TRANSFORMATION OF ORGANICS INPUTS TO ALUMINA REFINERIES

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Abstract

Carbohydrate and lignin dissolution has been studied under Bayer conditions. In the Bayer process for preparing alumina from bauxite small molecular weight compounds such as C_2-C_6 mono-, di- and tri- aliphatic carboxylic acids, which have hydroxy substituents, are formed from humic material. While involatile as anions under refinery conditions, upon acidification they become volatile and can be lost either in processing or in work up of process liquors in the laboratory. The origin of these organics is unknown, however this paper shows that they are directly derived from the carbohydrate fraction in the vegetation that is dissolved with the bauxite in preparing process liquors. Glucitol is shown to be a particularly stable carbohydrate to digestion and may therefore play an important role in Bayer poisoning processes. Using ^{13}C labelled compounds, rearrangements in alkaline solution have been demonstrated under Bayer conditions. They show that in the formation of lactate from glucose the carboxylate (COO^-) carbon is formed preferentially from C1 carbons but methyl (CH_3) carbon is formed preferentially from C6 carbons. From C1 labelled glucose, labelled carbon ends up as carboxylate (COO^-) carbon in glycolate, but from C6 labelled glucose the labelled carbon ends up as alcoholic (CH_2OH) carbon. The production of acetate and formate also discriminates between the C1 and C6 label. For the lignins the dissolution rates are *Corymbia calophylla* > *Eucalyptus marginata* > *Callitris rhomboidea* which is the same order as their syringyl contents. By means of carbon balances and solid state NMR spectroscopy it has been established that for *Callitris rhomboidea* aromatic carbon is rapidly hydroxylated on initial dissolution and converted to other carbon types. This differs from the angiosperm lignins where reactions of aromatic carbons are much slower.

1. Introduction

Elsewhere we [1–6] have published studies on organic matter in a plant operating at 145-150°C and a plant operating at around 250-255°C. The organic matter was investigated by separation on the basis of molecular weight by dialysis and analysis by spectroscopic (nuclear magnetic resonance and Fourier transform infrared spectroscopy) and pyrolysis techniques (thermogravimetric analysis, differential scanning calorimetry and pyrolysis gas chromatography).

The organic matter in Bayer liquors from a refinery operating at 250–255°C differs from that in a refinery operating at 150°C. Not unexpectedly, the material has a lower average molecular weight in the higher temperature process because many of the larger molecules are degraded to smaller molecular weight material. Upon pyrolysis the <1.2kD fraction appears to be mainly hydroxybenzene carboxylic acids and structurally resembles the highly oxidised humic acids that are found in podsols. However, some of this small molecular weight material forms molecular aggregates which behave during dialysis as if they have larger molecular weights. This aggregation behaviour affects water holding capacity. The 12-25kD fractions appear to be material more akin to kerogen while material of higher molecular weight behaves as a soluble char. Not surprisingly, pyrolysis products from the different molecular weight fractions differ and the differences are temperature dependent. Novel findings were that the 6-12kD fraction produces the most aromatic hydrocarbons and heteroaromatic hydrocarbons but also significant amounts of the less toxic materials such as aromatic carboxylic acids, alcohols, aldehydes and ketones. The less toxic materials are also produced by the fractions of lower molecular weight, but the higher molecular weight material is less volatile and produces little identifiable matter at this temperature. At 425°C all pyrolysis fractions start yielding significant amounts of aldehydes and ketones and the <1.2kD fraction produces large amounts of hydroxybenzoic acids. As the temperature is raised further to 450°C volatiles from the 25–50kD fraction particularly alcohols and aliphatic hydrocarbons become important. By 500°C all fractions contain significant quantities of aromatic hydrocarbons, phenols, carboxylic acids, alcohols, nitriles and aldehydes and ketones.

In this paper we present preliminary results which show the origin of these molecular weight fractions. The major plant matter types entering a refinery are lignins and carbohydrates. In this work three Klason lignins have been prepared from *Callitris rhomboidea* plants (a gymnosperm) and the roots of *Corymbia calophylla* and *Eucalyptus marginata* (both angiosperms).The dissolution of these materials in 3.5M sodium hydroxide at 145°C has been studied in order to understand β-O-4 aromatic carbon cleavage in lignin linkages, producing syringyl and guaiacyl units. In addition the carbohydrate fractions from these plants have been studied and there decomposition products followed. To elucidate mechanisms some ^{13}C labelled compounds have been investigated. Full details of these experiments will be published elsewhere [7–9] and are available in a thesis [10].

2. Experimental

2.1 *Plant species used*

The genus *Corymbia* comes from the family Myrtaceae. Taxonomists have recently renamed the genus that was previously classified as a Eucalypt. *Corymbia* are trees which mainly range in height from 10 to 15 m, although some species may reach almost 40 m. The species used in this

study is *Corymbia calophylla* (Marri). This angiosperm is predominantly found in association with bauxite deposits in Western Australia.

The genus *Eucalyptus* also comes from the family Myrtaceae. Over 700 Eucalypt species have been recognised, with only 4 species not endemic to Australia. Eucalypts dominate 124 million hectares of mallee (low growing) and open forest throughout Australia. They are large trees ranging from 10 to 40 m in height. *Eucalyptus marginata* (Jarrah), an angiosperm, is used in this study as it is this species that is almost exclusively found in the south west of Western Australia, particularly in association with bauxite deposits.

The genus *Callitris* comes from the family Cupressaceae. There are 140 species of *Callitris* worldwide with 17 of these species located in Australia. In this study the *Callitris* species chosen was the Australian cypress pine *Callitris rhomboidea*, commonly known as Port Jackson pine. *Callitris rhomboidea*, a gymnosperm, is a slender shrub or small tree that is 3 to 6 m in height. They often occur in association with a range of Eucalypt species and for this reason were used in this study.

2.2 *Isolation of plant components*

Plant components were isolated from *Callitris rhomboidea* (leaves, stems and roots of two year old plants), and *Eucalyptus marginata* and *Corymbia calophylla* (roots). The *Callitris rhomboidea* plants were obtained from a nursery and the *Eucalyptus marginata* and *Corymbia calophylla* roots were from a bauxite mine in Jarrahdale, Western Australia. The plant material was soaked overnight in distilled water and then washed thoroughly to remove soil. The three species were finely chopped, blended and freeze-dried at –55°C and 26.7 Pa and the batches (10 g) of each dried plant sample (200 g in total) were ring-milled in a tungsten carbide ring-mill carried out on an N. V. Tema ring-mill shaker (Type T.100), at 50 Hz per cycle. Each batch was milled for 1 to 2 min, then the contents were sieved to pass a 150 μm^2 grid. A sample of each ring-milled plant (40 g) was extracted in a soxhlet apparatus with a sequence of (1) absolute ethanol/toluene (1:2 v/v) for 48 h; (2) absolute ethanol (96% v/v) for 48 h; and (3) distilled water for 10 days (water-soluble, carbohydrate extract).

During the water extraction the water was changed every 3 days.The residual material was washed with acetone and dried in an oven at 65°C for 12 h. Extracts (1) and (2) were dried under vacuum at 26.7 Pa and 40°C while extract (3) was freeze-dried at 26.7 Pa and –55°C. The dried extracts were weighed and stored in a dessicator over silica gel.

Table 1 — Yields of extracts (% wt/wt) (errors are calculated as one standard deviation within the mean).

	Yields of extracts (% wt/wt)		
	1	2	3
Callitris rhomboidea	15.6±1.6	1.2±0.1	5.9±0.9
Corymbia calophylla	4.6±0.6	1.8±0.5	11.6±0.7
Eucalyptus marginata	1.6±0.8	0.4±0.1	2.9±1.1

2.3 *Isolation of Klason lignin*

A sub-sample (10.00 g) of each dried residual plant material was ground in a mortar and pestle and digested in 5% w/v sodium hydroxide (600 mL) under nitrogen (to avoid oxygen uptake) with constant stirring for 5 h at 50°C in a silicon oil bath. While still hot, glacial acetic acid (43.0 mL) was added and the solution was filtered. The residue was then washed until the washings were neutral to pH paper. This residue was dried in an oven at 65°C.

The dried residue (2-5 g) was treated with sulphuric acid 72% v/v (40.00 mL) for 12 h at room temperature, after which time distilled water (1.5 L) was added and the solution was refluxed for 4 h. This solution was then filtered while hot through a pre-weighed glass sintered crucible (No.3). The residue (Klason lignin) was washed with distilled water until the outlet was neutral to pH paper, then it was dried and weighed.

2.4 *Dissolution under Bayer conditions*

The digestions were carried out using the Parr reactor described elsewhere [7–10]. Lignins or carbohydrates of *Callitris rhomboidea, Corymbia calophylla* and *Eucalyptus marginata*, or labelled glucose compounds were were added to 3.5 M sodium hydroxide (10.00 mL), purged previously with nitrogen at room temperature in the Parr bomb reactor. The masses used correlated directly to 30 g/L total organic carbon (TOC). The bomb was sealed under 5.2×10^5 Pa of nitrogen and heated on a silicon oil bath at 145°C (±3°C). The temperature dropped to 120°C and then rose to 145°C in 30 min. The bomb was then held at this temperature for 0 h, 5 h, 24 h, 50 h and 96 h for the lignins and 0 h, 1.5 h, 14 h, 24 h and 48 h for the water-soluble carbohydrates. After each digestion the bomb was cooled for 5 min under cold tap water and the charge was emptied into distilled water (300 mL). The clear dark brown solution (310 mL) was passed through a H^+ cation-exchange column (Amberlite 120, 60 cm × 2 cm) to ensure it was in the protonated form and eluted with distilled water (200 mL). Preliminary studies showed that the total carbohydrate material (as a solid) could not be isolated in this form since many of the low molecular weight free acids were very volatile when rotary evaporated and significant losses were incurred during freeze-drying. To avoid this loss, the eluant pH was adjusted to 7.2 with 0.1 M sodium hydroxide and the solution freeze-dried at –55°C and 26.7 Pa overnight, then weighed.

The percentage yield of extract was determined at each digestion time on an ash free basis as:

%yield = 100 × [(weight of extract (g) – wt of ash in extract (g)) / (wt of biomaterial (g) – wt of ash in biomaterial (g))]

Details of the techniques used for analysis are given elsewhere.

3. Results and Discussion

3.1 *Lignins*

For all three lignins, dissolution occurs rapidly over the first 5 h then levels off after 50 h but does not fit a simple exponential decay. The data is best fitted to three empirical equations of the form:

$c_A = a + b \exp(-t/x) + c \exp(-t/y)$ where c_A is the concentration of residual lignin.

For *Callitris rhomboidea*, the line of best fit is:

$$c_A = 19.54 + 11.68e^{(-t/0.760)} + 23.19e^{(-t/19.68)}$$

For *Corymbia calophylla*, the line of best fit is:

$$c_A = 5.817 + 51.01e^{(-t/1.131)} + 23.68e^{(-t/8.629)}$$

And for *Eucalyptus marginata*, the line of best fit is:

$$c_A = 4.504 + 23.92e^{(-t/0.710)} + 48.57e^{(-t/16.06)}$$

The fact that the kinetics are not single order in lignin and need to be expressed effectively by a series of exponentials suggests that more than one bond is broken during dissolution, and that these break at different rates. It also suggests that there are different concentrations of these bonds and / or different bonds are involved for different lignins.

The integration of NMR data for the residues and extract fractions respectively, after correction for relaxation in itself is not particularly useful except they show trends in dissolution. However, by combining yield data it is possible to determine changes in structural group content as the original lignin dissolves. The amount of carbon in any functional group (Σf_C) is given in g/100g of original lignin by:

$$\Sigma f_C = [(\%\ C_{residue}\ f_{C\ residue}\ \%yield_{residue}) / 100] + [(\%\ C_{extract}\ f_{C\ extract}\ \%yield_{extract}) /100] \quad \text{eq 1}$$

This data is shown in Table 2. Here $\%C_{residue}$ and $\%C_{extract}$ are the percentage carbon in each Klason lignin, in the residue or extract respectively. The parameter f_C is the fraction of a particular carbon type in the residue or extract from integration of relaxation. Corrected solid-state NMR spectrum and % $yield_{residue}$ and % $yield_{extract}$ are the yields of the residue or recovered extract respectively**.**

For *Callitris rhomboidea* there appears to be an initial reaction which involves loss of 22% carbon as aromatic and methoxy carbon. Aromatic carbon drops by 53% of the original aromatic carbon. Some aromatic carbon must be converted by base to gas, carbonate or other potential volatiles probably carbon dioxide or small volatile molecules lost in work up. There is however an increase in aliphatic carbon. This has been described previously by us using syringyl and related compounds as hydroxylation followed by ring opening but with carbon capture. This probably occurs by intramolecularly captured hydrogen generated in any base catalysed organic matter oxidation reaction (schematically for a carboxylic salt, $RCH_3 + H_2O + NaOH \rightarrow 6H\cdot + RCOONa$). Table 2 shows that only a small amount (5% total) of further gasification occurs for *Callitris rhomboidea* with increasing time. The same processes appear to be occurring for *Corymbia calophylla* and *Eucalyptus marginata*. For these two lignins 11-12% is volatilised. The trend in loss of aromatic carbon is *Callitris rhomboidea* > *Eucalyptus marginata* > *Corymbia calophylla.* For *Corymbia calophylla* there is no loss.

These results are confirmed by the change in methoxy content. There is an initial rapid loss for *Callitris rhomboidea* due to aryl ring opening. For all three lignins this continues but at a much slower rate, if at all, and aromatic ring decomposition stops. The most interesting feature of Table 2 is the decrease in alkoxy carbon. *Callitris rhomboidea*, which has the lowest apparent content (6.4%), has a value of only 2.0% after 96 h. *Eucalyptus marginata* has 9.7% carbon of this type but shows a loss to 4.3% and a faster rate of dissolution. On the other hand *Corymbia calophylla* has 13.0% O-alkyl carbon and this reduces to 6.3%. Most of this loss is during the initial dissolution, and for *Corymbia calophylla*, O-alkyl cleavage is almost over after initial reaction but for the other lignins the reaction continues at a slower rate.

Although our results show that the rate of dissolution is clearly dependent on the syringyl content, the electron donating ability of a second methoxy group on the aryl ring would however destabilise the β-O-4 transition state through the 4 position, slowing the rate. However it is the gymnosperm which dissolves slowest not the angiosperms. A possible explanation is that because the methoxy group in gymnosperms can be replaced by a di-aryl linkage, this holds the lignin together preventing dissolution. However it is difficult to see how hydroxide slowly breaks this linkage and it appears dissolution requires the β-O-4 linkage to hydrolyse. Perhaps, in the early loss of aromatics there are internal rearrangements from β-O-4 to α-O-4 which then hydrolyse slower. Such reactions have been documented for model lignin dimers.

It is well established that many polyhydroxyphenols and oxidation products containing carboxylic acid functionalities can interfere with precipitation of both alumina and the by product sodium oxalate. The results show that the degree of β-O-4 linkages and hence the production of these phenols is plant specific, indeed Klason lignin type specific. Hence any technology which can remove specific plants may be of value.

3.2 *Carbohydrates*

Table 3 shows the yields of water-soluble extracts. They range from 11.6% wt/wt for *Corymbia calophylla* to 2.9% wt/wt for *Eucalyptus marginata.* Yields of extracts as a function of dissolution time in 3.5 M sodium hydroxide at 145°C are also shown in Table 3. These are shown on a dry ash free basis to determine loss in organic matter since ash contents are variable. This data shows that after 48 h *Callitris rhomboidea* and *Corymbia calophylla* had lost

Table 2 — Yield of different carbon types (g/100g original lignin) in residues and extracts.

Extraction time (h)	Assignment					
	Alkyl	Methoxy	O-alkyl	Aromatic	Carboxyl	S
Callitris rhomboidea[a]	15.1	4.1	6.4	30.4	2.8	58.8
0	21.0	2.8	6.5	14.3	1.2	45.8
1	21.0	3.4	4.9	18.6	0.9	48.8
5	16.1	3.3	5.2	18.1	1.1	43.8
24	20.2	3.5	3.2	18.7	0.8	46.4
50	17.0	2.8	2.1	22.8	1.7	46.4
96	15.6	2.7	2.0	21.2	1.6	43.1
Eucalyptus marginata[a]	13.2	7.0	9.7	27.0	1.0	57.9
0	13.8	6.1	9.6	21.3	0.6	51.4
1	12.8	6.9	6.6	25.7	1.2	53.2
5	13.7	5.8	5.2	24.4	1.3	50.4
24	13.9	5.4	3.4	25.5	0.9	49.1
50	16.2	4.8	4.7	23.4	0.9	50.0
96	14.6	4.2	4.3	27.2	1.1	51.4
Corymbia calophylla[a]	14.3	5.6	13.0	27.0	1.0	60.9
0	10.5	7.5	6.5	28.3	0.8	53.6
1	11.2	5.8	8.8	22.7	0.8	49.3
5	11.1	6.0	6.6	25.0	1.2	49.9
24	14.3	6.7	7.3	23.0	0.5	51.8
50	11.8	6.4	5.5	27.3	0.7	51.7
96	13.1	6.1	6.3	26.3	0.7	52.5

[a] Calculated from NMR spectrum and % carbon in lignin

10.5 and 16.1% wt/wt of organic material respectively while *Eucalyptus marginata* has lost considerably more, 29.7% wt/wt.

Gas chromatography mass spectrometry (GC/MS) chromatographs of the tetramethylsilane (TMS) derivatives of these extracts were useful. Each water-soluble extract digestion yielded a wide variety of compounds the majority of which were mono-, di- and tri- carboxylic and hydroxy aliphatic and aromatic carboxylic acids of low molecular weight and some carbohydrate species (Table 4). These types of species are known to accumulate in the lower molecular weight range of isolated humic substances from Bayer process liquor making up to 75% wt/wt isolated organics however little is known about their build up.

Compounds can be grouped into several classes according to their formation or destruction kinetics. These are those which: 1) decrease in concentration with time, 2) remain constant in concentration with time, 3) increase with time and have complex profiles. Important compounds will be discussed here to deduce trends. Carbohydrates such as D-xylose (a), β-D-arabofuranose (b), D-mannose (c), α-D-arabopyranose (d), D-lyxose (e), xylitol (f), D-ribose (g), D-glucose (h), D- altrose (i), D-allose (k), and α-D-glucopyranoside (l) decrease in concentration for all three digestions. Furans such as 2-furancarboxylic acid also decrease. It is well known that furans are derived from thermal decomposition of carbohydrates. Hence they are an intermediate that is rapidly decomposed. Polyalcohol structures are also known poisons[11]. The aliphatic chain structures could form alcoholic species that are undesirable. It does seem that the conditions are harsh enough to make these not a problem that arises from the lignin component of plant tissue. However, it is significant that the carbohydrate glucitol (j) remains almost constant in concentration for all three digestions. Carbohydrate stability was also observed by NMR. Almost all the small substituted aliphatic carboxylic acids increase in concentration. Lactic acid, hydroxyacetic acid, 2-hydroxybutanoic acid, propanedioic acid, 4-hydroxybutanoic acid and 2-hydroxypropanedioic acid are all examples. This is also true of oxalic acid. With one or two notable exceptions no significant differences were observed between the three plants, except concentrations differ.

During work up, compounds such as alpha hydroxy carboxylic acids while stable as sodium salts could almost certainly be potentially volatile in various amounts if acidified at room temperature in the isolation process required for mass balances since they form lactones. This was initially found to be a problem as yields obtained were variable and low. Experiments showed that lactic acid was a particularly difficult compound to isolate quantitatively. On acidification on the cation exchange column lactic acid forms a lactone (b.p = 142°C). This is readily removed along with water during volatilization. This is particularly true if low pressure rotary evaporator or freeze drier vacuums are used when preparing high concentrations of materials prior to their methylation and subsequent gas chromatographic analysis. The problem of quantitation was solved by titrating the extract after acidification to a pH of 7.2. This insured the lactic acid was in the salt form (without excess sodium) and that dimerisation to form the lactone and its subsequent volatilisation did not take place. The impact of all these species on the process is not in the open literature, but it is well recognised that low molecular weight aliphatic and aromatic carboxylic acids with adjacent, multiple acidic hydroxyl groups are highly detrimental to the precipitation sequence.

Table 3 — Yield data (% wt/wt) for *Callitris rhomboidea* (gymnosperm), *Corymbia calophylla* (angiosperm) and *Eucalyptus marginata* (angiosperm) water-soluble digestion products as a function of extraction time (h).

Extraction time (h)	Yield (% wt/wt) organic
Callitris rhomboidea	5.9[a]
0	97.8
1.5	93.9
5	96.2
14	88.9
24	90.7
48	89.5
Corymbia calophylla	11.6[a]
0	96.4
1.5	97.4
5	94.5
14	94.8
24	89.8
48	83.9
Eucalyptus marginata	2.9[a]
0	99.8
1.5	99.8
5	82.8
14	82.7
24	78.9
48	70.3

a) extract from plant

As noted above, the compounds formed from lignin during Bayer processing are different than many of the compounds shown here. Hence it is clear that selective removal of carbohydrates before Bayer processing will influence the nature of organics present in the Bayer liquor and this may affect yields. Water washing is obviously a potential methodology but drying costs could be prohibitive. Other options are thermal maturation. Table 5 shows the ^{13}C distributions of all the products identified from digestion of unlabelled and labelled 1-^{13}C-D-glucose and 6-^{13}C-D-glucose after 1 h digestion at 145°C in 3.5 M NaOH.

The mechanism by which carbohydrates yield small molecular weight compounds however is not simple. This is best illustrated by labeling studies which can indicate where carbons on different parts of the carbohydrate molecule end up. Table 5 shows enhanced yields of ^{13}C in products relative to that in the original unlabelled mixture of products. It is clear that these values are greater than one, and that label from 1-^{13}C-D-glucose and 6-^{13}C-D-glucose ends up in all carbons in the products.

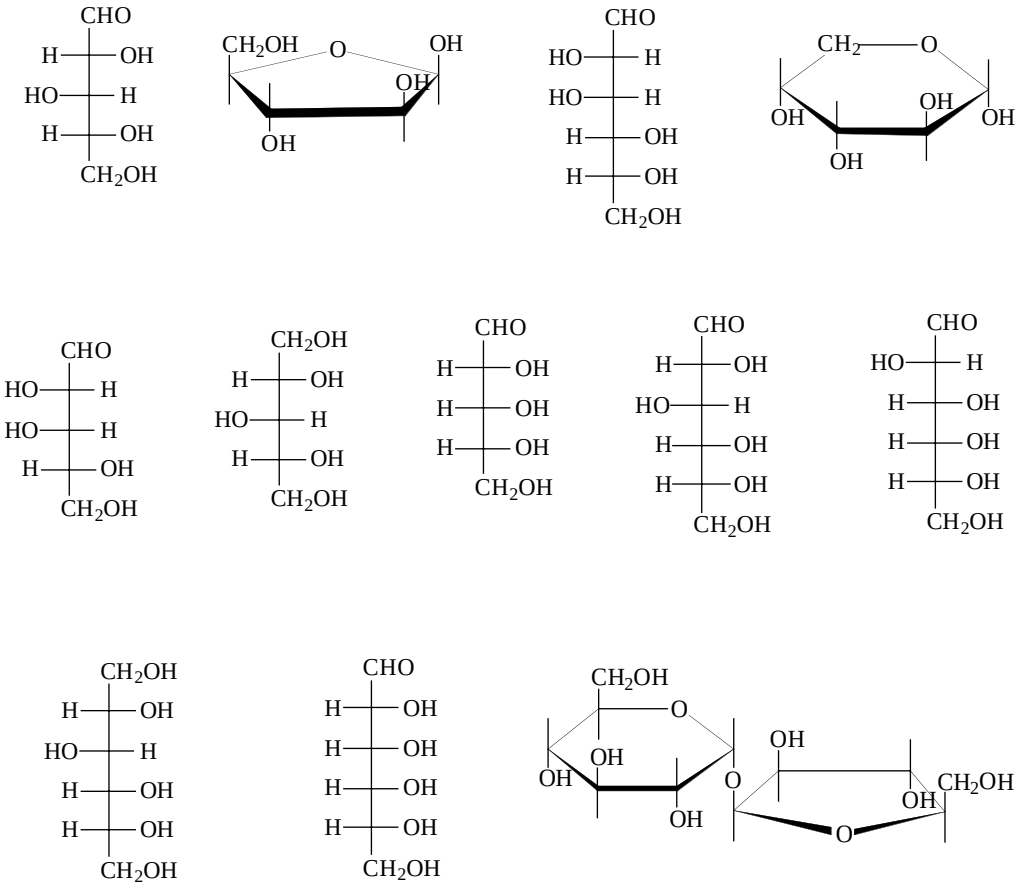
It is shown in Table 5 that labelled lactate is the predominant compound formed from both 1-^{13}C-D-glucose and 6-^{13}C-D-glucose under Bayer simulated laboratory conditions. The labelling occurs at all three lactate carbons but in different proportions. Table 5 shows that from 1-^{13}C-D-glucose the production of C1 labelled lactate (56.1%) is favoured while from 6-^{13}C-D-glucose the production of C3 labelled lactate (57.1%) is favoured. The distribution of label in other compounds is also very dependent on the position of label in glucose. In formate more label appears when a different source is used. In acetate more label occurs on methyl carbon from 1-C labeled than 6-C labeled carbon.

4. Conclusions

1. The dissolution rates at 145°C in 3.5 M sodium hydroxide for three lignins is best described by a double exponential equation at differ. For *Callitris rhomboidea*, the line of best fit is $c_A = 19.54 + 11.68e^{(-t/0.760)} + 23.19e^{(-t/19.68)}$, for *Corymbia calophylla* the line of best fit is $c_A = 5.918 + 51.01e^{(-t/1.131)} + 23.68e^{(-t/8.629)}$ and for *Eucalyptus*

Table 4 — Identified trimethylsilyl (TMS) derivatives from GC-MS of water-soluble digestions

	Compound		Compound		Compound
1	2-Hydroxypropanoic acid (lactic acid)	20	n-Pentadecane	39	3,4-Dihydroxybenzoic acid
2	Hydroxyethanoic acid (hydroxyacetic acid)	21	2-Hydroxybutanedioic acid (malic acid)	40	2-Hydroxy-1,2,3-propanetricarboxylic acid
3	3,7-Dimethyldecane	22	2,3,4-Trihydroxybutanoic acid	41	2,4,5,6-Tetrahydroxyhexanoic acid
4	2-Hydroxybutanoic acid	23	2-Hydroxypentanedioic acid	42	2,4,5-Trihydroxy-2-hydroxymethylpentenoic acid
5	Ethanedioic acid	24	D-Xylose	43	2,4,5-Trihydroxy-2-hydroxymethylpentanoic acid
6	2-Furancarboxylic acid	25	β-D-Arabofuranose	44	4-Hydroxybenzenepropanoic acid
7	Propanedioic acid	26	2,4-Dihydroxy-2-hydroxymethylbutanoic acid	45	D-Glucose
8	4-Hydroxybutanoic acid	27	D-Mannose	46	2,4,5-Trihydroxyhexanedioic acid
9	Benzoic acid	28	2,4-Dihydroxy-4-hydroxymethylpentanoic acid	47	D-Altrose
10	4-Methyltetradecane	29	α-D-Arabopyranose	48	D-Glucitol
11	Phosphoric acid	30	2-Hydroxyhexanedioic acid	49	3,4,5-Trihydroxybenzoic acid
12	2-Butenedioic acid (Z)	31	2,5-Dihydroxypentanoic acid	50	D-Allose
13	Succinic acid	32	D-lyxose	51	4-Hydroxy-3-methoxybenzenepropanoic acid
14	n-Dodecane	33	1,2,3-Propanetricarboxylic acid (tricarballylic acid)	52	D-Gluconic acid
15	2,3-Dihydroxy-2-methylpropanoic acid	34	Xylitol	53	3,4-Dihydroxycatachollactate
16	2,3-Dihydroxypropanoic acid	35	1,2,3-Propenetricarboxylic acid	54	Hexahydroxycyclohexane (myo-inositol)
17	2-Hydroxypropanedioic acid	36	4-Hydroxy-3-methoxybenzoic acid	55	Docosanoic acid (STANDARD) (100%)
18	2,4-Dihydroxybutanoic acid	37	D-Ribose	56	α-D-Glucopyranoside
19	3,5-Dihydroxy-3-methylpentanoic acid	38	1,4-Benzenedicarboxylic acid		



marginata the line of best fit is $c_A = 4.504 + 23.92e^{(-t/0.710)} + 48.57e^{(-t/16.06)}$ where c_A is the concentration of residual lignin. The rate of dissolution is *Corymbia calophylla* > *Eucalyptus marginata* > *Callitris rhomboidea* which is directly proportional to their syringyl content.

2. Carbohydrates are an important potential source of small molecular weight organics in Bayer liquors. They are responsible for the formation of a range of substituted aliphatic acids. Lactic acid, hydroxyacetic acid, 2-hydroxybutanoic acid propanedioic acid, 4-hydroxybutanoic acid and 2-hydroxypropanedioic acid are examples. By means of carbon balances and solid state NMR spectroscopy it has been established that for the gymnosperm lignin, aromatic carbon is rapidly hydroxylated on initial

Table 5 — ^{13}C distribution (%) and enhanced yield in products from unlabelled digested α-D-(+)-glucose and labelled 1-^{13}C-D-glucose and 6-^{13}C-D-glucose digestions in 3.5 M NaOH for 1 h at 145°C.

Product	Chemical shift δ (ppm)	Unlabelled α-D-(+)-glucose digestion (1 h)	1-^{13}C-D-glucose digestion (1 h)	6-^{13}C-D-glucose digestion (1 h)	Enhanced yield[a] 1-^{13}C-D-glucose digestion (1 h)	Enhanced yield[a] 6-^{13}C-D-glucose digestion (1 h)
Lactate COO^- | CHOH | CH_3	 185.6 | 71.1 | 23.2	 28.7 | 24.8 | 21.6	 49.5 | 1.0 | 37.8	 24.2 | 1.1 | 33.7	 155.2 | 3.7 | 157.9	 76.2 | 3.7 | 140.5
Glycolate COO^- | CH_2OH	 184.6 | 66.5	 2.7 | 2.8	 3.5 | 0.1	 2.9 | 31.7	 116.6 | 3.7	 96.4 | 1019.2
Acetate COO^- | CH_3	 184.1 | 26.3	 0.1 | 0.1	 0.1 | 1.3	 0.1 | 0.4	 90.0 | 1169.8	 90.0 | 359.9
Ethanol CH_2OH | CH_3	 57.0 | 17.6	 3.0 | 3.2	 0.1 | 0.3	 0.1[b] | 0.1	 2.8 | 8.3	 2.8 | 2.8
Formate $HCOO^-$	173.8	0.1	1.3	0.5	1169.8	449.9
Carbonate CO_3^{2-}	170.9	9.7	0.4	0.4	3.7	3.7
Other roducts		3.2	4.6	4.8	129.5	135.0

[a] Enhanced yield is defined as yield of functional group in ^{13}C labelled experiment (g/100g) / yield in unlabelled experiment (g/100g) = [(% distribution in labelled experiment (g/100g) x fraction of label enhancement in glucose, 0.99) / (% distribution in unlabelled experiment (g/100g) x fraction of natural label enhancement (0.011 for ^{13}C in natural glucose))]. [b] approximate, trace only.

dissolution and transformed into other carbon types. This differs from the angiosperm.

3. Not surprisingly carbohydrates are rapidly decomposed in the process and converted to compounds such as those described above. Significantly though glucitol remains and is important. Glucitol is shown to be a particularly stable carbohydrate to digestion and may therefore play an important role in Bayer poisoning processes.
4. Using ^{13}C label, rearrangements in alkaline solution have been demonstrated under Bayer conditions. They show that in the formation of lactate from glucose the carboxylate (COO^-) carbon is formed preferentially from C1 carbons but methyl (CH_3) carbon is formed preferentially from C6 carbons. From C1 labelled glucose, labelled carbon ends up as carboxylate (COO^-) carbon in glycolate, but from C6 labelled glucose the labelled carbon ends up as alcoholic (CH_2OH) carbon. The production of acetate and formate is almost indiscriminant between the C1 and C6 label and primarily produces carboxylate labelled carbon.

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