



OULUN YLIOPISTO
UNIVERSITY of OULU

TEKNILLINEN TIEDEKUNTA

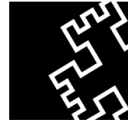
**DEPOLYMERIZATION OF LIGNIN:
SIGNIFICANCE OF FORMIC ACID**

Markus Honkanen

PROCESS ENGINEERING

Bachelor's thesis

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Instructors: Goldmann Werner Marcelo & Kangas Jani

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TIIVISTELMÄ

OPINNÄYTETYÖSTÄ Oulun yliopisto Teknillinen tiedekunta

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<p>Tiivistelmä</p> <p>Tämän työn tarkoituksena oli tutkia muurahaishapon toimivuutta vedynluovuttajana ligniinin depolymerisoinnissa ilman erillisen katalyytin käyttöä. Korkeissa lämpötiloissa ligniinin tiedetään kondensoituvan korkeasti polymerisoituneeksi hiileksi, mutta vedyn avulla tätä reaktiota voidaan ehkäistä. Muurahaishappo tunnetusti vapauttaa vetyä hajoamistuotteenaan.</p> <p>Työn toisena tavoitteena oli tuottaa teollisuuden sovelluksille käyttökelpoisia tuloksia. Tästä johtuen reaktiolämpötilat (250 °C ja 300 °C) ja liuoksen happamuus (8,82 m-% ja 17,64 m-%) pidettiin suhteellisen matalina. Tutkimus suoritettiin kahdessa osassa, joista ensimmäisessä keskityttiin löytämään reaktio-olosuhteet, joissa ligniiniä saataisiin depolymerisoitua mahdollisimman tehokkaasti. Reaktioissa syntyneet kaasumaiset ja nestemäiset reaktiotuotteet analysoitiin kaasukromatografilla. Reaktiossa käytettyä lämpötilaa sekä liuoksen happamuutta muunneltiin eri kokeiden välillä, jotta voitiin arvioida näiden tekijöiden vaikutusta reaktiotuotteiden koostumukseen. Tavoitteena oli tuottaa mahdollisimman paljon kaasua annettujen määreiden rajoissa, sillä teoreettisesti suurempi kaasuntuotto muurahaishapon hajotessa viittaa suurempaan vedyn määrään tuotteissa. Vety puolestaan on tärkeässä roolissa ligniinin polymerisaatiota ajatellen. Tutkimuksen toisessa vaiheessa ligniiniä lisättiin liuokseen olosuhteissa, jotka olivat ensimmäisen vaiheen tulosten mukaisesti parhaat ligniinin depolymerisointumiseen. Kaikkien kokeiden aikana syntyneiden kaasu- ja nesteseoksien koostumukset analysoitiin kaasukromatografilla.</p> <p>Työn tuloksena saatiin jatkotutkimukseen hyödyllistä dataa matalan lämpötilan ja laimean hapon reaktioitoiminnoista ligniinille. Toistaiseksi juuri kyseisiä laimeita olosuhteita on tutkittu suhteellisen vähän. Vastoin aiempaa tietämystä, myös laimealla happoliuksella kyettiin tuottamaan suhteellisen suuria määriä kaasua, mikä viittaa myös merkittävään vedyn määrään. Myös lämpötilan havaittiin vaikuttavan reaktioihin enemmän kuin alkuun oletettiin: korkeassa lämpötilassa suoritettavat kokeet nostattivat reaktorin paineen huomattavasti korkeammaksi kuin matalan lämpötilan kokeet, jolloin myös kaasua syntyi enemmän. Kaasun CO/CO₂-suhde käyttäytyi painetta epäjohdonmukaisemmin, sillä sen arvo vaihteli riippumatta reaktio-olosuhteista. Yleisesti ottaen tulokset viittasivat vedyn määrän kasvamiseen lämpötilan noustessa. Molemmissa ligniinikokeissa syntyi sama määrä tuhkaa (noin 2 g). Tuhkan korkean koheesion vuoksi kunnollisen näytteen kerääminen osoittautui hyvin vaikeaksi, eikä sen tarkkaa massaa voitu siten mitata.</p> <p>Muurahaishappo osoittautui testien perusteella lupaavaksi vedynluovuttajaksi ligniinin depolymerisointiin. Ligniinitestien aikana onnistuttiin tuottamaan selkeästi suurempi hiilidioksidimäärä kuin pelkillä ensimmäisten testien muurahaishapon hajoamisreaktioilla. Tämä viittaisi ligniinin osittaiseen dekarboksylaatioon reaktioiden aikana.</p> <p>Jatkotutkimuksen kohteina voisi olla ligniinin depolymerisoinnin tarkastelu pidemmillä reaktioajoilla, eri vedynluovuttajien käyttö tai lisätutkimus laimean happoliuoksen riittävydestä ligniinin rakenteen pilkkomiseen.</p>			
Muita tietoja			

ABSTRACT FOR THESIS

University of Oulu Faculty of Technology

Degree Programme (Bachelor's Thesis, Master's Thesis) Process Engineering		Major Subject (Licentiate Thesis)	
Author Honkanen, Markus		Thesis Supervisor Goldmann Werner Marcelo, M.Sc. (Eng.) Kangas Jani, Dr. (Tech.)	
Title of Thesis Depolymerization of Lignin: Significance of Formic Acid			
Major Subject	Type of Thesis Bachelor's thesis	Submission Date March 2016	Number of Pages 24 pages, 2 appendices
Abstract <p>The basis for this thesis was to explore how formic acid performs as a hydrogen donor in lignin depolymerization, when no additional catalyst is used. It is known that at high temperatures, lignin tends to recondense into highly polymerized fractions (char), and active hydrogen can cap these reactions to hinder char formation. Formic acid is known to release active hydrogen during its decomposition.</p> <p>Another goal was to make the results usable for the industrial applications. To succeed in this, only relatively low temperatures (250 °C and 300 °C) and acid content (8.82 wt % and 17.64 wt %) were used. The research was conducted in two stages, the first of which concentrated on finding the optimal reaction conditions for depolymerizing lignin into smaller fractions. The gas and liquid produced by the reactions were analysed by gas chromatography. The reaction temperature and acid content were changed to see how it affected the composition of the gas and liquid products. The goal was to achieve the greatest possible amount of gas within the defined parameters, because in principle more gas produced in the decomposition of formic acid suggests more potential hydrogen present in the product. The hydrogen in turn is essential for lignin depolymerization. In the second stage lignin was added to the reaction mixture at the conditions determined during the first stage. The products were analysed by gas chromatography.</p> <p>The research resulted in some useful data about the reactions occurring at low temperatures and acid contents. These conditions have remained relatively scarcely researched. Contrary to earlier knowledge, significant amounts of carbon dioxide could be produced even by using low acid content, which suggests that also notable amount of hydrogen was present. The temperature was also observed to affect the results more than was initially thought: the runs done at higher temperature saw an exponential increase in pressure and a greater gas yield than the ones done at low temperature. However, the CO/CO₂-ratio did not seem to be consistent, as it changed regardless of the conditions. These indicators suggested that more hydrogen was released by the reactions at higher temperature. Both depolymerisation experiments yielded about the same amount of char (ca. 2 g). However, due to the difficulty of char recovery given its high cohesion, the weight could not be accurately measured.</p> <p>Formic acid proved to be a promising hydrogen donor. During the lignin solvolysis experiments, a significantly larger amount of carbon dioxide was released than during the formic acid decomposition experiments. This suggests that lignin was partially decarboxylated during the reactions.</p> <p>Additional research should be conducted by using longer reaction times, having a different hydrogen donor or looking into the sufficiency of mild acid solution to depolymerize lignin.</p>			
Additional Information			

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ABSTRACT

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1 INTRODUCTION

Lignin is the second most abundant biopolymer on earth after cellulose and constitutes approximately 30 % of the organic carbon in the biosphere. Lignin is essential in the cell wall structure of vascular plants, accounting for the stiffness and strength of the stem, as well as waterproofing the cell wall, thus enabling the water transport through the vascular system. Additionally, lignin helps the plant to protect itself against pathogens. Lignin derives mainly from three alcohol monomers: coumaryl, coniferyl and sinapyl. However, there are more functional groups affecting the structure of lignin as well as different possible bonding patterns between individual units. Consequently, the structure of lignin is highly complex. Thus, it is difficult to have as precise knowledge of the chemical structure of lignin as with other polymers. (Boerjan et al., 2003)

There are two main processes to produce lignin commercially: kraft and sulfite pulping. The dominant chemical pulping process in the world is kraft (alkaline) pulping. It uses strong alkali with a sodium sulfide catalyst to delignify cellulose fibers. The cellulose fibers are then bleached to remove the residual lignin and produce a strong, white, stable paper pulp. The mixture of dissolved lignin, hemicellulose, and the spent pulping chemicals is known as black liquor. The black liquor is sent to a recovery system and ultimately burned. Even though sulfite pulping has been nowadays widely replaced by kraft pulping, it is the most important commercial source of lignin. Lignosulfonates are soluble in water within a much wider range of pH than kraft lignin, making the recovery of lignin from the sulfite pulping process more cost efficient. (UWO, 2016)

The purpose of this thesis was to explore the usefulness of formic acid in lignin depolymerization within conditions practical for industrial purposes. What makes this subject particularly important is the potential of lignin as a raw material, given that it can be efficiently separated from black liquor and valorized through depolymerization. This should preferably be done in a cost effective manner; thus, these experiments were made with no additional catalyst and in relatively mild conditions (<300 °C and <180 bar). The timing for this research seems rather well placed, since the industry is globally seeking ways to improve the production processes and make them more environmentally friendly, as well as looking into being more profitable.

2 LIGNIN DEPOLYMERIZATION

One way to refine lignin into more usable raw materials and products is to depolymerize it. Depolymerization means the breakdown of lignin structure into smaller molecules. There are several methods of accomplishing this, such as pyrolysis (thermolysis), gasification, hydrogenolysis, chemical oxidation, and hydrolysis under supercritical conditions. Studies on different lignin extracts suggests that the product properties achieved with depolymerization depend significantly on the method of isolation. (Kim and Pandey, 2010) Hydrolysis, or more accurately solvolysis (where the nucleophile is the solvent molecule), was chosen as the depolymerization method for the experiments in this study. The reaction conditions were set to relatively mild limits (250-300 °C, <180 bar), which are naturally easier to execute in larger scales than those with harsher conditions. In Fig. 1, a possible structure for a fragment of lignin is presented to show the complexity of the chemical structure of lignin.

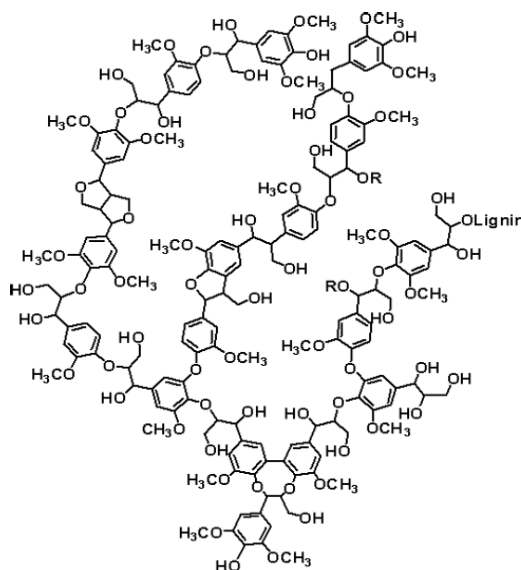
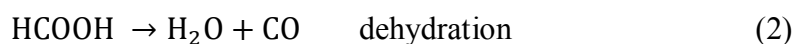


Fig. 1. One of the possible chemical structures of lignin. Taken from UWO (2016).

As can be seen in Fig. 1, the lignin is composed of multiple different functional groups primarily consisting of methoxyl and hydroxyl moieties, as well as bonds linking the groups. Therefore, it is generally difficult to reach high yields of a specific product through depolymerization.

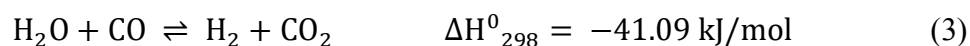
3 DECOMPOSITION OF FORMIC ACID

Formic acid is the simplest organic acid. It decomposes mainly to carbon monoxide and water in the gas phase (dehydration) and to carbon dioxide and hydrogen in aqueous phase (decarboxylation). When there is no water present in the reaction, dehydration is more favorable to occur. Though water reduces activation barriers for both decomposition pathways, decarboxylation is more favorable than dehydration when water is present. Water also strongly stabilizes formic acid isomers, acid-water complexes and transition states. It is generally agreed that the reaction network forms two parallel pathways (Savage and Akiya, 1998):



According to Savage and Yu (1998), in hydrothermal conditions (between 320 °C and 500 °C) most of the products of formic acid decomposition are carbon dioxide and hydrogen with traces of carbon monoxide. This suggests that increasing temperature turns decarboxylation into preferred reaction over dehydration, yet both reaction pathways remain available. However, the yield of carbon monoxide remains consistently lower than the yields of carbon dioxide and hydrogen. (Savage and Yu, 1998)

In addition to the decarboxylation and dehydration reactions (1) and (2), the water-gas shift reaction must be taken into account as well. In the water-gas shift reaction, water and carbon monoxide react into hydrogen and carbon dioxide (Smith et al., 2010):



The water-gas shift reaction is reversible and moderately exothermic. This means that the equilibrium constant of reaction (3) decreases when the temperature is increased.

4 LIGNIN SOLVOLYSIS

Solvolysis is defined generally as a type of nucleophilic substitution or elimination reaction in which the nucleophile is a solvent molecule. In many nucleophilic substitution reactions, the solvent is used as the nucleophilic agent. The name of the reaction changes based on the applied solvent. For example if water acts as a solvent, the reaction occurring is hydrolysis, but if it is an alcohol, it is called alcoholysis. (Robertson et al., 1977) In Fig. 2, one example of a substitution occurring in the aforementioned reactions is presented.

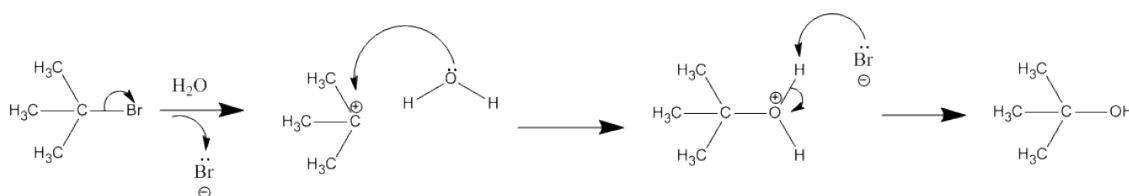


Fig. 2. Unimolecular nucleophilic substitution. Taken from Uggerud (2006).

In Fig. 2, an example of a substitution reaction is shown. In this particular reaction, a bromide group is substituted by a hydroxyl group. When this reaction mechanism is applied to lignin, the product consists of different monomers as well as water, char and different gases. To maximize the amount of monomers produced in the reaction, it is essential to optimize the role of formic acid as a hydrogen donor. Active hydrogen has been determined to cap the recondensation reactions during lignin depolymerization, decreasing the char yield and thus increasing the liquid yield. (Kim et al., 2013)

During lignin solvolysis, however, there are simultaneous reactions occurring. This makes the factors leading to a certain outcome difficult to predict. The main reactions occurring during lignin solvolysis are depolymerization and hydrodeoxygenation. Oxygen is removed from the lignin through the reactions with active hydrogen in the form of water and carbon dioxide. Removal of methoxy groups as carbon dioxide from lignin is referred to as decarboxylation. This whole complex reaction system in which lignin is depolymerized through solvolysis has been called as the lignin-to-liquid process (LtL). (Kim and Pandey, 2010)

5 MATERIALS AND METHODS

The experiments consisted of two stages: the formic acid decomposition stage (first stage) and lignin depolymerization stage (second stage). The former consisted of four runs, and the latter of two. The first four runs were done to investigate formic acid decomposition behavior and to select the conditions for the second stage that would result in the maximum amount of produced hydrogen whilst keeping the amount of byproducts as low as possible. In the second stage, the conditions that best met these goals were applied to depolymerize lignin. The selected reaction condition variables in the first stage runs were the reactor temperature and the initial acid content of the reactor solution. The temperature levels chosen for the experiments were 250 °C and 300 °C, hereby referred to as low and high temperature. As for the acid content, the low value was set to 15 ml and the high value to 30 ml, hereby referred to as low acid content and high acid content. The testing was started by first mixing the reagents, i.e. formic acid (98-100 vol. %), ultra-pure water, ethanol (AA quality) and isopropanol (>99.8 vol. %). In the second stage, Indulin AT lignin was added to obtain a solution with a lignin concentration of 50 g/L. The amounts of the chemicals used in the first stage experiments are listed in Table 1.

Table 1. The amounts of chemicals used in the first stage experiments.

	Ethanol	H ₂ O	Isopropanol	Formic acid	Total volume
Low acid content					
Volume (ml)	50	20	165	15	250
vol. %	20.00	8.00	66.00	6.00	
wt. %	19.03	9.64	62.51	8.82	
mol. %	18.95	24.55	47.71	8.79	
High acid content					
Volume (ml)	50	20	150	30	250
vol. %	20.00	8.00	60.00	12.00	
wt. %	19.03	9.64	53.69	17.64	
mol. %	18.95	24.55	38.92	17.58	

5.1 Analysis methods

The liquid and gas reaction products were analyzed through gas chromatography in a 6890N Network GC System equipped with an HP 19001A-102 packed column for the gas samples and a J&WScien 1259134 DB-ALC capillary column for the liquid samples, with helium as carrier gas in both cases. The liquid samples of the lignin depolymerization experiments were filtered through 0.2 μm PES filters (polyethersulfone) and diluted in acetone before the analysis. The gas produced in the experiment was also analyzed with the same gas chromatograph, and an example chromatogram can be seen in Fig. 3. The char produced by the lignin experiment was salvaged for later examination. However, the investigation of the char samples were not included in this thesis.

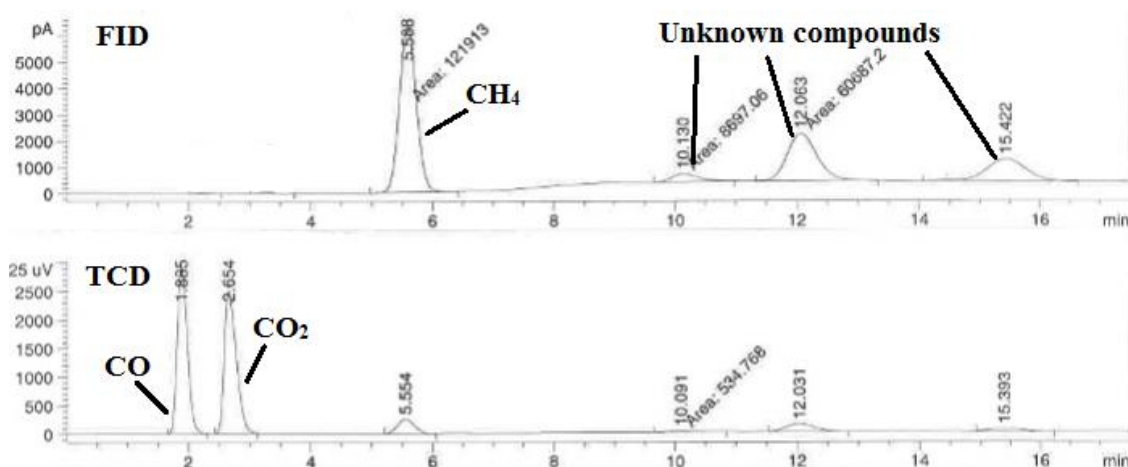


Fig. 3. Analysis diagram of the 6th run showing the FID (flame-ionization detector) and TCD (thermal conductivity detector) chromatograms.

In Fig. 3, the chromatogram peaks depict different compounds found. In this instance, carbon monoxide, carbon dioxide and methane, as well as some un-identified residual compounds were observed to be present in the gas example.

5.2 Batch reactor experimental set-up

Zirconium steel was chosen as the material for the reactor mainly due to its excellent resistance against formic acid-induced corrosion. In addition, zirconium does not have significant catalytic properties with respect to formic acid decomposition. Thus, it was assumed that the reactor material should have negligible effects on the results. In Fig. 4, the reactor used in the experiments is shown.

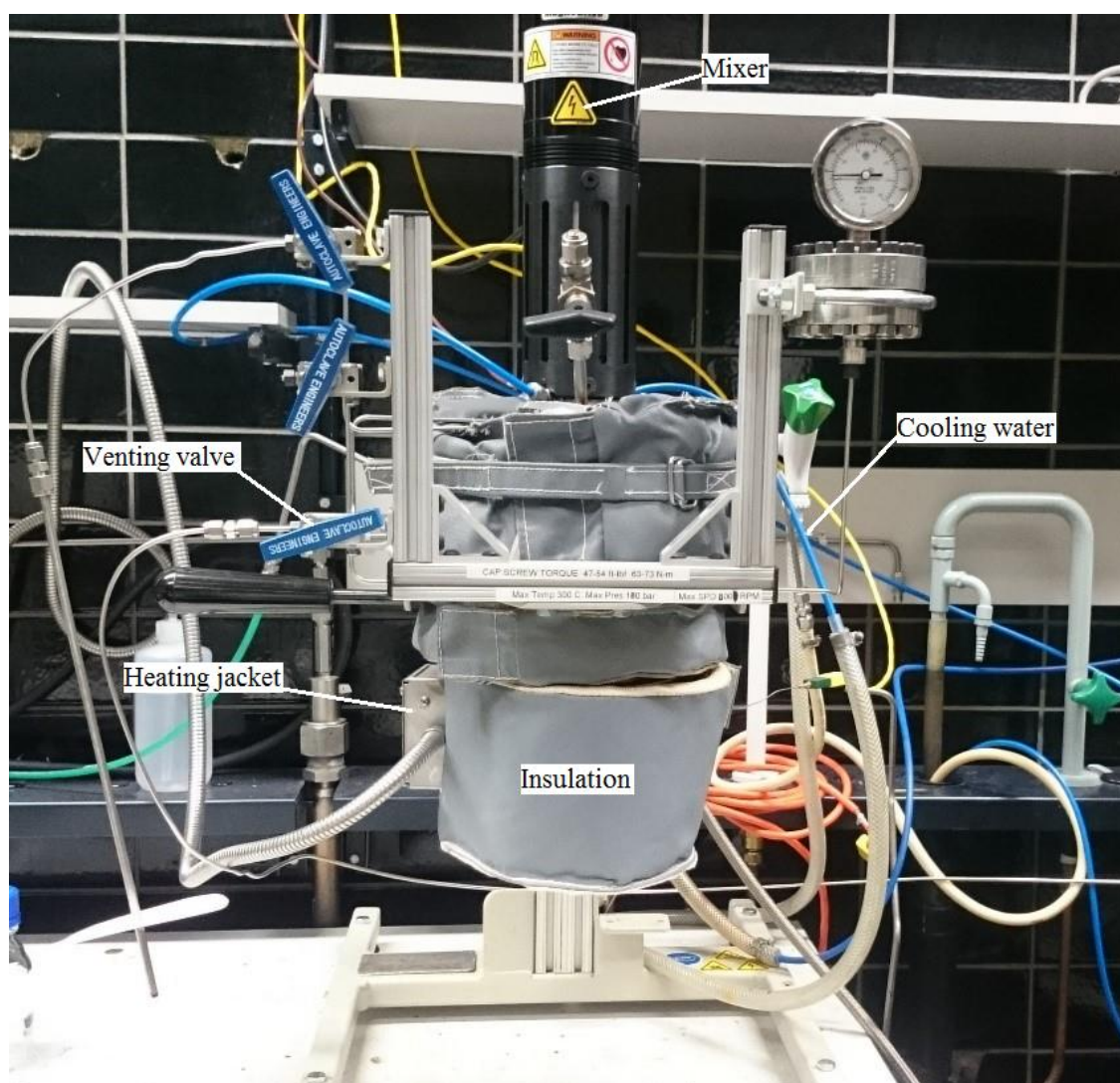


Fig. 4. Reactor equipment used in the experiments.

In all of the experiments, the stirring speed of the used mixer was set to 300 rpm (rounds per minute). The heating and the cooling phases of the reactor took each approximately 75 minutes to complete. The heating was done via a heating jacket, and insulation was also used as shown in Fig. 4. Cooling of the reactor was done with a water cooling coil. Due to working safety, the reactor was closed carefully. This was set as one of the core priorities when beginning the tests. To ensure an even tightening, an electronic torque wrench was used twice on each bolt. To make sure that the reactor pressure would stay within safety limits, a rupture disc was included in the experimental set-up as a safety measure. The rupture disc was rated at 187 bar and the safe operation limit was set to about 95% of the maximum allowed pressure (175 bar).

A mixture of ethanol, water, isopropanol and formic acid was fed into the reactor and heated for approximately five hours with the emphasis on when the reaction would reach the equilibrium and the rise of pressure halt. The goal for the first stage was to produce as much gas as possible, since that would potentially yield the greatest amount of active hydrogen. The two mixtures were tested at 250 °C and 300 °C resulting in a total of four runs for the first stage. For the second stage, the conditions that yielded the largest combined amount of carbon dioxide and carbon monoxide were applied to lignin.

6 RESULTS

6.1 Formic acid decomposition experiments

The selected experimental conditions of the first four runs (first stage) are listed in Table 2. From here on, each run is referred to by its number.

Table 2. Selected variables and conditions of the first stage runs.

Run	T ($^{\circ}\text{C}$)	Acid content	Lignin concentration (g/l)
1	250	Low	0
2	300	Low	0
3	250	High	0
4	300	High	0

In Fig. 5, the temperature profile is presented for the first stage experiments. The third run with low temperature and high acid content was operated longer than the other experiments. This was due to the fact that the pressure did not stabilize within the set time frame as shown in Fig. 6. This could mean there were still reactions occurring and the equilibrium had not been reached.

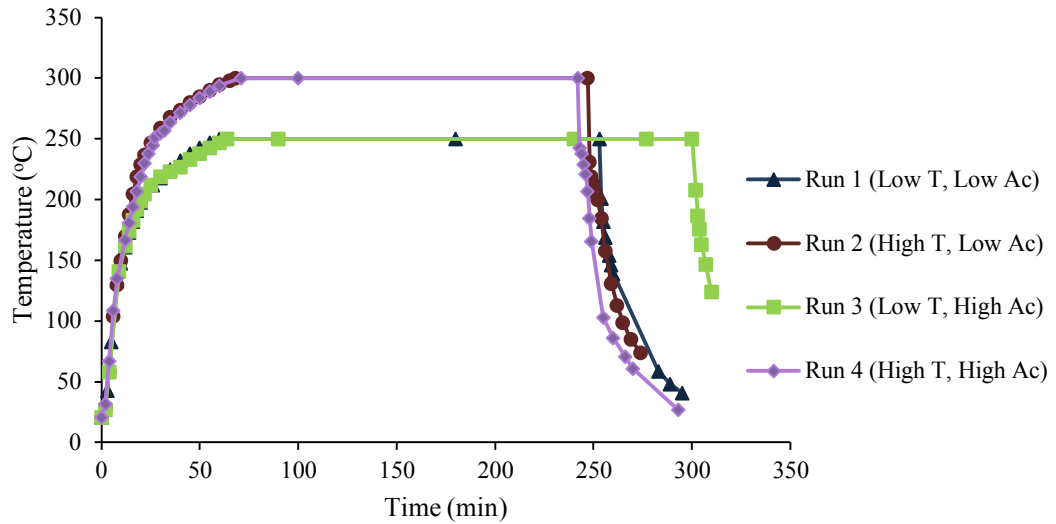


Fig. 5. Reactor temperature during the formic acid decomposition experiments.

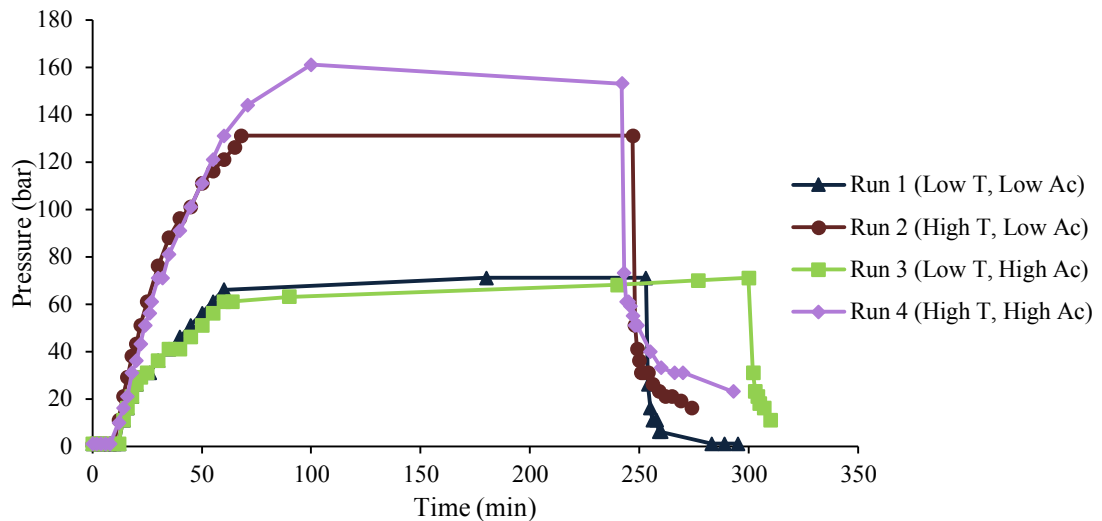


Fig. 6. Reactor pressure during the formic acid decomposition experiments.

It can be observed in Fig. 6 that performing the tests at higher temperature (300 °C) resulted in a higher maximum pressure at both low acid content (131 bar) and high acid content (161 bar) than at lower temperature at low acid content (68 bar) and high acid content (71 bar). The fourth run with high temperature and high acid content proved to generate higher maximum pressure (161 bar) than the other runs.

The final pressures in the runs done at the higher temperature were both higher than the final pressures of the runs done at the lower temperature. However, regardless of the temperature, the heating and cooling times (approximately 75 minutes) were the same in every run.

In Fig. 7, the concentrations of carbon monoxide and carbon dioxide in the gas samples of the first stage runs are shown.

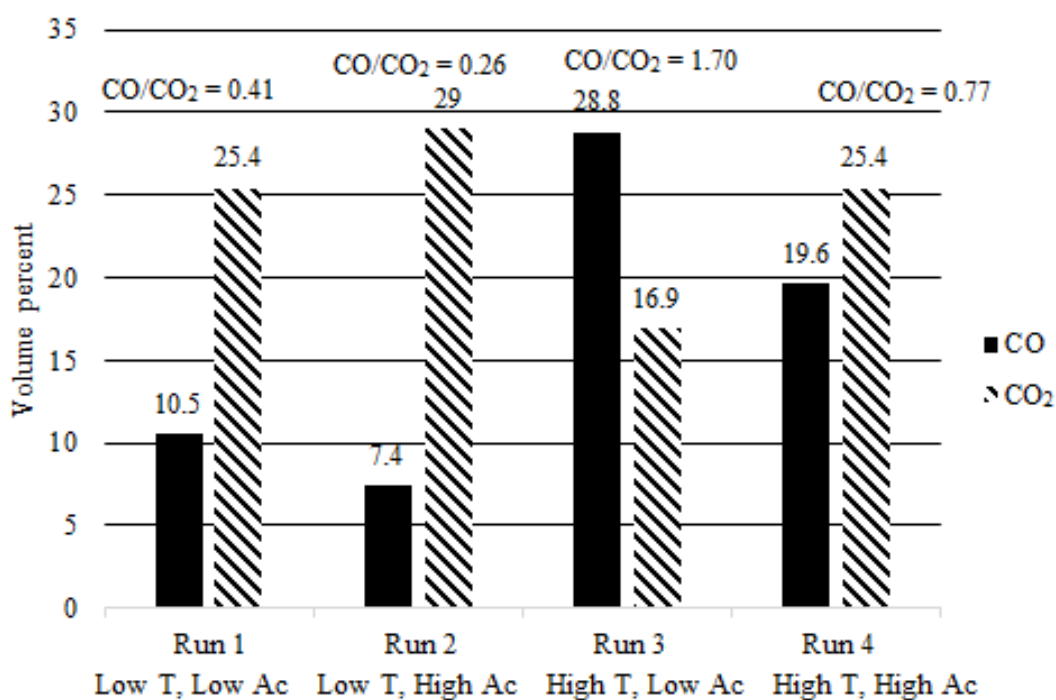


Fig. 7. Concentrations of CO and CO₂ in the gas products of the first stage experiments.

As can be noticed in Fig. 7, in the third and fourth run the carbon dioxide yield was generally lower than it was in the first and second run, but the combined concentration of CO/CO₂ was higher. A small CO/CO₂ ratio indicates that the formic acid decomposition, reactions (1) and (2), occurs mainly via the decarboxylation route, i.e. reaction (1). According to the stoichiometry of the decarboxylation reaction, one mole of hydrogen, in addition to CO₂, is formed. Therefore, the reaction conditions where the CO/CO₂ ratio is small and the concentration of carbon dioxide is high should result also in a high hydrogen

concentration. This would suggest that out of the four runs done during the first stage the first two produced the most hydrogen.

Despite of the presence of hydrogen being essential for lignin depolymerization, presence of carbon monoxide and water can lead to the production of more hydrogen through the water-gas shift reaction, while the lignin is consuming the readily available hydrogen. Hence the conditions that produced the most combined amount of carbon dioxide and carbon monoxide were chosen to be the conditions for the second stage with lignin. The analysis data also revealed that there was still formic acid present in the product and it could not be decomposed entirely. On that account there was still potential hydrogen from the residual formic acid after approximately 5 hours of decomposition.

6.2 Lignin depolymerization experiments

The characteristics of the last two runs (second stage) are listed in Table 3. From here on, the runs are referred to by their number. The temperature and acid content for the fifth run were the same as in the fourth run. For the sixth run, the conditions of the third run were applied.

Table 3. Characteristics of the experiments conducted in the second stage.

Run	T ($^{\circ}\text{C}$)	Acid content	Lignin concentration (g/l)
5	300	High	50
6	250	High	50

For the runs with lignin, the conditions were chosen according to which produced the largest amount of gas. As stated earlier, this was due to the reversibility of the water-gas shift reaction as seen from reaction (3) in Section 3. As the lignin consumed hydrogen, it was expected that the equilibrium composition would shift towards the reaction products resulting in more hydrogen released into the reaction. The following figures (Figs. 8 and 9) show how the temperature and pressure changed during these runs.

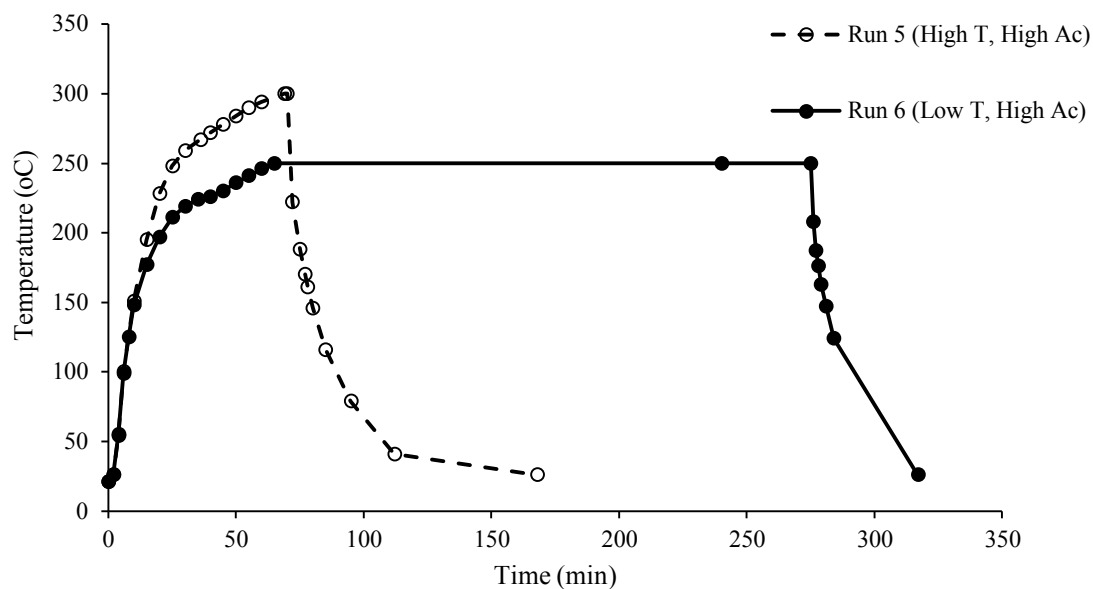


Fig. 8. Temperature during the lignin depolymerization experiments.

Fig. 8 shows the change of the temperature during the lignin experiments. The dashed line represents the fifth run done with high temperature (300 °C) and high acid content. This run had to be stopped because, as it is shown in Fig. 9, the pressure met the safety limit of 175 bar. At lower temperature (250 °C) during the following run, the pressure did not rise nearly as much. The results of both gases and liquids produced by these runs were analyzed by gas chromatography (shown in Appendices 1 and 2).

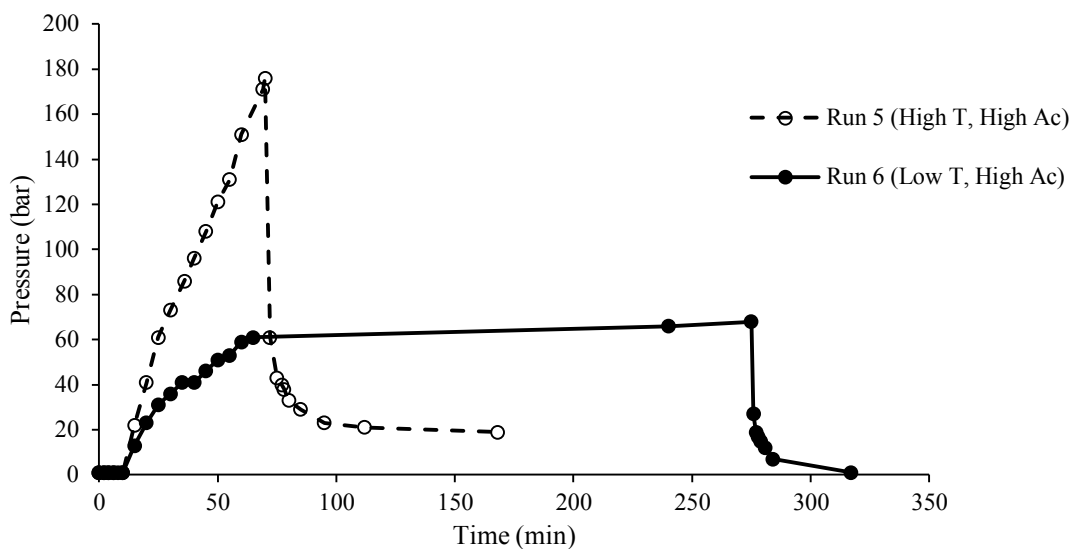


Fig. 9. Pressure during the lignin depolymerization experiments.

In Fig. 9 the sharp rise of pressure during the fifth run can be seen. This run produced a significant amount of gas. The gas chromatography results showed the presence of a large amount of an unknown gaseous component, as can be seen in the chromatograms in the appendices. Basically, the unknown component could have been hydrogen; however, hydrogen could not have been detected with the analysis setup. Therefore, the gaseous component was likely something other than hydrogen. According to Heeres et al. (2014), the lignin solvolysis gas product contains significant amounts of methane. Methane can be formed by the reactions between carbon monoxide and hydrogen or carbon dioxide and hydrogen. (Heeres et al., 2014)



Methane has a high hydrogen to carbon ratio. The flame ionization detector (FID) operation relies in the burning of the gas. Thus, the burning of methane gas would result in a large FID signal per volume of methane gas. Due to the large peak area of the unknown component in the FID signal of the gas chromatogram and the literature data, methane was deemed the most likely component.

During the sixth run, the pressure rose distinctly less pronouncedly than during the fifth run as shown in the Fig. 9. The sixth run produced higher concentration of carbon monoxide and carbon dioxide with a lower CO/CO₂-ratio (1.34) than the fifth one (2.06) as can be seen in Fig. 10. In both cases there was solid product formed (char). The mass was about 2 grams in both cases; however, due to the tackiness of the product, the recovery of char from the reactor vessel was considerably challenging and the actual amounts could have been underestimated.

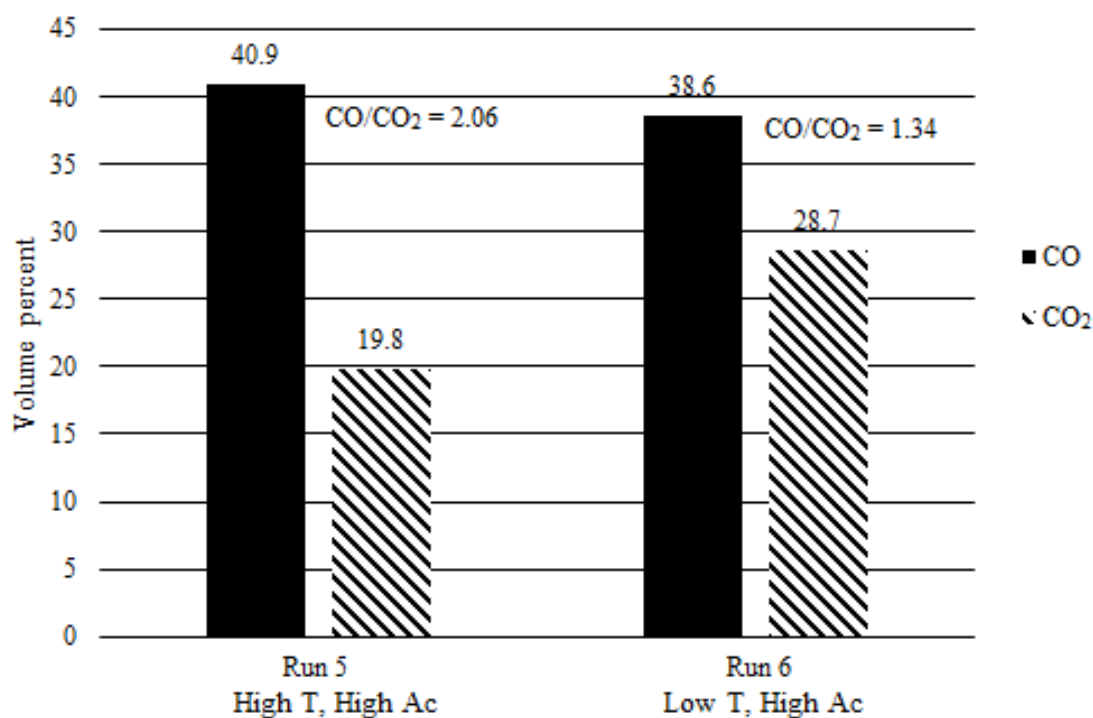


Fig. 10. CO and CO₂ in the reactor gas products in the second stage.

When the results of the second stage are compared to the runs with similar conditions from the first stage (run 3 and run 4), remarkable differences can be observed. The

CO/CO₂ ratio changed from 0.77 to 2.06 between runs 4 and 5, whereas between the third and the sixth run the CO/CO₂ ratio dropped from 1.70 to 1.34. This was not the only difference, as the change of pressure also changed between the conditions with and without lignin. When the fourth and the fifth runs are compared, the top pressure of the fifth run was 15 bar higher (176 bar) than the top pressure of the fourth run (161 bar), whereas the top pressure of the second run (71 bar) had almost the same top pressure as the sixth run (68 bar). As a recapitulation, the amounts of carbon monoxide and carbon dioxide are shown in Table 4.

Table 4. Summary of the CO and CO₂ yields in different runs

Run	Max P (bar)	CO/CO ₂	CO (Vol. %)	CO ₂ (Vol. %)	T (°C)	Acid content (Vol. %)
1	68	0.41	0.41	10.50	25.40	250
2	131	0.26	0.26	7.40	29.00	300
3	71	1.70	1.70	28.80	16.90	250
4	161	0.77	0.77	19.60	25.40	300
5	176	2.06	2.06	40.90	19.80	300
6	68	1.34	1.34	38.60	28.70	250

7 DISCUSSION

The results revealed that formic acid is a potential option as a hydrogen donor for depolymerizing lignin. It also turned out that the formic acid decomposition behavior in the reactor was far more complex than anticipated. Formic acid decomposition seemed to be also dependent on the progress of the water-gas shift reaction. In addition, the formed synthesis gases may have produced methane according to Heeres et al. (2014). Due to the combined effect of the reactions, hydrogen may have kept getting released and consumed in further reactions even after formic acid had decomposed completely. Thus, the equilibrium was possibly not achieved within the time frame of the experiments, in contrast to the anticipated behavior. On the other hand, it was highly likely that methane was formed in high amounts during the experiments. Adding lignin changed the characteristics of the reactions especially when both high temperature and high acid content were applied. For example the CO/CO₂-ratio varied considerably between different runs. The pressure changes turned out to be likewise unpredictable.

The conditions for the second stage were based on the total amount of carbon monoxide and carbon dioxide instead of considering the products individually. The reason for this was that a high amount of carbon monoxide and carbon dioxide were deemed to indicate a high amount of potential hydrogen in the reactor. The theory behind this choice was based on the water-gas shift reaction and its reversibility. The lignin was thus assumed to consume some of the hydrogen produced by the reaction and hence shift the equilibrium towards the reaction products releasing more hydrogen into the reactor.

The CO/CO₂ ratio appeared to rise when lignin was added to the reactor. This was possibly caused by the consumption of hydrogen by lignin, which lead to more carbon monoxide being produced, reducing the amount of carbon dioxide present in the reaction. When the pressures of the second stage experiments were compared to the pressures of the first stage experiments with similar temperatures and acid contents (runs 3 and 4), the results were dissimilar, most likely due to the presence of lignin which changed the relative significance of reactions. Though the difference in temperature was only 50 °C between the fifth and the sixth run, the difference in pressure was over 100 bar. This could signify that the high pressure in the fifth run might have been caused not only by the higher temperature, but also by decarboxylation of the lignin molecules.

8 CONCLUSIONS

The purpose of this study was to explore how lignin can be depolymerized with relatively low temperature and weak acid, which in this case was chosen to be formic acid. The main purpose of formic acid is to function as a hydrogen donor that aids in the breakdown of the lignin structure. To find an optimal temperature and acid content for the depolymerization, the decomposition of formic acid was investigated first. The reaction conditions for the subsequent lignin depolymerization experiments were chosen to be the same as the ones which produced the most carbon dioxide and carbon monoxide during in the first stage runs. The selection was based on the reasoning of literature data. According to reaction equilibria, carbon dioxide can be seen as an indicator for potential hydrogen available and the presence of carbon monoxide has potential of shifting the reaction equilibrium in such a way that hydrogen is further produced.

According to the results obtained by gas chromatography, it might be possible to have good results also by using lower temperature and lower acid content than the values chosen for these experiments. Also, longer reaction times might be needed to see whether the results would change. Furthermore, optimization of these variables would be advised.

The most important findings were that formic acid can be used successfully in depolymerizing lignin even at low temperatures and without any auxiliary catalyst. Additionally, some useful data about the behavior of lignin when exposed to formic acid was collected. To form reliable conclusions more tests would be required. This is mainly due to the high complexity of lignin. This resulted in some inconsistencies regarding the variation of the reaction pressure and yields of carbon dioxide and carbon monoxide. To achieve more reliable results it would be recommended to conduct more experiments and verify the repeatability of the results. The reactor pressure plays an essential role in the occurring phenomena, so the small leaks observed during the test may have been enough to change the outcome of the runs. Naturally, additional experimentation would also lower the amount of error in results caused by the equipment, operator and other factors.

9 REFERENCES

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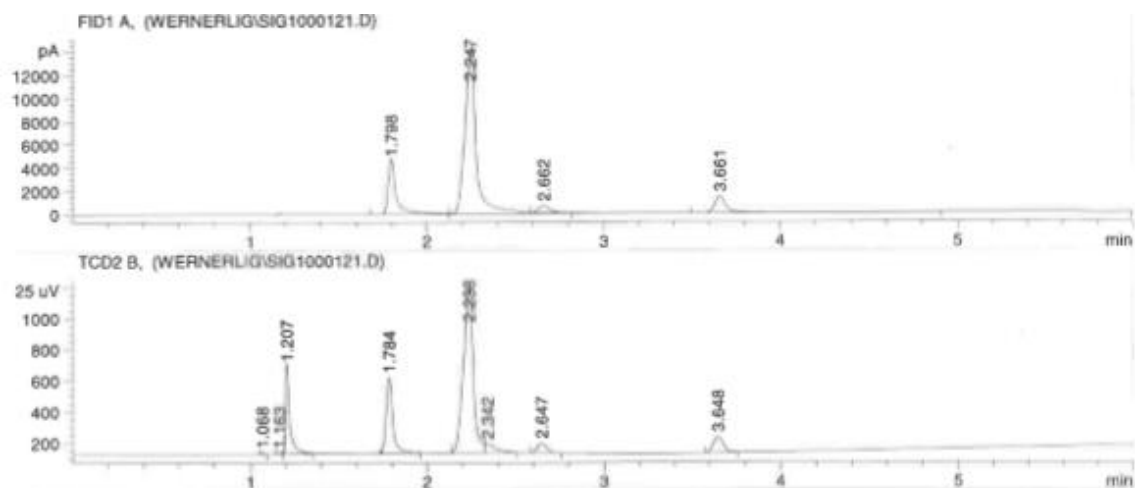
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APPENDICES

Appendix 1: Liquid analysis chromatograms



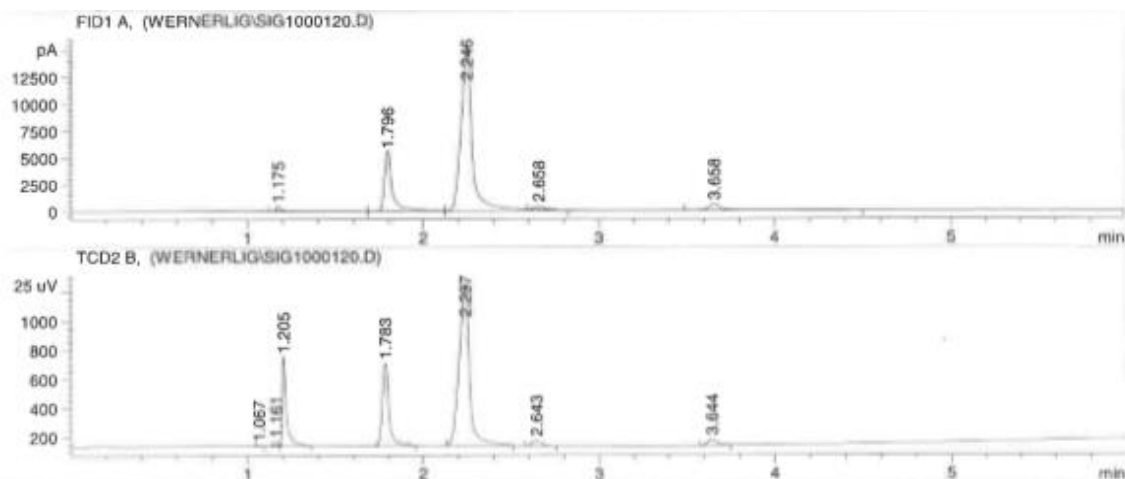
Signal 1: FID1 A,

RetTime [min]	Type	Area [pA*s]	Amt/Area	Amount [wt%]	Grp	Name
1.165	-	-	-	-	-	???
1.798	VV	1.50128e4	1.04301e-3	15.65843	-	Ethanol
2.247	VBAS	6.76846e4	8.64595e-4	58.51978	-	Isopropanol
2.662	BB X	2289.81494	1.47533e-3	3.37822	-	Acetone
4.068	-	-	-	-	-	Acetic Acid
5.327	-	-	-	-	-	EthyleneGlycol
7.393	-	-	-	-	-	Phenol
10.075	-	-	-	-	-	2-PhenylEthanol
Totals :				77.55643		

Signal 2: TCD2 B,

RetTime [min]	Type	Area [25 uV*s]	Amt/Area	Amount [wt%]	Grp	Name
1.068	BB	5.58465	0.00000	0.00000	-	???
1.207	VB	930.51715	1.13128e-2	10.52672	-	Water
2.342	VB	246.33452	1.81062e-2	4.46019	-	Formic Acid
3.648	BB	393.32397	0.00000	0.00000	-	EthylFormate?
4.053	-	-	-	-	-	Acetic Acid
5.300	-	-	-	-	-	EthyleneGlycol

Fig. A1. Run 1 (low temperature, low acid).



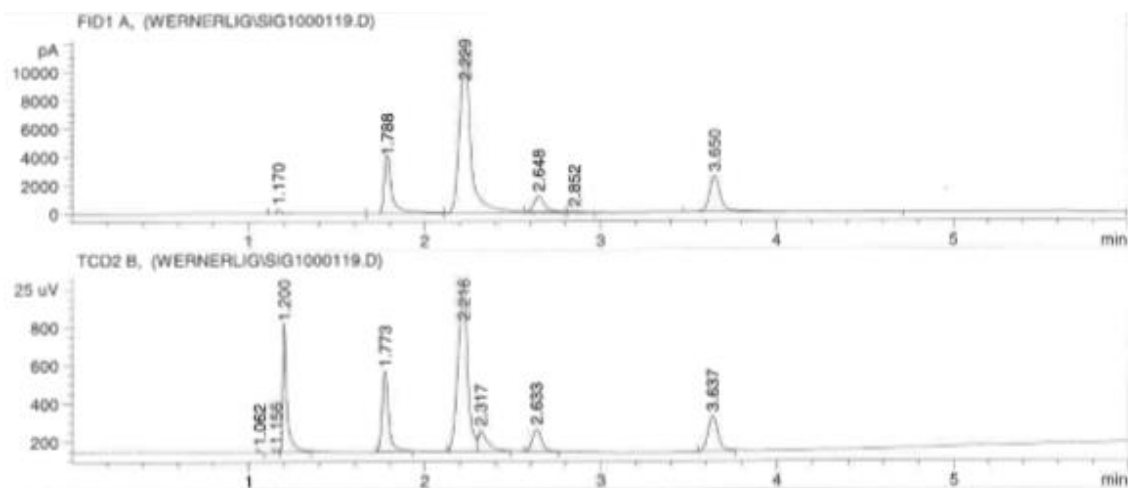
Signal 1: FID1 A,

RetTime [min]	Type	Area [pA*s]	Amt/Area	Amount [wt%]	Grp	Name
1.175	VV	973.88257	0.00000	0.00000		???
1.796	VV	1.77545e4	1.04301e-3	18.51806		Ethanol
2.246	VBAS	7.21715e4	8.64493e-4	62.39177		Isopropanol
2.658	BV X	1304.94751	1.98867e-3	2.59512		Acetone
4.068	-	-	-	-		Acetic Acid
5.327	-	-	-	-		EthyleneGlycol
7.393	-	-	-	-		Phenol
10.075	-	-	-	-		2-PhenylEthanol
Totals :				83.50495		

Signal 2: TCD2 B,

RetTime [min]	Type	Area [25 uV*s]	Amt/Area	Amount [wt%]	Grp	Name
1.067	BB	3.31391	0.00000	0.00000		???
1.205	VB	1007.27032	1.13312e-2	11.41356		Water
2.350	-	-	-	-		Formic Acid
3.644	BB	160.13623	0.00000	0.00000		EthylFormate?
4.053	-	-	-	-		Acetic Acid
5.300	-	-	-	-		EthyleneGlycol

Fig. A2. Run 2 (low temperature, high acid)



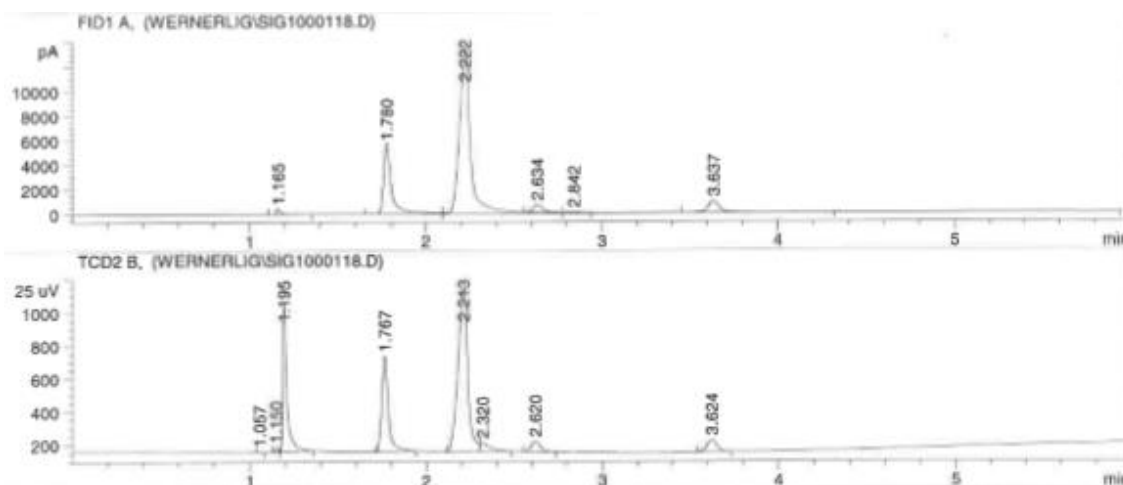
Signal 1: FID1 A.

RetTime [min]	Type	Area [pA*s]	Amt/Area	Amount [wt%]	Grp	Name
1.170	VV	559.71942	0.00000	0.00000	---	???
1.788	VV	1.28722e4	1.04301e-3	13.42573	---	Ethanol
2.229	VBAS	5.55615e4	8.64953e-4	48.05812	---	Isopropanol
2.648	BV X	4498.42383	1.14137e-3	5.13438	---	Acetone
4.068	-	-	-	-	---	Acetic Acid
5.327	-	-	-	-	---	EthyleneGlycol
7.393	-	-	-	-	---	Phenol
10.075	-	-	-	-	---	2-PhenylEthanol
Totals :				66.61822		

Signal 2: TCD2 B.

RetTime [min]	Type	Area [25 uV*s]	Amt/Area	Amount [wt%]	Grp	Name
1.062	BB	9.50847	0.00000	0.00000	---	???
1.200	VB	1113.09753	1.13524e-2	12.63633	---	Water
2.317	VB	401.23318	1.75451e-2	7.03966	---	Formic Acid
3.637	BB	716.49707	0.00000	0.00000	---	EthylFormate?
4.053	-	-	-	-	---	Acetic Acid
5.300	-	-	-	-	---	EthyleneGlycol

Fig. A3. Run 3 (high temperature, low acid).



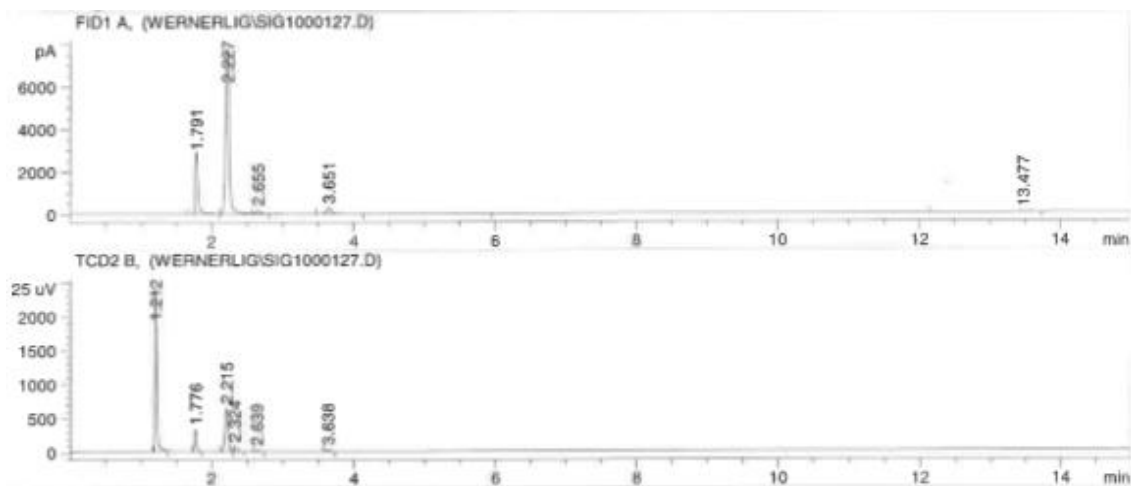
Signal 1: FID1 A.

RetTime [min]	Type	Area [pA*s]	Amt/Area	Amount [wt%]	Grp	Name
1.165	VV	842.33545	0.00000	0.00000	???	
1.780	VV	1.80432e4	1.04301e-3	18.81915		Ethanol
2.222	VBAS	6.30457e4	8.64716e-4	54.51666		Isopropanol
2.634	BV X	2394.18530	1.44567e-3	3.46121		Acetone
4.068	-	-	-	-		Acetic Acid
5.327	-	-	-	-		EthyleneGlycol
7.393	-	-	-	-		Phenol
10.075	-	-	-	-		2-PhenylEthanol
Totals :				76.79703		

Signal 2: TCD2 B.

RetTime [min]	Type	Area [25 uV*s]	Amt/Area	Amount [wt%]	Grp	Name
1.057	BB	2.40119	0.00000	0.00000	???	
1.195	VB	1465.65881	1.14010e-2	16.70996		Water
2.320	VB	212.43912	1.83382e-2	3.89574		Formic Acid
3.624	BB	279.88232	0.00000	0.00000		EthylFormate?
4.053	-	-	-	-		Acetic Acid
5.300	-	-	-	-		EthyleneGlycol

Fig. A4. Run 4 (high temperature, low acid)



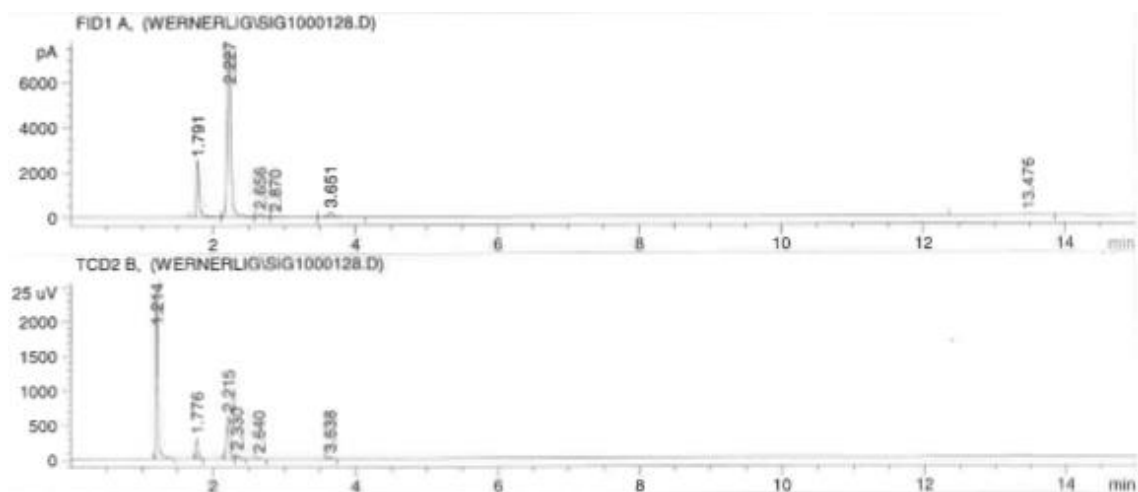
Signal 1: FID1 A,

RetTime [min]	Type	Area [pA*s]	Amt/Area	Amount [wt%]	Grp	Name
1.165	-	-	-	-	-	???
1.791	VV	7733.15381	1.04301e-3	8.06572	-	Ethanol
2.227	VB S	2.85208e4	8.66848e-4	24.72319	-	Isopropanol
2.655	BV X	578.60846	3.48694e-3	2.01757	-	Acetone
4.068	-	-	-	-	-	Acetic Acid
5.327	-	-	-	-	-	EthyleneGlycol
7.393	-	-	-	-	-	Phenol
10.075	-	-	-	-	-	2-PhenylEthanol
Totals :				34.80649		

Signal 2: TCD2 B,

RetTime [min]	Type	Area [25 uV*s]	Amt/Area	Amount [wt%]	Grp	Name
1.057	-	-	-	-	-	???
1.212	BB S	5096.39063	1.15103e-2	58.66086	-	Water
2.324	VB	215.86581	1.83114e-2	3.95281	-	Formic Acid
3.638	BB	80.80634	0.00000	0.00000	-	EthylFormate?
4.053	-	-	-	-	-	Acetic Acid
5.300	-	-	-	-	-	EthyleneGlycol

Fig. A5. Run 5 (high temperature, high acid, lignin present).



Signal 1: FID1 A.

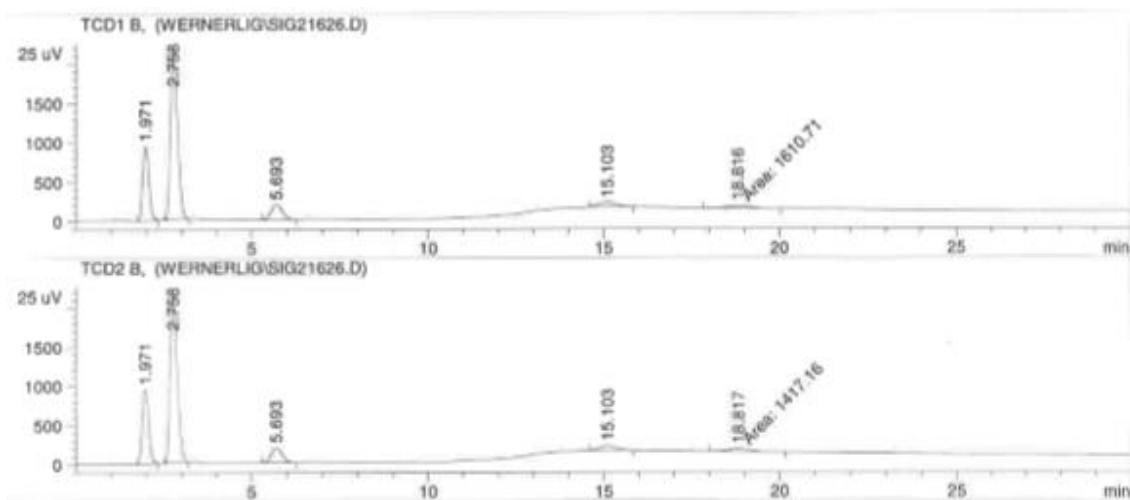
RetTime [min]	Type	Area [pA*s]	Amt/Area	Amount [wt%]	Grp	Name
1.165	-	-	-	-	-	???
1.791	VV	6831.34863	1.04301e-3	7.12514	-	Ethanol
2.227	VV	2.63849e4	8.67163e-4	22.87998	-	Isopropanol
2.656	VV	603.39716	3.37636e-3	2.03728	-	Acetone
4.068	-	-	-	-	-	Acetic Acid
5.327	-	-	-	-	-	EthyleneGlycol
7.393	-	-	-	-	-	Phenol
10.075	-	-	-	-	-	2-PhenylEthanol
Totals :				32.04240		

Signal 2: TCD2 B.

RetTime [min]	Type	Area [25 uV*s]	Amt/Area	Amount [wt%]	Grp	Name
1.057	-	-	-	-	-	???
1.214	BB S	5403.67090	1.15128e-2	62.21130	-	Water
2.330	VB	183.35468	1.86055e-2	3.41141	-	Formic Acid
3.638	BB	62.86036	0.00000	0.00000	-	EthylFormate?
4.053	-	-	-	-	-	Acetic Acid
5.300	-	-	-	-	-	EthyleneGlycol

Fig. A6. Run 6 (low temperature, high acid, lignin present).

Appendix 2: Gas analysis chromatograms



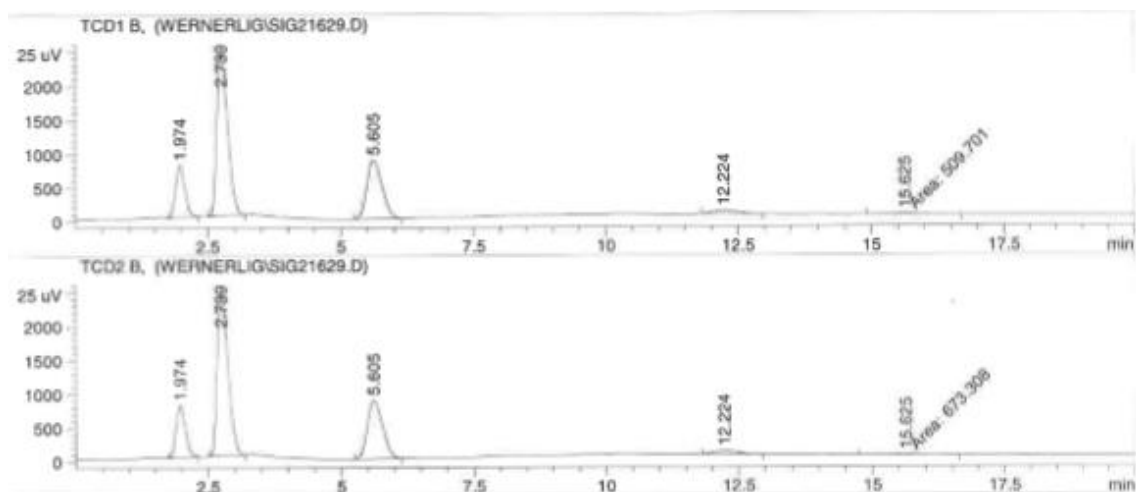
Signal 1: TCD1 B.

RetTime [min]	Type	Area [25 uV*s]	Amt/Area	Amount [%]	Grp	Name
1.971	BB	1.16954e4	8.94960e-4	10.46694		CO
2.758	BB	2.99635e4	8.47521e-4	25.39466		CO2
3.533		-	-	-		???
4.565		-	-	-		???
5.693	BB	4247.34033	0.00000	0.00000		???
6.378		-	-	-		???
9.000		-	-	-		???
10.307		-	-	-		???
12.408		-	-	-		???
15.103	BB	2065.19336	0.00000	0.00000		???
18.816	MM	1610.70862	0.00000	0.00000		???
25.941		-	-	-		???

Totals :

35.86160

Fig. A7. Run 1 (low temperature, low acid).



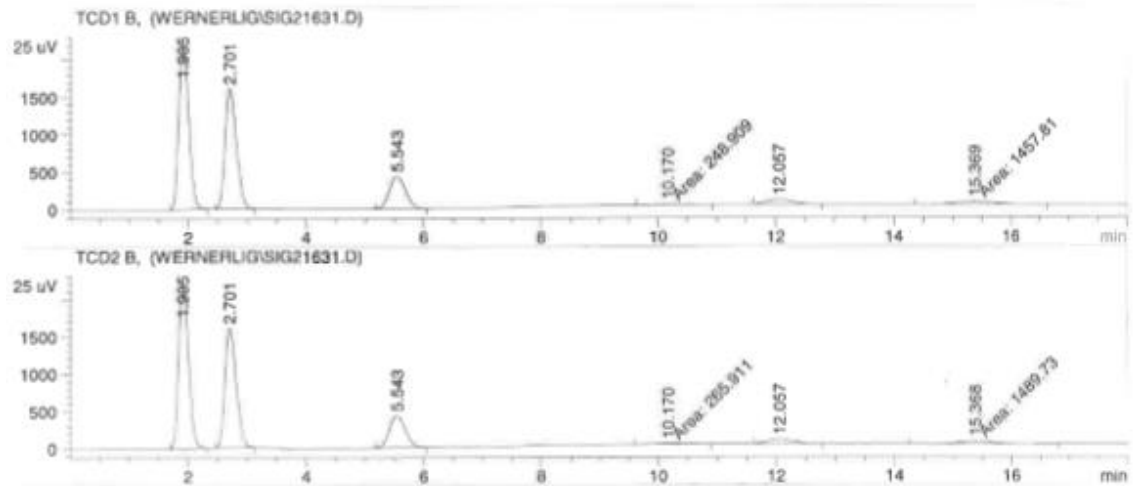
Signal 1: TCD1 B,

RetTime [min]	Type	Area [25 uV*s]	Amt/Area	Amount [%]	Grp	Name
1.974	BB	9275.36035	7.93194e-4	7.35716		CO
2.739	BB	3.36861e4	8.61086e-4	29.00664		CO2
3.533	-	-	-	-		???
4.565	-	-	-	-		???
5.605	BB	1.72844e4	0.00000	0.00000		???
6.378	-	-	-	-		???
9.000	-	-	-	-		???
10.307	-	-	-	-		???
12.224	BB	1835.09741	0.00000	0.00000		???
15.625	MM	509.70053	0.00000	0.00000		???
18.799	-	-	-	-		???
25.941	-	-	-	-		???

Totals :

36.36380

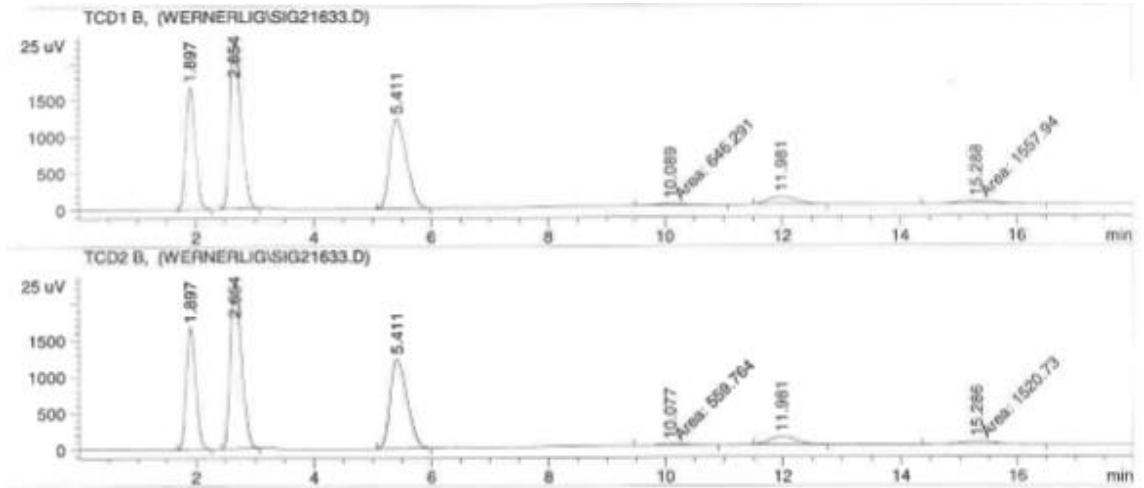
Fig. A8. Run 2 (high temperature, low acid).



Signal 1: TCD1 B.

RetTime [min]	Type	Area [25 uV*s]	Amt/Area	Amount [%]	Grp	Name
1.905	BB	2.59687e4	1.10934e-3	28.80806	CO	
2.701	BB	2.12576e4	7.97249e-4	16.94763	CO2	
3.533	-	-	-	-	???	
4.565	-	-	-	-	???	
5.543	BB	8329.75000	0.00000	0.00000	???	
6.378	-	-	-	-	???	
9.000	-	-	-	-	???	
10.170	MM	248.90895	0.00000	0.00000	???	
12.057	BB	1877.94873	0.00000	0.00000	???	
15.369	MM	1457.80798	0.00000	0.00000	???	
18.799	-	-	-	-	???	
25.941	-	-	-	-	???	
Totals :				45.75569		

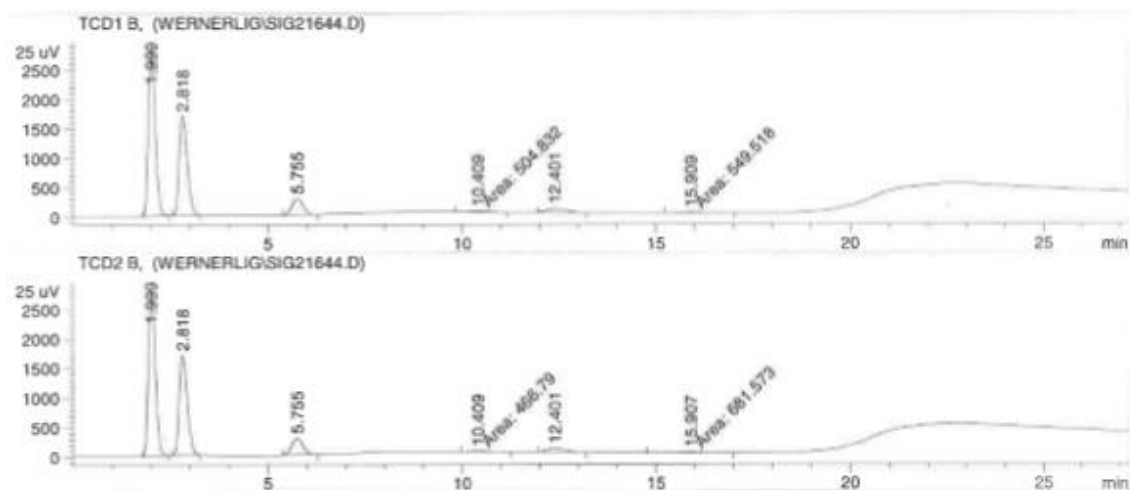
Fig. A9. Run 3 (low temperature, high acid).



Signal 1: TCD1 B,

RetTime [min]	Type	Area [25 uV*s]	Amt/Area	Amount [%]	Grp	Name
1.897	BB	1.87913e4	1.04224e-3	19.58515	CO	
2.654	BB	2.99566e4	8.47492e-4	25.38799	CO2	
3.533	-	-	-	-	???	
4.565	-	-	-	-	???	
5.600	-	-	-	-	???	
6.378	-	-	-	-	???	
9.000	-	-	-	-	???	
10.089	NM	646.29144	0.00000	0.00000	???	
12.408	-	-	-	-	???	
15.288	NM	1557.94482	0.00000	0.00000	???	
18.799	-	-	-	-	???	
25.941	-	-	-	-	???	
Totals :				44.97313		

Fig. A10. Run 4 (high temperature, high acid).



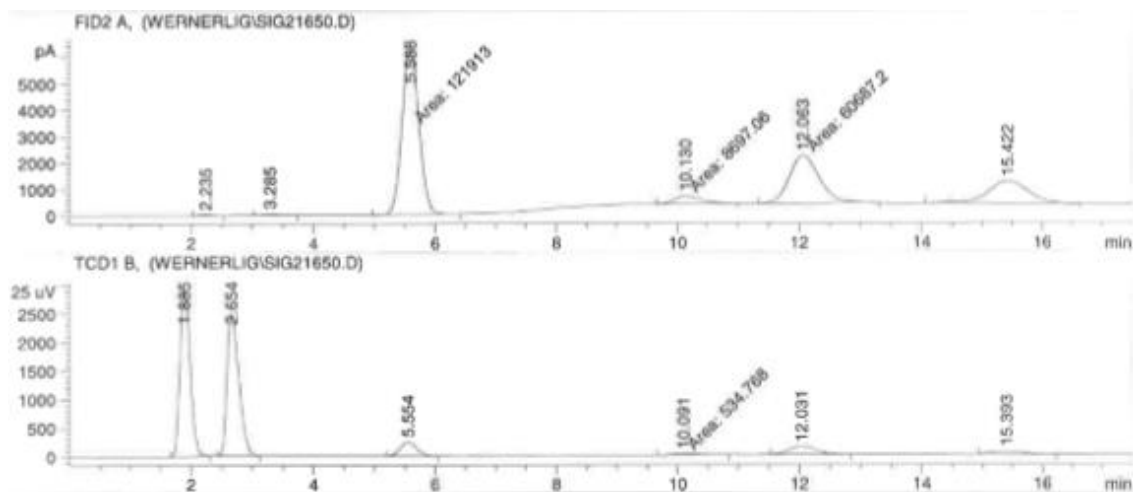
Signal 1: TCD1 B.

RetTime [min]	Type	Area [25 uV*s]	Amt/Area	Amount [%]	Grp	Name
1.999	BB	3.53561e4	1.15598e-3	40.87079		CO
2.818	BB	2.41893e4	8.18219e-4	19.79216		CO2
3.533		-	-	-		???
4.565		-	-	-		???
5.600		-	-	-		???
6.378		-	-	-		???
9.000		-	-	-		???
10.409	MM	504.83163	0.00000	0.00000		???
12.401	BB	2332.77197	0.00000	0.00000		???
15.103		-	-	-		???
18.799		-	-	-		???
25.941		-	-	-		???

Totals :

60.66295

Fig. A11. Run 5 (high temperature, high acid, lignin present).



Signal 1: FID2 A,

RetTime [min]	Type	Area [pA*s]	Amt/Area	Amount [%]	Grp	Name
2.235	BB	279.08813	0.00000	0.00000		
3.285	BB	915.64728	0.00000	0.00000		
Totals :				0.00000		

Signal 2: TCD1 B,

RetTime [min]	Type	Area [25 uV*s]	Amt/Area	Amount [%]	Grp	Name
1.885	BB	3.35742e4	1.14913e-3	38.58100	CO	
2.654	BB	3.33960e4	8.60137e-4	28.72519	CO2	
3.533		-	-	-		???
4.565		-	-	-		???
5.554	BB	4681.57471	0.00000	0.00000		???
6.378		-	-	-		???

Fig. A12. Run 6 (low temperature, high acid, lignin present).