VALORISATION OF WASTE LIGNIN FOR PHENOL DERIVATIVE COMPOUNDS USING HYDROTHERMAL LIQUEFACTION

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ABSTRACT: Approximately 95% of global phenolic compounds (such as catechol, guaiacol, syringol, and vanillin) used in the pharmaceutical, fragrance and industrial industries are produced from petroleum-based phenolics such as benzene. Lignin waste, a by-product from industrial processes such as paper mills, is rich in bio-based phenolic groups that could be utilised to replace or supplement fossil-based products. Generally, lignin valorisation can be divided into three categories, power/fuel, macromolecules and aromatics. The highly aromatic nature of lignin makes lignin the highest value-added valorisation constituent of biomass and research is needed to improve lignin valorisation processes for commercial application. A promising technology able to extract phenolic derivatives from lignin at moderate temperatures and pressures is hydrothermal liquefaction (HTL). The effect of HTL on the yield of phenolic derivatives using a South African waste lignin in the aqueous product phase has not yet been investigated in detail. This research is necessary to develop a more economically viable HTL process as biochar and bio-oil alone could not justify an economic option for the HTL process. Thus, other streams produced during the HTL process must be developed to produce a more economical process through value added chemicals from lignin. In this study the effect of hydrothermal liquefaction on the phenolic derivatives in the aqueous phase was investigated through using a two-level factorial design approach. This was done as a first step to identify possible interactions between process variables and to identify the bio-products obtainable during the HTL of South African sodium lignosulfonate. Experiments were conducted in a SS316 high-pressure autoclave of 0.954 L with a heating mantle of 6 kW. All HTL products were quantified and analysed. Main phenolic derivatives in the aqueous phase were vanillin (0.67 g/kg biomass), guaiacol (3.74 g/kg biomass), *p*-cresol (1.72 g/kg biomass), and catechol (2.18 g/kg biomass). Compared to other research obtaining vanillin with a relative yield of 33% at 250°C, and guaiacol of 19% using supercritical H_2O:CO2 as solvent vanillin production was lower, however guaiacol production was higher and other value added chemicals such as *p*-cresol were produced with the use of simple untreated biomass and water HTL, simplifying the process and lowering costs. Also, selective conversion of lignin is a challenge due to the complex nature of lignin. However, in this study it was proven that the manipulation of HTL parameters can favour the production of specific phenolic compounds. This proves that waste lignin can not only be depolymerised into economically value-added phenolic products but can also lessen the reliance on fossil fuels to produce phenolic compounds for the pharmaceutical, fragrance and industrial industries and may contribute to a more economically HTL process.
Keywords: Hydrothermal liquefaction, waste, lignin, phenolic compounds, experimental design approach.

1 INTRODUCTION

Current world crises and regulatory demands on governments, require innovative ways to meet the demand for fossil fuels with carbon-neutral alternatives [1]. One such way is the use of renewable sources of energy originating from previously discarded wastes of either agricultural (lignocellulosic material) or industrial activities [2]. However, disadvantages associated with the used of wastes as energy sources (fouling, lower efficiencies, and high moisture content) necessitate upgrading of these materials. Current bio-processes predominantly focus on the use of cellulose and hemicellulose for the production of bio-products with little attention paid to the second most abundant terrestrial polymer, lignin, that constitutes from 15-30 wt% and 40% by energy of terrestrial plants [3].

Vast amounts of wastes in the form of lignin is produced as by-product from the paper and pulping- and bioethanol industries, containing varying amounts of cellulose, hemicellulose and lignin [3]. Different types of lignin produced, depending on the manner in which it was processed. Mostly, lignin ends up as either a fuel for boilers in the form of black liquor or processed, dried and used as dust suppressant.

Lignin in its basic structure consists of a large number of cross-linked phenolic polymers interlocked with ether and carbon-carbon bonds [4]. Three main types of lignols (all of which are derivatives of phenylpropane)are: 4-hydroxy-3-methoxyphenylpropane, 3,5-dimethoxy-4-hydroxypenlypropane, and 4-hydroxyphenylpropane and three monolignol monomers are: *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. All of which form part of larger molecules called *p*-hydroxyphenyl, guaiacol, and syringol. Thus, the value-added potential of lignin as precursor for the production of high-quality phenolics for the pharmaceutical and industrial applications is of interest [3].

Due to the nature of lignin and its resistance to decay, ordinary bio-processes is not enough for the cleavage of chemical bonds to liberate lignols and monolignol monomers. These units are bonded by means of carbon-carbon (C-C bonds named aryl-aryl; aryl-aliphatic and aliphatic-aliphatic) and carbon-oxygen bonds (C-O bonds named ether and aryl ether bonds) [5]. Thus, thermochemical processes are of interest. Current thermochemical conversion technologies include gasification, hydrothermal liquefaction, pyrolysis, combustion, and supercritical fluid extraction [6].

Hydrothermal liquefaction (HTL), operating at moderate temperatures (250-374°C) and pressures (4-22 MPa) offers several advantages over pyrolysis and other thermochemical processes [4]. One of these advantages is the usage of a feedstock of varying moisture content, thus circumnavigating the costly drying process required for other processes. Another advantage is the use of water alongside the feedstock, where the water acts as solvent and catalyst for the reactions [7]. A major advantage in using near critical water with moderate

temperatures and pressures, is that the aromatic rings in the lignin polymer remain intact [8].

HTL produces four distinctive products: biochar, bio-oil, an aqueous phase, and biogas [6]. Each of which can be used as value added products. Bio-oil production from lignin has extensively been investigated and shown to contain precious phenolic compounds such as phenol, catechol, guaiacol, syringol and vanillin [9]. Although a lot of work has been done on the analysis and quantification of phenol derivatives present in the bio-oil phase, little has been reported on the effect of operating conditions on the type and amount for phenol derivatives in the aqueous HTL product phase.

Thus, in this study the statistical effect of operating parameters such as temperature, biomass loading, volume loading and residence time on the production and distribution of phenolics in the aqueous phase from industrial South African sodium lignosulphonate was investigated.

2 MATERIALS AND METHODS

2.1 Feedstock preparation

Industrial sodium lignosulphonate was obtained from a local Paper and Pulping manufacturer in South Africa (with GPS coordinates of 29°09'13.4"S 31°24'25.7"E) as a dry brown powder. No further purification was done on the sodium lignosulphonate was used as is in all experimental work. A rotary sample splitter was used to quarter, mix and separating the samples into six homogeneous samples, which were stored in air tight containers in a desiccator.

Compositional analysis on the untreated sodium lignosulphonate was done by a South African accredited laboratory (Agricultural Research Council (ARC), Irene). The results of this compositional analysis can be seen in Table I.

Table I: Compositional analysis of sodium lignosulfonate (wet basis)

Property	Standard Method	Content (wt%)
Dry matter	ASM 013	96.46
Total moisture	ASM 013	3.54
Ash	ASM048	55.72
Protein (N x 6.25)	ASM 078	1.21
Lipids (ether extracted)	ASM 044	0.39
Total carbohydrates*	ASM 075	39.14
Cellulose		0.1
Hemicellulose		0.28
Lignin		1.03

*As monomeric sugars

2.2 Experimental method

The effect of HTL operating conditions on phenolic derivatives in the aqueous phase was done using batch hydrothermal liquefaction and a 2-level factorial design with 4 factors (process temperature, residence time, biomass loading, and volume loading). A factorial design was chosen to investigate the simultaneous effects these parameters may have on the production and quality of bio-products obtained and to ascertain the most significant process parameters in terms of bio-product yield and quality. The parameters levels used in the factorial design is given in Table II.

ANOVA of the data was done at a 95% confidence level and statistical models could be derived from this to describe the effect of individual and interaction effect of manipulated variables on phenolic derivative yields.

Table II: Levels used for parameters in the factorial design

Parameter	Minimum	Maximum	Unit
Temperature	280	300	°C
Residence time	15	45	min
Biomass loading	10	50	wt%
Reactor volume loading	25	75	vol%

The process constant was the feed to the HTL reactor being industrial sodium lignosulphonate obtained through a local paper and pulp producing company, the inert atmosphere of nitrogen and using a heating rate of 2°C/min. Bio-product yield (biochar, bio-oil and biogas) and phenolic content as composition was used as response variables in the ANOVA.

Batch HTL was carried out in a SS316 high-pressure autoclave with an inside diameter of 90 mm, height of 150 mm and a volume of 954 mL, equipped with a removable sleeve with a working volume of 700 mL.

The autoclave has a maximum operating pressure and temperature of 200 bar and 360 °C respectively. The autoclave was heated using a removable electric heating jacket with a heating capacity of 6 kW. A schematic representation of the HTL set-up can be seen in Figure 1.

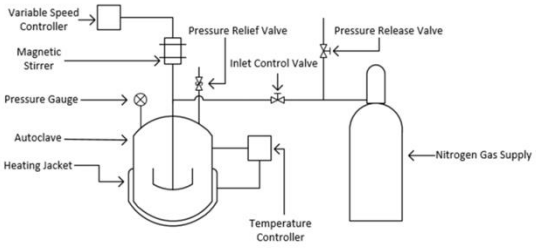

Figure 1: Schematic representation of HTL reactor

For each experiment, the required biomass and water slurry was poured into the reactor and the lid of the reactor was fastened. The reactor system was then purged three times with nitrogen gas and pressurised to a starting pressure of 10 bar. The reactor was heated at a heating rate of 2 °C/min until the desired temperature inside the reactor was reached.

Once the desired temperature was reached, the temperature was kept constant for the desired retention time (15-45 min), after which several fans were used to cool the reactor to ambient temperatures. The pressure in the reactor was responsibly released to the atmosphere and the reactor sleeve was removed the gas yield gravimetrically measured. The other HTL product mixture, bio-oil, biochar, and aqueous phase was quantitatively extracted for product purification and quantification.

2.3 Analysis

2.3.1 Product recovery

After the reactor has reached ambient temperature the reactor was vented to atmospheric pressure without

analysing the biogas formed. Non-polar oils were extracted by adding 250 mL hexane to the reaction mixture in the sleeve. After mixing, the mixture was separated into an aqueous/hexane oil phase and a biochar phase by Büchner filtration. The biochar was then washed again with 250 mL hexane. The aqueous and hexane-oil phases were separated through gravity settling in a separating funnel. The polar oil-phase was extracted from the biochar by washing the biochar with 500 mL of acetone in a separate Büchner funnel. Both oil phases were recovered from the solvents by evaporation (RII Buchi RO Rotovap) and the total weight recorded. The biochar was dried in an oven at 60 °C for a minimum of 3 hours to remove all residual solvents and the mass was recorded. All of the aqueous phase recovered from the non-polar oil/hexane mixture was collected and stored for analysis in a Labocool fridge at 5°C. Product yields were then calculated using the following equations:

$$\text{Biochar yield} = m_{char}/m_{biomass} * 100\% \quad (1)$$

$$\text{Bio-oil yield} = m_{oil}/m_{biomass} * 100\% \quad (2)$$

$$\text{Biogas yield} = m_{after\ HTL}/m_{before\ HTL} \quad (3)$$

2.3.2 Phenolic content of aqueous phase

The phenolic content of the aqueous phase was quantified using an Agilent Technologies 1260 Infinity II HPLC. The HLC is fitted with an InfinityLab Poroshell 120 EC-C18 4.6 x 100 mm and a 4-micron column ID and the HPLC oven was set on 40 °C. The volume of sample used during the quantification was set to 10 µL with a diode array detector with wavelength of 275 nm and bandwidth of 4 nm. Two mobile phases were used during the HPLC process namely a 1% formic acid in water mixture and a 1% formic acid in acetonitrile mixture. The phenolic content of the aqueous phase was then calculated using the following equation:

$$\text{Phenol yield} = (\text{phenolic concentration} * \text{solvent volume})/m_{biomass} \quad (4)$$

Where the phenol yield will be in g/kg biomass used, the phenolic concentration in g/L, solvent volume in L, and $m_{biomass}$ in kg of biomass used.

3 RESULTS AND DISCUSSION

In the following sections the statistically significant process parameters found for biochar, bio-oil, biogas, and the phenolic content of the aqueous phase will be discussed. Stat-Ease, Inc., Design-Expert version 11 was used for calculations and interpretation.

3.1 Effect on biochar yield and quality

The significant process parameters for biochar was found to be biomass loading ($p < 0.0001$) and temperature ($p = 0.0598$). The effect these parameters has on the biochar yield can be seen in Figure 2.

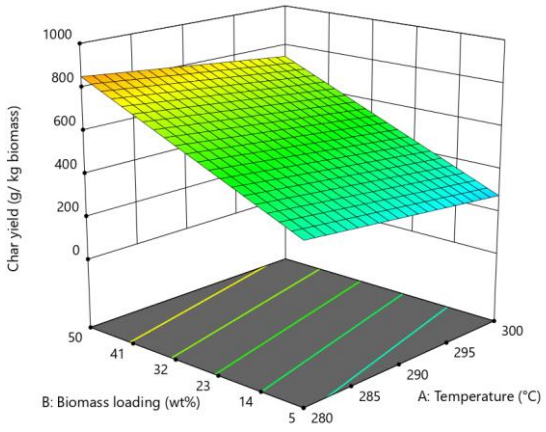

Figure 2: Biochar yield as function of temperature and biomass loading

Biochar is produced by the recombination and repolymerisation of reactive fragments in the absence of hydrogen donors or if the concentration of the free radicals are excessively abundant, form high molecular weight compounds [4]. Thus, from Figure 2 it can be seen that by increasing the concentration of biomass increases the amount of biochar produced. This fits perfectly with that explained from literature [4], where by with the increase of free radicals in excess, recombination and repolymerisation reactions are favoured to produce biochar. Similarly, with a larger weight percentage of biomass less water is added to the reactor, thus decreasing the amount of hydrogen donor species available. Thus, with both these factors playing synergetic effects increases the biochar yield. Furthermore, the production of biochar can be approximated by the following statistically obtained equation:

$$\text{Char yield} = 1834.17 - 5.35840*(\text{Temperature}) + 10.35*(\text{Biomass loading}) \quad (5)$$

This shows the dependency of the biochar yield on temperature and biomass loading. It is further known that carbohydrates and lignin contribute to the biochar formation [10]. When considering the biomass used during this experiment, it can be seen that the content of carbohydrates and lignin far outweighs the content of bio-oil forming components thus leading to biochar production.

3.2 Effect on bio-oil yield and quality

Significant process parameters for the production of bio-oil was found to be biomass loading ($p < 0.0001$) and volume loading ($p = 0.0026$). The effect these parameters has on the bio-oil yield can be seen in Figure 3.

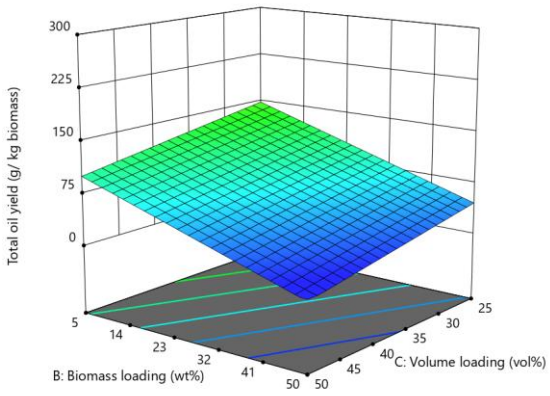

Figure 3: Bio-oil yield as function of temperature and biomass loading

Bio-oil production from lignin was extensively investigated in literature, using various operating conditions. It was found that temperature, residence time, and biomass to water ratios played crucial roles in the production of bio-oil. From these investigations temperature was found to play the dominant role in bio-oil production, where at specific temperature, depending on the feedstock, the amount of bio-oil produced reaches a limit and cracking reaction occur at the cost of bio-oil to form biogas and repolymerisation reactions to form biochar [11].

It is known that carbohydrate content (including saccharides and lignin content) does not contribute to the formation of bio-oil and produces more biochar as compared to protein and lipids [10]. Thus, in this study using biomass with far greater combined carbohydrate and lignin content resulted in less bio-oil forming and more biochar. This can be due to recombination reactions responsible for the breakage of carbohydrates, sugars, phenolics, and bio-oil constituents formed during HTL to form larger molecules and alongside unreacted lignin and thus produce more biochar. A possible reason for the higher bio-oil production with lower biomass loading can be attributed to the limitation of biomass present in the reaction where fewer recombination reactions would occur to form larger molecules for biochar production. The statistically obtained equation for the bio-oil yield can be seen below as:

Bio-oil yield =
208 – 2.30*(Biomass loading) – 1.93*(Volume loading) (6)

This shows the dependency of bio-oil production on biomass and volume loading, whereby the effect of biomass loading plays a more dominant role as compared to volume loading. It is thus suggested that by increasing the volume loading (an increase in the reaction pressure) lowers the final bio-oil production. This may be due to the forceful recombination reactions forming biochar at the expense of bio-oil.

3.3 Effect on biogas yield

The biogas yield was determined through the difference between the starting mass (raw lignosulphonate, water, and reactor sleeve) and mass after HTL (containing all bio-products). It is suggested that HTL light gasses, primarily comprises of CO_2 and small amounts of CO, H_2, and CH_4. Furthermore, it was found that the average yield of biogas formed can range from 10-25 wt.% [11]. Furthermore, from literature it is suggested that the production of biogas is negligible and not often fully quantified or left out entirely. It was found in this investigation that biomass loading (amount of biomass present during HTL) and volume loading (final reaction pressure) played roles in the production of biogas. The influence biomass loading ($p < 0.0001$) and volume loading ($p < 0.0001$) on the production of bio-oil can be seen in Figure 4.

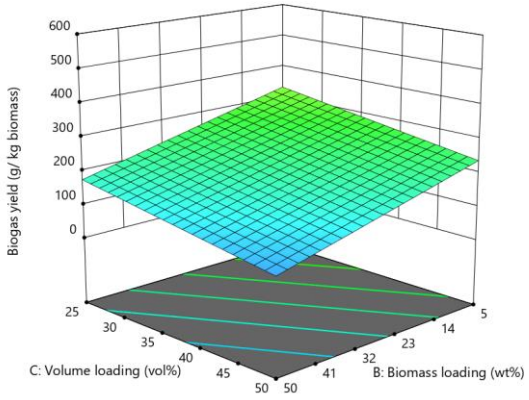

Figure 4: Biogas yield as function of temperature and biomass loading

In this study it was found that the biogas yield ranged from 10-30wt% which is in accordance with literature.

However, at low volume loading and low biomass loading a high of 30wt% was obtained which is higher than other studies. This can be due to the synergistic effect of more free radicals forming from the small amount of biomass used and lower reaction pressures at lower volume loading. Thus, when using a lower biomass loading alongside a lower reaction pressure would favour the reactions responsible for the conversion of biochar and bio-oil into biogas. The statistically obtained equation for the biogas yield can be seen below as:

Biogas yield =
44.61 – 3.51*(Biomass loading) – 3.85*(Volume loading) (7)

This shows the yield of biogas is dependent on the biomass loading and volume loading of reaction where lower reaction pressures and lower biomass loadings will favour the production of biogas.

3.4 Effect on phenolics in the aqueous phase

Small polar organic compounds produced during HTL are recovered mainly in the aqueous phase and not in the oil phase [11]. Another possible element affecting the phenolic yields may be due to the pH of the aqueous phase. Usually the pH of HTL waste water is of acidic nature (pH of 5.28-6) due to organic acids forming in normal lignocellulosic biomass [12]. However, all experiments showed a pH in the range of 8-9.5. This can be due to the sodium content of the raw sodium lignosulfonate dissociating into the aqueous phase and combining with OH^- groups resulting in a basic medium.

Due to the decreasing nature of bio-oil with increasing biomass loading, suggesting fewer phenolics forming, the aqueous phase showed a similar trend to bio-oil which produces the phenolic compounds.

Suggesting the inter-dependence of phenolics in the aqueous phase to the production of bio-oil. However, it must be taken into account the solubility of phenolics in water and that of the extractive solvent being hexane, a non-polar solvent. Thus, the concentration of phenolics in the aqueous phase relies on the solubility of each component in water and the non-polar solvent.

Another effect on the phenolic yield may be attributed to the manner in which the solvent (hexane) is extracted via evaporation at 40°C, at which some lighter phenolics could end up in the distillate lowering the total phenolic content.

After the HTL of sodium lignosulphonate the four most abundant products in the recovered aqueous phase was identified as vanillin, guaiacol, *p*-cresol, and catechol through HPLC. The highest yield of combined phenolic compounds was obtained at 280°C, 5wt%, 50 vol%, and 15min and was approx. 9.53 g/kg biomass. This run contained: vanillin 1.11 g/kg biomass, guaiacol 4.17 g/kg biomass, *p*-cresol 2.49 g/kg biomass, and catechol 2.37 g/kg biomass. In the following subsections the influence on all these phenolic compounds will be discussed and the most statistically significant factors will be included alongside the statistically obtainable linear equation relating the yield of phenolics to the most statistically favourable parameters.

3.4.1 Effect on guaiacol yield

The production of guaiacol was influenced by biomass loading ($p < 0.0001$), volume loading ($p = 0.0378$) and the interaction of both ($p = 0.0390$) as can be seen in Figure 5.

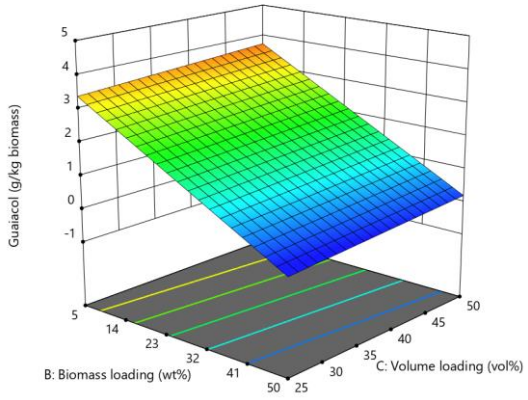

Figure 5: Guaiacol yield as function biomass loading and volume loading

The highest guaiacol yield (4.17 g/kg biomass) was obtained at 280°C, 5 wt%, 50 vol%, and 15 min and 280°C, 5 wt%, 50 vol%, and 45 min. Thus, the production of guaiacol will be influenced by the amount of biomass present (amount of free radicals forming) in the reactor where a lower biomass content will favour the reactions to form guaiacol. This can be due to the forceful transformation undergone to the sodium lignosulfonate where a lower amount of biomass is present thus, limiting the reaction steps that could possibly be enhanced when more biomass is present.

Furthermore, a statistically obtainied equation for the production of guaiacol yield can be seen below as:

$$\text{Guaiacol yield} = 3.42 - 0.08*(\text{Biomass loading}) + 0.01*(\text{Volume loading}) \quad (8)$$

This equation relates the linear dependancy of guaiacol yield to biomass loading and volume loading.

Thus, when a high volume loading is used, resulting in a higher reaction pressure, forcess water in the reactor to be in a subcritical condition will promote the formation of guaiacol. This may be attributed to the increased decomposition and penetration reactions on biomass to form bio-oil and subsicuently water soluable guaiacol.

3.4.2 Effect on catechol yield

The production on catechol was influenced by temperature ($p = 0.0252$), biomass loading ($p < 0.0001$) and the interaction of both ($p = 0.0128$) as can be seen in Figure 6. The highest yield of catechol (2.37 g/kg lignin) was obtained at 280°C, 5 wt%, 50 vol%, and 15 min.

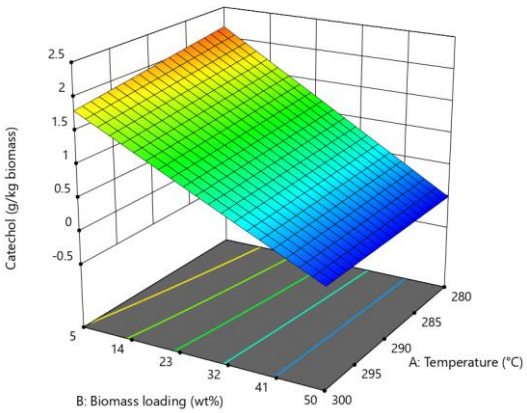

Figure 6: Catechol yield as function biomass loading and temperature

The decreasing nature of catechol yield with increasing temperature with a low biomass loading suggest that using harsher conditions will lead to the degradation of catechol

$$\text{Catechol} = 8.35 - 0.02*(\text{Temperature}) - 0.17*(\text{Biomass loading}) + 0.0004*(\text{Temperature}*\text{Biomass loading}) \quad (9)$$

3.4.3 Effect on *p*-cresol yield

p-Cresol production was mainly influenced by biomass loading ($p = 0.0003$) as can be seen in Figure 7.

The highest yield of p-cresol (2.49 g/kg lignin) was obtained at 280°C, 5 wt.%, 25 vol.%, and 15 min.

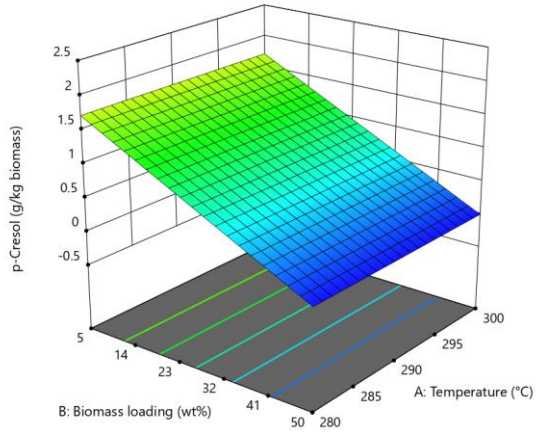

Figure 7: *p*-Cresol yield as function biomass loading and temperature

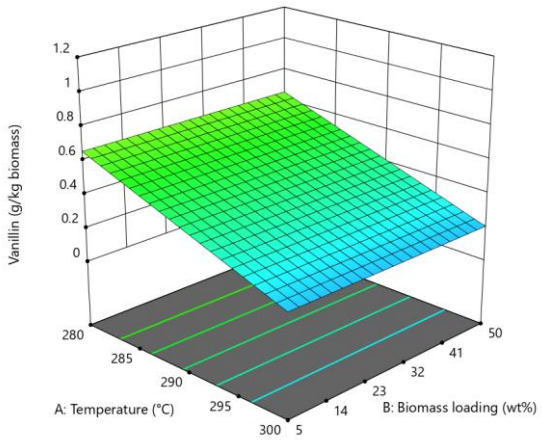

Figure 8: Vanillin yield as function biomass loading and volume loading

p-Cresol production will be optimised by the amount of biomass present during HTL. The more carbon available the more *p*-cresol can be produced. The highest yield of *p*-cresol and catechol corresponded to the same operating parameters showing a possible independent relationship between the production of *p*-cresol and catechol. This can be confirmed by literature suggesting that *p*-cresol is produced from the protein content of the biomass [13]. Thus, in this study the biomass had a protein content of 1.2wt% as compared to 1.03wt% lignin, showing the possible independent formation of *p*-cresol and catechol. Furthermore, *p*-cresol yield can be statistically approximated by the following equation:

p-Cresol yield =
1.91 – 0.04*(Biomass loading) (10)

The only factor influencing *p*-cresol can be seen as biomass loading, thus more protein available in the reaction more *p*-cresol can be produced. Another possible explination of *p*-cresol production is the demethoxylation reactions of guaiacol and syringol in the precence of a strong base during the reaction [14]. This can also be a plausable reason for the formation of *p*-cresol due to the high pH of all the aqueous phase.

3.4.4 Effect on vanillin yield

The production of vanillin was influenced by temperature ($p = 0.0097$), as shown in Figure 8.

Temperature of reaction, controls the degree of depolymerisation of the biomass [11]. Thus with a low temperature, fewer free radicals would form and a lesser degree of depolymerisation would occur resulting in fewer biochar and biogas production and a higher bio-oil yield, thus resulting in a higher phenolic content in the aqueous phase. This is in accordance to [17] which showed that by increasing temperate above a certain threshold would result in more char forming at the expense of bio-oil constituents.

The highest yield of vanillin (1.11 g/kg biomass) was produced at 280°C, 5 wt%, 50 vol% and 15 min. This suggest the production of vanillin would be favoured at a lower temperature allowing for fewer depolymerisation reactions to occur [15]. Thus, it is proven that vanillin can be produced through no additional oxidative catalytic reaction pathways or complex solvent additions, making the HTL process more economically viable. An increase in temperature will favour phenolic compounds through demethoxylation and alkylation [16]. From the statistical data a linear equation was obtained showing the influence of temperature on the production of vanillin and can be seen below:

Vanillin yield =
7.02 – 0.02*(Temperature) (11)

This shows that by increasing temperature would negatively influence the production of vanillin. The destruction of vanillin rings may be attributed to the formation of biochar through recombination reactions making a more complex structure which would contribute to biochar formation.

4 CONCLUSIONS

Suitable statistical equations for the yields of bioproducts (biochar, bio-oil and biogas) and phenolics in the aqueous phase was obtained. This can now be utilised to further develop and test these equations for its applicability to real life scenarios and to further develop these equations. From a statistical point of view the main influencers for bioproducts was identified as biomass loading and temperature for biochar, biomass loading and volume loading for bio-oil production and biomass loading and volume loading for biogas. For the phenolics it was found that biomass loading and volume loading for guaiacol, biomass loading and temperature for catechol, biomass loading for *p*-cresol, and temperature for vanillin. It can also be concluded that residence time (15-45 min) had no effect on the production of phenolics and thus shorter residence times could be used for phenolic production.

5 REFERENCES

[1] UNFCCC, "Adoption of the Paris Agreement. Proposal by the President.," in Paris Climate Change Conference - November 2015, COP 21, 2015, vol. 21932, no. December, p. 32.

[2] K. Tekin, S. Karagöz, and S. Bektaş, "A review of hydrothermal biomass processing," Renew. Sustain. Energy Rev., vol. 40, pp. 673–687, 2014.

[3] H. Wang, Y. Pu, A. Ragauskas, and B. Yang, "From lignin to valuable products–strategies, challenges, and prospects," Bioresour. Technol., vol. 271, no. September 2018, pp. 449–461, 2019.

[4] A. R. K. Gollakota, N. Kishore, and S. Gu, "A review on hydrothermal liquefaction of biomass," Renew. Sustain. Energy Rev., vol. 81, no. April, pp. 1378–1392, 2018.

[5] R. Beauchet, F. Monteil-Rivera, and J. M. Lavoie, "Conversion of lignin to aromatic-based chemicals (L-chems) and biofuels (L-fuels)," Bioresour. Technol., vol. 121, pp. 328–334, 2012.

[6] A. Dimitriadis and S. Bezergianni, "Hydrothermal liquefaction of various biomass and waste feedstocks for biocrude production: A state of the art review," Renew. Sustain. Energy Rev., vol. 68, no. September 2016, pp. 113–125, 2017.

[7] J. A. Ramirez, R. J. Brown, and T. J. Rainey, "A review of hydrothermal liquefaction bio-crude properties and prospects for upgrading to transportation fuels," Energies, vol. 8, no. 7, pp. 6765–6794, 2015.

[8] K. R. Arturi, M. Strandgaard, R. P. Nielsen, E. G. Sogaard, and M. Maschietti, "Hydrothermal liquefaction of lignin in near-critical water in a new batch reactor: Influence of phenol and temperature," J. Supercrit. Fluids, vol. 123, pp. 28–39, 2017.

[9] A. M. Numan-Al-Mobin, P. Kolla, D. Dixon, and A. Smirnova, "Effect of water–carbon dioxide ratio on the selectivity of phenolic compounds produced from alkali lignin in sub- and supercritical fluid mixtures," Fuel, vol. 185, pp. 26–33, 2016.

[10] J. Yang, Q. (Sophia) He, K. Corscadden, H. Niu, J. Lin, and T. Astatkie, "Advanced models for the prediction of product yield in hydrothermal liquefaction via a mixture design of biomass model components coupled with process variables," Appl. Energy, vol. 233–234, no. September 2018, pp. 906–915, 2019.

[11] B. de Caprariis, P. De Filippis, A. Petrullo, and M. Scarsella, "Hydrothermal liquefaction of biomass: Influence of temperature and biomass composition on the bio-oil production," Fuel, vol. 208, pp. 618–625, 2017.

[12] T. H. Pedersen et al., "Continuous hydrothermal co-liquefaction of aspen wood and glycerol with water phase recirculation," Appl. Energy, vol. 162, pp. 1034–1041, 2016.

[13] R. B. Madsen et al., "Chemometric analysis of composition of bio-crude and aqueous phase from hydrothermal liquefaction of thermally and chemically pretreated Miscanthus x giganteus," Biomass and Bioenergy, vol. 95, pp. 137–145, 2016.

[14] A. Toledano, L. Serrano, and J. Labidi, "Organosolv lignin depolymerization with different base catalysts," J. Chem. Technol. Biotechnol., vol. 87, no. 11, pp. 1593–1599, 2012.

[15] H. Luo and M. M. Abu-Omar, Chemicals From Lignin, vol. 3, no. 2016. Elsevier, 2017.

[16] L. Cao et al., "Lignin valorization for the production of renewable chemicals: State-of-the-art review and future prospects," Bioresour. Technol., vol. 269, no. June, pp. 465–475, 2018.

[17] J. M. Lavoie, W. Baré, and M. Bilodeau, "Depolymerization of steam-treated lignin for the production of green chemicals," Bioresour. Technol., vol. 102, no. 7, pp. 4917–4920, 2011.

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