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**Extraction of phenolic compounds from hydrothermal processing
of black liquor: Effect of reactor type and pH of recovered liquid
phase**

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Graphical abstract



Integration of black liquor gasification in a pulp mill without disturbing upstream processing by partial utilization of black liquor

Abstract

The goal of this work was to study the effect of pH on the extraction yield of phenolic compounds from liquid phases recovered after the hydrothermal treatment of black liquor in the batch and continuous reactors at 280 °C and 350 °C. The pH values of recovered liquid phases under investigation were adjusted to 9, 8, and 7. The liquid-liquid extraction was subsequently performed using ethyl acetate for 4 h at room temperature. The identification and quantification of phenolic products were conducted using GC-Mass analysis. The main monomeric compounds identified in the aqueous phase were phenol, guaiacol, and syringol. The results indicated that reducing the pH improved slightly the extraction of the phenol and guaiacol from the various recovered liquid phases after hydrothermal treatment. However, the extraction yield of syringol greatly improved by reducing the pH of liquid phases. This was very noticeable for the recovered liquid phases after treatment at 280 °C, where the quantity of syringol was initially high. Moreover, lower pH hinders the ethyl acetate hydrolysis during liquid-liquid extraction. The extraction experiments with various pH also confirmed the superior performance of the continuous reactor over the batch reactor to obtain the phenolic compounds. In addition, the phenolic products have been degraded with increasing treatment temperature from 280 °C to 350 °C.

Keywords: Black liquor; Liquid-liquid extraction; Phenolic compounds; Hydrothermal treatment; Lignin

1. Introduction

All plant-based fibers are lignocellulosic materials, mainly composed of cellulose, lignin, and hemicellulose. Other molecules that can be found in woody biomass are pectin, resins, waxes, minerals, etc. Lignin is a major polymeric component in biomass and is known as the second most abundant organic substance on the earth, after cellulose. The structure of lignin is highly branched with ether linkages and C-C bonds formed through oxidative radical polymerization (Bamdad et al., 2017). Moreover, it is the largest phenolic polymer in the plant cell walls and is composed of monomeric subunits called monolignols. The content of lignin in biomass varies by the type of plant and interacts with two other biopolymers, cellulose and hemicellulose. For example, in softwood and hardwood, the contents of lignin represent about 18-25 wt% and 27–33 wt%, respectively. Currently, the main challenge is to remove lignin in a selective manner, where cellulose and hemicelluloses are preserved to the greatest possible extent to valorize all the components (Llano et al., 2015).

The pulp and paper industry is known as a traditional source of industrial lignin. Black liquor obtained from pulping processes is a toxic liquor with 10-20% solid content that includes degraded lignin, sodium salts of organic acids, and degraded polysaccharides (Wang et al., 2019). Currently, 60-70 million tons of lignin are generated annually from the pulp and paper industries worldwide. It is estimated that by 2030, this number will increase by 225 million tons per year (Bajwa et al., 2019). Industrial lignin can be divided into two types based on its sulfur content: sulfur-containing lignin and sulfur-free lignin. The sulfur-containing lignin, which is by far the most important includes Kraft lignin, liginosulfonates, and enzymatic hydrolyzed lignin with sulfur contents of 1.0-3.0%, 3.5-8.0%, and 0-1.0%, respectively (Aro and Fatehi, 2017; Bajwa et al., 2019). Organosolv lignin, soda lignin, and lignin from second-generation biorefinery processes are known as sulfur-free lignin. Due to its high abundance, availability, and eco-friendly properties, lignin is a candidate for

producing high-value compounds such as phenolic compounds, syngas, carbon fiber, various oxidized products, and multifunctional hydrocarbons (Bajwa et al., 2019). However, due to its complex and heterogeneous structure, lignin of pulping liquor has obstacles in utilization, thus leading to its main exploitation in a recovery boiler to produce a low-value fuel to generate electricity and heat. The development of value-added lignin-derived co-products can help to make the second-generation biorefineries and paper industry more profitable by valorizing their byproduct lignin.

The conventional Kraft pulp mills could be transformed into a multi-product biorefinery to produce pulps, biofuels, and chemicals. In newly developed platform, pre-extraction of the low heating value of hemicelluloses (13.9 kJ/kg) by an autohydrolysis stage before the pulping allows the production of bioethanol or various valuable chemicals from the extracted hemicelluloses (Chirat et al., 2012). Due to altered structure and more accessibility, pre-extracted lignocelluloses are cooked under moderate conditions to give chemical pulps with the appropriate properties, enabling the utilization of sulfur-free process alkaline pulping, which facilitates the gasification and valorization of the resulting black liquor (Huet et al., 2016). The sulfur-free black liquor could then be treated in the more efficient gasification facilities developed in recent decades, where high moisture content alkaline black liquor can promote the conversion of biomass and organic waste (Fig. 1).

Hydrothermal treatment increases the potential of black liquor to generate energy, synthetic biofuels, or chemicals, where black liquor is evaporated in a pressurized reactor under reducing conditions, and converted into a gaseous phase (a mixture of H₂, CH₄, C₂H₆, CO, CO₂), aqueous phase (including mineral and intermediate phenolic compounds), along with solid/char phase (Pola et al., 2019; Mañas et al., 2022). The converting yield of black liquor biomass to various compounds depends significantly on several parameters, including treatment temperature, reaction time, and reactor type (Lee et al., 2021). For simultaneous

production of pulp, fuel and phenolic compounds, the preferred mode of hydrothermal operation would involve only partial treatment of the black liquor of the pulp mill. Furthermore, the liquid-liquid extraction efficiency of phenolic compounds from the aqueous phase, one preferred option, was influenced by the process parameters such as the number of extraction stages, nature of solvents, sample-to-solvent ratios, temperature, and also the initial pH value of the aqueous phase (Llano et al., 2015; Mante et al., 2019; Tsouko et al., 2019).

Previously, we investigated the extraction of phenolic compounds from the recovered liquid phase after hydrothermal treatment of sulfur-free black liquor in a batch reactor (Curmi et al., 2022). It was found that the phenolic compounds were better extracted with ethyl acetate than methyl isobutyl ketone (MIBK). The pH value of the aqueous phase is another key factor influencing the liquid-liquid extraction performance of phenolic compounds. It should be adjusted to ensure that they are uncharged, which reduces the solubility of analytes in the aqueous phase and promotes the transfer of analytes into the organic phase (Llano et al., 2015). In batch reactor the highest yield for extraction of phenolic compounds obtained at 280°C. However, the higher treatment temperature (350°C) might facilitate the release and recovery of sodium (Na) from the organic acid salts which is of the utmost importance for the pulp mill.

Following our previous study, the present work aimed to assess the influence of the hydrothermal treatment reactor type (batch and continuous reactors) and pH of the extraction medium on the production and extraction efficiency of individual and total phenolic compounds from the recovered liquid phases. The pH values of recovered liquids were adjusted to 9, 8, and 7 using H₂SO₄. Then, the liquid-liquid extraction was done using ethyl acetate for 4 h at room temperature. The identification and quantification of phenolic products were conducted using GC-Mass analysis.

2. Materials and method

2.1. Materials

2.1.1. Chemicals

All commercial chemicals were purchased and used as received. List of chemicals used for the experiments: Sulfuric acid H₂SO₄ 4 N (97%, Fluka), sodium hydroxide NaOH (99%, Carl Roth), vanillin C₈H₈O₆ (99%, Sigma Aldrich), kit poly(styrene sulfonate) sodium salt (PSS), ethyl acetate (99.9%, Carl Roth), phenol (Sigma Aldrich), guaiacol (Carl Roth), syringol 2,6-dimethoxyphenol (Sigma Aldrich), and phenol-d₆ (99 atom% D, Sigma Aldrich). The pure cellulose, and alkaline lignin were purchased from Sigma Aldrich.

2.1.2. Black liquor

The raw material used in this study was sulfur-free black liquor provided by our project partner Fibre Excellence R&D Kraft, a wood Kraft pulp producer located in Saint-Gaudens (France). To produce the black liquor, an industrial mix of hardwood chips composed of beech, poplar, oak, and chestnut was cooked to make black liquor. The first step was hemicellulose hydrolysis (hot water extraction at 170 °C for 1 h). Then, a soda cooking (32% NaOH, 5.1 liquid/wood mass ratio, 170 °C for 55 min) was applied to these hydrolyzed wood chips, and the black liquor was recovered.

2.2. Hydrothermal treatment

Hydrothermal treatments were performed in batch and continuous reactors. A 0.6 L stainless steel (type 316) reactor sealed with a screwed jaw from Parr Instruments (France), and a 0.5 L stainless steel (type 1.4980) batch reactor sealed with dowels and nuts from TOP Industrie (France) were used. A 0.5 L continuous reactor from TOP Industrie (France) was also used. There are major differences between the batch and the continuous reactors,

especially concerning the heating rate and distribution of the residence time influencing the results.

For each batch experiment, depending on the temperature, between 60 mL and 300 mL of black liquor is introduced in the reactors, and N₂ is added to create an inert atmosphere and reach an initial pressure of about 10 bar relative. Then the reactor was heated by a heating collar to the desired temperature (280 and 350 °C) by a resistance-type heating collar (2 kW for the Parr reactor and 4 kW for the TOP reactor). The heating time depends on the targeted temperature (from 30 min for 280 °C and 50 min for 350 °C). Once the reaction temperature is reached, the reaction conditions are maintained for 30 min before quenching with an air coil around the reactor. During the reaction, the temperature is monitored by a thermocouple in an immersion sleeve inside the reactor. A relative pressure sensor associated with a pressure gauge indicates the pressure. Data from both sensors (temperature and pressure) are automatically recorded during the experiment in a computerized file.

Continuous experiments were performed on a 1.5 L/h test bench (TOP Industrie) in the similar temperature conditions of the batch experiment. While the batch reactors are heated up together with the reaction mixture, the continuous reactor is continuously heated, fluids are admitted in the already hot reactor changing the heating profile and thus the chemistry. The installation is described in more detail, including residence time and distribution measurements, in the literature (Briand et al., 2022). The reactor is heated while operating on a water feed. Once the installation is stable the switch to the biomass slurry tank is made. Operation takes typically between 5 and 30 h. The effective internal volume of the reactor is 0.5 L, leading to an averaged residence time of 20 min. Gas production is measured by the pressure increase on the product tank, followed by gas analysis by micro-chromatography.

2.3. Samples preparation

2.3.1. Lignin extraction

Lignin was extracted from black liquor and liquid phase after hydrothermal treatment. About 20 g of the sample under stirring was gradually acidified to pH 3 using H₂SO₄ 4 N. A centrifugation step for 30 min at 3076 g in a centrifuge made it possible to recover the precipitated lignin. The lignin was washed three times with deionized water previously acidified to pH 2 with H₂SO₄ 4 N and centrifuged after each washing for 30 min at 3076 g in a centrifuge. Finally, the washed lignin was dried using a freeze-dryer.

2.3.2. Liquid-liquid extraction

To recover the small phenolic compounds from the liquid phase after hydrothermal treatment, liquid-liquid extraction with ethyl acetate was performed. Ethyl acetate was added to the sample in a volumetric ratio of 1:1. After stirring, the mixture was centrifuged for 30 min at 3076 g in a centrifuge to separate the two phases distinctly.

2.4. Analysis

2.4.1. Gel permeation chromatography (GPC)

Molar mass distributions of precipitated lignin were determined using gel permeation chromatography. First, 0.025 g of lignin was dissolved in ultrapure water (4.5 mL) previously adjusted at pH 12 with NaOH. After filtration with a membrane (0.45 µm PTFE), the samples were injected into chromatography device equipped with a pump (SP Thermo Spectra System P1500), an autosampler (SP Thermo Spectra System AS3500), a guard-column (TOSOH TSKgel PWH 0006762), three columns in series (TOSOH TSKgel G3000PW 0005762, TSKgel G4000PW 0005763, and TSKgel G3000PW 0005762), and a UV-detector (SP

Thermo Spectra System UV6000LP). Elution solvent was aqueous NaOH solution of pH 12 at flow rate of $0.6 \text{ mL}\cdot\text{min}^{-1}$, injection volume was $10 \text{ }\mu\text{L}$, and detection was done at 280 nm. To determine the molar mass distributions of the lignin, polystyrenes with a mass range between 580 Da and 3250,000 Da, and vanillin were used to create a calibration curve and analyze the results.

2.4.2. Gas chromatography-mass spectroscopy (GC-MS)

After liquid-liquid extraction, ethyl acetate extracts were analyzed by GC-MS (PerkinElmer GC Clarus 680 and PerkinElmer MS Clarus SQ 8 T). Helium is used as carrier gas at a flow rate of $1 \text{ mL}/\text{min}$. In the GC oven, the capillary column (Elite 1701–60 m x 0.25 mm inner diameter; $1.0 \text{ }\mu\text{m}$ film thickness) is initially held at the temperature of $45 \text{ }^\circ\text{C}$ for 10 min, and the temperature increase by $6 \text{ }^\circ\text{C}/\text{min}$ to $230 \text{ }^\circ\text{C}$ where it is finally held for 9 min. The identification of compounds was made by comparing mass spectra with the NIST library. For the quantification, standard compounds (phenol, guaiacol, and syringol) were injected at different concentrations to create a calibration curve, and phenol-d6 was used as the internal standard.

2.4.3. FTIR analysis

FTIR analysis was used to evaluate the structural and composition of the residual solid phases after hydrothermal treatment of black liquor. The FTIR analysis was carried out using a Bruker Tensor 27 spectrometer (Germany). The ATR module is from Specac, model GS10800. The spectral range from 400 to 7800 cm^{-1} and a scanning resolution of 4 cm^{-1} .

3. Results and discussion

3.1. General characterization of recovered liquid phases

The main characteristics of the sulfur-free black liquor, liquid phases, solid phase recovered after hydrothermal treatment are presented in Table 1. Data for untreated black liquor and recovered liquid phase after black liquor treatment in a batch reactor at 280 °C as the best condition for phenolic products production were obtained from Curmi et al. (2022). Precipitated lignin includes a high molar mass fraction of lignin that was extracted from original black liquor and liquid phases after hydrothermal treatment by gradual acidification to pH 3 and then centrifugation. By comparing the calculated values based on the weight of aqueous black liquors (values in parentheses in the Table 1), it was found that the weight percentage of precipitated lignin in liquid phase decreased significantly by over 89% and 96% respectively, upon treatment of black liquor in batch and continuous reactors at 350 °C, indicating significant degradation of lignin during hydrothermal treatment. Moreover, the weight percentage of ash has also decreased by over 41% and 58%, respectively, upon treatment in batch and continuous reactors at 350 °C, presumably due to the separation of inorganic compounds as solid waste. As seen from Table 1, the recovered solid waste after hydrothermal treatment in continuous reactor at 350 °C exhibited high ash content, which could be mixed with black liquor in the case of sulfur-free black liquor and fed to the recovery boiler for sodium recovery. The overall mass balance for the performed experiments is given in Table 2, exhibiting that the lignin is degraded significantly during the hydrothermal treatment. For instance, lignin degradation during hydrothermal treatment in batch and continuous reactors at 350 °C were 91.3% and 96.65%, respectively.

3.2. GPC analysis

The molecular mass distribution of lignin was determined by GPC analysis on the entire recovered liquid phases after hydrothermal treatments and also their precipitated lignin. The results are presented in Fig. 2. The whole of the liquid phase after hydrothermal treatment in continuous reactor (350 °C) showed a slightly higher molecular weight and a lower quantity of small molar mass compounds than the batch reactor. The obtained small molar mass fraction of degraded lignin presumably corresponds to the dimers, and trimers of phenolic products which also are interesting for different applications (Hashemi et al., 2017). However, the precipitated lignin from the treated black liquor from the continuous reactor exhibited a slightly lower molar weight than that of the batch reactor, indicating lower condensation of lignin products during treatment in the continuous reactor.

3.3. GC-Mass analysis

The liquid-liquid extraction was done using an equal volume of ethyl acetate and the whole recovered liquid phase after hydrothermal treatment of sulfur-free black liquor. The identification and quantification of phenolic products were carried out using GC-Mass analysis (Figs. 3 and 4). As shown in Fig. 3, the identified phenolic products for treated black liquor in batch reactor included phenol as the major product (33.51 min), guaiacol (34.86 min), p-cresol (35.72 min), and dimethyl-phenol (36.98 min). Likewise, the identified phenolic products for treated black liquor in a continuous reactor included phenol as the major product (33.51 min), guaiacol (34.64 min), 2-methyl-phenol (34.86 min), p-cresol (35.72 min), dimethyl-phenol (36.98 min), creosol (37.23 min), and ethylphenol (37.91 min) (Fig. 4). The highest concentration of phenolic compounds (3.54 g/L) has been obtained for treating the same black liquor at 280 °C in a continuous reactor (Fig. 5). However, their concentration decreased to 0.3 g/L when the treatment temperature increased to 350 °C. The total concentration of identified phenolic compounds for treated black liquor in a batch reactor at

280 °C and 350 °C was calculated to be 3.1 g/L and 0.17 g/L, respectively. As can be seen in Fig. 5, in the same condition of treatment temperature, the continuous reactor provided more phenol (+38%) and guaiacol (+40%) than the batch reactor, indicating lower condensation reaction between the products during hydrothermal treatment of black liquor in the continuous reactor. In summary, at the same temperature condition, the continuous reactor resulted in more various phenolic compounds with higher concentration than the batch reactor.

The quantity of the phenolic products was calculated based on the volume of the initial black liquor by considering the volume ratio of the recovered liquid phase to the initial black liquor. In addition, the yield of phenolic products was calculated based on the quantity of lignin present in the initial black liquor. The results are given in Table 3. The results indicated that the phenolic products had been degraded with increasing treatment temperature from 280 °C to 350 °C, as demonstrated in literature (Kang et al., 2015). For example, 4.14% and 5.58% of the lignin content of black liquor were converted to phenolic compounds by hydrothermal treatment at 280 °C for batch and continuous reactors, respectively. Whereas these values decreased to 0.24% and 0.43% for treatment at 350 °C.

3.4. FTIR analysis of residual solid phase

The structure of cellulose, alkaline lignin, precipitated black liquor lignin, untreated black liquor, and recovered solid phases after hydrothermal treatment of black liquor at 280 °C and 350 °C were determined using FTIR spectroscopy (Fig. 6). The spectra of cellulose, and alkali lignin were presented as reference. The residual solid phases after hydrothermal treatment demonstrated very different signal profiles in comparison to those of the cellulose, alkali lignin and untreated black liquor, suggesting destruction of organic compounds of black liquor under different hydrothermal treatment conditions. From the comparison of the peaks,

it can be concluded that a sharp increase in peak intensity of 1421 cm^{-1} can be attributed to the aromatic skeletal vibration with C-H deformation. An increase in the sediment, the amount of minerals, and carbonate compounds were observed at a peak of 877 cm^{-1} . Based on this, the remaining solid materials can be burned in the recovery furnace and their minerals can be used to prepare white liquor. Thus, the problem of the imbalance of chemical materials in preparing chemical pulp is solved to a great extent. By increasing the treatment temperature to $350\text{ }^{\circ}\text{C}$ (sample HT $350\text{ }^{\circ}\text{C}$), the peak of 1700 cm^{-1} , attributed to the carboxyl and carbonyl groups of lignin, was completely destroyed and disappeared. Elimination of aromatic compounds at 1560 and 1460 cm^{-1} regions as well as the band at 1160 cm^{-1} (related to C–O–C pyranose ring skeletal vibration) were observed. Also, removed bands at 1313 and 1205 cm^{-1} regions, which respectively related to CH_2 and C–C stretching in carbohydrates, were caused by the decomposition of carbohydrates in the black liquor. In the black liquor sample, the peak area at 799 cm^{-1} was assigned to the condensation reactions and carbon-carbon self-bonding which intensified in the residual solid phases, suggesting the formation of charcoal and the increasing the lignin condensation reactions during hydrothermal treatment of black liquor.

3.5. Effect of pH on the extraction yield

The pH values of recovered liquid phases during the liquid-liquid extraction are presented in Table 4, and the effect of the pH of the liquid phase on the extraction yield of phenolic compounds from various recovered liquid stages is illustrated in Fig. 6. The influence of pH on the extraction yield was significant. For the liquid phase obtained after black liquor treatment in the batch reactor at $280\text{ }^{\circ}\text{C}$, the quantity of phenol increased from 0.42 g/L to 0.54 g/L , by decreasing the pH value from 13 (unchanged pH) to 8. In addition, the amount of extracted guaiacol was almost unaffected by reducing the pH from 13 to 8. Generally, the

total concentration of phenolic compounds declined with decreasing the pH of the extraction from 13 to 9 and then increased with further reducing the pH from 9 to 8 and 7. For the recovered liquid phase after hydrothermal treatment at 280 °C in the continuous reactor, the extraction yield of all phenolic compounds increased by reducing the pH value from 13 to 8. The pH value of 7 resulted in a slightly lower yield than 8.

In contrast to the recovered liquid phase after hydrothermal treatment at 280 °C, the influence of pH value on the extraction yield from the recovered liquid phases after hydrothermal treatment at 350 °C in both reactors was less marked (Fig. 7). However, in all tested pH, the products from the continuous reactor exhibited a relatively higher phenol extraction than from the batch reactor. The lack of guaiacol and syringol in the recovered liquid phases after hydrothermal treatment at 350 °C could be attributed to the higher reactivity and degradation of these phenolic compounds, which process through demethoxylation and hydrogenolysis reactions to produce phenol and cresol (Venkatesan et al., 2021).

Regarding the influence of reactor type, Fig. 7 shows that the continuous reactor resulted in only slightly higher extraction of phenol and guaiacol than the batch reactor at the same condition of extraction pH and treatment temperature of 280 °C. However, the continuous reactor provided a significantly higher concentration of syringol than the batch reactor, leading to a greater value of total phenolic compounds. The same phenomena, but with lower values, were observed for the liquid phase recovered after hydrothermal treatment at 350 °C. This confirms the fewer condensation reactions in the continuous reactor during hydrothermal treatment.

Fig. 8 (a, b, c, and d) shows the influence of pH extraction on the relative abundance of individual phenolic compounds in the recovered liquid phases after hydrothermal treatment at various conditions. As can be seen, by reducing the pH of the recovered liquid phase after hydrothermal treatment of black liquor in the continuous reactor at 350 °C, the phenol concentration in the extraction solvent was increased. However, the peaks related to guaiacol (retention time of 34.36 min) and some other identified compounds such as 2-methyl-phenol (retention time of 34.86 min), 4-ethyl-1,3-benzenediol (retention time of 36.98 min), and creosol (retention time of 37.23 min) disappeared from the chromatograms. This behavior was observed only for the recovered liquid phases after hydrothermal treatment at 350 °C, with a lower impact for the batch reactor.

Liquid-liquid extraction of alkaline hydrothermally treated black liquor using ethyl acetate may involve irreversible hydrolysis of ethyl acetate by sodium hydroxide. This reaction reduced the pH of the medium (Hadkar et al., 2018) and could improve the extraction efficiency of phenolic compounds due to their protonation and enhancing their affinity toward nonpolar solvents (Llano et al., 2015). However, the degradation of ethyl acetate reduced its recycling efficiency and increased the extraction cost. To estimate the hydrolysis extent of ethyl acetate, the pH values of the ethyl acetate mixture with treated black liquors at different conditions were measured after 1 h and 2 h agitation. As indicated in Table 5, the pH reduction was significant only for the mixture of treated liquors at a lower temperature (280 °C), where the pH of recovered liquid phases was sufficiently high. The hydrolysis of ethyl acetate with sodium hydroxide is a stoichiometric reaction, hence decreasing the pH from 13 to about 10 equals to degradation of 0.1 mole L⁻¹ of ethyl acetate. This corresponds to the saponification of 0.1% of applied ethyl acetate. Therefore, reducing the pH of the recovered liquid phase after hydrothermal treatment not only improved the extraction efficiency but also

inhibited the ethyl acetate saponification, which is an important parameter for economical extraction.

Table 6 shows the effect of extraction pH on the yield of phenolic compounds from the recovered liquid phases based on the lignin content of the initial black liquor. As can be seen, the highest yield of phenolic compounds was 6.85% (based on the lignin content of the initial black liquor), which was obtained after hydrothermal treatment of black liquor in the continuous reactor at 280 °C. The hydrothermal treatment at 350 °C in both reactors resulted in a lower yield of phenolic compounds. In contrast, the highest product of phenolic compounds (0.43% based on the lignin content of black liquor) was obtained under unchanged pH in the continuous reactor. This is presumably due to the degradation of these compounds in the applied severe condition. However, these results are considerably higher than the values of 1.7% and 0.18%, respectively, reported for the production yield of guaiacol and phenol for lignin hydrothermal treatment at 300 °C for 30 min in a mini-batch reactor (Schuler et al., 2017). On the other hand, Kang et al. (2015) reported a value of 17% (based on initial lignin) for phenol extraction after hydrothermal liquefaction of lignin at 320°C for 30 min. The difference is presumably due to the experimental conditions such as reaction time and temperature and extraction solvent.

4. Conclusions

The influence of extraction pH on the extraction yield of phenolic compounds was investigated. The pH of the recovered liquid phase was adjusted, and then the liquid-liquid extraction was performed. The results indicated that reducing the pH improved slightly the extraction of the phenol and guaiacol from the various recovered liquid phases after hydrothermal treatment. However, the extraction yield of syringol greatly enhanced by

reducing the pH of liquid phases. This was very noticeable for the recovered liquid phases after treatment at 280 °C, where the quantity of syringol was initially high. The extraction experiments with various pH also confirmed the superior performance of the continuous reactor over the batch reactor to obtain the phenolic compounds after hydrothermal treatment of black liquor, showing that the heating rate of the mixture is an important parameter. Furthermore, GPC data revealed that the whole liquid phase after hydrothermal treatment in continuous reactor (350 °C) had slightly higher molecular weight and lower quantity of small molar mass compounds than the batch reactor. The GC-Mass analysis confirmed that the phenolic compounds for treated black liquor in a batch reactor (at 280 °C) included phenol as the major product with a concentration of 3.1 g/L, which was 10-fold more than the phenol concentration in a continuous reactor (at 350 °C). However, their concentration decreased considerably when the treatment temperature increased to 350 °C. Overall, hydrothermal treatment of black liquor at 280 °C in continuous reactor is more preferable considering the production of phenolic compounds and recovery of sodium.

Author Contributions:

Yahya Hamzeh: Investigation, Methodology, Formal Analysis, Writing-Original draft preparation, Visualization, Validation.

Christine Chirat: Conceptualization, Supervision, Validation, Resources, Funding acquisition.

Geert Haarlemmer: Conceptualization, Investigation, Validation, Methodology, Supervision, Resources, Funding acquisition.

Dominique Lachenal: Conceptualization, Supervision, Methodology, Validation, Writing - Review & Editing.

Alireza Ashori: Validation, Methodology, Writing - Review & Editing.

Gerard Mortha: Validation, Methodology, Supervision, Resources, Funding acquisition.

Hary Demey Cedeno: Investigation, Methodology, Formal Analysis.

All authors have read and agreed to the published version of the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors are unable or have chosen not to specify which data has been used.

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Captions of Tables:

Table 1. Analysis of original sulfur-free black liquor and liquid phases recovered after hydrothermal treatments at different conditions, and resulting solid waste (% based on dry content of samples)

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Fig. 3. GC-Mass chromatogram of ethyl acetate extracts after hydrothermal treatment of sulfur-free black liquor in batch reactor at 350 °C

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Fig. 5. Concentration of phenol, guaiacol and syringol and their total concentration in liquid phases after hydrothermal treatments of sulfur-free black liquor at different conditions

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Fig. 7. GC–MS chromatograms of the extracted compounds at various pH and temperatures from the recovered liquid phase after hydrothermal treatment of black liquor in the continuous and batch reactors

Table 1. Analysis of original sulfur-free black liquor and liquid phases recovered after hydrothermal treatments at different conditions and resulting solid waste

(% based on dry content of samples)

Sample	Dry content (%)	Weight percentage of precipitated lignin	Weight percentage of ash content at 800 °C	Initial pH
Untreated black liquor	19.4	31 (6.014)	41 (7.95)	13.6
B-280 °C	7.5	4.9 (0.368)	39.3 (4.52)	13.0
B-350 °C	11.8	5.16 (0.609)	39.5 (4.66)	10.1
C-280 °C	6.21	3.24 (0.721)	39.3 (4.51)	13.3
C-350 °C	8.3	2.85 (0.236)	40.1 (3.33)	9.8
Solid waste (C-350 °C)	50.6	n.d.	31.8 (16.1)	n.d.

Table 2. Mass balance of hydrothermal experiments at various temperatures

Hydrothermal treatment condition	Batch reactor				Continuous reactor			
	280 °C		350 °C		280 °C		350 °C	
	(g)	(%)	(g)	(%)	(g)	(%)	(g)	(%)
Initial dry mass of black liquor	1487.32	100.00	828.12	100	55.41	100	1928.16	100
Dry mass of recovered liquid phase	461.25	31.01	433.06	52.29	17.27	31.2	703.01	36.46
Dry mass of recovered solid phase	30.61	2.06	88.55	10.69	2.72	3.74	330.92	17.16
Transformed dry mass to gas	995.46	66.93	306.51	37.01	36.06	65.08	894.23	46.38
Dry mass of lignin in black liquor initial	461.07	31.00	256.72	31.00	17.17	31.00	597.73	31.00
Dry mass of lignin in recovered liquid phase	22.60	4.90	22.35	2.70	0.56	3.24	20.04	1.04
Degraded lignin during hydrothermal treatment	438.47	95.10	234.37	91.30	16.71	96.7	577.69	96.65

Table 3. The quantity of phenolic compounds in the recovered liquid phase based on the initial volume of black liquor and its lignin content.

	Treatment	Phenol	Guaiacol	Syringol	Total
Concentration in recovered liquid phase (g/L)	Batch reactor at 280 °C	0.8	1.62	1.10	3.10
	Batch reactor at 350 °C	0.7	0.00	0.00	0.17
	Cont. reactor at 280 °C	0.44	1.31	1.80	3.54
	Cont. reactor at 350 °C	0.3	0.07	0.00	0.30
Concentration based on initial volume of black liquor (g/L)	Batch reactor at 280 °C	0.2	1.38	0.94	2.64
	Batch reactor at 350 °C	0.16	0.00	0.00	0.16
	Cont. reactor at 280 °C	0.12	0.37	0.50	0.99
	Cont. reactor at 350 °C	0.20	0.06	0.00	0.26
Yield based on initial lignin content in the initial black liquor (%)	Batch reactor at 280 °C	0.51	2.16	1.47	4.14
	Batch reactor at 350 °C	0.24	0.00	0.00	0.24
	Cont. reactor at 280 °C	0.69	2.06	2.84	5.58
	Cont. reactor at 350 °C	0.33	0.10	0.00	0.43

Table 4. Initial pH values and adjusted pH of liquid phases

	Treatment conditions			
	Batch reactor		Continuous reactor	
	280 °C	350 °C	280 °C	350 °C
Unchanged pH	13.0	10.1	13.2	9.8
	9.0	9.0	9.0	9.0
Decreased pH	8.0	n.d.	8.0	n.d.
	7.5	7.5	7.0	7.5

Table 5. pH of the mixture of ethylene acetate with hydrothermal treated black liquor at different conditions as a function of mixing time

Sample	Initial pH	pH after 60 min agitation	pH after 120 min agitation
Batch reactor (280 °C)	13.3	11.39	10.96
Continuous reactor (280 °C)	13.23	11.23	10.78
Batch reactor (350 °C)	10.36	10.23	10.3
Continuous reactor (350 °C)	9.70	9.83	9.74

Table 6. Extraction yield of phenolic compounds from the recovered liquid phases based on the lignin content of the initial black liquor (%).

Extraction pH	Treatment	Phenol	Guaiacol	Syringol	Total
Unchanged	Batch reactor at 280 °C	0.51	2.16	1.47	4.14
	Batch reactor at 350 °C	0.24	0.00	0.00	0.24
	Cont. reactor at 280 °C	0.69	2.06	2.84	5.58
	Cont. reactor at 350 °C	0.33	0.10	0.00	0.43
9	Batch reactor at 280 °C	0.50	1.44	0.97	2.91
	Batch reactor at 350 °C	0.23	0.00	0.00	0.23
	Cont. reactor at 280 °C	0.66	2.05	3.26	5.97
	Cont. reactor at 350 °C	0.30	0.00	0.00	0.30
8	Batch reactor at 280 °C	0.72	2.07	0.91	3.70
	Batch reactor at 350 °C	0.25	0.00	0.00	0.25
	Cont. reactor at 280 °C	0.78	2.35	3.72	6.85
	Cont. reactor at 350 °C	0.30	0.00	0.00	0.30
7	Batch reactor at 280 °C	0.65	1.85	1.30	3.80
	Batch reactor at 350 °C	0.25	0.00	0.00	0.25
	Cont. reactor at 280 °C	0.72	2.27	3.65	6.64
	Cont. reactor at 350 °C	0.30	0.00	0.00	0.30

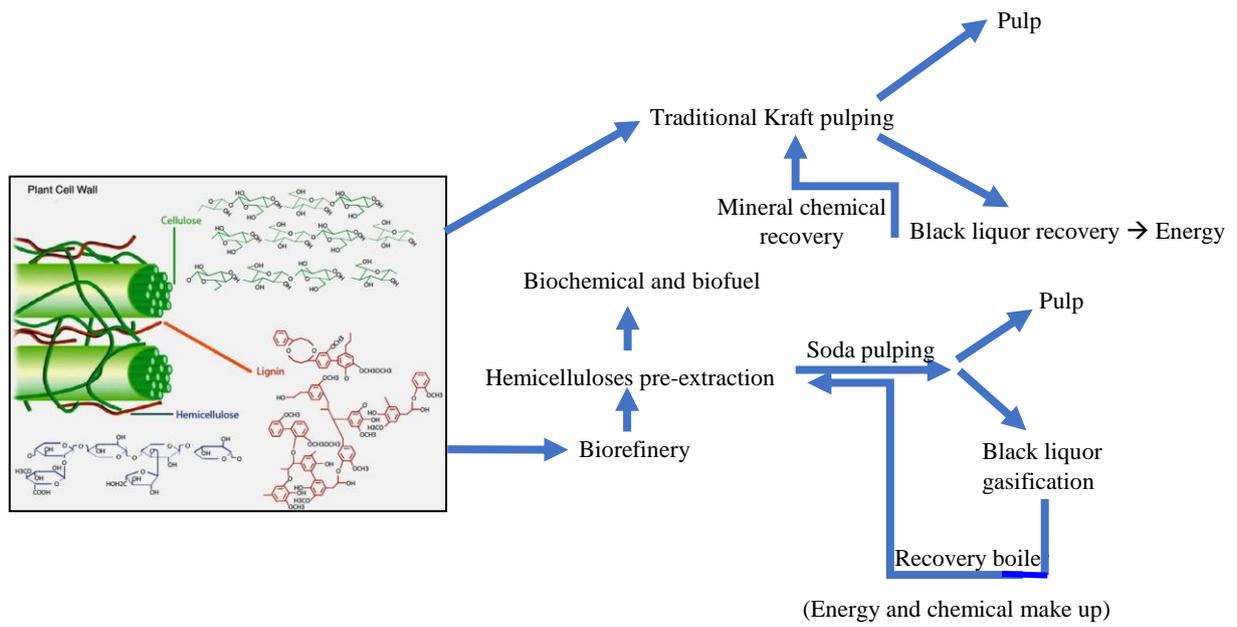


Fig. 1. Integration of black liquor gasification in a pulp mill without disturbing upstream processing by partial utilization of black liquor.

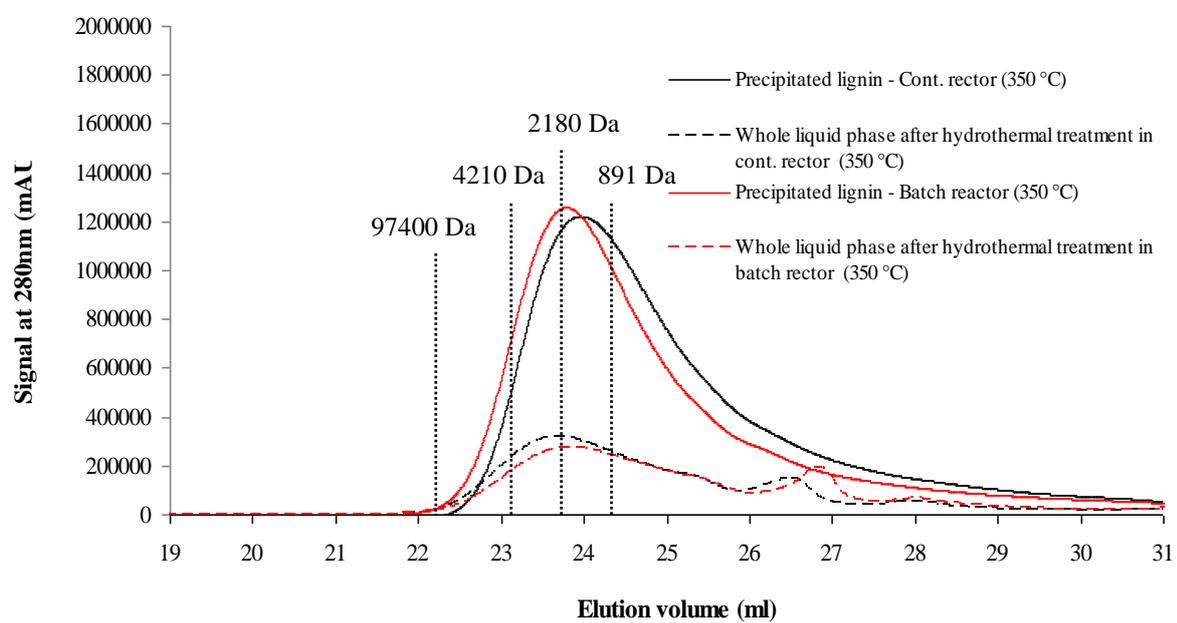


Fig. 2. GPC analysis of whole liquid phases recovered after hydrothermal treatments and precipitated lignin from them.

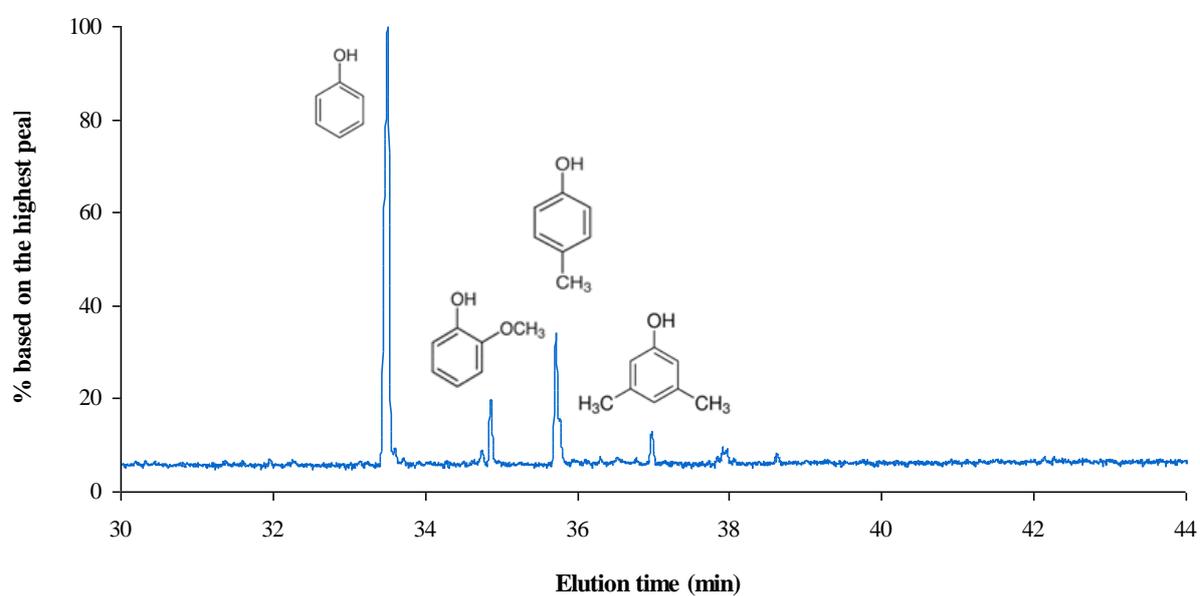


Fig. 3. GC-Mass chromatogram of ethyl acetate extracts after hydrothermal treatment of sulfur-free black liquor in batch reactor at 350 °C.

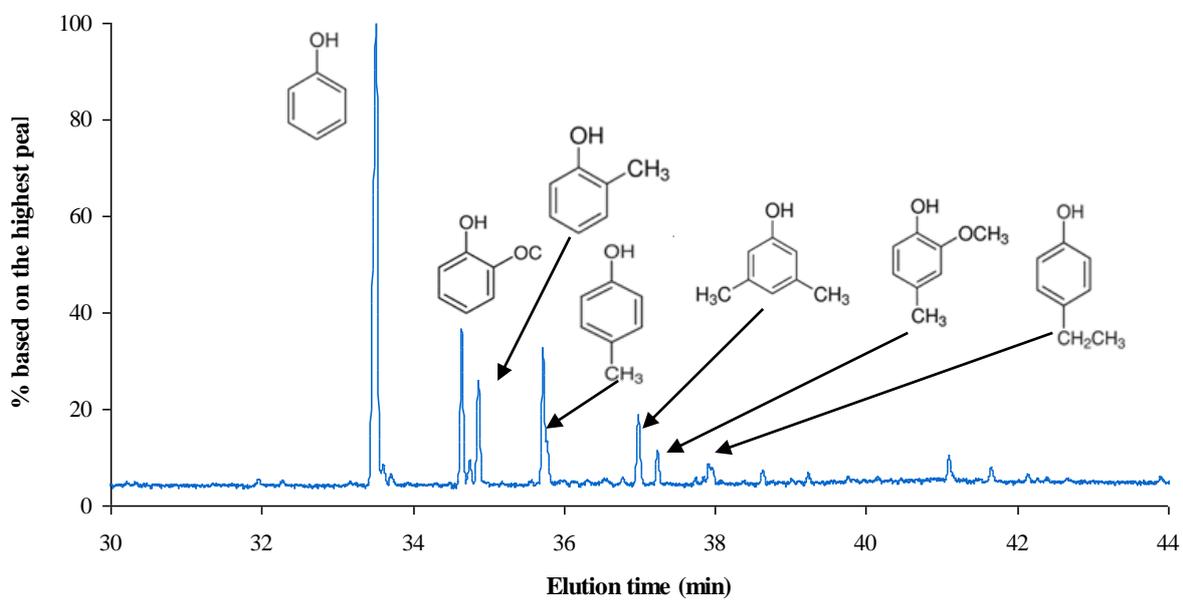


Fig. 4. GC-Mass chromatogram of ethyl acetate extracts after hydrothermal treatment of sulfur-free black liquor in continuous reactor at 350 °C.

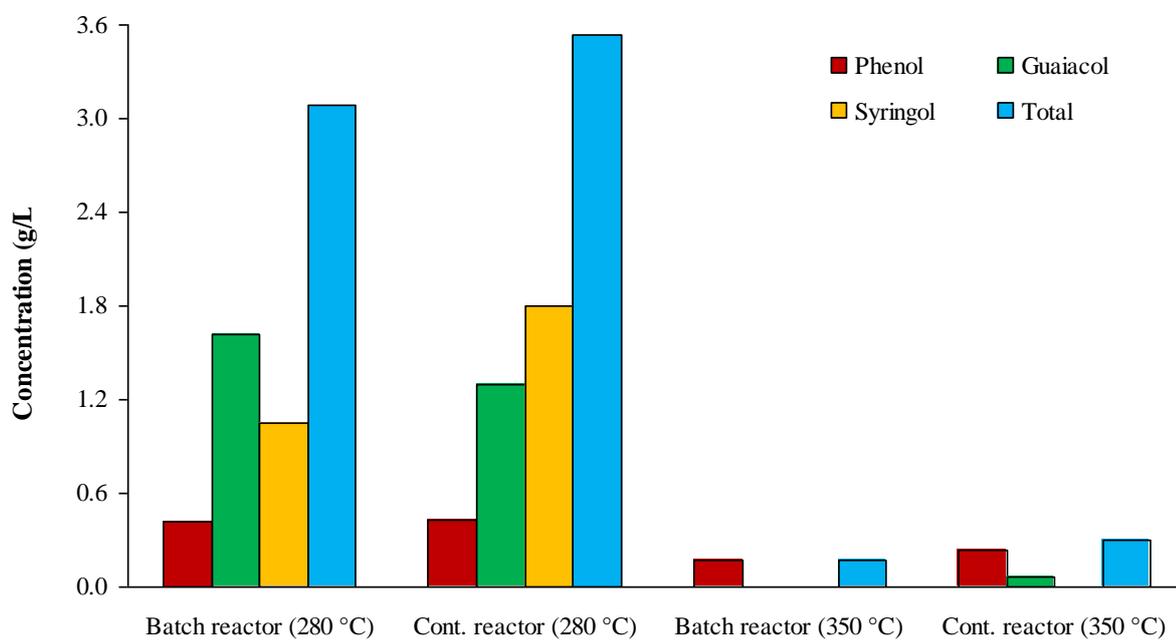


Fig. 5. Concentration of phenol, guaiacol and syringol and their total concentration in liquid phases after hydrothermal treatments of sulfur-free black liquor at different conditions.

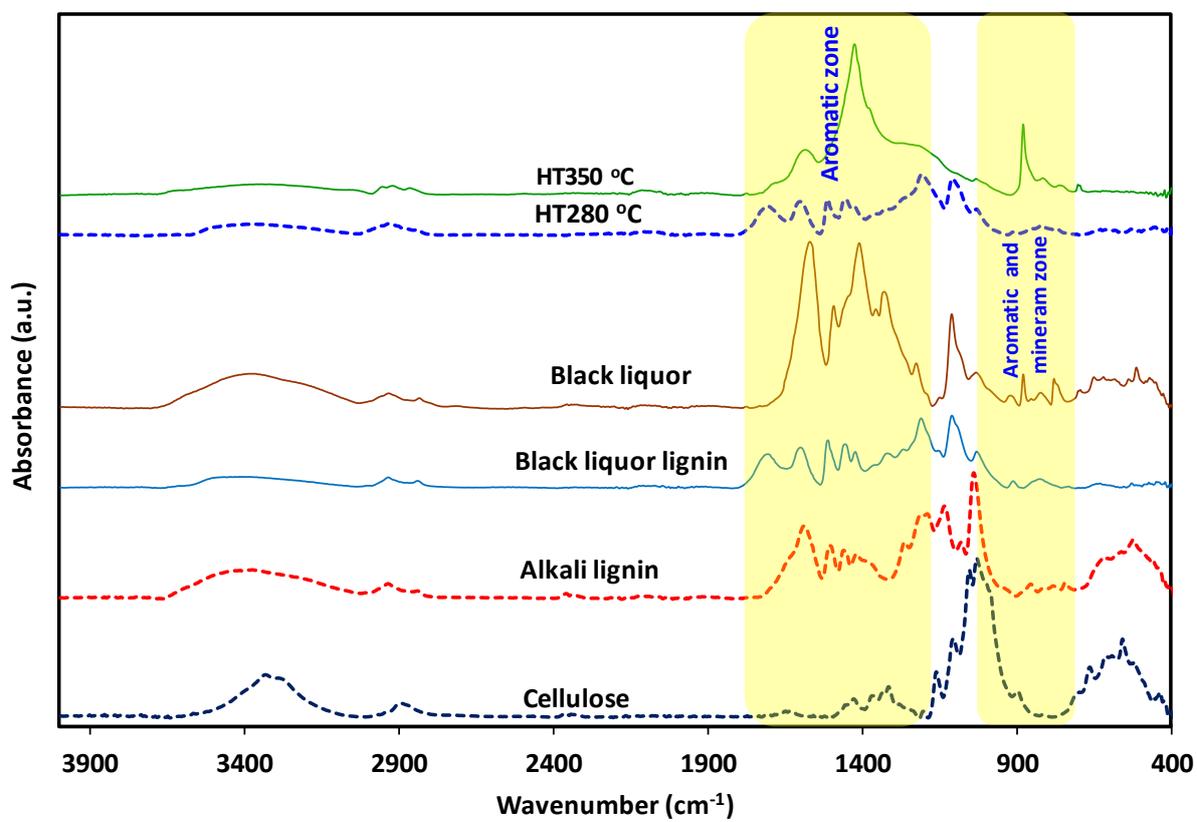


Fig. 6. FTIR analysis of the residual solid phases after hydrothermal treatment of black liquor.

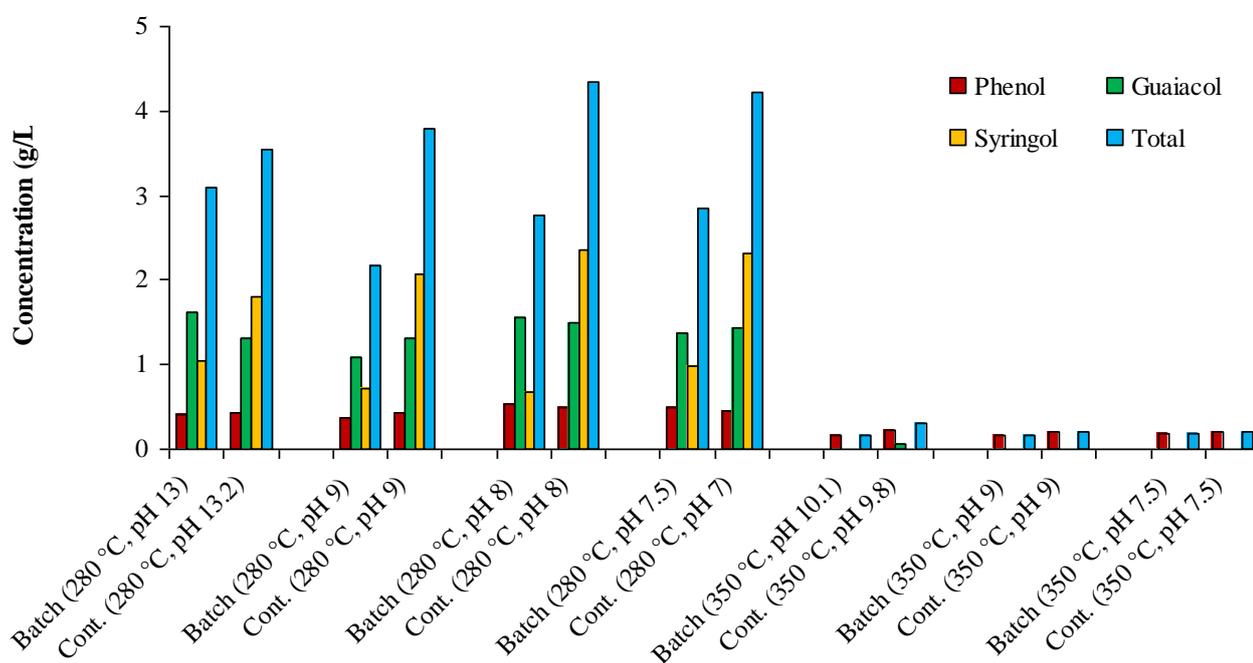


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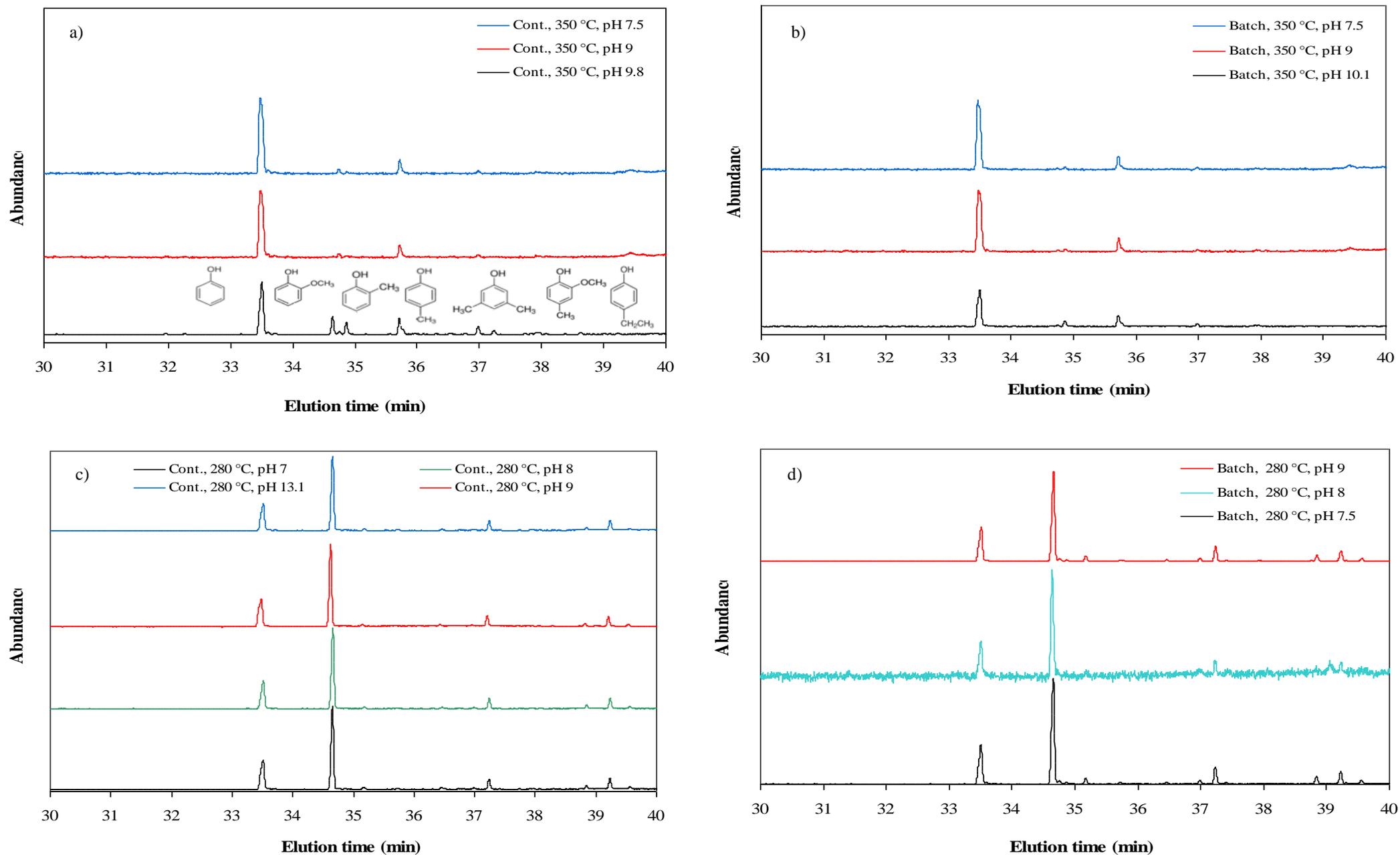


Fig. 8. GC-MS chromatograms of the extracted compounds at various pH and temperatures from the recovered liquid phase after hydrothermal treatment of black liquor in the continuous and batch reactors.