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Lignin to liquids over sulfided catalysts

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ABSTRACT

Direct lignin conversion into valuable chemicals (phenols and hydrocarbons) was explored in a semi-continuous tubular reactor in the presence of a heterogeneous hydrotreating catalyst at 320–380 °C and hydrogen pressure 4–7 MPa. The catalyst to lignin mass ratio was varied in the range 0.25–1. The hydrolysis lignin was fully converted under the experimental conditions to yield gaseous, liquid and solid products. The amount of the undesired solid products decreased with the increasing severity of reaction conditions. The liquid products consisted mainly of aromatics and naphthenes in the organic phase and phenols in the aqueous phase. The proximity of the catalyst active sites and of the primary reaction intermediates originating from thermal depolymerization of lignin was shown to be crucial for product distribution.

1. Introduction

Renewable energy resources have attracted considerable attention as they are the only viable alternative for modern chemical production that does not rely on the use of fossil energy resources. The most abundant renewable resource for chemical utilization is the lignocellulosic biomass. While cellulose and hemicellulose are promising raw materials for carbohydrate-based chemistry, lignin could become a cornerstone of hydrocarbon chemistry platform owing to its unique composition. By estimation from the pulp production for paper manufacture in 2009, the worldwide lignin production was 50 million tons [1]. However, lignin is currently regarded as industrial solid waste and is almost exclusively being "only" burned for heat and energy production, and recovery of spent delignification chemicals.

Thanks to its interesting macromolecular structure based on phenolic monomeric units – typically, sinapyl, coniferyl and p-coumaryl alcohols (Fig. 1), lignin decomposition (depolymerization) could be used as a large scale source for valuable chemicals. Phenolics, aromatics and hydrocarbons represent the theoretical products of lignin depolymerization during pyrolysis or hydroprocessing, as discussed widely by several authors investigating lignin depolymerization [2–8].

Lignin (and wood) pyrolysis product, so called bio-oils, consist of wide range of chemicals (aromatics, olefins, oxygenates, *etc.*). Typically, these complex mixtures contain large amounts of water and have been described as unstable [9]. Moreover, to utilize bio oil for fuel or chemicals production it has to be stabilized first and only then it can be upgraded to the final products [10]. Consequently, transformation of lignin relying on its hydroprocessing that consists of the primary lignin liquefaction (thermal decomposition) followed by immediate hydrogenation and deoxygenation of reaction intermediates has been proposed to arrive at stable upgraded products in a single reaction step [2,11–18]. Two principal approaches have been proposed – (i) lignin to liquids (LtL) based on lignin solvolysis with formic acid and alcohol in a non-stirred autoclave at 350–400 °C for 4–16 h [11,12] and catalytic hydropyrolysis/hydrocracking of lignin [2,13–18].

The present work is focused on exploring the possibilities of hydrolysis lignin transformation using the latter approach. The aim is to convert hydrolysis lignin to liquid hydrocarbons and phenols using a semi-continuous reactor set-up in order to facilitate the transport of reaction intermediates to the catalyst active sites and of the products from the reaction zone to minimize their subsequent condensation reactions.

2. Experimental

Semi-continuous tubular reactor has been used to study the transformation of spruce enzymatic hydrolysis lignin (provided by Sekab–Processum, powder <0.1 mm, characterized by elemental composition and thermo-gravimetric analysis given below) over a sulfided catalyst under hydrotreating reaction conditions. A commercial NiMoP/γ-Al_2O_3 catalyst (17.0% MoO_3, 2.95% NiO, and 5.71% P_2O_5) was used for semi-continuous experiments. Catalyst particles were crushed and sieved; particles with diameter 0.25–0.5 mm were used for experiments. The influence of catalyst activation method (low temperature in situ vs. high

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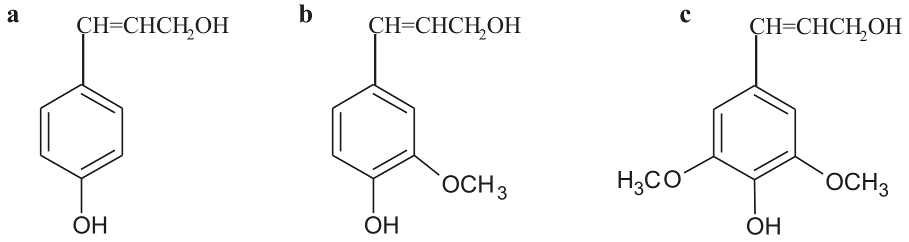

Fig. 1. Basic building blocks of lignin – coniferyl alcohol (a); sinapyl alcohol (b); p-coumaryl alcohol (c).

temperature pre-sulfiding), catalyst-to-lignin (C/L) mass ratio (C/L = 0.25–1), hydrogen pressure (4–7 MPa) and reaction temperature (320–380 °C) have been investigated.

Prior to each experiment, the tubular reactor (stainless steel, inner diameter 17 mm) was filled with 60 g of lignin and catalyst mixture. Depending on the specific catalyst activation method, the catalyst in mixture with lignin was either in oxide or sulfided form (pre-sulfided). The in situ catalyst activation was based on catalyst sulfiding by 50 g/h of 5 vol.% dimethyldisulfide (DMDS) in isooctane under hydrogen flow of 50 Nl/h and overall pressure of 4 MPa. The sulfiding was carried out in the temperature range 200–220 °C that was selected to minimize the decomposition of lignin during catalyst activation. The chosen temperature range coincides with DMDS decomposition yielding H_2S and is close to the recommended temperature range for the low temperature sulfidation stage (220–250 °C). The initial temperature 200 °C was increased at a heating rate of 10 °C/h until the final temperature 220 °C was reached. At this temperature, the activation continued for 6 h under constant conditions. Then the reactor was flushed with nitrogen and cooled down to temperature 200 °C. The actual experiment was started by heating the reactor to the desired reaction temperature (320–380 °C) at a heating rate 20 °C/h under the hydrogen flow of 50 Nl/h. After reaching the reaction temperature, the experiment has continued for 4 h under constant reaction conditions. The experiments were stopped by replacing hydrogen by nitrogen and cooling the reactor down to ambient temperature. When pre-sulfided catalyst was employed, the same experimental procedure was followed except for the sulfiding step. The sulfiding of the catalyst was carried out ex situ. Again, 5 vol.% dimethyldisulfide (DMDS) in isooctane under hydrogen flow of 50 Nl/h and pressure of 4 MPa has been used. However, the temperature has been risen at a heating rate 10 °C/h up to 340 °C where it was kept constant for 8 h.

The reaction products consisted of gaseous, liquid and solid products. The liquid products were collected in a gas–liquid separator. The plausible residual lignin and condensation products (solids) were removed from the reactor together with the catalyst. They were separated by sieving. The condensation products deposited on the catalyst were determined by burning off the deposits in an oven at 500 °C in air atmosphere. The liquid products consisted of two phases – an organic liquid phase and an aqueous phase. They were analyzed individually after their separation.

The organic liquid phase was analyzed by the comprehensive two-dimensional gas chromatograph equipped with a flame ionization detector (GCxGC-FID) to determine its type composition (paraffins, isoparaffins, olefins, naphthenes, aromatics and compounds containing heteroatoms). The identity of the main components was confirmed by the GC–MS technique. The aqueous phase products were analyzed by GC-FID using the SPME (solid phase micro-extraction) technique to extract selectively the organic compounds dissolved in the aqueous phase. Once again, the identity of the main components was confirmed by the GC–MS technique. The total concentration of phenols in aqueous phase was determined by UV spectrometry using double-beam spectrometer Specord 210 (Analytik Jena). The measurements were carried out in a quartz cell having optical path of 10 mm and the samples were diluted with distilled water. The sample absorbance at 270 nm was evaluated.

The effect of the lignin feedstock (hydrolysis lignin and lignosulfonate) and reaction temperature on the evolution of gaseous products have been studied in a stirred batch reactor using a commercial pre-sulfided NiMo/γ-Al_2O_3 catalyst (6.30% NiO, 23.5% MoO_3). Prior to the actual experiment, the autoclave vessel was filled with lignin (10 g), pre-sulfided catalyst (2 g) and solvent (100 g). Then the reactor was closed and flushed first with nitrogen and then with hydrogen. The reactor was rapidly heated to reach the reaction temperature (270, 320 and 350 °C). The reaction mixture was slowly stirred during the heating. When the desired temperature was reached, the reactor was pressurized to 7 MPa by hydrogen. When the pressure dropped by 0.2 MPa, reactor was re-pressurized to the initial pressure. After 1 h of reaction time, the stirring was stopped and the reactor vessel was rapidly cooled by external nitrogen flow. The mixture of hydrogen and evolved reaction gases was sampled after the temperature decreased below 23 °C. The gaseous products were then analyzed off-line by gas chromatograph equipped with FID and TCD detectors. The liquid phase consisting of the solvent and liquid products was separated from the catalyst, residual lignin and condensation products by filtration.

3. Results and discussion

The basic aim of the study was to understand the principal parameters affecting lignin conversion under hydrotreating conditions. Hence, the experiments were carried out in an exploratory manner focusing on the effect of (i) catalyst activation method, (ii) reaction mixture composition (mass ratio of catalyst to lignin), (iii) reaction (hydrogen) pressure, and (iv) reaction temperature. The experiments were performed in a tubular reactor that was operated in a semi-batch mode, i.e. under continuous flow of hydrogen and withdrawal of reaction products. As it was not possible to collect the gaseous products from the reactor setup representatively due to their considerable dilution by hydrogen, typical batch experiments were carried out to evaluate quantitatively the composition of the gaseous products.

3.1. The influence of the reaction parameters on the yields of lignin decomposition products

The conventional hydrotreating catalysts, such as NiMo used in this study, have to be converted to sulfide form to ensure their activity. This requires a special pretreatment of the catalyst using H_2S or a compound that decomposes under the sulfiding conditions and yields H_2S. Typically, sulfiding is carried out using dimethyl disulfide (DMDS) in the temperature range 200–360 °C, which is also a temperature region where lignin thermal decomposition takes place (Fig. 2). To avoid lignin decomposition during catalyst pretreatment, the in situ activation of the catalyst was carried out only

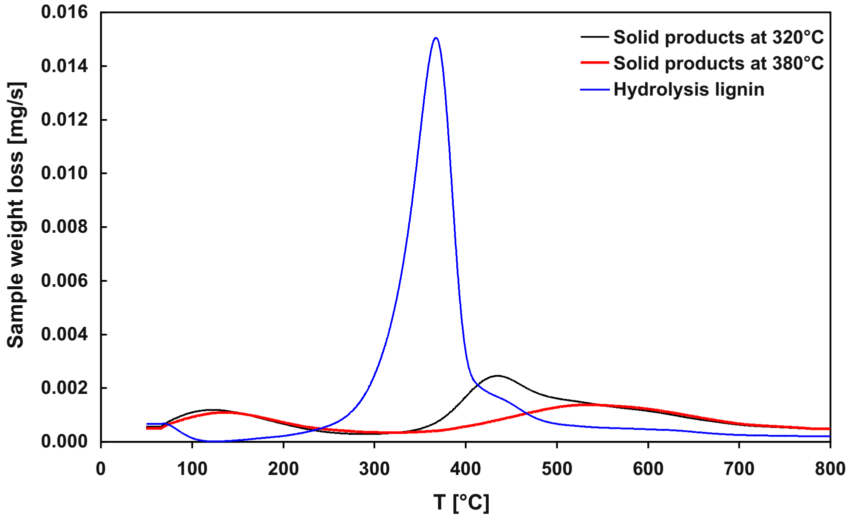

Fig. 2. The sample weight loss during thermal decomposition (N_2, 10 °C/min) of hydrolysis lignin (▬), and solid products from hydrolysis lignin hydrotreatment at 320 °C (–) and 380 °C (▬) (determined as derivative of the measured TGA curves).

at the low temperature sulfidation region, i.e. 200–220 °C where the decomposition of DMDS takes place and lignin decomposition is not yet significant (Fig. 2). Alternatively, the catalyst was sulfided separately (pre-sulfided catalyst) and after that it was mixed with lignin and loaded in the reactor. While proper sulfidation could be achieved, the pre-sulfided catalyst was briefly exposed to air during its mixing with lignin and loading of the mixture in the tubular reactor.

In all experiments four main product groups were distinguished – organic liquid phase products, aqueous phase products, solids and gaseous products. The solid products consisted in fact of condensation products and plausibly unconverted lignin, as these could not be separated. Nonetheless, the thermo-gravimetrical analyses results strongly suggest that virtually all lignin was converted under the reaction conditions and that the recovered solids consists of condensation products that can be thermally decomposed to a significantly lesser extent and in comparison with neat hydrolysis lignin only at a higher temperature (Fig. 2). The organic liquid product consisted of hydrocarbons and oxygenates having lower solubility in water. The aqueous phase product contained mainly phenol and its derivatives dissolved in water. The main products found in the gaseous phase included CO_2, CH_4, H_2S (particularly when sodium lignosulfonate was hydroprocessed) and low concentrations of other light hydrocarbons and CO.

The results have indicated (Fig. 3) that the lignin hydrotreating over pre-sulfided catalysts is slightly more efficient in comparison with the in situ sulfided catalyst. It is clear particularly from the increased yield of liquid products and the decreased yield of solid products. It can be ascribed to the intrinsically higher deoxygenation activity of the pre-sulfided catalyst that originates from the more complete conversion of the catalyst into its sulfide form. Elemental analysis of both sulfided catalysts confirmed higher sulfur content in presulfided catalyst (9.9 wt.%; Mo/S ratio = 1.49 w/w) in comparison with the in situ activated catalyst (7.9 wt.%; Mo/S = 1.86 w/w). Moreover, catalyst pre-sulfiding allows avoiding of lignin decomposition during activation. The advantage of in situ activation, on the other hand, is connected with the experimental procedure itself as the handling of a pre-sulfided catalyst can be avoided.

The principal role of the catalyst lies in the rapid stabilization of the primary products of lignin decomposition that helps in preventing their condensation to high molecular weight products. Therefore, the key issue is to ensure a close contact between the catalyst active centers, on the one hand, and the lignin pyrolysis intermediates, on the other hand. A comparison of the main product yields at various catalyst-to-lignin mass ratios was hence performed at two reaction temperatures (Fig. 4). It can be clearly seen that with the increasing catalyst-to-lignin ratio that can be considered as an indicator of the proximity of the catalytically active sites and reactants the yields of gaseous and liquid products increase while the yield of the solid products drops. At the same time, however, the concentration of active sites, relative to lignin, is increased and consequently higher conversion can be expected as well. For example, at 380 °C the yield of solid products dropped from roughly 45 wt.% to about 20 wt.% (Fig. 4b). The drop is accompanied particularly by the increase in the yield of the gaseous products, among which mainly CO_2 and light alkanes originating from the elimination of side chains and alkoxy groups were detected (see below).

As expected, hydrogen pressure affects the product distribution as well (Fig. 5). Similarly to hydrocracking, an increase in hydrogen pressure results in a larger extent of the hydrocracking reactions and to deeper upgrading, which may be characterized by a more pronounced products deoxygenation and hydrogenation (see below). Moreover, the increase in hydrogen partial pressure will increase the rate of stabilization of the primary lignin

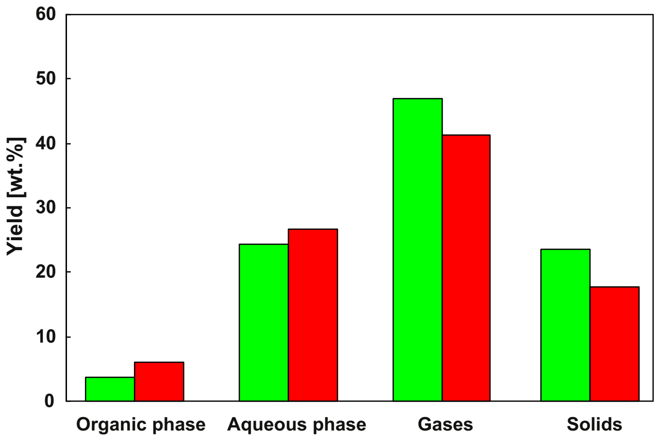

Fig. 3. Product distribution obtained over in situ sulfided (▬) and pre-sulfided (●) catalysts (320 °C, p = 4 MPa C/L = 1.0), wt.% of lignin weight.

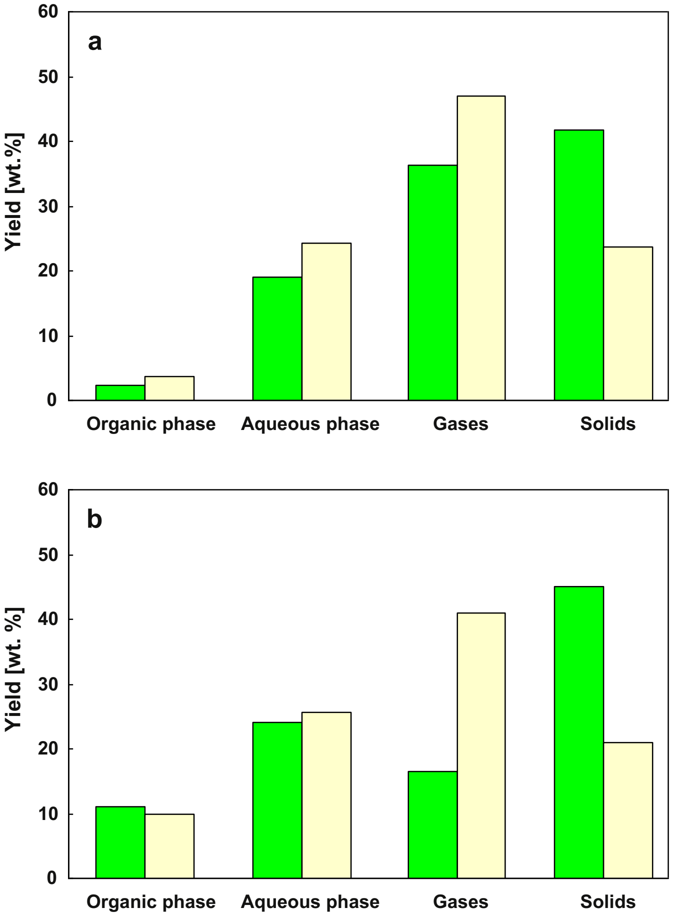

Fig. 4. Effect of the catalyst to lignin ratio (C/L) on product distribution (● C/L = 0.25, ● C/L = 1.00, p = 4 MPa, in situ activation); (a) 320 °C; (b) 380 °C; wt.% of lignin weight.

decomposition products. The slight decrease in aqueous phase products could be attributed to deoxygenation of phenol and its derivatives to in the aqueous phase insoluble hydrocarbons. Their yield does indeed increase (Fig. 5).

The data in Fig. 4 reveal also the effect of the reaction temperature on the yields of products for the in situ sulfided catalyst. It can be seen that the higher reaction temperature promotes the formation of liquid products, particularly of the organic liquid products. On the other hand, the yield is surprisingly lower at the catalyst-to-lignin ratio equal to 0.25 while it is approximately the same at the catalyst-to-lignin ratio equal to 1 (Fig. 4). The effect of the reaction temperature was also investigated for the pre-sulfided catalyst (Fig. 6). In accord with the results obtained for the in situ sulfided catalysts (Fig. 4), also with the pre-sulfided catalysts the yield of liquid products, both organic liquid products and aqueous phase products, has increased at the expense of the solid products. The yield of gaseous products remained virtually unaltered (Fig. 6).

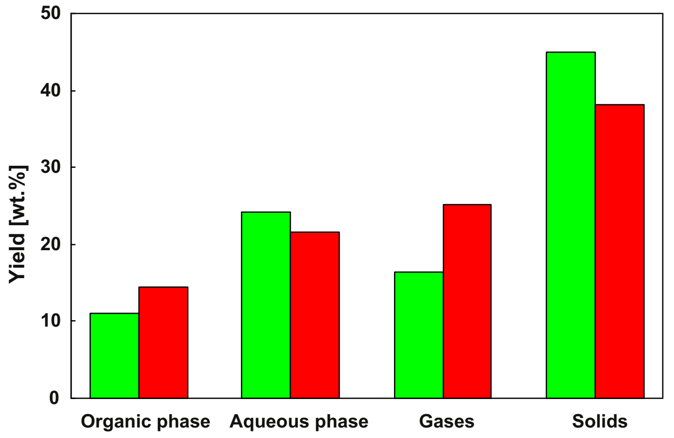

Fig. 5. Effect of hydrogen pressure on product distribution (○ p = 4 MPa, ● p = 7 MPa, 380 °C, C/L = 0.25, in situ activation); wt.% of lignin weight.

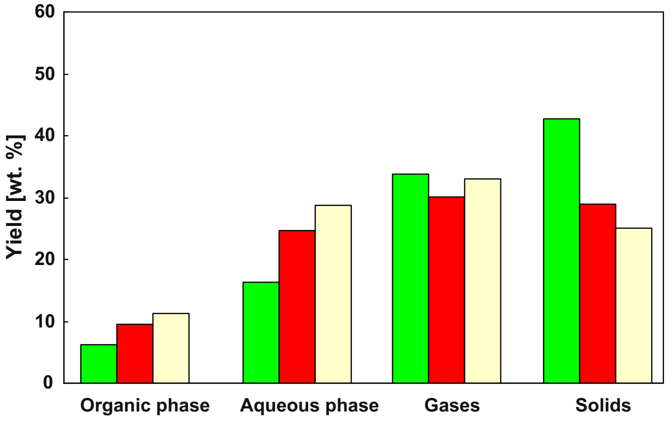

Fig. 6. Product distributions for various reaction temperatures (● 320 °C, ● 360 °C, ● 380 °C, pre-sulfided catalyst, C/L = 0.5; p = 7 MPa); wt.% of lignin weight.

The exploratory tests have shown that all selected reaction parameters influence significantly the yield of products of lignin hydrotreatment. Based on the results it can be inferred that the most important parameters are the catalyst-to-lignin ratio, i.e. the proximity of the catalytically active centers and the primary decomposition intermediates, and the reaction temperature. The impact of pre-sulfiding or in situ sulfiding and of hydrogen pressure was, for the selected sets of parameter values, less pronounced.

3.2. The influence of the reaction parameters on the detailed composition of the liquid products originating from lignin decomposition

Two separate liquid product phases were obtained in all experiments – an organic liquid phase and an aqueous phase. The formation of the aqueous phase can be attributed to those deoxygenation reactions that yield water as the principal deoxygenation product. These include hydrodeoxygenation, dehydration and possibly also reversed water–gas shift reaction. In addition to water, carbon dioxide and monoxide are typical deoxygenation products as well. They are formed as a result of decarboxylation and decarbonylation reactions, respectively. Phenols originating from the building blocks of lignin (Fig. 1) were the main organic products found in the aqueous phase. On the other hand, the concentration of oxygenated compounds in the organic liquid product phase was low. The predominant products were aromatics and naphthenes, i.e. products of phenols deoxygenation and subsequent aromatics hydrogenation, respectively. They were accompanied by paraffins and isoparaffins. Only traces of olefins were observed in the products suggesting that any cracking products were hydrogenated or underwent rapid condensation.

As shown in Fig. 4, the increased concentration of the catalyst in the mixture with lignin (i.e. a higher C/L ratio) resulted in decreased formation of condensation products. The yields of both liquid phases increased only slightly at 320 °C and remained virtually unchanged at 380 °C (Fig. 4). Nonetheless, the composition of both phases was changed dramatically (Fig. 7). The increased concentration of the catalyst resulted in a deeper upgrading of the

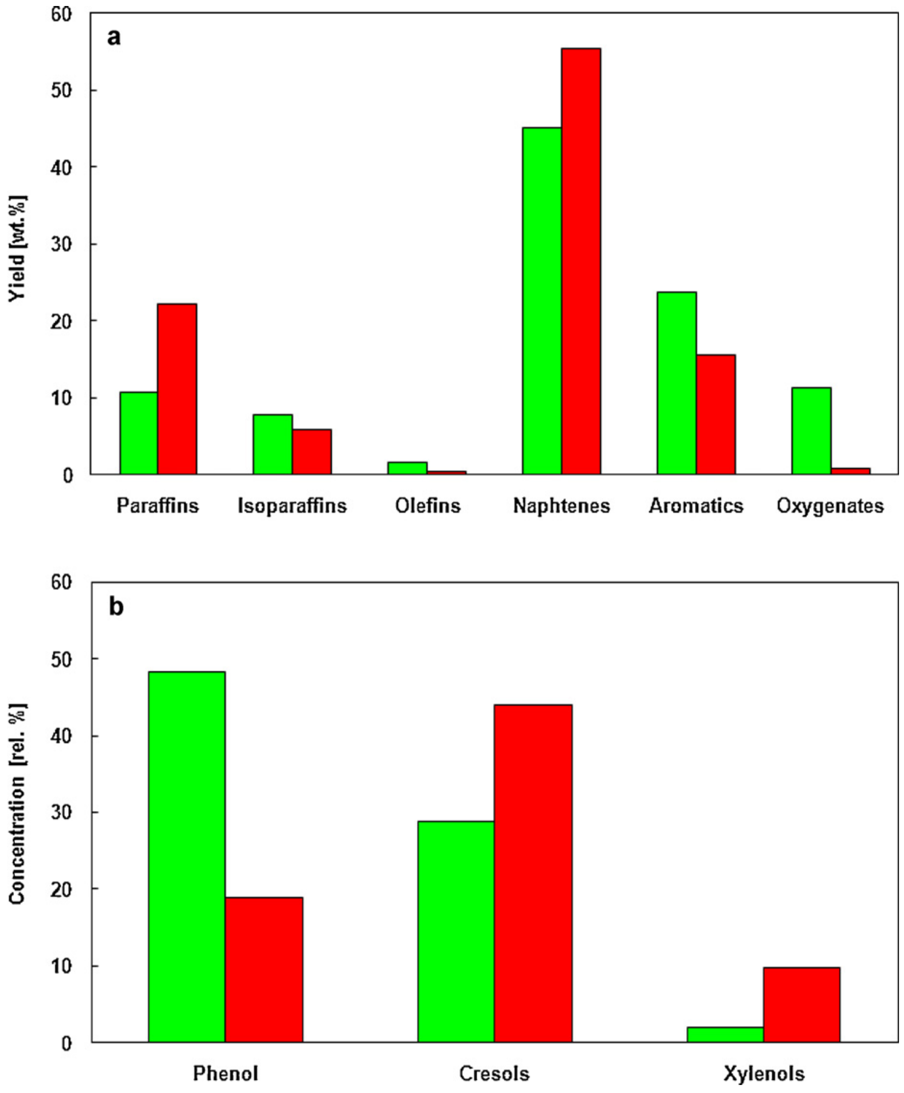

Fig. 7. The effect of catalyst-to-lignin (C/L) ratio (🟢 C/L = 0.25, 🔴 C/L = 1.00, 380 °C, 4 MPa, in situ activation) on the composition of the organic liquid phase, wt. % of organic liquids (a) and aqueous phase, rel.%, obtained by SPME-GC–MS (b) during hydrolysis lignin hydrotreatment.

reaction products, confirming thus the concept of better availability of active sites (both higher concentration and better proximity), on the one hand, and reaction intermediates, on the other hand. Consequently, the formation of naphthenes and paraffins was enhanced at the expense of aromatics and oxygenated compounds (Fig. 7a). These products are less prone to condensation reactions and may hence explain the suppressed formation of condensation products (Fig. 4). Moreover, changes in the relative composition of phenolic compounds dissolved in the aqueous phase have been observed as well (Fig. 7b). The relative concentration of phenol dropped sharply when C/L ratio was increased from 0.25 to 1. On the contrary, the relative concentrations of cresols and xylenols increased. This could be attributed to the better availability of active sites. The absolute concentrations of phenols in aqueous phase are reported in Table 1. However, the results are rather inconclusive due to the distribution of some compounds between both liquid phases.

Table 1
Concentrations of phenols in aqueous phase (wt. %) obtained from hydrolytic lignin upgrading at various reaction conditions.

Temperature [°C]	380	380	320	360	320	380	380
Pressure [MPa]	4	4	4	7	7	7	7
Catalyst/lignin ratio	0.25	1	1	0.5	0.5	1	0.5
Activation	In situ	In situ	presulf.	presulf.	presulf.	presulf.	presulf.
Benzene ring moiety	0.62	0.19	0.50	0.56	0.23	0.57	0.28
Phenol	0.35	0.04	0.26	0.30	0.14	0.25	0.12
o-Cresol	0.07	0.04	0.09	0.10	0.04	0.10	0.06
m- and p-Cresols	0.17	0.06	0.15	0.14	0.05	0.22	0.08
Xylenols	0.02	0.02	0.03	0.03	0.01	0.03	0.02

Note: The concentration of benzene ring moiety was determined by UV spectrometry, the concentrations of the individual phenols were determined by combining the total concentration of benzene ring moiety by UV spectrometry and relative concentrations of individual phenols obtained by SPME-GC assuming equal efficiency of SPME for the measured phenols.

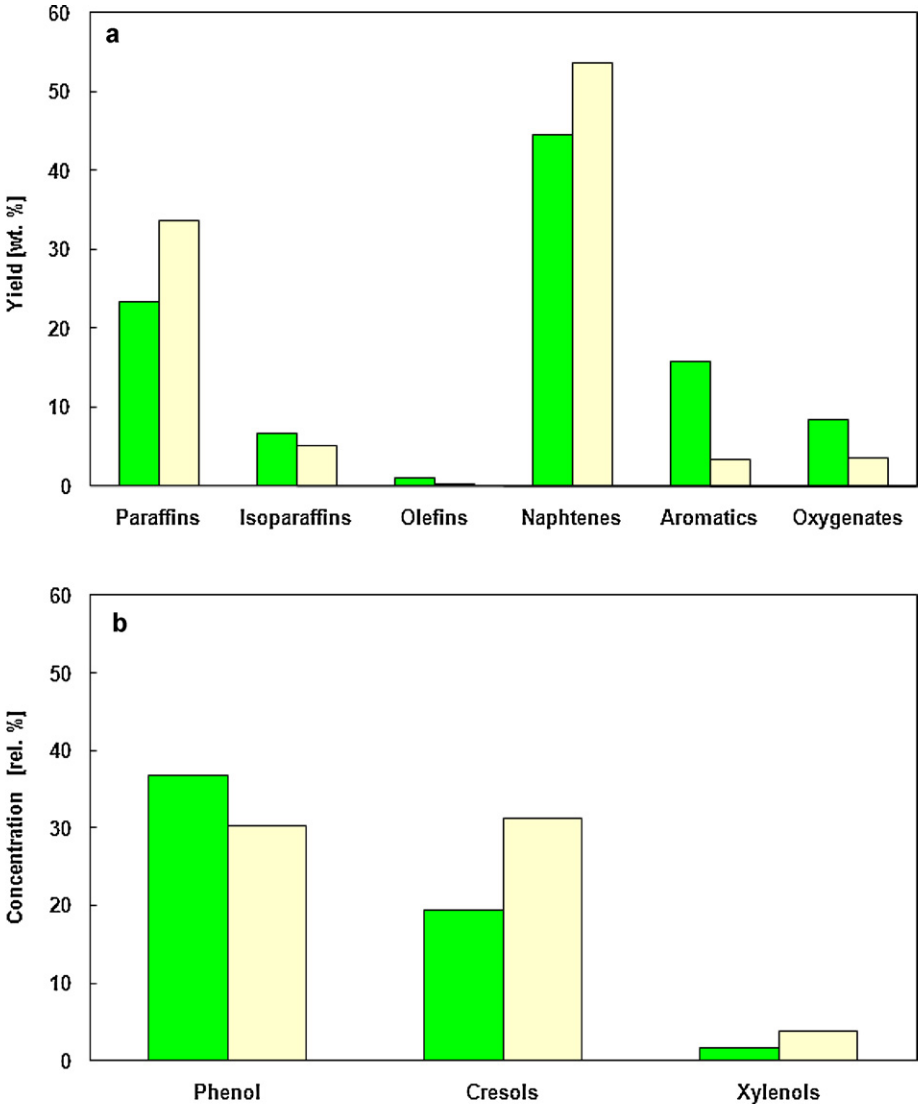

Fig. 8. The effect of reaction temperature (● 320 °C, ○ 380 °C, pre-sulfided catalyst, C/L=0.5; p=7 MPa) on the compsition of the organic liquid phase, wt.% of organic liquids (a) and aqueous phase, rel.% obtained by SPME-GC–MS (b) during hydrolysis lignin hydrotreatment.

The influence of the increased reaction temperature on the composition of the liquid product phases was similar to that of the increased catalyst concentration. As the rate of the deoxygenation and hydrogenation reaction was enhanced by the increase of the reaction temperature from 320 to 380 °C, the products obtained at the higher temperature were more rich in saturated products (paraffins and naphthenes) while the yields of aromatics and oxygenates decreased (Fig. 8a). The increased reaction temperature contributed also to an increase in the relative concentration of cresols and xylenols in the aqueous phase (Fig. 8b). It can be suggested that the rate of guaiacol (methoxyphenol), dimethoxybenzenes and other alkyl methoxy benzenes is enhanced due to the rise in temperature and these are hence converted into cresols and xylenols.

Based on the detailed analysis of liquid products, it can be concluded that the catalyst plays a vital role in hydrogenolysis of bonds connecting the monomeric units as well as in deoxygenation and hydrogenation of the reaction intermediates. Obviously, the choice of reaction conditions, including the relative distance that the reaction intermediates released due to the thermal depolymerization (pyrolysis) of lignin have to travel to catalyst active centers, determines the composition of products both in the organic and aqueous phase.

3.3. The composition of gas phase products originating from lignin decomposition

Due to the dynamic character of the semi-continuous experiments it was not feasible to obtain reliable information on composition of the gaseous products. Therefore, a set of experiments with hydrolysis lignin and lignosulfonate were carried out in a stirred batch reactor to obtain information about the composition of gaseous products. It should be noted that these experiments provided, in relation to the semi-continuous experiments, only qualitative information about gas phase products due to the differences of both experimental set-ups. Hence the exact gas-phase composition reported here for the batch experiments should not be interpreted as gas-phase composition representing the semi-continuous experiments. Besides hydrolysis lignin, lignosulfonate was used as an alternative feedstock. As it contains sulfur (sulfonic groups) lignosulfonate could be used as a source of H_2S that is important for preserving the activity of hydrotreating catalysts [19]. During the experiments, fresh hydrogen was added only to compensate the hydrogen consumption (i.e. the pressure drop).

The composition of gaseous products as a function of reaction temperature is depicted in Fig. 9. It can be seen that the main gaseous products during hydroprocessing of hydrolysis lignin as

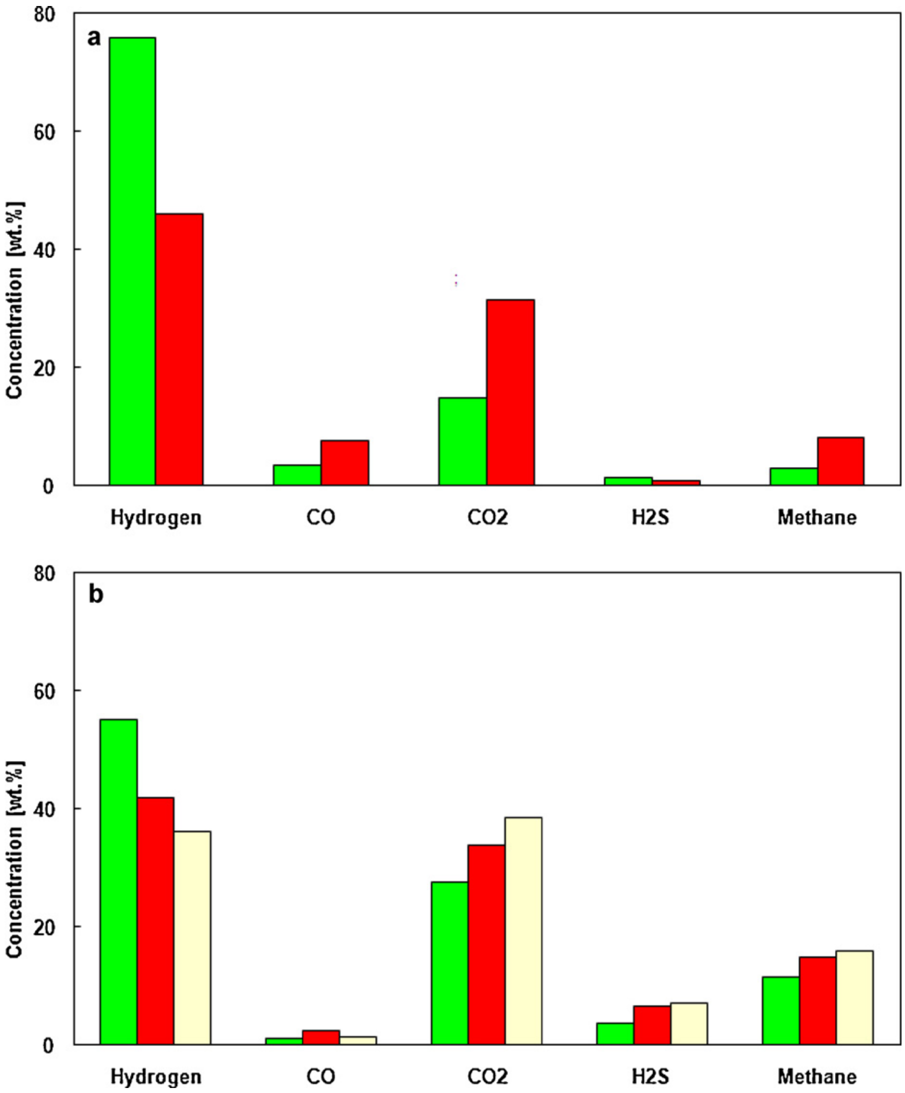

Fig. 9. The composition of gas products sampled after lignin hydrothermal depolymerization at various temperatures (● 270 °C, ● 320 °C, ○ 350 °C) – hydrolysis lignin (a) and sodium lignosulfonate (b); wt.% of reaction gas.

well as lignosulfonate were carbon dioxide and methane. The concentration of both products increased with the increasing reaction temperature (Fig. 9), which supports the explanations given above for the observed changes in the aqueous phase products composition. The formation of methane can be linked with the conversion of methoxy groups in various (di)-methoxy-(alkyl) benzenes. While in the case of hydrolysis lignin formation of carbon monoxide was observed (Fig. 9a), only traces of carbon monoxide were found among the products of lignosulfonate hydroprocessing (Fig. 9b). Only traces of hydrogen sulfide that originated due to the reductive conditions most probably from the catalyst were found among the products of hydrolysis lignin hydroprocessing. On the other hand, significant concentrations of hydrogen sulfide were detected in the gaseous products of lignosulfonate hydroprocessing. It can be inferred that in this case the hydrogen sulfide is a product of the reduction of the present sulfonic groups (5.7 wt.% of sulfur). Other gaseous hydrocarbons (C_2–C_3) were detected in hydroprocessing of both lignin types only in very low concentrations.

4. Conclusions

The effect of basic reaction parameters (temperature, hydrogen pressure, catalyst-to-lignin (C/L) ratio, catalyst activation method) on the transformation of hydrolysis lignin into gaseous and liquid products has been investigated. It has been demonstrated that the studied parameters affect significantly the basic product distribution. The formation of solid products, i.e. of the undesired condensation products, has been suppressed when more severe reaction conditions were used (high temperature, pressure and C/L ratio). Moreover, pre-sulfiding of the catalyst has been beneficial as well. The higher severity of the reaction conditions has resulted also in more deeply upgraded products. Typically, the yield of naphthenes and paraffins has increased at the expense of aromatics and oxygenates due to the higher severity. The hydrocarbon products included typically C_6–C_9 alkyl-naphthenes, C_6–C_9 aromatics and C_5–C_8 n- and isoparaffins. The predominant oxygenates were phenol, cresols and xylenols. Finally, it has been concluded based on batch experiments that the gaseous phase products from hydrotreating of hydrolysis lignin and lignosulfonate consist mainly of carbon dioxide and methane. They have been accompanied by light hydrocarbons, carbon monoxide and hydrogen sulfide.

Acknowledgements

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