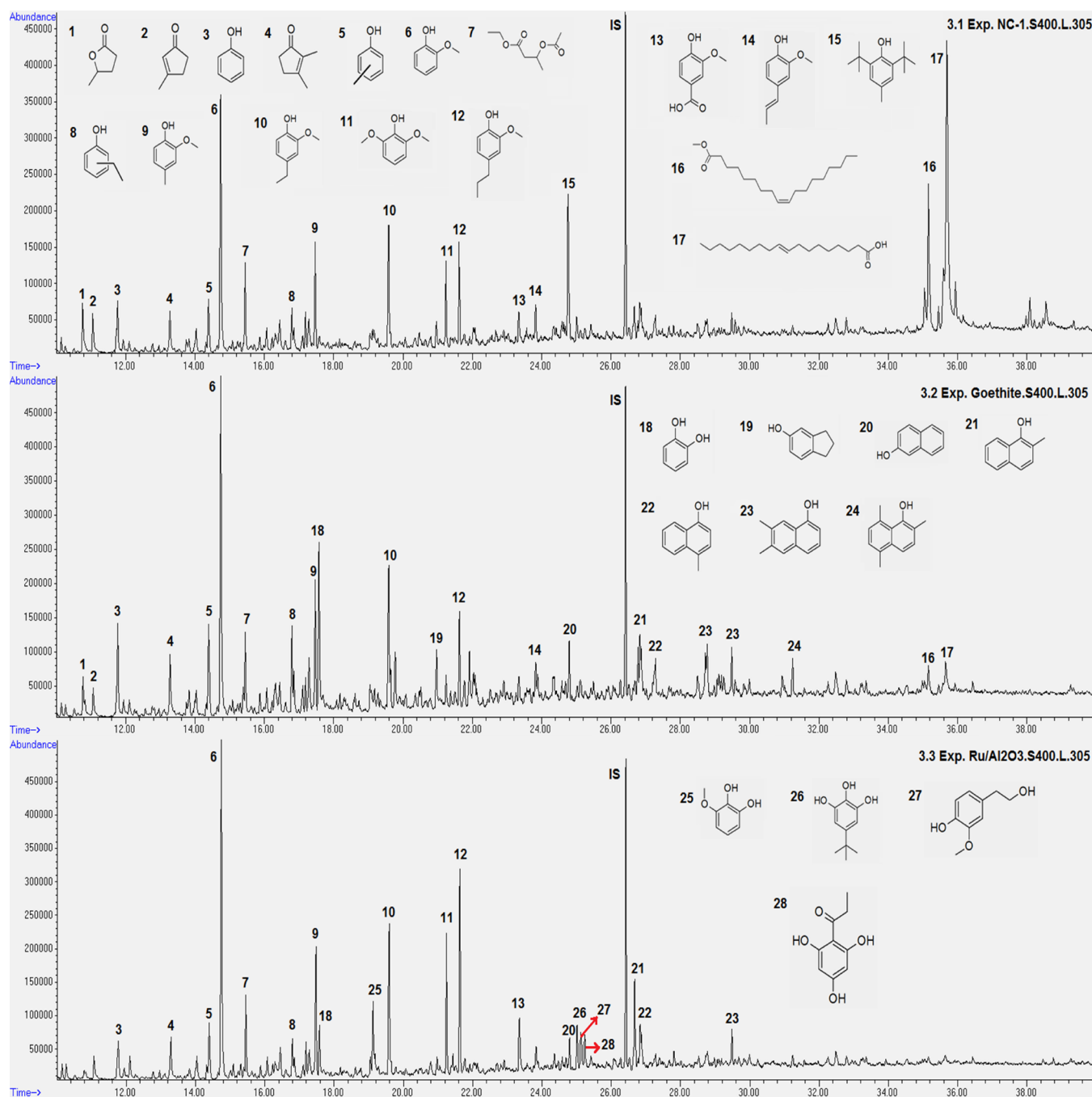
No significant variation in the H/C and O/C ratios of bio-oils has been observed as a function of catalyst use (catalyzed vs noncatalyzed) and catalyst type (goethite vs ruthenium on alumina) when keeping other parameters constant, confirming that the distribution of the elemental composition is primarily based on the temperature of the conversion process. However, among all experiments conducted at 305 °C (both catalyzed and noncatalyzed), the highest H/C ratio belongs to experiment Ru/Al<sub>2</sub>O<sub>3</sub>.S1000.Max.305 indicating that a combination of the maximum stirring rate and maximum level of loading in the reactor leads to better hydrogenation of the lignin-derived components.

In addition to recovery by mass, carbon balance calculations are also performed for all LtL-process experiments carried out in this work, see Table 1. Mass fractions (wt %) of carbon in raw materials, bio-oils, and solid products (chars) are determined using elemental compositional data. The carbon

balance data includes input of carbon in the form of lignin and output of carbon in the form of organic products (bio-oils and chars) and thus will be dependent on the product recovery by mass. However, a major source of uncertainty is the lack of data for aqueous and gas-phase products. In a study reported by Løhre et al. (2017), high levels of dissolved organic carbons are detected in the aqueous phase using <sup>1</sup>H NMR analysis.<sup>25</sup> The results from <sup>1</sup>H NMR have shown a presence of methanol, ethanol, and considerable amounts of aromatics and carboxylic acids in addition to the extraction solvents, ethyl acetate and tetrahydrofuran.<sup>25</sup> Hydrogenation of a methoxy substituent in methoxyphenol will lead to the formation of phenol and methanol. The methanol formed will be found in the aqueous phase and will be removed during a work-up procedure.<sup>37</sup> However, the other components such as aromatics and carboxylic acids are believed to originate from lignin and formic acid, respectively. Therefore, due to lack of aqueous phase analysis, the carbon balance data are most useful for comparative use.

Calculations show a carbon balance ranging from 75 to 108 wt %. Carbon balances over 100 wt % indicate a potential carbon contribution from formic acid to bio-oils. As given in Table 1, the carbon balance has increased considerably as a function of an increased stirring rate (from 89 to 108 wt %), which can indicate better incorporation of carbon from formic acid to the lignin structure at elevated stirring conditions. Changes in the carbon balance as a function of different levels of loading in the reactor did not show to follow a specific trend. However, a carbon balance of approximately 101 wt % has been achieved in the experiment performed at the maximum level of loading (NC.S400.Max.350). Moreover, carbon balance does not seem to have been affected by catalyst use at 305 °C. Meanwhile, comparison of the catalyzed experiments with the noncatalyzed experiments performed at 350 °C showed that the carbon balance increased by approximately 10. and 24.7 wt % when using goethite and Ru/Al<sub>2</sub>O<sub>3</sub> as catalysts, respectively.

**2.3. Bio-Oil Composition from Gas Chromatography–Mass Spectrometry.** The more volatile compounds of the bio-oils have been identified using GC–MS analysis. The

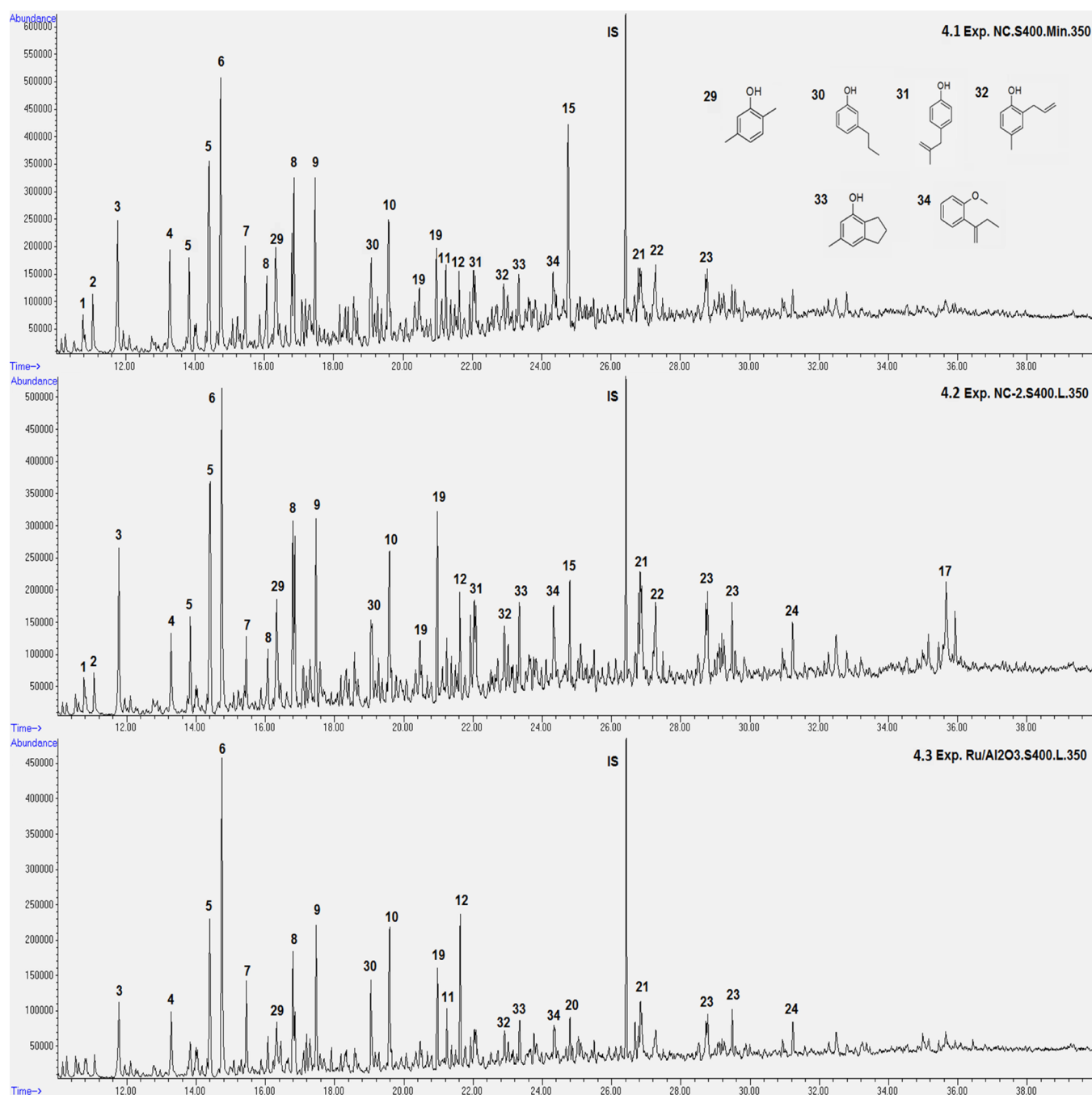


**Figure 3.** GC–MS chromatograms of (3.1) experiment NC-1.S400.L.305 at the top, (3.2) experiment Goethite.S400.L.305 in the middle, and (3.3) experiment Ru/Al<sub>2</sub>O<sub>3</sub>.S400.L.305 at the bottom.

LtL oils comprise a complex mixture of phenolic compounds. Figure 3 shows chromatograms containing representative compound distributions from six different bio-oils. The chromatograms presented in Figure 3 show that the composition of the GC–MS detectable part of the bio-oils is quite similar in different oils performed at the same reaction temperature, while the abundance varies with other reaction conditions, for example, catalyst type, stirring rate, and level of loading in the reactor.

The GC–MS analysis confirms the results obtained by elemental analysis. Figure 3-3.1–3.3 illustrates this, showing that the most abundant compounds are the same in oils performed at 305 °C regardless of catalysis conditions (bio-oils

from experiment: NC-1.S400.L.305, Goethite.S400.L.305, and Ru/Al<sub>2</sub>O<sub>3</sub>.S400.L.305). However, the proportion of the compounds relative to the internal standard (hexadecane) varies between the oils in a way that can tentatively be explained by the effect of different catalysis conditions. Furthermore, GC–MS chromatograms shown in Figure 4 confirm also that the composition of the GC–MS detectable part of oils produced at 350 °C is quite similar, while the abundance varies as a function of raw material freshness, loaded level in the reactor, and catalyst use. Since the profile of the monomers is essentially the same for catalyzed and noncatalyzed experiments, the main effect of the catalyst is interpreted to be hydrogenation of the depolymerized lignin



**Figure 4.** GC-MS chromatograms of (4.1) experiment NC.S400.L350 at the top, (4.2) experiment NC-2.S400.L350 in the middle, and (4.3) experiment Ru/Al<sub>2</sub>O<sub>3</sub>.S400.L350 at the bottom.

monomers. The stabilization of the depolymerized lignin monomers through hydrodeoxygenation reactions hinders their repolymerization into char.<sup>31</sup> Therefore, the higher bio-oil yields obtained in the catalyzed experiments can mainly be due to the catalyst activity in the formic acid-aided aliphatic ether bond cleavage.

A general observation is that 2-methoxyphenol (guaiacol, #6) is the most abundant compound in almost all of the chromatograms depicted in Figures 3 and 4. GC-MS chromatograms depicted in Figure 3-3.1-3.3 show that the bio-oils produced at 305 °C consist mainly of methoxy-substituted phenols in high concentrations. The compounds numbered as 1, 2, and 4 (five-membered rings) are most

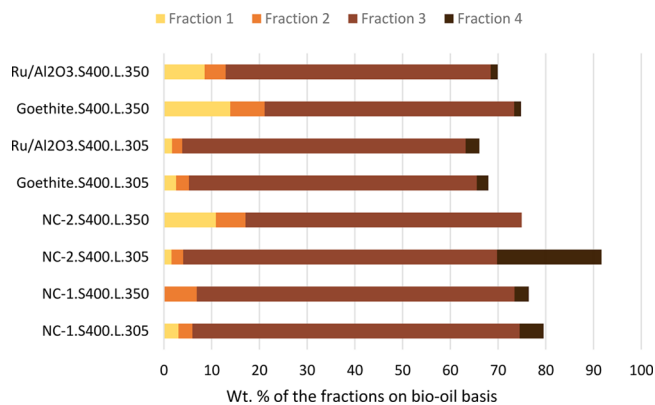
probably degradation products from the sugar residues in the raw material. In addition to guaiacol (#6), 2-methoxy-4-methylphenol (#9), 4-ethyl-2-methoxyphenol (#10), 2,6-dimethoxyphenol (#11), and 2-methoxy-4-propylphenol (#12) are the most abundant compounds identified in the bio-oils performed at 305 °C. In addition, catechol (#18) is also one of the major components in the bio-oil produced using goethite. However, the proportion of these compounds relative to 2-methoxyphenol (guaiacol) differs between the bio-oils produced at different reaction conditions. The higher content of oxygen in oils produced at 305 °C results in higher O/C ratios of the oils, confirming the results obtained from elemental analysis, shown in Figure 2. Compounds identified



as #16 (a fatty acid methyl ester) and #17 (a fatty acid) are present in all bio oils produced at 305 °C from fresh Eucalyptus lignin. These two components are most probably products derived from plant waxes, which have been degraded by the microorganisms present in the feedstock. This observation confirms the results presented in Figure 2, which show that the H/C ratio of lignin is significantly reduced after a two-year storage period that may be due to the consumption of plant fat by living microorganisms.

Identification of the most abundant peaks in the bio-oils produced at 350 °C show a higher amount of alkylated phenols. Phenol (#3), 2,3-dimethyl-2-cyclopenten-1-one (#4), methyl- and ethylphenol (#5 and #9), 3-propylphenol (#30), 2,3-dihydro-1*H*-inden-5-ol (#19), and butylated hydroxytoluene (#15) are the most abundant compounds identified in the chromatograms shown in Figure 4-4.1–4.3. The higher content of hydrogen in bio-oils produced at 350 °C results in significantly higher H/C ratios of the oils, corroborating again the results obtained from the elemental analysis.

#### 2.4. In-Depth Analysis of the Solid Phase-Extracted Bio-Oil Fractions Using GC–MS Analysis. Figure 5 shows a



**Figure 5.** Mass percentage of the four different fractions based on the bio-oil input.

schematic illustration of the results obtained from the solid phase extraction where fraction 1 contains the least polar compounds and fraction 4 contains the most polar compounds eluted from the column.

As shown in Figure 5, more than 65 wt % the input bio-oils are fractionated using the eluents given in Section 4.5.3. However, the bio-oil produced in experiment NC-2.S400.L.305 was shown to have the highest degree of elution on bio-oil intake (above 90 wt %). A general observation is that bio-oils from noncatalyzed experiments have shown better recovery from separation using normal-phase fractionation compared to bio-oils from catalyzed experiments performed at the same reaction temperature. In addition, bio-oils produced at 350 °C seem to contain a larger proportion of nonpolar or less-polar fractions (fractions 1 and 2) in comparison with bio-oils produced at 305 °C. Furthermore, there are no significant differences observed in the quantity of the different fractions between the catalyzed experiments performed at the same reaction temperature. Nevertheless, increased reaction temperature from 305 to 350 °C seems to have positively influenced the tendency of fractionation of bio-oils produced using catalysts. In addition, Figure 5 shows that approximately 10–35 wt % the input bio-oils either is left in the SPE column (are not eluted using the most polar eluent) or consists of volatile

components that have evaporated along with the separation solvents. Thus, the amount of the collected fractions and the rest left in the SPE column can again confirm that approximately 80 wt % the bio-oils consists of polar phenolic compounds. The majority of the polar phenolic compounds in the bio-oils are hard to quantify using gas chromatography due to poor GC properties. However, silylation of the polar compounds enhances the elution properties and has improved the quantification of the different phenolic compounds.

Figure 6 depicts that the composition of the fractionated samples also depends on the reaction temperature used during production of the bio-oils. Based on results from GC–MS analysis, bio-oils produced at 350 °C contain many phenolic compounds that are not found and/or identified in fraction 2 from bio-oils produced at 305 °C. This observation confirms the results shown in Figure 5, indicating that the portion of fraction 2 increases with increased reaction temperature from 305 to 350 °C.

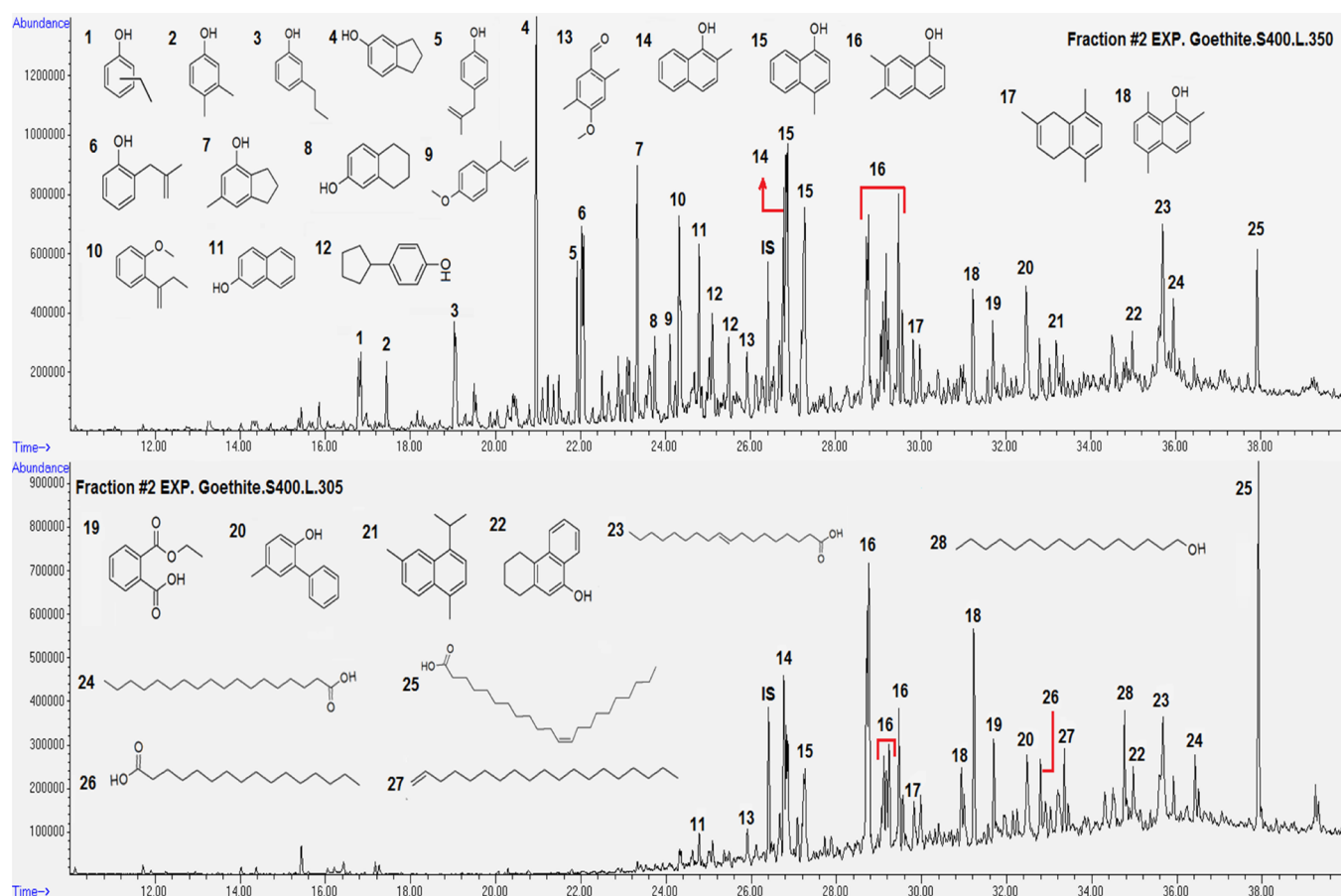
A general observation is that the majority of compounds identified on the right side of the GC–MS chromatograms from fraction 2 are fatty acids and alcohols with long hydrocarbon chains. This observation is expected since the polarity of alcohols and carboxylic acids decrease with the chain length increase. In addition, based on results obtained from elemental analysis, bio-oils produced at 305 °C have a higher content of oxygen and therefore are expected to be poorly eluted with a nonpolar or less polar eluent such as hexane:DCM (90:10 v:v).

Figure 7 shows that the most abundant components identified by GC–MS in fraction 3 from experiment NC-2.S400.L.350 at the top, experiment Ru/Al<sub>2</sub>O<sub>3</sub>.S400.L.350 in the middle, and experiment Goethite.S400.L.350 at the bottom are quite similar and independent of the reaction temperature and catalyst use. Furthermore, the GC–MS-identified compounds seem to be more polar compared to the compounds identified in fraction 2 (shown in Figure 6), which is expected due to increased polarity of the eluent. The major components identified in fraction 3 are catechol (#3), 3,5-dihydroxytoluene (#4), 2-(2-hydroxyethyl)phenol (#5), and 2-hydroxymandelic acid ethyl ester (#8).

### 3. CONCLUSIONS

The aim of this study was to provide an insight into the impact of different reaction conditions on LtL solvolysis conducted at a 5 L pilot scale. The overall result shows a major increase in the oil yield and a significant decrease in the char yield as a function of an increased stirring rate at 305 °C, increased reactor loading at 350 °C, and use of Ru/Al<sub>2</sub>O<sub>3</sub> at both reaction temperatures. A general observation is that the oil yield decreases as a function of increased reaction temperature due to repolymerization of lignin components for char formation at higher reaction temperatures. The use of goethite as a reaction catalyst does not affect the oil and char yields at either reaction temperatures. However, Ru/Al<sub>2</sub>O<sub>3</sub> has been found to be very efficient for LtL solvolysis showing the highest oil yields and the lowest char yields.

Furthermore, the significant reduction in the H/C ratio of the feedstock from storage over time, which can be due to degradation of carbohydrate residues and/or plant waxes, did not affect the H/C ratios of the bio-oils significantly. Results from elemental analysis and GC–MS analysis show effective deoxygenation and depolymerization when comparing the starting material with the produced bio-oils. However, for bio-



**Figure 6.** GC–MS chromatograms of fraction 2 from experiment Goethite.S400.L.350 at the top and experiment Goethite.S400.L.305 at the bottom.

oils produced from fresh lignin, bulk hydrogenation did not seem to have occurred since the H/C ratio of the bio-oils was also reduced relative to the starting material. In addition, the H/C ratio of the oils has not been influenced by the use of a catalyst. An increase in the H/C ratio has been found as a function of an increased stirring rate due to an increased reaction rate and improved mass transfer. Guaiacol is the major component in most of the LTL oils. The most abundant compounds identified in bio-oils produced at 305 °C are mainly alkyl-substituted methoxyphenols. However, alkylated phenols are the most abundant compounds identified in the bio-oils produced at 350 °C. One of the main benefits of bio-oil production at a 5 L scale is the large product volume, which makes testing of different separation, fractionation, and upgrading processes, for example, distillation and solid phase extraction, possible. Overall, the results from SPE show good perspectives for further development and indicate that other separation methods such as flash chromatography can even be more suitable for separation of the bio-oil components.

## 4. EXPERIMENTAL SECTION

**4.1. Chemicals.** Formic acid (mass fraction of  $\geq 98\%$ ), ethyl acetate (mass fraction of  $>99.8\%$ ), and tetrahydrofuran (mass fraction of  $>99.9\%$ ) were purchased from Sigma-Aldrich and used without any further purification.

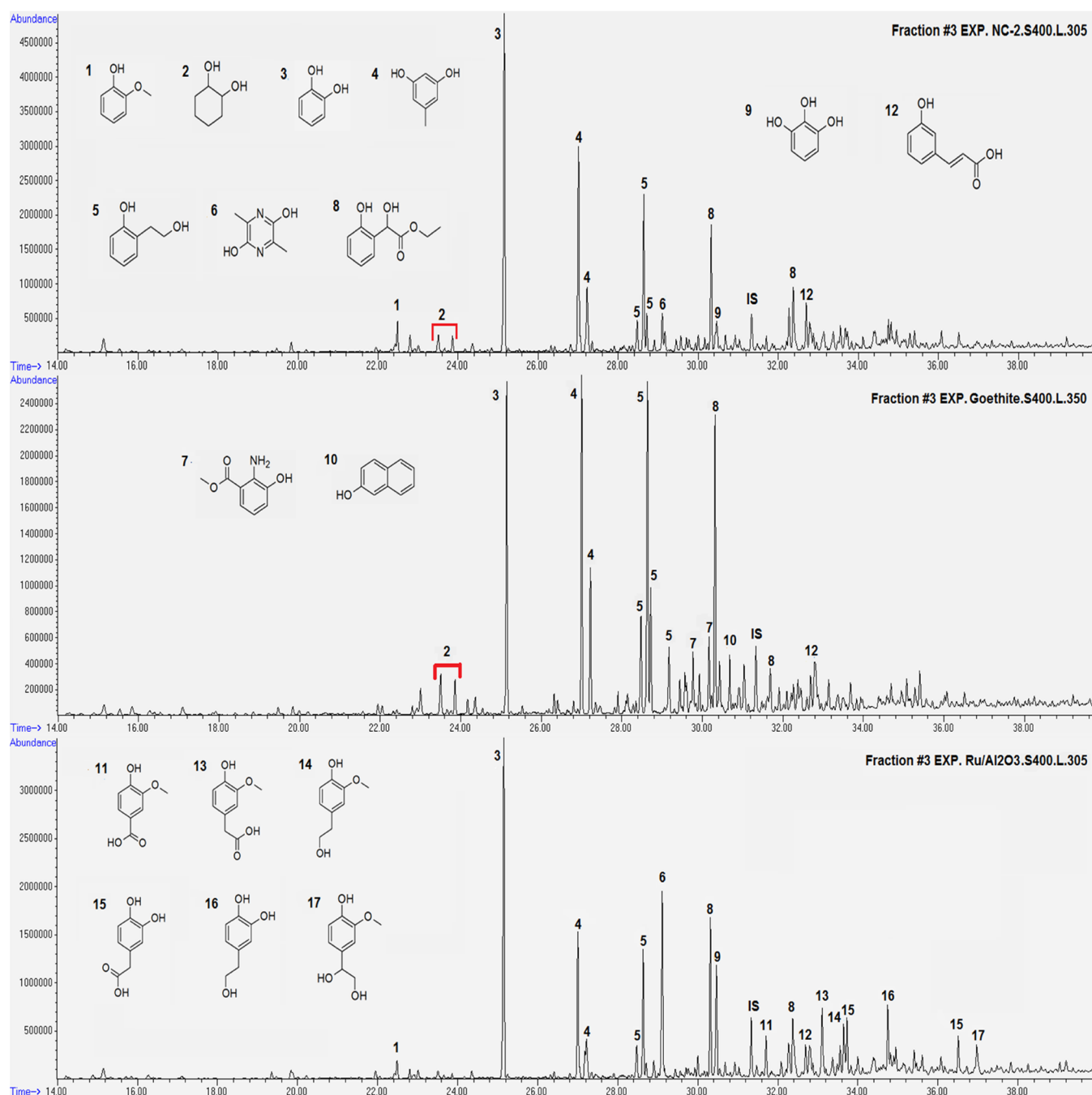
**4.2. Catalysts.** Ruthenium on alumina (Ru mass fraction of 5%, catalogue no. 381152, and batch no. Lot#10714KYV), and goethite (Fe mass fraction 30–63%, catalogue no. 71063, and

batch no. Lot#BCBQ8228V) were purchased from Sigma-Aldrich and used without any further work-up.

**4.3. Feedstock.** The feedstock used in this work is a lignin-rich residue isolated from weak acid and enzymatic hydrolysis of Eucalyptus wood, which was produced at the Biorefinery Demo Plant (BDP) in Örnköldsvik, Sweden. The lignin content of the feedstock was estimated from elemental composition to be  $\sim 50.1$  wt %. The ash content of the feedstock was determined to be approximately 4.4 wt % according to protocol NREL/TP-510-42622.<sup>38</sup> Eucalyptus lignin was received as a wet sample and was dried in an oven at 60 °C until constant mass before further grinding and sieving to a dry powder of  $<500$   $\mu\text{m}$  in particle size. The dried lignin powder was used without further purification.

The H/C and O/C ratios of the feedstock were 1.41 and 0.59 when fresh and 1.13 and 0.54 after long-term storage. The high oxygen content of this feedstock compared to pure lignin is attributed to a certain amount of residual sugars/carbohydrates.

**4.4. Lignin to Liquid Solvolysis System and Conditions.** **4.4.1. Experimental Conditions.** Lignin (150–350 g), formic acid (183–427 g), water (375–875 g), and the catalyst (ca. 5 g) were added to a stirred 5 L high-pressure autoclave reactor from ESTANIT GmbH. The autoclave was then closed and heated to the desired temperatures (305–350 °C) with a stirring rate of 0–1000 rpm for a reaction time of 2 h. The heating time from room temperature to the desired temperature (305–350 °C) was tested in a range of 60–70 min, giving an approximate heating rate of 5 °C  $\text{min}^{-1}$ . The



**Figure 7.** GC–MS chromatograms showing the most abundant compounds in fraction 3 from experiments NC-2.S400.L.305 at the top, Goethite.S400.L.350 in the middle, and Ru/Al<sub>2</sub>O<sub>3</sub>.S400.L.305 at the bottom.

reaction time (2 h) was measured in addition to the heating period. The pressure and torque of the stirrer were continuously monitored during the experiments. The maximum level of loading in the reactor is defined by the pressure limits of the equipment. The experimental conditions of all the experiments are given in Table 2. The experiments are coded as shown below:

X.Y.Z.T where X is the catalytic condition, Y is the stirring condition, Z is the level of loading, and T is the reaction temperature.

**4.4.2. Sample Work-Up.** After the completed reaction time, the reactor was cooled to ambient temperature by flowing cold water through the reactor's cooling coil. The final products

from the LtL process consisted of a gas phase, a liquid phase, and a solid phase (containing both the unreacted starting material and char produced during the conversion). However, previous results indicate that the bulk of the solid phase will mainly be char.<sup>39</sup> The produced gas was vented by opening the gas valve. Analysis of the gas composition was not performed as a part of this study, but relevant data for the gas composition can be found in a previous work reported by Oregui-Bengoechea et al. (2015) showing that decomposition of formic acid is the source of the major part of the produced gas.<sup>31</sup>

After the gas phase was vented, the reactor was opened and the liquid phase was separated from the solid phase. The liquid

**Table 2. Experimental Conditions Investigated in the LtL Experiments**

experiments	temperature (°C)	stirring rate (rpm)	lignin <sup>a</sup> (g)	water (g)	formic acid (g)	catalyst (g)
Different stirrer rates						
NC.NSL.305	305	0	191	500	244	–
NC.S100.L.305	305	100	191	500	244	–
NC-1.S400.L.305	305	400	191	500	244	–
NC.S700.L.305	305	700	191	500	244	–
NC.S1000.L.305	305	1000	191	500	244	–
Different loading levels						
NC.S400.Min.350	350	400	143	375	183	–
NC-1.S400.L.350	350	400	191	500	244	–
NC.S400.Med.350	350	400	239	625	305	–
NC.S400.H.350	350	400	287	750	366	–
NC.S400.Max.350	350	400	335	875	427	–
Prolonged storage						
NC-2.S400.L.305	305	400	191	500	244	–
NC-2.S400.L.350	350	400	191	500	244	–
Different catalysts						
Goethite.S400.L.305	305	400	191	500	244	5.25
Ru/Al <sub>2</sub> O <sub>3</sub> .S400.L.305	305	400	191	500	244	5.07
Goethite.S400.L.350	350	400	191	500	244	5.36
Ru/Al <sub>2</sub> O <sub>3</sub> .S400.L.350	350	400	191	500	244	5.01
Ru/Al <sub>2</sub> O <sub>3</sub> .S1000.Max.305	305	1000	335	875	427	5.16

<sup>a</sup>Feedstock amount measured on an ash-free basis.

phase consisted of a single aqueous phase and the LtL oil was adsorbed to the solid phase. The liquid phase was separated from the solid phase by opening the valve on the container bottom. Then, the organic phase was extracted by adding a solution of ethyl acetate:tetrahydrofuran (90:10 v/v), and the solid phase was filtered off.

The extracted organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated at a reduced pressure (20–25 kPa) at 40 °C to yield a dark brown liquid. The final oil and solid yields were determined by mass after solvent evaporation and drying and are given in a mass fraction percentage, as specified in eq 1.

$$\text{product yield (wt \%)} = \frac{\text{dry mass of oil or char (g)}}{\text{dry mass of input lignin (g)}} \times 100 \quad (1)$$

The solid yield for the catalyzed systems was calculated after subtracting the amount of catalyst introduced and thus refers to the organic solids (char). The mass balance was calculated as the sum of oil and char mass fractions.

**4.5. Characterization of the Products.** **4.5.1. Elemental Analysis.** All samples were analyzed for their elemental composition in the CHNS mode with a Vario EL III instrument using helium as the carrier gas. The amount of oxygen was calculated by the difference of CHN.

**4.5.2. Gas Chromatography–Mass Spectroscopy.** The LtL oils (1.0 mg) were dissolved in 1 cm<sup>3</sup> ethyl acetate:tetrahydrofuran (90:10 v/v) with hexadecane (1 μL/L) as the internal standard, and the sample was analyzed using an Agilent Technologies 7890A GC system with an autosampler coupled with an Agilent 5977A mass-selective detector (MSD). The injection was run in the splitless mode at 280 °C (injector temperature) on a 30 m HP-5ms column with 250 μm i.d. and thickness of 0.25 μm from Agilent Technologies. The following GC–MS instrumental conditions were applied:

Start temperature: 40 °C (held for 5 min), heating rate 1: 6 °C min<sup>-1</sup> to 280 °C, and heating rate 2: 40 °C min<sup>-1</sup> to 300 °C (held for 5 min).

The GC–MS interphase valve delay was set to 4.60 min and the MS detector was operated in the positive mode at 70 eV with an ion-source temperature of 250 °C. Compounds were identified using Enhanced MSD Chemstation software F.01.00.1903 and the NIST 2.0 library.

**4.5.3. Solid Phase Extraction.** In this work, normal-phase separation has been applied using a column material consisting of silica modified with cyanopropyl groups, which is more suitable than silica and C18 columns for separation of lignin-derived compounds due to its intermediate polarity.

Approximately 70 mg of the LtL oil was dissolved in 100 μL of DCM:MeOH (93:7 v/v). The SPE column was wetted with the first eluent before the dissolved oil sample was gently applied to the top of the column material. Then, the column was placed on top of the SPE vacuum manifold by Supelco Visiprep, the extraction vacuum was kept on 20 mHg, and the flow rate through the column was adjusted to 0.3 cm<sup>3</sup>/min. Three different eluents were used in an increasing polarity order as given in Table 3. The different fractions were collected in sample vials, concentrated, and then weighted. Fractions 2 and 3 were prepared for GC–MS analysis.

**Table 3. Eluents Used in Solid Phase Extraction (SPE)**

eluent	ratio (v/v)	used volume (cm <sup>3</sup> )
hexane:dichloromethane	90:10	20
hexane:dichloromethane	90:10	20
dichloromethane:methanol	93:7	20
methanol:dichloromethane	70:30	20

**4.5.4. Silylation.** The collected fractions using eluent 3 (DCM:MeOH) from solid phase extraction were silylated by measuring 10 mg of the sample into a vial, adding 3 mL of the internal standard solution (0.01 mg/mL hexadecane in ethyl acetate:tetrahydrofuran (90:10 v/v)), thus giving a sample concentration of 3.33 mg/mL. A volume of 1 mL of the prepared sample solution was transferred to a GC vial, and 150



$\mu\text{L}$  of pyridine and 150  $\mu\text{L}$  of BSTFA were added. The GC vial was capped and heated to 70 °C for 30 min before cooling to room temperature. To a new GC vial, a volume of 0.7 mL of the silylated sample was transferred and diluted with 0.7 mL of pentane. The GC vial was capped and cooled to 5 °C overnight and filtered through a 0.5  $\mu\text{L}$  syringe filter before analyzing by GC–MS.

**4.5.5. Gas Chromatography–Mass Spectroscopy (for Silylated Samples).** The prepared samples above were analyzed using an Agilent Technologies 7890A GC-system with an autosampler, coupled with an Agilent 5977A MSD. The injection was run in the splitless mode at 280 °C (injector temperature) on a 30 m HP-5ms column with 250  $\mu\text{m}$  i.d. and thickness of 0.25  $\mu\text{m}$  from Agilent Technologies. The following GC–MS instrumental conditions were applied:

Start temperature: 40 °C (held for 5 min), heating rate 1: 6 °C  $\text{min}^{-1}$  to 73 °C (held for 5 min), heating rate 2: 6 °C  $\text{min}^{-1}$  to 280 °C, and heating rate 3: 40 °C  $\text{min}^{-1}$  to 300 °C (held for 5 min).

The GC–MS interphase valve delay was set to 11 min, and the MS detector was operated in the positive mode at 70 eV with an ion-source temperature of 230 °C. Compounds were identified using Enhanced MSD Chemstation software F.01.00.1903 and the NIST 2.0 library.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02629.

Oil, char, and organic mass balance data together with the pressure readings (Table S1) and elemental composition as well as H/C and O/C ratios of all LTL oils and chars (Table S2) (PDF)

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### Notes

The authors declare no competing financial interest.

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