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Organosolv delignification of willow: Kinetics, recovery and use

by

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A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy in Engineering

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Abstract

Pretreatment is critical to the conversion of biomass into valuable chemicals. Willow (Salix spp), consisting mainly of polysaccharides and lignin, was used in this study of lignin in three stages. The delignification reaction using the organosolv process, the recovery of lignin from organosolv spent liquor by precipitation and dissolved air flotation, and the use of lignin for polymer production were studied.

A novel method of determining delignification activation energy using fewer pulping experiments was developed. Several reaction rate constants were determined during a single pulping run by examining kinetics at different reaction times with a slowly increasing temperature. The effects of changing ethanol concentration were then investigated using this method. Only the change in pH caused by changing ethanol concentration had a significant effect on delignification rate.

Prehydrolysis has been used to selectively remove hemicellulose prior to organosolv pulping. De-ashing is a treatment to remove the acid-neutralising components (ash and extractives) of biomass. It was previously thought that organosolv delignification proceeded faster after prehydrolysis due to increased accessibility of solvent to lignin. However, prehydrolysis did not result in faster subsequent delignification compared to de-ashing. De-ashing and prehydrolysis treatments removed the acid neutralising components of wood while prehydrolysis also removed a portion of the polysaccharides. It may be the lower pH resulting from prehydrolysis that increases subsequent organosolv delignification rate compared to untreated feedstock.

Upon dilution of organosolv black liquor, lignin forms a precipitate, which is typically removed by filtration or centrifugation. The use of dissolved air flotation (DAF) presents a low cost alternative that utilizes the hydrophobicity of organosolv lignin. The parameters important to the dissolved air flotation of organosolv lignin were studied using fractional factorial design. Fastest flotation occurs when saturation pressure is high and black liquor-water mixing is rapid resulting in the redistribution of micro-bubbles.
during floc formation. Precipitation must occur below 35°C to cause sufficient flocculation.

Phenol formaldehyde resins were prepared with 20% w/w of the phenol replaced by lignin (lignin-PF resin). Lignin-PF resins prepared from the most depolymerised lignin had comparable strength to pure PF resin when strength was compared using a lap joint test.
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# Table of Contents

Abstract .............................................................................................................................. ii
Acknowledgements .......................................................................................................... iv
Table of Contents .............................................................................................................. v
List of Tables .................................................................................................................. viii
List of Figures ................................................................................................................... ix
List of Equations .............................................................................................................. xi
Notation ............................................................................................................................ xii
Glossary .......................................................................................................................... xiii

1 **Introduction** ............................................................................................................... 1
   1.1 Technical objectives .................................................................................................. 3
   1.2 Scope ........................................................................................................................... 4

2 **Background** ............................................................................................................... 6
   2.1 Biorefining ................................................................................................................... 6
      2.1.1 Fuel ethanol production ....................................................................................... 6
      2.1.2 Wood chemistry .................................................................................................. 7
         2.1.2.1 Lignin ........................................................................................................... 9
      2.1.3 Conversion of wood to ethanol ............................................................................ 12
      2.1.4 The biorefining concept ..................................................................................... 14
   2.2 Pretreatment ............................................................................................................. 16
      2.2.1 Pretreatment technology for lignocellulosics ....................................................... 16
   2.3 Organosolv pulping .................................................................................................. 19
      2.3.1 Reactors and reaction methods ............................................................................. 27
      2.3.2 Re-condensation ............................................................................................... 28
      2.3.3 Mechanisms of organosolv delignification ......................................................... 31
      2.3.4 Kinetic parameters of organosolv delignification .............................................. 34
      2.3.5 The effect of pH during ethanol-water pulping ................................................. 36
      2.3.6 Lignin and polysaccharide selective pulping sequences .................................... 39
   2.4 Problem statement .................................................................................................. 43

3 **Organosolv materials and methods** ........................................................................... 45
   3.1 Feedstock preparation .............................................................................................. 45
      3.1.1 Re-precipitation experiments .............................................................................. 45
      3.1.2 Autocatalysed, buffered and catalysed delignification ....................................... 46
         3.1.2.1 Autocatalysed delignification feedstock ....................................................... 46
         3.1.2.2 Buffered and catalysed delignification feedstock .......................................... 47
         3.1.2.3 Klason lignin analysis ................................................................................... 47
         3.1.2.4 De-ashing .................................................................................................... 50
         3.1.2.5 Prehydrolysis .............................................................................................. 52
      3.1.3 Klasson lignin analysis ....................................................................................... 47
   3.2 Organosolv pulping .................................................................................................. 54
      3.2.1 Lignin re-precipitation experiments .................................................................. 54
# Table of Contents

7.1 Background ......................................................................................................................... 151
  7.1.1 Lignin products ........................................................................................................... 152
  7.1.2 Phenol formaldehyde resin and replacing phenol with lignin ..................................... 154
  7.1.2.1 Lignin-PF resin synthesis .................................................................................. 155
  7.1.2.2 Determining curing activation energy by differential scanning calorimetry (DSC) .................................................................................................................. 156
  7.1.2.3 Lignin-PF resin strength .................................................................................. 158
  7.1.3 Analysis of lignin ........................................................................................................... 159

7.2 Materials and methods ......................................................................................................... 160
  7.2.1 Resin synthesis for screening replacement level and curing time ............................... 161
      7.2.1.1 Resin synthesis procedure ........................................................................... 161
  7.2.2 Resin synthesis for testing different lignins ................................................................. 161
      7.2.2.1 Resin synthesis procedure ........................................................................... 163
  7.2.3 Differential scanning calorimetry (DSC) ..................................................................... 163
  7.2.4 Lap joint preparation and tensile testing ...................................................................... 164
  7.2.5 Lignin characterisation ................................................................................................. 165
      7.2.5.1 UV visible spectrophotometry ..................................................................... 165
      7.2.5.2 Size exclusion chromatography (SEC) .......................................................... 166
      7.2.5.3 2-D nuclear magnetic resonance (2D NMR) .................................................. 166

7.3 Results and discussion ......................................................................................................... 166
  7.3.1 Screening tests ............................................................................................................. 167
      7.3.1.1 Screening resin synthesis ............................................................................. 167
      7.3.1.2 Lap joint strength testing ............................................................................. 167
  7.3.2 Testing PF resins containing different lignins .............................................................. 169
      7.3.2.1 Resin synthesis ............................................................................................. 170
      7.3.2.2 Curing kinetics by dynamic DSC .................................................................. 171
      7.3.2.3 Strength testing of resin containing different lignins ..................................... 173
  7.3.3 Lignin characterisation ................................................................................................. 177
      7.3.3.1 UV visible absorbance ................................................................................ 178
      7.3.3.2 2-D Nuclear absorbance ............................................................................. 179
      7.3.3.3 Size exclusion chromatography ................................................................. 183

7.4 Conclusions ......................................................................................................................... 183

8 Summary of conclusions ....................................................................................................... 185
  8.1 Organosolv pulping ......................................................................................................... 185
  8.2 Lignin recovery ................................................................................................................ 186
  8.3 Lignin use in phenol formaldehyde resin ........................................................................ 186

9 Future recommendations ...................................................................................................... 187

10 References ........................................................................................................................... 189

Appendix 1. Chip size analysis ................................................................................................. 211
Appendix 2. HPAEC-PAD data ............................................................................................... 213
Appendix 3. Pulping conditions and final lignin content ......................................................... 219
Appendix 4. Mathematical model ............................................................................................ 221
Appendix 5. 2-D NMR spectra ............................................................................................... 228
Appendix 6. Size exclusion chromatography data ................................................................. 235
Appendix 7. DSC thermograms .............................................................................................. 250
List of Tables

Table 2-1. Methods of pretreatment and typical solubilisation yield of hemicellulose and lignin .......... 17
Table 2-2. Activation energies of bulk delignification reported in literature. ........................................ 36
Table 3-1. Untreated Salix schwerinii composition using the modified NREL protocol. ................... 48
Table 3-2. Untreated S. schwerinii composition using the School of Biological Sciences (SBS) protocol, University of Auckland. .............................................................. 50
Table 3-3. De-ashed S. schwerinii composition by the modified NREL protocol. .............................. 51
Table 3-4. Untreated S. schwerinii composition using the School of Biological Sciences (SBS) protocol, University of Auckland. .............................................................................................................. 51
Table 3-5. De-ashed S. schwerinii composition by the modified NREL protocol. .............................. 51
Table 3-6. De-ashed S. schwerinii composition by the SBS protocol. .................................................... 51
Table 3-7. De-ashed S. schwerinii composition by the modified NREL protocol. .............................. 51
Table 3-8. De-ashed S. schwerinii composition by the SBS protocol. .................................................... 51
Table 3-9. Prehydrolysed S. schwerinii composition by the modified NREL protocol. .............................. 53
Table 3-10. Prehydrolysed S. schwerinii composition by the SBS protocol. ........................................ 53
Table 4-1. Delignification k values measured at different times and temperatures in 35% v/v ethanol. .... 80
Table 4-2. Delignification k values measured at different times and temperatures in 70% v/v ethanol. .... 81
Table 4-3. Activation energy and frequency factor of delignification in 35% and 70% Ethanol. .......... 82
Table 4-4. The kinetic parameter of delignification corrected for differences in [H+] between 30% and 50% v/v ethanol buffered pulping. ................................................................. 90
Table 4-5. Bulk rate constant of untreated and de-ashed willow delignifications corrected for [H+]. ........ 98
Table 4-6. Kinetic data for delignification of de-ashed willow at three temperature levels. .......... 108
Table 4-7. Kinetic data for delignification of prehydrolysed willow at 3 temperature levels. .............. 110
Table 4-8. Activation energy and frequency factor for delignification of de-ashed willow and prehydrolysed willow. ............................................................. 111
Table 4-9. Kinetic constants and effective temperatures for delignification of de-ashed willow. .......... 114
Table 4-10. Kinetic constants and effective temperatures for delignification of prehydrolysed willow. .... 115
Table 4-11. Activation energy and frequency factor for delignification of de-ashed willow and prehydrolysed willow. ............................................................. 116
Table 4-12. Forward and reverse reaction rate constants for each pulping experiment fit with a reversible first order model. ............................................................. 124
Table 6-1. Parameter values for the 2^6 factorial design. ................................................................. 142
Table 6-2. Level of parameters for the 2^6 factorial design. ................................................................. 142
Table 6-3. Value of parameters for the second set of factorial designed experiments. ....................... 143
Table 6-4. Level of parameters for the second set of factorial designed experiments. ....................... 143
Table 6-5. Precipitate volume ratio (mL/mL of black liquor) for each parameter at low and high level. .. 144
Table 6-6. Precipitate volume ratio (mL/mL of black liquor) for each parameter at low and high level. .. 144
Table 6-7. Precipitate volume ratio (mL/mL of black liquor) for each parameter at low and high level. .. 145
Table 6-8. Yield of precipitate for each parameter at low and high level (mg lignin/mL black liquor). .... 149
Table 7-1. Lignin samples for analysis and resin synthesis: extraction conditions and klason lignin content. .......................................................................................................................... 162
Table 7-2. Lignin samples for analysis only. ...................................................................................... 165
Table 7-3. Resin density and viscosity. .............................................................................................. 170
Table 7-4. Failure load at the 120s hot pressing time and statistical significance. ......................... 175
Table 7-5. Failure load at the 240s hot pressing time and statistical significance. ......................... 175
Table 7-6. Failure load at the 480s hot pressing time and statistical significance. ......................... 176
Table 7-7. Relative peak volumes of lignin structures by 2-D NMR. ................................................. 181
List of Figures

Figure 2-1. Components of wood. ................................................................. 8
Figure 2-2. Structure and labelling of phenyl-propanoid units comprising lignin. ......................................................... 9
Figure 2-3. Possible structure of softwood lignin indicating complexity. Adler [15]. ......................................................... 11
Figure 2-4. Fermentation and gasification routes for converting lignocelluliosics into ethanol. ................................. 12
Figure 2-5. Xu et al. [111] showing lignin precipitated after drying of ethanol-lignin solution on a wood fiber held by adhesive tape. .............................................................. 29
Figure 2-6. % lignin remaining (PLR) during HCl catalysed acetic acid pulping. Parajo et al. [84]. ................ 30
Figure 2-7. Solvolytic cleavage of an α-aryl ether linkage by nucleophilic substitution. R and R’=H or CH3; R’=another lignin unit; B=OH, OCH3 (basic species). McDonough [113]. ........................................ 31
Figure 2-8. Delignification kinetics showing three distinct phases. Shatalov and Periera [115]. ................. 32
Figure 3-1. 7L aluminium pressure cooker .................................................................................................. 52
Figure 3-2. 100mL batch organosolv reactor ................................................................................................. 55
Figure 3-3. Organosolv reactor consisting of the vessel and external recycle loop with heating element and motor driven circulating pump. .......................................................... 58
Figure 3-4. Cross-section of reaction vessel .................................................................................................. 59
Figure 4-1. Untreated S. alba .................................................................................................................................. 66
Figure 4-2. S. alba after organosolv treatment in 70% v/v ethanol and solvent removal at 200°C. ............ 67
Figure 4-3. SEM of willow treated at 180°C in 70% v/v ethanol for 80 minutes followed by ethanol removal at 180°C. ........................................................................................................... 68
Figure 4-4. SEM of willow treated at 180°C in 70% v/v ethanol for 80 minutes followed by ethanol removal at 180°C. Willow fiber showing spheres of lignin of size range 0.2-1µm. .......................................................... 68
Figure 4-5. S. alba after organosolv treatment at 200°C in 70% v/v ethanol and cooling to 40°C before solvent removal .................................................................................................................. 69
Figure 4-6. Effect of process temperature on structure of willow during 70% v/v ethanol pulping for 100 minutes at 180°C, 190°C and 200°C. ............................................................................. 71
Figure 4-7. Lignin concentration during autocatalysed pulping. ........................................................................ 73
Figure 4-8. Mass of lignin and polysaccharides in wood before and after treatment. .................................. 74
Figure 4-9. Comparison of inlet, outlet, effective and average temperatures. ................................................ 75
Figure 4-10. Effective temperature of packed bed reactor during each delignification. .................................. 76
Figure 4-11. Kinetic plot of delignification in 35% v/v ethanol. ........................................................................ 77
Figure 4-12. Kinetic plot of delignification in 70% v/v ethanol. ........................................................................ 78
Figure 4-13. Linear plot of ln(α) versus 1/T_g showing a linear regression with good correlation. .................. 82
Figure 4-14. Temperature control during buffered pulping in 30% and 50% v/v ethanol. .............................. 83
Figure 4-15. pH during buffered pulping in 30% and 50% v/v ethanol. ......................................................... 84
Figure 4-16. Mass of wood components before and after pulping in 30% v/v and 50% v/v ethanol. ............ 85
Figure 4-17. Mass of precipitate in liquor sample and final dissolved lignin based on a mass balance analysis of the pulp. Comparison of buffered 30% v/v and 50% v/v ethanol pulping. ................................. 87
Figure 4-18. Mass of dissolved solids in liquor sample and final dissolved total solids based on a mass balance analysis of the pulp. Comparison of 30% v/v and 50% v/v ethanol pulping. .................................................. 88
Figure 4-19. Lignin remaining in pulp as a fraction of input total mass. Comparison of buffered pulping in 30% v/v and 50% v/v ethanol. ........................................................................................................... 89
Figure 4-20. Kinetic plot of buffered pulping in 30% v/v and 50% v/v ethanol showing minimal difference in delignification rate. ............................................................................................................. 89
Figure 4-21. Effective temperature during catalysed pulping experiments .................................................... 93
Figure 4-22. Mass input and output of de-ashing and prehydrolysis treatments. ........................................ 94
Figure 4-23. De-ashed willow (A) and prehydrolysed willow (B). ............................................................... 95
Figure 4-24. pH of liquor samples from pulping at 180°C in 70% v/v ethanol. .............................................. 96
Figure 4-25. Kinetic plot of willow delignification at 180°C in 70% v/v ethanol and 0.04% w/w H2SO4. .... 97
Figure 4-26. Kinetic plot of willow delignification at 180°C in 70% v/v ethanol and 0.08% w/w H2SO4. .... 97
Figure 4-27. pH of liquor for delignification of willow in 70% v/v ethanol and 0.08% w/w H2SO4. ......... 100
Figure 4-28. % of lignin dissolved during pulping at the low temperature level, comparison of de-ashed and prehydrolysed willow delignification with 70% v/v ethanol and 0.08% w/w H₂SO₄.....................101
Figure 4-29. % of lignin dissolved during pulping at the mid temperature level, comparison of de-ashed and prehydrolysed willow delignification with 70% v/v ethanol and 0.08% w/w H₂SO₄.....................102
Figure 4-30. % of lignin dissolved during pulping at the high temperature level, comparison of untreated, de-ashed and prehydrolysed willow delignification with 70% v/v ethanol and 0.08% w/w H₂SO₄..............103
Figure 4-31. Mass remaining during treatment sequences, pulping at mid temperature level in 70% v/v ethanol with 0.08% w/w H₂SO₄ ..........................................................104
Figure 4-32. Percentage total solids dissolved in 70% v/v ethanol. Mid temperature level with preorganosolv treatment and high temperature level untreated.................................................................105
Figure 4-33. Mass flows of willow components (g/100g feed) during either de-ashing or prehydrolysis and then pulping at the mid temperature level in 70% v/v ethanol with 0.08% w/w H₂SO₄..........................106
Figure 4-34. Kinetic plot of delignification of de-ashed willow at different temperatures.......................108
Figure 4-35. Kinetic plot of delignification of prehydrolysed willow at different temperatures..............109
Figure 4-36. Relationship between temperature and rate constant for delignification of de-ashed willow and prehydrolysed willow.................................................................111
Figure 4-37. Calculation of rate constant from 7 points after neglecting the first 25 minutes of reaction. 113
Figure 4-38. Activation energy plot for delignification of de-ashed willow and prehydrolysed willow.....116
Figure 4-39. De-ashed willow delignifications showing a transition to residual phase kinetics ..........119
Figure 4-40. Prehydrolysed willow delignifications showing a transition to residual phase kinetics ...119
Figure 4-41. All other delignifications displaying a transition to residual phase kinetics ....................120
Figure 4-42. First order reversible model fit to pulping of de-ashed willow. ......................................123
Figure 4-43. First order reversible model fit to pulping of prehydrolysed willow. ...............................123
Figure 4-44. First order reversible model fit to other pulping experiments........................................124
Figure 4-45. Best fit of simple reversible model that is 1st order with respect to L₅ .........................127
Figure 4-46. Best fit of simple reversible model that is 2nd order with respect to L₅ .........................127
Figure 4-47. Data fitted with model for dissolution and re-condensation to residual lignin .........129
Figure 4-48. Model using re-condensed lignin fit to the data of Parajo et al. [84] .................................130
Figure 4-49. Data from literature fit with the L₅ to L₅ to L₅ reversible model .............................131
Figure 4-50. Model incorporating a second species of soluble lignin, L₅, L₅ ...............................132
Figure 6-1. Mechanisms of DAF. Rubio et al. [152] .................................................................137
Figure 6-2. Illustrates a final flotation volume of 6mL ..............................................................140
Figure 6-3. 50% clarification time of 35 minutes and 38 seconds ..................................................141
Figure 6-4. Effect of temperature on clarification time and final filtered yield during dissolved air flotation of organosolv lignin.................................................................146
Figure 6-5. Precipitates 24 hours after dilution. At 30°C (far left), an interface is visible. At 40°C (far right), no floated precipitate can be distinguished from the continuous phase..........................146
Figure 6-6. Effect of N₂ saturation pressure and black liquor-water addition rate on clarification time..148
Figure 7-1. Structure of lignin and position of formaldihyde addition onto phenol. R = H or O-CH₃ 154
Figure 7-2. Common linkages present in the structure of lignin....................................................160
Figure 7-3. Lap joint made from 0.6mm thick Rock maple veneer ................................................164
Figure 7-4. Failure load of lap joints after heat-pressing for 120 seconds at 145°C.............................168
Figure 7-5. Resin strength increase with time for pure PF and 16% lignin-PF resin ......................169
Figure 7-6. Dynamic DSC thermograms of pure PF resin 3.......................................................171
Figure 7-7. Curing activation energy of pure PF and lignin-PF resins ...........................................172
Figure 7-8. Failure load of resins selected for testing at three hot pressing times ............................173
Figure 7-9. No relationship between failure load and resin viscosity is observed .......................177
Figure 7-10. UV absorbance spectra of lignins A to G and AILG ..............................................178
Figure 7-11. Comparison of absorbance of lignin A, lignin G and AILG .................................179
Figure 7-12. Lignin 2-D NMR spectra with signals of aliphatic C-H bonds labeled ....................180
Figure 7-13. Labelled 2-D NMR spectra of lignin B .............................................................180
Figure 7-14. Extent of delignification versus % Guaiacyl/Syringyl lignin .................................182
Figure 7-15. Relationship between pulping pH and lignin linkages identified by 2-D NMR........183
## List of Equations

| Equation 2-1 | 21 |
| Equation 2-2 | 35 |
| Equation 3-1 | 61 |
| Equation 3-2 | 62 |
| Equation 4-1 | 75 |
| Equation 4-2 | 76 |
| Equation 4-3 | 77 |
| Equation 4-4 | 86 |
| Equation 4-5 | 87 |
| Equation 4-6 | 90 |
| Equation 4-7 | 118 |
| Equation 4-8 | 121 |
| Equation 4-9 | 121 |
| Equation 4-10 | 121 |
| Equation 4-11 | 122 |
| Equation 4-12 | 122 |
| Equation 4-13 | 122 |
| Equation 4-14 | 122 |
| Equation 4-15 | 125 |
| Equation 4-16 | 126 |
| Equation 4-17 | 128 |
| Equation 4-18 | 128 |
| Equation 4-19 | 129 |
| Equation 4-20 | 131 |
| Equation 7-1 | 156 |
| Equation 7-2 | 157 |
| Equation 7-3 | 157 |
| Equation 7-4 | 174 |
| Equation 7-5 | 174 |
Notation

DM<sub>0</sub>  Dry mass of wood prior to organosolv treatment (g)
DM<sub>f</sub>  Dry mass of wood after organosolv treatment (g)
E<sub>a</sub>  Activation energy (kJ/mol)
E<sub>ai</sub>  Activation energy of reaction i (kJ/mol)
k  Rate constant (min<sup>-1</sup>)
k'  pH corrected rate constant (min<sup>-1</sup>)
k<sub>i</sub>  Rate constant of reaction i (min<sup>-1</sup> or L·g<sup>-1</sup>·min<sup>-1</sup>)

k<sub>0</sub>  Frequency factor (min<sup>-1</sup>)

k<sub>0i</sub>  Frequency factor of reaction i (min<sup>-1</sup> or L·g<sup>-1</sup>·min<sup>-1</sup>)
k<sub>r</sub>  Rate constant for the residual phase (min<sup>-1</sup>)

K  Equilibrium constant for 1<sup>st</sup> order reversible reaction (k<sub>2</sub>/k<sub>1</sub>)

TL<sub>0</sub>  Total lignin content before organosolv treatment (g/g of dry wood)
TL<sub>f</sub>  Total lignin content after organosolv treatment (g/g of dry wood)

L  Lignin concentration (g/g of dry wood)
L<sub>0</sub>  Lignin concentration at t=0 (g/g of dry wood)
L<sub>N</sub>  Native lignin content (g/g of dry wood)
L<sub>R</sub>  Re-condensed lignin content (g/g of dry wood)
L<sub>S</sub>  Soluble lignin concentration (g/L)

R  Gas constant (8.314 J·K<sup>-1</sup>·mol<sup>-1</sup>)

RWL  Wood to liquor ratio (g dry wood/L)

<sub>t</sub>  Time (minutes)
<sub>t</sub><sub>0</sub>  Time at the beginning of measurement (minutes)

T  Temperature (°C or K)
T<sub>IN</sub>  Temperature at inlet of packed bed reactor (°C or K)
T<sub>OUT</sub>  Temperature at outlet of packed bed reactor (°C or K)
T<sub>eff</sub>  Effective temperature (kinetic mean temperature, °C or K)
T<sub>average</sub>  Arithmetic average temperature (°C or K)
T<sub>p</sub>  Temperature at peak maximum of the DSC exotherm (K)

V  Volume (L)

δ  Order of reverse reaction with respect to L<sub>S</sub>
ε<sub>i</sub>  Order of reaction i with respect to H<sup>+</sup> concentration
ϕ  Heating rate during differential scanning calorimetry (K/s)
μ  Average failure load during resin testing (N)
σ  Sample standard deviation

AIL  Acid insoluble lignin from acid hydrolysis
ASL  Acid soluble lignin from acid hydrolysis
G/S  Guaiacyl to syringyl lignin ratio
PF  Phenol formaldehyde
Glossary

**Autocatalysed** – Synonymous with uncatalysed since virtually all biomass releases acetic acid, which catalyses further reaction during hydrothermal treatment.

**Cellulose** – Main component of wood. A linear chain polymer of D-glucose units linked together by $\beta$ (1,4) glycosidic bonds.

**De-ashing** – Method of removing acid neutralising components of biomass (ash and protein) by soaking in dilute acetic acid followed by thorough washing with deionised water.

**Delignification** – Act of removing lignin from a lignocellulosic material.

**Effective temperature** – An Arrhenius average of temperature. The temperature giving the same rate constant as the average reaction rate constant for a series of temperatures.

**Hemicellulose** – The non-cellulosic polysaccharides consisting of several 5 and 6 carbon sugars.

**Holocellulose** – Total of cellulose and hemicellulose, the polysaccharide fraction of biomass.

**Hydrolysis** – Depolymerisation by addition of water.

**Klason lignin** – The solid fraction of a lignocellulosic retained after two-stage acid hydrolysis to remove polysaccharides. Acid insoluble lignin (AIL).

**Lignin** – A major component of woody materials. A complex 3-D polymer consisting of cross-linked phenyl-propanoid units.

**Lignocellulosic** – Woody or herbaceous material consisting of lignin, cellulose and hemicellulose.

**Native lignin** – Lignin as it exists in the plant cell wall without any modification by physical or chemical methods.

**Polysaccharide** – A polymer consisting of sugar monomers.

**Prehydrolysis** – A treatment that hydrolyses polysaccharides. In this thesis it is used to describe a separate dilute acid treatment to remove a portion of hemicellulose from willow prior to organosolv pulping.
1 Introduction

Fuel ethanol produced from biological material has the potential to replace some if not all oil derived transport fuel. Feedstocks for the production of so called bioethanol include sugarcane and corn as well as lignocellulosic feedstocks such as wood, agricultural residues and dedicated energy crops. The energy gain for converting biomass into fuel is a measure of the energy equivalent the fuel produced less the energy requirement for all steps in the conversion. Energy gains for ethanol production from corn are estimated at only 30% to 37% due to the large energy requirement of growing corn. In contrast, the production of ethanol from lignocellulosic feedstocks has an estimated net energy gain ranging from 300% to 570% [1]. There is also an ethical debate as to whether a food source such as corn should be used for fuel production. The use of a dedicated energy crop that is able to be grown on marginal land with higher biomass yield is a possible solution. The fast growing, short rotation coppice willow, *Salix schwerinii*, is an ideal crop for many areas around the world including the North Island of New Zealand. However, the processing of lignocellulosic material into ethanol is more challenging than processing corn into ethanol. Pretreatment is required to render the cellulose portion of lignocellulosic materials more digestible by cellulase enzymes.

Many methods of lignocellulosic pretreatment exist. Organic solvent pulping is considered in this thesis for several reasons. Firstly, it produces a lignin free of sulphur and suitable as a replacement for phenol in polymers. Secondly, this method does not pose an environmental waste problem because solvent can be easily recovered and recycled by distillation. Many solvents have been studied regarding pulp and paper production in order to circumvent the pollution problems caused by the Kraft™ process. Ethanol is the preferred solvent for bioethanol production because it is available in the bioethanol process. The focus of this thesis is on improving lignin extraction using the organosolv method and making lignin more accessible using existing pre-organosolv treatments.

The extra cost of pretreatment can be more than offset by the production of valuable by-products released during the pretreatment step. Using aqueous ethanol, lignin is
extracted in a form that can be utilised for the production of paint, resin and adhesive. Kraft lignin is typically used as boiler fuel and in 1985 had a fuel value of US$0.048/kg (US$0.095/kg in 2008) as reported by Glasser [2]. Whereas organosolv lignin, sold as a chemical feedstock, had an estimated net value of US$0.34/kg (US$0.67/kg in 2008). One of the most promising applications for un-sulphonated lignin is the replacement of phenol in phenol-formaldehyde resin. However, the adoption of lignin for use in such applications has been slow due to uncertainties over the chemical heterogeneity of lignin.

This thesis investigates the selective fractionation of willow. The polysaccharide fraction may be converted into many products including fuel ethanol. However, the utilisation of the lignin fraction for the production of resins and adhesives will have a major impact on the overall economics of the process. Due to inter-species variation of the lignin molecule in both molecular size and structure, defining the lignin molecule is difficult. However, proving its utility in resin is both practical and useful. Lignin recovered from ethanol pulping of *Salix schwerinii* was tested as a partial replacement for phenol in phenol-formaldehyde resin.

Ethanol pulping has previously been used for the production of pulp and paper and the extraction of high value lignin. In most cases, 50% v/v ethanol concentration is used with an inorganic acid catalyst to increase the rate of hemicellulose and lignin removal. However, the effects of pH on delignification kinetics are not well understood. Low pH increases lignin reaction rate but can also increase re-condensation of lignin on the wood matrix as well as selectively increasing hemicellulose removal. These conflicting effects may have a bearing on the onset of “residual delignification”, a slow phase of delignification often attributed to a lignin chemical structure more resistant to depolymerisation.

Organosolv pulping using different ethanol concentrations were compared to see if liquor properties were responsible for the onset of residual delignification. It became apparent that ethanol concentration was inherently linked to liquor pH and an attempt was made to control pH during further delignification experiments to ascertain the effect of only changing ethanol concentration (see § 4.2).
An attempt was made to link the onset of residual phase delignification to feedstock properties by comparing delignification of untreated willow with that of willow that had been prehydrolysed to selectively remove hemicellulose. Instead, the effect of feedstock condition on liquor pH proved to be more important than any differences in lignin-polysaccharide interaction. This led to a comparison of feedstocks that had pre-organosolv treatments to remove acid neutralising components of wood such as ash and protein (see § 4.3).

The lignin-rich liquor (black liquor) from willow pulping can be diluted to precipitate lignin. Typically this mixture is then centrifuged or filtered to recover lignin. However, after lignin was often found to float after dilution, dissolved air flotation was investigated as a recovery method and parameters affecting rapid and complete clarification were investigated (see Chapter 6). Water at equilibrium with pressurised nitrogen was used for dilution of black liquor and simple methods were used to compare the rate of clarification and recovery yield.

Lignin was investigated as a direct replacement for phenol in Chapter 7. Lignin can be used in the manufacture of phenol formaldehyde resin and the properties of resins containing lignin from different pulping conditions were investigated. DSC was used to compare curing kinetics and lap joint samples were used to compare adhesive strength. The size and structure of the lignins used were also analysed using size exclusion chromatography and nuclear magnetic resonance respectively.

### 1.1 Technical objectives

The technical objectives of this thesis can be summarized in four stages.

1. Developing a method of determining reaction kinetics at various times and temperatures using a slow heat up period with measurement of lignin content in liquor samples (see § 4.2.1).
2. To determine the mechanisms controlling delignification and elucidate between reaction mechanism, mass transfer control and lignin-polysaccharide interaction for the cause of residual delignification.

3. Recovering lignin by precipitation and testing a novel method of recovery for organosolv lignin, dissolved air flotation (see Chapter 6).

4. Producing phenol formaldehyde (PF) resin containing organosolv lignin extracted under various conditions and comparing them to pure PF resin (see Chapter 7).

1.2 Scope

Chapters 2, 3, 4 and 5 relate to the organosolv fractionation of *S. schwerinii* (willow wood). Lignin extraction is the major concern in this thesis. The removal of other components such as hemicellulose and extractives is considered only in the context of how it affects the rate of lignin removal. Chapter 2 covers the concepts of biorefining and wood chemistry before delving into the existing literature on the organosolv method.

Cellulose conversion to glucose is not covered in this thesis as this has proven to be relatively easy provided the primary objective of this work, high lignin removal, is achieved. Literature suggests that lignin has an inhibitory role in enzymatic cellulose conversion and hydrolysis rate is highly dependent on the available surface area of cellulose [3-5]. Removal of lignin removes this inhibitory effect and alters the structure of the substrate such that available surface area is increased. Pretreated *S. schwerinii* from this work has also been hydrolysed by partners and shows a comparable hydrolysis rate and glucose yield to that of pure cellulose [6].

Chapter 6 describes a method of recovering lignin from organosolv black liquor and determines the parameters important to achieve rapid recovery. Chapter 7 examines the use of lignin prepared from organosolv pulping for incorporation into polymer products. Chapters 6 and 7 each contain a background, materials and methods, results and
discussion and conclusions. This is done for readability such that the reader is made familiar with the literature in the context of the following original work.

Thus, this thesis follows the lignin process stream in the biorefining of lignocellulosics and neglects the area of solvent recovery and the process streams containing primarily carbohydrates. The work is split into three areas pertaining to lignin, each affecting the subsequent process, but requiring different treatment and understanding. These areas are removal of lignin from willow (delignification) by the organosolv process, recovery of lignin from organosolv black liquor and use of organosolv lignin in PF resin.
2 Background

The separation and product valorisation of a lignocellulosics material is commonly referred to as biorefining. As such, an overview of the biorefining concept is presented. A basic knowledge of wood chemistry and the peculiar properties of the lignin reaction is introduced in this chapter. Current knowledge in the field of organosolv pulping is then reviewed. The current preferred method of extraction is justified and the other studies of kinetics and important parameters are reviewed to show theories, flawed or otherwise, of delignification mechanisms.

2.1 Biorefining

The ultimate goal of biorefining is to separate the components of biomass cleanly into components having the highest value resulting in favourable process economics. This is an ambitious goal since any attempt to remove one major component results in some degradation of another. A review of wood chemistry is given in Section 2.1.2.

The earliest conversion of biomass to energy by use as firewood is today considered a low value use but the desire to produce another type of fuel, ethanol, is a major part of the evolution of the biorefining concept. Fuel ethanol is a replacement for oil based liquid fuel and has been produced from various feedstocks. A variety of processing methods are currently considered and the merit of each is reviewed in Section 2.1.3. Modern biorefining is born from the realisation that combustion is of low value by comparison to fine chemicals and Section 2.1.4 shows that modern thinking is to utilise as much of the biomass at as high a value as possible.

2.1.1 Fuel ethanol production

The production of ethanol from biological material has been performed for thousands of years as the age old practice of beer and wine brewing. More recently it has been produced for use as a liquid fuel. Ethanol was once praised as the fuel of the future and the first Model T Ford was run on ethanol [7]. Fuel ethanol was later produced from wood as part of the German war effort before oil became abundant [8].
Interest was renewed in fuel ethanol production in the 1970’s due to the effects of the oil embargo in 1973 and ethanol was blended with gasoline in increasing proportions. Brazil quickly became the world’s foremost producer of ethanol using sugarcane as a feedstock. The US followed later when the fuel additive MTBE was phased out following concerns that the carcinogenic oxygenate had been found in groundwater systems. Their feedstock of choice was maize. Both of these are food sources and this has caused an ongoing ethical debate as well as criticism over the energy efficiency of producing ethanol from these crops [9, 10].

Lignocellulosic feedstocks, such as the short rotation hardwood coppice, Willow, are considered to be a superior source for the production of ethanol [1]. Willow is fast growing on marginal land and requires less fertilizer and energy compared to most agricultural crops [9, 11]. The drawback of using lignocellulosics is that further processing is required to separate cellulose, hemicellulose and lignin.

### 2.1.2 Wood chemistry

Wood is made up of three main components as shown in Figure 2-1. These are cellulose, hemicellulose and lignin. The term holocellulose encompasses both hemicellulose and cellulose.

Cellulose is a polymer of glucose that makes up 40-60% w/w of the cell wall. Cellulose consists of D-glucose units linked by the β (1-4) glycosidic bond in long linear chains. These chains, typically 10000 to 15000 glucose units long, easily pack into crystalline arrays called microfibrils. Microfibrils are held together by an amorphous network of hemicellulose and lignin. Each wood cell is made from a cell wall consisting of several layers of microfibrils, each layer in a different orientation. Water can penetrate the gaps between microfibrils and weaken the hydrogen bonds. This is called swelling. However, water does not penetrate so easily into the microfibrils [12].
Hemicellulose is a group of polysaccharides making up 20-40% w/w of wood and is made up of several different five and six carbon sugars. The main constituent of the hemicellulose in hardwoods is xylose. Arabinose, glucose, galactose and mannose are also part of the amorphous branched polymer that makes up hemicellulose. Hemicellulose unlike cellulose is easily hydrolysed to simple sugars by a process termed autohydrolysis. Above temperatures of 140°C acetyl groups on hemicellulose are released forming acetic acid. Acetic acid catalyses further hydrolysis of hemicellulose.

Lignin is a large macromolecule consisting of 3 variously cross-linked phenylpropanoid monomers as shown in Figure 2-1. Softwoods contain mainly guaiacyl (G) lignin. Hardwoods contain roughly equal proportions of guaiacyl and syringyl (S) lignin with para-hydroxyphenyl (H) lignin a minor component in both hardwood and softwood [13-15]. The removal of lignin from wood is the main topic of this thesis and as such, lignin and its association with wood is reviewed in more detail in Section 2.1.2.1.

Other constituents that make up less than 5% w/w of wood are categorised as either extractives or non-extractives. Extractives, also referred to as extraneous material, include a wide range of organic compounds. In terms of quantity and economic utilisation, polyphenols and oleoresin are the most important components. Polyphenols include tannins, anthocyanins, flavones, catechins, kinos and lignans. Oleoresin is used for the production of turpentine, tall oil and rosin. Other extractives include fatty acids,
waxes, volatile hydrocarbons and protein such as chlorophyll. Non-extractives, also called ash, mainly consist of calcium, magnesium and potassium compounds. Manganese can also be present in some species such as hard maple. Silica may be present and can cause the premature dulling of mechanical cutting tools during processing. Overall ash content in willow is usually between 0.1% and 0.5% w/w and is not discussed further in this thesis.

2.1.2.1 Lignin

Lignin has a number of functions in the plant cell wall. These include controlling fluid flow, protecting polysaccharides from microbial attack, storing energy and most importantly, providing strength and rigidity to the cell wall. In hardwoods such as willow, monomers are derived from either trans-sinapyl alcohol or trans-coniferyl alcohol. These precursors give rise to syringyl lignin (S) and guaiacyl lignin (G) respectively. The structure arising from free radical cross-linking of these monomers is neither random nor completely ordered. It is built up as an organised binding structure in the plant. Different structures may have different functions in the cell wall. In addition to the diversity of repeating units and bonding patterns characterising native lignin, the reaction of lignin for its recovery causes changes to functional groups and size creating further complication [16].

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>phenyl-propanoid unit</th>
<th>Lignin type</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-</td>
<td>-H</td>
<td>P-coumaryl alcohol</td>
<td>para-Hydroxyphenyl Lignin (H)</td>
</tr>
<tr>
<td>H-</td>
<td>-OCH₃</td>
<td>Coniferyl alcohol</td>
<td>Guaiacyl Lignin (G)</td>
</tr>
<tr>
<td>CH₃O⁻</td>
<td>-OCH₃</td>
<td>Sinapyl alcohol</td>
<td>Syringyl Lignin (S)</td>
</tr>
</tbody>
</table>

Figure 2-2. Structure and labelling of phenyl-propanoid units comprising lignin.

A comprehensive review of lignin chemistry is given by Adler [15]. Many potential structures of lignin are proposed but lignin is accepted as a 3-dimensional network.
polymer consisting of the three phenyl-propanoid units shown in Figure 2-2. A long list of reactions has been used for determining the various bond types in lignin and the predominant bonds (50-60%) between phenyl-propanoid groups are always reported to be β-O-4 (β–aryl ether) bonds. Lignins are divided into two classes, namely “guaiacyl”, comprising the majority of lignin in gymnosperms (softwoods) and “guaiacyl-syringyl” lignins, predominating in angiosperms (hardwoods). The guaiacyl-syringyl lignin is composed of varying proportions of coniferyl and sinapyl alcohol. P-coumaryl alcohol is present in all lignins in amounts less than 5% except in the compression wood of conifers, which can contain up to 20% p-coumaryl units. There is convincing evidence of covalent bonding between lignin and hemicellulose although the nature of these bonds is not entirely understood.

Lignin can form links between various combinations of the α, β, 4, 5 or 1 positions, making lignin extremely complex and difficult to define [17]. Figure 2-3 shows a possible structure of only a small part of lignin containing sixteen phenyl-propanoid units determined by Adler [15]. Although the most common bond between phenyl-propanoid units in lignin is the β-O-4 bond [16, 18], activation energies of delignification show that hydrolysis of α-O-4 linkages control the depolymerisation of lignin in hydrothermal processes [19-21].
Not only is it difficult to define lignin and its reactions due to the complexity and size of the lignin molecule, it is also known that lignin structure and reactivity can vary greatly in different species or ages of wood. Forss and Fremer [22] have written a 558 page book to postulate that the Spruce lignin monomer is made from 18 coniferyl alcohol units. The model may be applicable to other similar softwoods, but is vastly different to hardwood lignin.

Research up until 1977 indicates that lignin is linked to hemicellulose through arabinose and galactose units. A lignin-galactoglucomannan complex was isolated from spruce wood and further processing indicated that a bond exists between the lignin and galactose. Other researchers have shown evidence of glycosidic linkages between lignin and D-galactose, L-arabinose and D-xylose [15, 23-25].
2.1.3 Conversion of wood to ethanol

Several process routes exist for the conversion of wood into ethanol. They can be classified into two categories as shown in Figure 2-4. The gasification route, which uses extremely high temperatures to degrade wood polysaccharides and lignin into light gases, then convert a portion of the gases into ethanol using a Fischer-Tropsch catalyst. And the fermentation route, which usually requires a separation or pretreatment step followed by a combination of chemical and biological reactions to convert cellulose and hemicellulose into sugar monomers (hydrolysis) followed by the fermentation of those sugars into a dilute mixture of ethanol and water.

![Diagram](image)

**Figure 2-4. Fermentation and gasification routes for converting lignocellulosics into ethanol.**

Gasification has not been proven economic and there are problems with gas cleaning [11]. There is no opportunity for producing valuable products such as lignin by this method. Gasification requires that wood chips are subjected to temperatures from 1200 to
1400°C in limited oxygen and converted into synthesis gas, which is a mixture of H₂ and CO. CH₄, H₂O and CO₂ are also unavoidably produced. Gas cleaning and rectification then modifies the gas stream to the ideal conditions for conversion to ethanol by a Fischer-Tropsch catalyst. There are numerous problems with gasification technology for ethanol production despite thorough research into the topic.

By contrast, the hydrolysis method requires mild process conditions and a high mass conversion into ethanol. Hydrolysis can be performed by chemical means, using concentrated acid, or enzymatic conversion of cellulose into glucose. Concentrated acid hydrolysis is more highly researched than dilute acid hydrolysis and has higher yields. The ethanol yield however, is only 76-85% of theoretical for concentrated acid hydrolysis processes reviewed by von Sivers and Zacchi [26]. Processes using H₂SO₄, HF and HCl are reviewed.

Acid recovery and recycle is both essential and costly [27, 28]. Acid recovery and neutralisation is estimated to contribute to 8-11% of the capital cost of ethanol production from corn stover using concentrated acid. Concentrated acid hydrolysis is shown to have a lower capital cost than dilute acid hydrolysis for a 500 tonne/day plant. However, concentrated acid hydrolysis has a higher production cost [29].

In work by von Sivers and Zacchi [27] the substrate is subjected to two separate dilute hydrolysis steps. The first involves steaming at 188°C and 12bar with SO₂ catalyst to hydrolyse hemicellulose with a subsequent washing step to remove hemicellulose sugars. The second step involves hydrolysis of cellulose with dilute hydrochloric acid at 230°C. The yield of glucose and xylose are 82% and 54% of theoretical respectively.

Most research since 1990 focuses on enzymatic hydrolysis [26]. This is mainly due to a recent reduction in cost of cellulase enzymes and the problems associated with acid hydrolysis such as acid recycle costs and production of fermentation inhibiting compounds like furfural. Enzymatic hydrolysis is considered by some to be economically advantageous compared to acid hydrolysis [9].
Enzymatic hydrolysis can give glucose yields approaching 100%. It is performed at 40-50°C and requires long reaction times of hours to days depending on the substrate and pretreatment step employed. Commercially available cellulase enzymes are a mixture of three enzymes. Endoglucanase breaks the cellulose in the middle of chains to reduce the degree of polymerisation. Exoglucanase works at the ends of the chains to break the chains into cellobiose, the dimer of glucose. Beta glucosidase breaks the cellobiose into glucose monomers.

Fermentation of glucose can be carried out by a range of fermentation yeast such as those used for beer and wine production (Saccharomyces cerevisiae), or fermentation bacteria such as Zymomonas mobilis [30-33].

The move towards enzymatic hydrolysis has been in part driven by successful research into lowering the cost of cellulase production. A twelve-fold reduction in enzyme costs has been announced by Novozymes. However, for hydrolysis to be economically viable, pretreatment is required to obtain cellulose that can be accessed by those enzymes [34].

Both gasification and concentrated acid hydrolysis are discounted for the current work since both result in significant loss of wood components and immediately disadvantage the economics of biorefining. It should be noted that while acid hydrolysis using excessive amounts of acid or resulting in significant product losses is discounted, low temperature (<125°C) prehydrolysis using minimal amounts of acid (<0.05M) is considered feasible provided product losses are negligible. All parts of the biomass must be used just as all parts of a barrel of crude oil are utilised for maximum profit in the petroleum industry.

2.1.4 The biorefining concept

Biorefining is not merely a process for producing fuel from biomass. A fundamental shift is required in sourcing industrial raw materials. In order for biorefining to become competitive with the petroleum industry a range of high value products must be
produced. Polymer feedstocks of considerably greater value than fuel can be made from biomass [35].

Myerly et al. [36] have proposed a “forest refinery” concept whereby lignocellulosics in the form of wood are fractionated and converted into raw chemical feedstocks. A pulp mill is not a suitable biomass refinery due to degradation of hemicellulose and lignin into low value products. Each component of wood should be converted into a high value product such as feedstuff or polymers.

A review of the technology for pretreatment of lignocellulosics for fuel ethanol production states that the ideal pretreatment will efficiently fractionate lignocellulosics into multiple streams of sufficient purity to obtain value added products. Lignin inhibits cellulose enzymes used for hydrolysis of cellulose. Cellulose contaminated by lignin requires higher enzyme loadings than pure cellulose and therefore significant additional expenditure. Although pretreatment is one of the most expensive steps of fuel ethanol production it enables a reduction in costly enzyme production and improves the potential for higher value products [37].

Enzymatic hydrolysis rate is governed by the surface area of cellulose available to the enzyme [38]. Other important factors include degree of polymerisation and crystallinity. In order for cellulase to bind to cellulose, there must be large enough gaps in the structure of the substrate for the enzymes to penetrate. Surface area can be increased by disrupting the structure of wood or by solubilising one component of wood. The hydrolysis step is identified as being critical in the economic conversion of wood to ethanol. Pretreatment must be optimised to provide a high initial hydrolysis rate of cellulose and minimise the degradation of hemicellulose-derived sugars [39].

Lignin reduces the available surface area of cellulose by acting as a sheath around the cellulose fibers. Hardwoods are comprised of 20-30% w/w lignin. Lignin also binds irreversibly with cellulase enzymes removing them from the reaction [3]. There is evidence that phenolic structures present in lignin have a greater inhibitory effect on enzymatic hydrolysis than the non-phenolic structures [5]. Sutcliffe and Saddler [40] have also shown that cellulase adsorption is dependent on the nature of the lignin.
The advantages of using the hydrolysis-fermentation process include relatively mild process conditions and the selectivity of the product formed. However, a processing step is required to make cellulose susceptible to enzymatic hydrolysis. This can be turned into an economic advantage by selecting a pretreatment that allows the utilisation of lignin as well as polysaccharides. Therefore, the ideal pretreatment enables high rates and yields of enzymatic hydrolysis while allowing the recovery of non-cellulosic polysaccharides and lignin for use in high value products.

2.2 Pretreatment

Many pretreatments for solubilising one or more components of wood have been studied with varied success in terms of subsequent hydrolysis rate. Some pretreatments, such as steam explosion or liquid hot water, not covered in depth in this thesis, may be suitable for certain feedstocks, particularly those with low lignin content. Pretreatment has recently been identified as the most important and costly step in the production of low cost ethanol from cellulose. Pretreatment impacts on the performance and cost of all other operations in the conversion process [41].

2.2.1 Pretreatment technology for lignocellulosics

Table 2-1 lists several methods of pretreating lignocellulosics material. Cellulose generally undergoes negligible degradation while different proportions of the lignin and hemicellulose components are extracted.

Dilute sulphuric acid pretreatment of corn stover, poplar and switch grass was studied at temperatures from 140 to 180°C and acid concentration from 0.6 to 1.2% w/w H₂SO₄ (0.06M-0.12M). Poplar has a high neutralising ability (16.7mg H₂SO₄/g dry substrate) compared to other hardwoods. This was attributed to its ash content [50]. A low yield of xylose was obtained from dilute acid pretreatment of aspen wood due to partial degradation to furfural [51].
Table 2-1. Methods of pretreatment and typical solubilisation yield of hemicellulose and lignin.

<table>
<thead>
<tr>
<th>Method</th>
<th>% Component solubilised</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hemicellulose</td>
<td>Lignin</td>
</tr>
<tr>
<td>Dilute acid percolation [42]</td>
<td>94%</td>
<td>54%</td>
</tr>
<tr>
<td>Alkali [43]</td>
<td>Not reported</td>
<td>80%</td>
</tr>
<tr>
<td>Wet oxidation [44]</td>
<td>80%</td>
<td>55%</td>
</tr>
<tr>
<td>Steam explosion [45]</td>
<td>84%</td>
<td>75%&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Steam explosion [46]</td>
<td>74%</td>
<td>94%&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Liquid hot water [47]</td>
<td>100%</td>
<td>38%</td>
</tr>
<tr>
<td>Ammonia [48]</td>
<td>40-60%</td>
<td>70-85%</td>
</tr>
<tr>
<td>Organosolv [49]</td>
<td>91%&lt;sup&gt;b&lt;/sup&gt;</td>
<td>87%</td>
</tr>
<tr>
<td>Organosolv(pH~2.4) [46]</td>
<td>90%</td>
<td>99%</td>
</tr>
</tbody>
</table>

<sup>a</sup>With subsequent alkaline extraction, <sup>b</sup>xylene and mannose only

Alkalis such as NaOH, ammonia (NH₃) and lime (Ca(OH)₂) can be used to increase the digestibility of lignocellulosics. Chang [52] explored the digestibility of switch grass and poplar wood using lime. The effectiveness of alkali pretreatment is highly dependent on lignin content. Alkali pretreatment is effective for wheat straw and grasses but results in less digestibility improvement for hardwoods and substrates with high lignin content [53].

Wet oxidation is a term used to describe any autohydrolysis process involving water, high-pressure oxygen or air and elevated temperature. Conditions of 185°C, 6.5g/l Na₂CO₃ and 12 bar O₂ for 15 minutes resulted in recoveries of 95% cellulose and 60% hemicellulose from wheat straw while 55% of lignin was solubilised. At temperatures above 185°C, recoveries fall due to conversion of cellulose and hemicellulose sugars into undesirable products [44].

During hydrothermal treatments, hemicellulose end chains release acetic acid, which lowers the pH resulting in catalysed degradation of hemicellulose. It is the de-acetylation
of O-acetyl-4-O-methyl-glucuronoxylan in hardwoods and glucomannan acetate in softwoods that forms acetic acid. This is referred to as autohydrolysis [54].

Steam explosion is a process whereby the lignocellulosic feed is subjected to saturated steam at high pressure and temperature of 160-220°C. As severity (a combined parameter defined as a function of temperature and time by Overend and Chornet [55]) increases a higher proportion of hemicellulose sugars are degraded to non-fermentable products. Several studies aim to optimise economics by finding a balance between xylose and glucose yield [45, 56, 57]. The addition of SO₂ or H₂SO₄ catalyst to willow prior to steam pretreatment improves recovery of hemicellulose sugars. A theoretical yield of 95% glucose can be obtained with SO₂ impregnation at the expense of having only a 62% xylose recovery [56]. An acid catalysed post-hydrolysis step at lower temperature (120°C) can further improve xylose recovery with minimal reduction in glucose yield [58]. Steam exploded lignin has been found to absorb cellulose enzymes considerably more than lignin from other aqueous treatments [59].

Corn stover has been treated by ammonia recycled percolation resulting in a 70-85% reduction in lignin content and an enzymatic digestibility of 99%. SEM analysis showed that pretreatment deformed the structure of wood and exposed the fibers [48].

Lignocellulosics can be treated with supercritical carbon dioxide as a solvent. Kim and Hong [60] show that the effectiveness of supercritical CO₂ depends on the moisture content of the substrate. Untreated aspen wood with no moisture has a similar enzymatic digestibility to aspen wood pretreated with supercritical CO₂. When moisture content was increased, enzymatic digestibility of pretreated aspen wood increased giving a maximum glucose yield of 84.7% of theoretical.

Organosolv pulping has been advocated as the environmentally benign version of the kraft process. Unlike other pretreatment methods, organic solvents can easily be recycled and reused. Hardwoods (such as willow) delignify faster than softwoods by organosolv pulping. The lignin dissolved by organosolv pulping is easily recovered by dilution and is unsulphonated and relatively unmodified [61, 62]. Claims that organosolv pulping obtains high recovery of hemicellulose and lignin have been confirmed according to
Myerly et al. [36] and the cellulose produced is suitable for pulp and paper production or conversion into sugars. Organosolv pulping is considered to have a lower investment cost, greater potential for by-products and reduced emissions and effluent when compared to conventional kraft pulping [63-67].

Recent publications reviewing biorefining of lignocellulosics identify pretreatment as the most costly step in the conversion of wood to biofuels [68]. Recent industrial activity regarding cellulosic ethanol has resulted in a number of publications reviewing the various pretreatments. In many of these, organosolv is regarded as favourable due to the environmental advantages and potential for by-products [69-71].

The ability to recover high quality lignin, coupled with low emissions makes organosolv pulping an attractive method of pretreatment. In addition, hardwoods are easily delignified by organosolv. Lower molecular weight alcohols are commonly employed due to their easy recovery [72, 73] and the possibility of using ethanol as the solvent makes ethanol based organosolv a logical choice for a process converting willow into bioethanol.

### 2.3 Organosolv pulping

Organosolv is a pretreatment that uses an organic solvent to solubilise lignin and hemicellulose. It has been considered in the context of both pulp and paper manufacture and biorefining for subsequent conversion of cellulose to fuel ethanol.

Organosolv has several advantages when compared to other popular methods such as kraft pulping or dilute acid hydrolysis. In particular, the ability to obtain relatively high quality lignin adds value to a process stream otherwise considered as waste. Numerous authors report that pulping with ethanol-water solutions gives a lignin free pulp yield 4-4.5% higher than that of kraft pulp [63-67].

The commonly used solvents acetone and ethanol have been examined with respect to pulp properties. The pulping of wheat straw with 40% mixtures of acetone or ethanol with water requires 60 minutes at 180°C to give good pulp properties [64]. Organic
solvents are almost always used as a mixture with water for process considerations such as reducing the vapour pressure and lowering the pH in order to also solubilise hemicellulose.

Baeza et al. [74] uses acetone and formic acid on softwoods, which are known to be resistant to organosolv delignification. High pressure was needed for good penetration of solvent into the porous wood structure. Formic acid:acetone ratio of 7:3 gave the best results with Kappa number (a measure of lignin content) of 24.7 and pulp yield of 41%. Kappa number is proportional to lignin content and is calculated from the amount of potassium permanganate absorbed by the pulp. It is used extensively in the pulp and paper industry as a measure of how much bleach a pulp will consume to achieve a given brightness.

Work by Oliet et al. [75] compares methanol to ethanol. Methanol is found to extract more lignin from *Eucalyptus globulus* on average, but ethanol extracts more lignin at the higher temperature tested of 194°C. Methanol-water pulping is recommended by Oliet et al. due to the higher viscosity of methanol pulps. However, pulp viscosity is irrelevant when considering the effectiveness of pretreatment for lignin and bio-fuels production.

Formic acid is also an effective delignifying agent for the production of pulp. Formic acid pulping allows the use of lower temperatures (120°C) but results in a high proportion of cellulose loss (5-16%) compared to ethanol pulping [76]. An investigation of phenol-water mixtures as a solvent shows the influence of independent variables on the properties of wheat straw pulp. Despite being highly toxic, it is claimed that the use of phenol in a closed solvent cycle should not create contamination issues [77].

When selecting a pulping solvent, high boiling solvents have the advantage that a lower process pressure can be used. However, this is balanced by increased difficulty in recovering the solvent by distillation [78]. Ethylene glycol at a temperature of 220°C can effectively remove up to 89% of lignin from *Populus deltoides*. The subsequent separation of lignin by evaporation is considered rather time consuming by Thring et al. [79].
Aronovsky and Gortner [80] report that normal primary alcohols are better pulping agents than secondary or tertiary alcohols. Butyl alcohols yielded better pulped residues than lower alcohols although there was some disparity between the pulping temperatures used for each alcohol.

Chum et al. [81] developed a combined severity parameter relating temperature, reaction time and pH to the extent of delignification. Severity, \( R_0 \), is calculated as shown in Equation 2-1.

\[
R_0 = t \cdot e^{\frac{(T_r - T_b)}{14.75}}
\]

Equation 2-1

where \( t \) is time spent at the reaction temperature, \( T_r \), and \( T_b \) is a chosen reference temperature, usually 100°C. The combined severity factor is defined as \( \log(R_0) - \text{pH} \). Hence, reducing pH increases severity.

Higher severity treatment with organic solvent-water mixtures causes more degradation of lignin side-chains and resulted in lower carbon numbers in the repeating unit of lignin. Aspen wood was treated with a liquor to wood ratio of 4:1 by weight in 70% v/v methanol at 165°C for 2.5 hours using different acid catalysts. A batch reactor was used and allowed to cool overnight after the reaction. This resulted in some re-precipitation of lignin onto the wood. Liquors were evaporated in a rotary evaporator at temperatures lower than 60°C [62].

The use of formic acid as the catalyst for organic solvent delignification is promising according to Baeza et al. [82]. Although only delignification is considered in this work, formic acid pulping appears to have greater potential than many other organosolv processes. Solids with composition 88% w/w cellulose and 8% w/w klaslon lignin were obtained when Eucalyptus grandis wood chips were treated with 99% formic acid at 95°C.
Another popular solvent is acetic acid, which has proven to be adequate for delignification of both hardwoods [21, 83] and softwoods [20, 84]. The greater severity required for softwood delignification promotes lignin condensation reactions [20].

Eucalyptus treated with 95% acetic acid and up to 0.2% HCl catalyst gave pulp yields from 51.5-90.6%. Residues with less than 4% lignin were obtained. Considerable conversion of pentose to furfural occurred during the most severe pulping conditions [85].

The organocell process uses two stage organosolv with roughly 50% methanol solutions. Sodium hydroxide is added in the second stage at a loading of 30% w/w of the dry wood. The lignin from the second stage is isolated by adding phosphoric acid until a pH of 4.0 is reached [86]. The first stage extracts hemicellulose and lignin from norway spruce at 190°C. The mixture forms a colloidal suspension when methanol is removed. Bennani et al. [87] reports a method for isolating these components using strong acid and weak basic ion exchangers. 28% w/w of the hemicellulose can be recovered and considered for more valuable by-products while only 20% w/w lignin was recovered.

Pasquini et al. [88] studied the ethanol-water delignification of *Pinus teada* and sugar cane bagasse under sub and supercritical CO₂ pressure. 93% delignification was achieved after 150 minutes. Higher pressure reduced the delignification slightly whereas higher temperature increased delignification significantly. Pressure of 15-25MPa and temperatures from 142-198°C were tested. Greatest delignification was achieved using 50% v/v ethanol concentration. However, 75% v/v was considered the best result due to a higher pulp yield. Concentrations of ethanol from 50-100% v/v were tested.

Lora and Aziz [89] describes an Alcohol Pulping and Recovery (APR) process in which wood chip is treated in 3 stages, each using increasingly cleaner solvent. The four most important process parameters are extraction time, temperature, solvent composition and pH. A pilot plant operation has shown that ethanol pulping produces pulp superior to sulphite pulp at a lower cost. Lignin and hemicellulose are recovered in high yields. In 1987 the APR process was renamed the Alcell process. The process uses aqueous ethanol solutions (40-60% v/v) to delignify wood at temperatures from 180-210°C and 2-3.5MPa.
This is described in more detail in a patent by Diebold et al. [90]. Solvent is recovered with flash evaporation, vapour condensation and vacuum stripping.

The economy of several alcohol pulping processes have been examined for the production of pulp and paper. Katzen et al. [91] reports a payback period of 4.4 years without by-product credits (revenue from the lignin and hemicellulose stream) and 3.2 years with these credits. Due to the need for removal of lignin for enzymatic hydrolysis, by-product credits will be important for the success of an organosolv process producing bioethanol.

A demonstration organosolv pulp mill has operated in Mirimichi, New Brunswick, Canada from 1989-1996 using the Alcell process. Repap owned the IP to the process when taken over by hedge funds in 1997. The pilot plant boasted superior environmental performance, excellent bleached pulp, an economically attractive scale of 300tons/day and commercially attractive by-products. It is said that the technology can be used to exploit small regions of hardwood resource that could not support a modern sized kraft mill [67].

Although these technologies have been developed for the pulp and paper industry to reduce environmental impacts or reduce the commercially viable size of a pulp mill, the organosolv process has been considered recently for the purposes of biorefining.

When considered in the context of bio-ethanol production, organosolv pretreatment of aspen wood using methanol followed by enzymatic hydrolysis can obtain glucose yields 70-88% of theoretical. A range of organosolv conditions can yield a highly digestible substrate. Several acid catalysts were tested with methanol concentrations ranging from 30 to 70% v/v [92].

High enzymatic hydrolysis yields are reported using *Miscanthus x giganteus* subjected to a dilute H₂SO₄ prehydrolysis followed by ethanol organosolv pretreatment. 95% of the glucan fraction was retained in the solid fraction and 98% of this was recovered as glucose after a 48 hour enzymatic hydrolysis. The prehydrolysis resulted in greater xylose yields and faster fractionation of lignin [93].
Zhao et al. [73] reviews the recent advances in organosolv pretreatment for cellulosic ethanol production. The degree of delignification for enzymatic hydrolysis is less that that required for high quality pulp production. For complete hydrolysis with cellulase, the removal of lignin should be >70% for pine and >80% for beech wood. Although organosolv pretreatment is currently more expensive than other pretreatment technologies, such as steam explosion and dilute acid pretreatment, the potential for by-products is more promising for organosolv processes. Low boiling alcohols are identified as having easy recovery and lower cost than high boiling solvents. However, high pressure generated by these solvents leads to high capital cost. Organic acids are examined less in the literature due to their corrosive nature. Zhao et al. concludes that future work on organosolv should focus on both increasing the value of by-products and reducing solvent use.

Ethanol yields of 99.5% of theoretical (based on glucan in pretreated material) have been obtained by simultaneous saccharification and fermentation (SSF) of acetone organosolv treated *Pinus radiata*. The conditions of organosolv were acetone:water ratio of 1:1, 195°C for 5 minutes at pH=2 [94].

A two stage process was investigated for the conversion of woody legume species into ethanol and paper. *Chamaecytisus proliferus* was treated with water at 185°C to remove hemicellulose sugars for subsequent fermentation. The solids fraction was treated with 60% v/v ethanol at 175°C for 90 minutes to obtain a cellulose pulp yield of 58.2% [95]. The fast growing hardwood *Paulownia fortunei L.* has been considered for a similar two stage process. After autohydrolysis to obtain a xylose rich soluble phase, ethanol-soda pulping using an ethanol concentration of 20-30% v/v, 180°C and 30 minutes is recommended to give good pulp properties [96].

Teramoto et al. [97] used an ethanol/water/acetic acid organosolv method to remove lignin and hemicellulose from eucalyptus and bagasse. A 60 minute treatment at 200°C, an ethanol:water weight ratio of 3:1 and 1% (w/w ethanol-water solution) acetic acid allowed 96.6% enzymatic conversion of cellulose to glucose in 48 hours. Field emission
scanning electron microscopy confirmed that the sulphur free organosolv pretreatment resulted in pores of size 10 to 100nm being formed in the substrate.

*P. radiata* and *Acacia dealbata* have been subjected to 30 day treatment with white rot fungi followed by organosolv treatment in 60% v/v ethanol at 200°C for 1 hour. The white rot fungi treatment resulted in greater delignification during organosolv for both species. For *P. radiata*, the white rot fungi and organosolv treated pulp had greater enzymatic digestibility compared to pulp that was only organosolv treated. This was due to a significantly higher lignin content in the pulp of *P. radiata* that was only organosolv treated [98].

Pan et al. [99] examines the organosolv pretreatment and bioconversion to ethanol of lodgepole pine that has been killed by the mountain pine beetle. The beetle killed lodgepole pine would otherwise be a forestry waste. Beetle killed pine had a lower lignin content and greater enzymatic digestibility following organosolv pretreatment than healthy pine. However, the beetle killed pine showed a lower yield due to cellulose losses during the pretreatment. Conditions of 170°C, 1.1% w/w H2SO4, 65% v/v ethanol for 60 minutes resulted in recovery of 79% of the lignin. The recovered cellulose was converted to glucose with a conversion of 97% [100].

Substrate characteristics such as cellulose crystallinity, degree of polymerisation and fiber size were investigated using various conditions during organosolv pulping. The temperature, time and catalyst concentration can be altered to achieve predictable characteristics and substrate losses [101].

Lignol™, a company specialising in biorefinery technology uses the approach that wood must be separated into several products of high value for biorefining to become economically viable. Lignol™ cites a more valuable form of lignin, compared to Kraft lignin, as a substantial advantage over a plant based solely on ethanol production. Testing the utility of organosolv lignin with phenol-formaldehyde resin is identified as a possible high revenue gainer for a Lignol™ biorefinery [102].
The Lignol™ process for bioethanol production uses 40-60% v/v ethanol with sulphuric acid catalyst to delignify mixed softwoods. Temperatures of 185-198°C were used for 30-60 minutes and liquor to wood ratio was 7:1 to 10:1. More than 90% enzymatic conversion was obtained in 48 hours for all pulps using 40FPU/g (filter paper units/g, a measure of enzyme loading). Chemical and physical analysis showed that lignin from this process can be used for production of lignin based adhesives and other products. Requirements for this are high purity, low molecular weight and abundance of reactive groups. The value of by-products is key to the Lignol™ concept [103]. Although softwoods are in abundance due to waste from forestry, a hardwood to ethanol process using organosolv will result in higher conversions. This is due to the difficulty in pulping softwoods by the organosolv process.

Organosolv pulping is more environmentally friendly and has potential for by-products from the lignin stream. However, pulp washing is difficult due to the re-condensation of lignin and there is a greater risk of fire or explosion using organic solvents. Methanol and ethanol are the most realistic solvents to use in the organosolv process. Kleinert first suggested these solvents in the early 1930’s [104]. Softwoods can be pulped to kappa numbers of 85-100 but then delignification virtually ceases. If organosolv pretreatment is to be used to pulp softwoods, acid catalysts must be used. 0.01M sulphuric acid can reduce the temperature of pulping from 200°C to 170°C. However, any more than 0.01M causes cellulose degradation [105]. Tirtowidjojo et al. [19] confirms that adding 0.01M sulphuric acid catalyst reduces temperature from 180°C to 150°C with the same rate of delignification of black cottonwood.

Ethanol-water pulping shows some benefits over methanol-water pulping including a higher recovery of lignin using flash precipitation and acidified water dilution. The optimal dilution ratio is a trade off between lignin recovery and capital cost of the subsequent distillation step [63].
2 - Background

2.3.1 Reactors and reaction methods

Small scale laboratory reactors can be classified into two types: Batch and flow-through reactors. The ideal industrial scenario is the counter-current reactive extraction of lignin using a solvent. However, the cost and technical complexity of injecting coarse particulate material into a pressurised system of volatile liquid has restricted lab scale work to simulating this by sequential batch or flow through systems.

Tirtowidjojo et al. [19] details the effects of batch versus flow through reactors. The benefits of using a flow through reactor are significant as shown by an increase in reaction rate of 1.8 times. Improvement in rate was significant even at very low flow-rates suggesting the improvement is due to a constant replenishment of hydronium ions. Lignins removed by flow through reactor also had higher molecular weights than batch produced lignins. It is likely that removal of products from the reactor prevented further degradation.

A flow through reactor was used to examine the structure of five lignin fractions extracted at different times. Different proportions of lignin linkages were observed in lignin eluting from the reactor at different times. β-1 structures in recovered lignin decreased with reaction time whereas β-5 structures increased. It is thought that the β-1 structures are more prevalent in easily reacting lignin. β-5 structures may be present in more recalcitrant lignin or lignin may re-condense into lignin containing higher proportions of β-5 links. Either hypothesis results in a greater relative proportion of β-5 being extracted later in the cook [106].

The use of a batch reactor usually requires that the reaction be cooled before the solid and liquid fractions are separated. Lignin reactions may continue during the cooling period, particularly the re-condensation of lignin onto pulp fibers [107].

In order to study re-condensation during organosolv pulping, a batch reactor should be used to promote the reverse reaction of soluble lignin into insoluble lignin. However, reactions during the cooling period should be avoided.
2.3.2 Re-condensation

Re-condensation or re-precipitation, of lignin is the conversion of soluble lignin into solid lignin, which adheres to the wood structure [19, 107, 108]. Re-condensation constitutes a loss of lignin yield and causes a reduction of the rate of subsequent enzymatic hydrolysis due to deactivation of enzymes by lignin [3, 5].

However, some distinction should be made between lignin that re-condenses due to a reaction and lignin that precipitates due to a change in solubility. Sarkannen [109] suggests a re-condensation reaction occurs whereby soluble lignin re-polymerises to a more resistant form of solid lignin. It is reported by Sarkannen that irreversible re-condensation of lignin also occurs during cooling and washing of batch reactors as reported in a Tappi conference report [110].

Several factors may affect the rate and proportion of lignin that re-condenses. Xu et al. [111] examined the effects of washing organosolv pulp and found that lignin precipitates on during pulp washing due to lowering the ethanol concentration or temperature. Figure 2-5 shows the colloidal structure of lignin after drying on a wood fiber. It is also reported that lignin can form a glassy coating like structure.
Precipitation may be caused by a change of the solvent conditions such as lowering temperature or dilution of the organic solvent with water. Lignin then becomes insoluble. Thring et al. [79] uses this effect to recover lignin from organosolv black liquor. The terms re-condensation and re-precipitation are used interchangeably in the literature when referring to organosolv delignification. Lignin precipitated by dilution as a recovery method re-dissolves readily.

The precipitation of lignin back onto pulp fibers is well documented. An increase in solid-liquid ratio in the autocatalysed organosolv process has a minimal effect on delignification due to two opposing factors. High solids ratio increases the acetic acid concentration caused by a release of acetic acid from hemicellulose, lowering pH and increasing delignification while higher lignin concentration results in greater re-condensation of lignin [112].

In contrast, Tirtowidjojo et al. [19] reports that adding isolated lignin to a batch reactor prior to pulping does not increase the final lignin content of the pulp suggesting that higher soluble lignin concentration does not increase re-condensation. No
information is given on the conditions of isolation for the added lignin. Re-precipitation may be exacerbated by lowering the solvent temperature before draining a batch reactor. Use of a flow through reactor eliminates re-precipitation of lignin and gives a rate constant for delignification 1.8 times that for a batch reactor.

Percentage lignin remaining (PLR) during HCl catalysed acetic acid pulping reaches a minimum as shown in Figure 2-6. The subsequent increase of PLR is reportedly due to a mechanism of irreversible consecutive reactions of natural lignin to soluble lignin to re-condensed lignin according to Parajo et al. [84].

![Figure 2-6. % lignin remaining (PLR) during HCl catalysed acetic acid pulping. Parajo et al. [84].](image)

Paszner and Cho [54] show SEM images of lignin precipitated onto pulp fibers. They appear as spheres ranging in size from 1-10μm. Low final liquor pH is blamed for lignin re-condensation.
2.3.3 Mechanisms of organosolv delignification

Lignin extraction requires a combination of solvolysis, solvation and dissolution. Solvolysis is the cleavage of the lignin macromolecule (primarily via cleavage of α-aryl ether bonds), solvation is the association of the lignin fragment with surrounding solvent molecules and dissolution is the transport of the lignin-solvent complex into the bulk fluid [78]. The consensus is that solvolysis is the rate limiting step in lignin extraction.

The most easily hydrolysed bonds in lignin are the α-aryl ether linkages. β-aryl ether (β-O-4) linkages are more resistant to hydrolysis and outnumber α-aryl ethers by 8-10:1 in hardwoods. Activation energies of organosolv delignification agree with the notion that cleavage of α-aryl ether linkages is the controlling mechanism [78].

The cleavage of α-aryl ether linkages by nucleophilic substitution is given by McDonough [113] in Figure 2-7. The reaction can be acid catalysed using mineral acid or by the release of acetic acid from hemicellulose (termed autohydrolysis). Hydrolysis of β-ether linkages, a much slower reaction, cannot be ruled out.

β-ether cleavage may be far more important in the delignification of softwoods. Bose and Francis [114] found a correlation between β-O-4 content of lignin and pulp lignin content of softwood and concluded that β-ether cleavage determines the extent of delignification.

Shatalov and Periera [115] claim that there are several pre-existing structures of lignin with different delignification rates. They determine the delignification kinetics of...
Arundo donax L. using ethanol-alkali mixtures and compare experimentally determined lignin content of treated material to a mathematical model. A set of three parallel reactions is shown to model delignification better than a set of three consecutive reactions as reported in previous work [116]. Lignin types are labelled as initial, bulk and residual and are present in the proportions of 61%, 23% and 16% respectively. Figure 2-8 shows the three distinct kinetic phases having progressively slower reaction rates. The fiber crop Arundo donax L is rather different to most wood feedstocks. In the pulping of most woods, the initial phase of delignification is not observed. The large portion of initial lignin observed for *Arundo donax L* may be due to differences in lignin structure or the differences in plant morphology leading to easier transport of lignin out of the lignocellulosic matrix.

Chip size is not considered critical in ethanol delignification due to the low viscosity and hence high penetration of the organic solvent used [112]. However, this does not rule out the possibility that the three phases of delignification do not relate to lignin in different layers of the cell wall. A change in chip size would not affect the rate of delignification if solvent accessibility is hindered on a microstructural level.
Gilarranz et al. [116] has shown similar results with three phases of delignification observed for the methanol pulping of *Eucalyptus globulus*. The initial phase is only reported to occur during removal of the first 10% of lignin and is not clearly visible at temperatures above 140°C. The rate of residual delignification appears to change little with reaction temperature. This is in contrast to bulk delignification, which changes considerably with temperature. Consequently the activation energies reported were 98.4kJ/mol for bulk delignification and only 31.8kJ/mol for residual. This results in residual delignification being indiscernible from bulk delignification at some temperatures. The percentage of lignin reacting by residual phase kinetics was 21%.

However, work by Tirtowidjojo et al. [19] shows that a change in solvent conditions such as increased acidity or temperature can reduce the proportion of lignin reacting by residual phase kinetics. If the phases are represented by a different lignin structure in the wood, changing the proportion of each would not be possible by simply changing the solvent system. It is more likely that changing the solvent parameters influences the re-condensation reaction or transport properties by altering the solubility of lignin or altering the structure of wood allowing more lignin to react. A lower proportion of residual lignin in *Eucalyptus globulus* is also reported by Santos et al. [117] when a strong acid catalyst is employed (3% w/w dry wood).

In 1941, Hewson et al. [108] refer to the organosolv reaction as ‘ethanolysis’. Treatment with 30% ethanol and 2% HCl shows two distinct phases of reaction. The second, slower phase, termed residual delignification did not increase in rate when fresh liquor was introduced. It was concluded that residual lignin must be different in structure to native lignin. Re-treating lignin recovered by precipitation results in the formation of less soluble lignin presumed to be related to residual lignin. 93% of Maple wood lignin was removed by constant replacement of liquor. This could be an indication of reliance on solubility limit of lignin in the liquor or the recalcitrance of re-condensed lignin.

Hansen and April [118] show the existence of an isokinetic temperature for various types of solvents, indicating that the mechanism for delignification is not affected by the solvent system used. Rate constants at two temperatures for each solvent system were
determined and the activation enthalpy plotted against activation entropy. A straight line relationship was found for two distinct phases of delignification.

Sidiras and Koukios [119] apply a generalised pseudo first order kinetic model to delignification and polysaccharide hydrolysis of wheat straw. Lignin is considered to exist in two fractions. These were called ‘reaction resisting’ lignin (a negligible amount in the feedstock used) and ‘easily reacting’ lignin. Activation energy of 89.3 kJ/mol and frequency factor of $1.2 \times 10^{11}$ min$^{-1}$ was determined for easily reacting lignin. The easily reacting lignin is likely to be analogous to bulk lignin based on the activation energy and proportion present.

Buffered solvent pulping of tulip poplar has been proven to reduce polysaccharide degradation. Sodium bicarbonate was added to the liquor to maintain a pH of 7.2 during pulping. Methylanthraquinone was added to reduce re-condensation of lignin. Residence times of less than 20 minutes were achieved with high temperatures (above 200°C). This was made possible by a reduction of cellulose degradation due to the neutral pH. Two reaction phases were observed having activation energies of 56.4 kJ/mol and 58.1 kJ/mol for the slow and the fast stage of delignification respectively [120].

Virtually all research indicates a slow final stage of delignification now commonly referred to as the residual phase. Kleinert [121] has modified spruce and poplar sawdust by drying under different conditions prior to ethanol-water pulping. Convective drying of spruce at 90°C for 24 hours resulted in a rate of residual delignification 32.1% of that achieved with fresh spruce. A similar effect was observed using wood that had been stored for 15 years before pulping. Kleinert concludes that the aging of the microgel structure of lignin causes this effect.

### 2.3.4 Kinetic parameters of organosolv delignification

Kinetics of delignification for several wood feedstocks and process conditions have been analysed. Here, the delignification kinetics of methanol and ethanol systems will be discussed. In most cases authors analyse lignin reactions as pseudo first order reactions with respect to the lignin concentration of the wood. In 1974, Kleinert [66] identified two
pseudo first order phases during ethanol pulping of spruce and poplar. April et al. [122] applies Equation 2-2 to irreversible first order bulk hydrolysis for each component of wood where A is the percentage of component remaining.

\[
\frac{dA}{dt} = -kA,
\]

Equation 2-2

Several authors report delignification occurring in three distinct phases labelled initial, bulk and residual lignin reactions. The bulk phase is most often the largest portion of the lignin while residual lignin is slower reacting and observable in the later stages of delignification. An initial phase is not often observed. The activation energy (E_a) and proportion of each lignin varies with feedstock and process conditions. For initial lignin, Gilarranz et al. determined E_a=93.1 kJ mol⁻¹ compared to 64 kJ mol⁻¹ by Shatalov and Pereira. For bulk lignin, Gilarranz et al. determined E_a=98.4 kJ mol⁻¹ compared to 89kJ mol⁻¹ determined by Shatalov and Pereira. For residual delignification, Gilarranz et al. determined 31.8kJ/mol compared to 96kJ/mol found by Shatalov and Pereira [115, 116]. Kleinert [121] calculated the activation energy of the slow phase (residual) to be 117.6kJ/mol for the ethanol-water pulping of spruce wood sawdust.

Table 2-2 shows literature values of activation energy and frequency factor for the bulk phase of delignification. Bulk lignin is the major proportion of lignin to the extent that initial and residual delignification kinetics is often not reported. Table 2-2 illustrates the wide range of activation energies (E_a) that have been reported for bulk delignification using different process conditions or different feedstocks. Organosolv pulping has been performed under alkali, acidic and autocatalysed conditions. Autocatalysed organosolv pulping refers to processes in which no catalyst is added and the pH drops as acetic acid is liberated from hemicellulose in the wood. Faass et al. [120] uses a sodium bicarbonate buffer to negate this effect.
2 - Background

Table 2-2. Activation energies of bulk delignification reported in literature.

<table>
<thead>
<tr>
<th>Bulk ( E_a ) (kJ/mol)</th>
<th>( k_0 ) (min(^{-1}))</th>
<th>Condition</th>
<th>Feedstock</th>
<th>Author</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.9</td>
<td>Not reported</td>
<td>Acid</td>
<td>Hardwood</td>
<td>Aravamuthan et al. [123]</td>
<td>1989</td>
</tr>
<tr>
<td>26</td>
<td>9.74E+00</td>
<td>Auto*</td>
<td>Hardwood</td>
<td>Pereira et al. [124]</td>
<td>1986</td>
</tr>
<tr>
<td>57.4</td>
<td>1.63E+04</td>
<td>Alkali</td>
<td>Hardwood</td>
<td>Park and Phillips [125]</td>
<td>1988</td>
</tr>
<tr>
<td>58.1</td>
<td>3.26E+05</td>
<td>Neutral pH</td>
<td>Hardwood</td>
<td>Faass et al. [120]</td>
<td>1989</td>
</tr>
<tr>
<td>80.3</td>
<td>Not reported</td>
<td>Acid</td>
<td>Hardwood</td>
<td>Tirtowidjojo et al. [19]</td>
<td>1988</td>
</tr>
<tr>
<td>82.9</td>
<td>1.72E+06</td>
<td>Auto*</td>
<td>Softwood</td>
<td>Aravamuthan et al. [123]</td>
<td>1989</td>
</tr>
<tr>
<td>89</td>
<td>1.62E+10</td>
<td>Alkali</td>
<td>Grass</td>
<td>Shatalov and Pereira [115]</td>
<td>2005</td>
</tr>
<tr>
<td>89.3</td>
<td>1.20E+11</td>
<td>Acid</td>
<td>Wheat straw</td>
<td>Sidiras and Koukios [119]</td>
<td>2004</td>
</tr>
<tr>
<td>98.4</td>
<td>2.59E+10</td>
<td>Acid</td>
<td>Hardwood</td>
<td>Gilarranz et al. [116]</td>
<td>1999</td>
</tr>
</tbody>
</table>

*Autocatalysed/uncatalysed

The activation energy for the delignification of model lignin compounds was determined by Meshgini and Sarkanen [126] to fall between 79 and 118kJ/mol. This was close to the activation energy for hydrolysis of \( \alpha \)-aryl ether linkages. The hydrolysis rate of \( \beta \)-aryl ether bonds was found to be two orders of magnitude slower. Thus, cleavage of \( \alpha \)-aryl ether linkages was concluded to be the rate limiting step of delignification.

2.3.5 The effect of pH during ethanol-water pulping

The important parameters in acidified ethanol pulping are pH and temperature. While the importance of temperature is expected due to the Arrhenius relationship with reaction rate constant, the effect of pH is less well understood.

The importance of pH is evident in the acetic acid pulping of *Pinus pinaster* wood. Acetic acid concentration was found to be an important factor and a concentration of 90%
v/v was suggested as the best by Vazquez et al. [20]. The addition of HCl catalyst reduced the activation energy of delignification from 78.8 to 69.7kJ/mol.

Several factors change the pH during ethanol pulping. Acetyl groups on hemicellulose end chains depolymerise to acetic acid at the temperatures used during ethanol pulping, increasing acidity. Work by Hewson et al. [107] shows that water ionises the catalyst making delignification faster. Thus, lower ethanol concentrations result in faster reaction.

This is confirmed by the work of Goyal et al. [127] showing that delignification is higher at 50% v/v ethanol concentration than at 70% v/v ethanol concentration. Higher hydronium ion concentration at lower ethanol concentrations was identified as the cause. Goyal et al. also noted that syringyl lignin is removed faster than guaiacyl lignin.

Goyal and Lora [128] measure the pH during autocatalysed organosolv pulping of white birch and incorporate hydronium ion concentration into the kinetics. The reaction is assumed first order with respect to H⁺ concentration and a modified rate constant, k’, is defined such that k’=k/[H⁺]. Activation energy of 82.9kJ/mol is calculated without pH correction and 67.8kJ/mol with pH correction.

Others have reported that hardwood lignin is more easily removed by the organosolv process compared to softwood lignin due to the higher syringyl lignin content of hardwoods [66, 123]. The resistance of softwoods to solvent pulping is well documented. It is hypothesised that guaiacyl lignin has fewer easily cleaved α-O-4 linkages [78].

The use of an acid catalyst is found to be essential for significant delignification of softwood. For solvent-water mixtures, molar concentration of acid is an inferior measure of acidity compared to an acidity function. However, pH is difficult to measure above temperatures of 100°C and the literature has little information on pH variation with temperature [114].

A treatment prior to organosolv delignification has been used to remove acid neutralising components from the wood. The term ‘de-ashing’ has been used to describe the soaking of biomass in dilute acetic acid to solubilise and remove components of wood.
that otherwise neutralise the acid catalyst used in organosolv. Although the acid neutralising components are likely to be proteins (extractives), the term de-ashing will be used in this thesis to indicate the same treatment described by Tirtowidjojo et al. [19].

Bulk delignification rate constant is nearly proportional to catalyst concentration when de-ashed black cottonwood is used. Tirtowidjojo et al. [19] demonstrated that the better performance of a flow-through versus batch reactor is due to the constant addition of fresh liquor thereby reducing lignin re-condensation reactions and eliminating the neutralising effect of biomass by continuous replacement of the acid catalyst. Activation energy of 80.3kJ/mol was measured for delignification of Black cottonwood with 70% v/v methanol and 0.01M H₂SO₄. This work also showed that the onset of residual delignification occurs at lower lignin content when either a flow through reactor is used or reaction severity is increased. This indicates that either the equilibrium of the re-condensed lignin depolymerisation and re-polymerisation is affected by the liquor conditions, or that the liquor conditions are affecting the transport properties of lignin through the wood matrix.

Gilarranz et al. [116] has determined the dependence of initial, bulk and residual delignification on H⁺ concentration. Lignin conversion rate is proportional to hydronium ion concentration to the power of 0.293, 0.214 and 0.97 for initial, bulk and residual phases respectively. Other researchers have used a power law relationship of bulk rate constant to H⁺ concentration with an exponent of unity [19, 21]. Gilarranz et al. used very low solid:liquid ratios of 1:50 (kg:L) with buffered methanol water solutions to determine the kinetic parameters for fitting a model to organosolv delignification. This causes the pH to remain constant for accurate determination of model data. A model for delignification comprising three consecutive reactions for initial, bulk and residual delignification is then verified by autocatalysed delignification at a liquor-wood loading of 7L/kg. The pH is shown to change significantly from 7.5 to below 4 during the autocatalysed experiments.

Yawalata [72] investigates the effect of different catalysts in the selectivity of lignin removal with the goal of fiber separation. Final pulping liquor with pH between 3.8 and
4.2 was necessary for high fiber yield and quality. Delignification was reduced when pH dropped below 3.5 and citric acid was the most effective organic acid for fiber liberation. Structural studies of organosolv lignin show that higher severity results in greater degradation of lignin side-chains, losing functionality of lignin [62].

Delignification has been shown to occur first in the secondary cell wall during the aging of spirits. Acetic acid inducing a pH of 4.25 was found to reduce secondary reactions [129].

Presoaking has a profound effect on delignification rate. The role of solvent system and catalyst type is not clearly understood, but high catalyst concentrations have been found to be less selective towards delignification and cause increased re-condensation. Selectivity is independent of the type of catalyst used provided that low levels of catalyst are employed [78, 130].

The effect of added acid catalysts is complicated by a combination of the release of acetic acid and the neutralising effect of ash and extractives. Much of the literature does not report the pH during pulping or consider the neutralising effect of biomass. In such cases, the catalyst concentration at low catalyst loadings is not a true indication of acidity.

High catalyst loading is known to favour hemicellulose removal over lignin [110]. Selectivity of conditions and treatments prior to organosolv delignification will now be discussed in more detail.

### 2.3.6 Lignin and polysaccharide selective pulping sequences

Pan et al. tested a set of 17 different conditions and the greatest percentage glucose detected in the water soluble fraction was 8.6% (w/w glucose in feed) at conditions of 195°C, 80 minutes, 1.5% H₂SO₄ (g/g dry wood) and 65% v/v ethanol. A small fraction of hydroxymethyl furfural (a degradation product of glucose) was also detected. Under the centre point conditions of 180°C, 60 minutes, 1.25% H₂SO₄ (g/g dry wood) and 50% v/v ethanol, 88% of glucose was retained in the pulp while only 28% of the lignin and 19%
of the xylose was retained. Changing the conditions showed changes in selectivity towards hemicellulose and lignin [49].

The term prehydrolysis is used by some researchers to describe hydrolysis of hemicellulose during the organosolv pulping process. To avoid confusion, prehydrolysis is used henceforth to describe a hydrolysis step prior to organosolv pulping. Prehydrolysis is usually selective to dissolution of hemicellulose. It is not to be confused with pre-soaking, which logically does not remove any major constituents of a lignocellulosics material. The purpose of pre-soaking is the swelling of the wood matrix, which is considered to be the driving force of fiber liberation [118].

Patel and Varshney [131] investigate the effect of presoaking and prehydrolysis of bagasse prior to organosolv delignification. 40-50% of hemicellulose can be removed by prehydrolysis with minimal degradation of other components. Removal of solids with a 4 hour treatment in 0.1% H₂SO₄ at 125°C was 41.1% of the pentosan, 5.17% of the cellulose and lignin loss reported as 1.22% making a total of 12.9% of input dry mass solubilised. Subsequent ethanolysis at 200°C removes 90% of lignin. Prehydrolysis without catalyst at 175°C resulted in significant solubilisation of both hemicellulose (67% w/w) and lignin (31% w/w).

The kinetics of organosolv delignification of hardwoods and softwoods following a prehydrolysis step with SO₂ and water is reported by Aravamuthran et al. [123]. The activation energy of uncatalysed ethanol water pulping was found to be 82.9kJ/mol. In the 0.01M H₂SO₄ catalysed ethanol-water pulping system, the activation energy was 20.9kJ/mol. Softwood pulping without catalyst restricted the removal of lignin to only 50% of the original amount whereas removal of 90% of hardwood lignin was achieved using an acid catalyst.

Wheat straw was subjected to one of two treatments prior to organosolv by Lawther et al. [132]. Either an alkali pretreatment at 75°C or an acid prehydrolysis at 99°C was performed. Each treatment was then followed by organosolv delignification at 75°C using 60% v/v ethanol with a 1.0N H₂SO₄ catalyst. The alkali treatment removed more lignin
(51.2% of lignin present) than the acid prehydrolysis (23.0%). However, the acid prehydrolysis resulted in a faster subsequent organosolv delignification rate.

Hasegawa et al. [133] claims that lignin cannot be extracted until hemicellulose is removed. Hasegawa et al. used a hot water pretreatment and acetone lignin extraction each at 180°C for extracting lignin from oil palm shells. However, Wang and Avgerinos [134] show that 65% of lignin can be removed from corn stover with only a 5% removal of hemicellulose using a long reaction time (80 hours) at 25°C in base catalysed ethanol-water solutions (50% v/v).

Hemicellulose is extracted in a highly selective manner under dilute acid conditions of 0.5-2.5N H₂SO₄ in water at reflux temperatures. Lignin is then extracted, also in a selective manner, by acid catalysed ethanol-water treatment at 81°C. Higher ethanol concentration results in reduced fractionation of hemicellulose [135]. Whether this is only due to pH difference caused by changing the ethanol concentration is not verified.

April et al. [122] claims that a lower resistance to solvent penetration is the cause of higher delignification rates when southern yellow pine is prehydrolysed with water at 180°C to 250°C prior to organosolv delignification with butanol-water mixtures.

Differences in lignin chemical structure were observed when *Populus deltoides* (an aspen hybrid) woodmeal was subjected to ethylene glycol pulping with or without a prehydrolysis in water at temperatures up to 223°C. The greater degradation of lignin fractions isolated from prehydrolysed and organosolv pulped aspen was attributed to modification of the lignin during the prehydrolysis [136].

Chemi-thermo mechanical pulp (CTMP) delignifies to a greater extent than thermo mechanical pulp (TMP) when subjected to the same 50% v/v ethanol pulping with 0.1M acetic acid at 175°C in a flow through reactor. Thermo mechanical pulping employs high temperatures (usually by steaming) and mechanical action to de-fiberise wood. Chemi-thermo mechanical pulping also uses Na₂SO₃ to further dissolve lignin. The difference in organosolv delignification is attributed to presence of sulphonic acid groups in the lignin
in CMPT improving dissolution of lignin or that the CMPT has greater accessibility brought about by greater surface area or hydrophilicity [106].

Delignification using ethanol pulping was more effective when applied to severe steam explosion treated corn stover. This is presumed to be due to the structure of corn stover being more accessible to the ethanol solvent after being ripped apart by explosive decompression [137]. However, if delignification is indeed reaction controlled, the effect must be attributed to alteration of lignin by the acidic conditions of steam explosion. It is possible that removal of hemicellulose is facilitating mass transfer of lignin deep within the structure, allowing greater solubilisation and dissolution of depolymerised lignin that would otherwise be inaccessible.

An organosolv step is incorporated into two-stage acid hydrolysis by Aravamuthan et al. [138] in order to prevent the re-condensation of acid soluble lignin. The process consists of an SO$_2$/H$_2$O prehydrolysis at mild temperatures to hydrolyse hemicellulose followed by an acid catalysed ethanol/H$_2$O delignification step. The SO$_2$ treatment stage gave xylose yields of 81% and 86% w/w for 2 and 3 hour treatment respectively. The use of 0.25 to 0.5% w/w SO$_2$ and temperatures from 125 to 130°C are given as the optimum conditions. For the organosolv delignification step, increasing ethanol concentration was beneficial up until a concentration of 70% v/v and it was noted that any further study should be conducted for ethanol concentration 60 to 70% v/v and temperature from 150 to 160°C for times of approximately 2 hours.

Patel and Varshney [131] and April et al. [122], compare prehydrolysed feedstock delignification with untreated feedstock delignification without any mention of pH measurement of the liquor. Vast improvements in delignification rate are observed following prehydrolysis but the effects of these treatments on the pH of organosolv treatment are not mentioned. If pH measurements are taken, it is still not possible to determine the actual H$^+$ ion concentration in the wood chips at the site of the reaction nor is it easy to obtain an accurate value of pH at elevated temperature [139]. Tirtowidjojo et al. [19] used de-ashing to ensure that the bulk solvent pH is representative of the pH throughout any wood chip. Faass et al. [120] uses a buffer and, like many others, an
impractically small chip size (<1mm) to minimise H⁺ concentration gradient from the bulk liquor into the wood chip.

**2.4 Problem statement**

Literature indicates the existence of re-condensed lignin and shows that it has a lower reaction rate than native lignin. Lignin content at which residual delignification occurs can be changed by altering the liquor conditions. This rules out the possibility of more resistant types of lignin pre-existing in wood. However, it is unclear as to whether the residual phase is caused by a change in the rates of various reactions occurring during organosolv delignification or a transition of the rate controlling mechanism from reaction to mass transfer.

There are three possible explanations for the transition to a residual phase.

1. **Equilibrium is reached between de-polymerization and re-polymerization reactions of re-condensed lignin.**

   The rate of the forward and reverse reaction is affected by the reaction conditions. The parameters that might affect lignin re-condensation rate are pH, solvent concentration and temperature.

2. **There is a change in mechanism from reaction controlled to solubilisation and dissolution controlled.**

   The transport properties of lignin out of the wood matrix are affected by the conditions of the liquor. A change of the solvent concentration (liquor viscosity) or temperature will change diffusion rates.

3. **The removal of lignin is halted by the presence of hemicellulose.**

   At lower pH, the hemicellulose is readily removed allowing rapid bulk phase delignification of lignin that would otherwise exist in a complex with hemicellulose. The conditions of the liquor would only affect the transition to a residual phase if hemicellulose removal was also affected. Therefore, pH
and temperature would affect the lignin concentration at the point of transition to residual kinetics but solvent concentration would not.

There is a confounding effect between ethanol concentration and pH during ethanol-water pulping. The pH must be controlled in order to study the effect of ethanol concentration in isolation. A change in the transport properties of the liquid and accessibility of the solvent can then be investigated to exclude a mass transport controlled mechanism from the cause of residual delignification. Section 4.2.2 examines different ethanol concentrations while attempting to control pH using a buffer.

Literature using prehydrolysis shows that delignification is very fast when hemicellulose is removed from the wood prior to ethanolysis [122, 131]. This adds weight to the third possibility since removal of only hemicellulose would increase the accessibility of lignin. However, the literature does not confirm the cause of faster delignification rates using prehydrolysed feedstocks. Prehydrolysis may improve the subsequent organosolv delignification rate due to improved mass transfer resulting from lower hemicellulose content. De-ashing, as described by Tirtowidjojo et al. [19], removes neutralising components of wood. Prehydrolysis also removes neutralising components. In order to confirm the effect of hemicellulose content and accessibility of the solvent to lignin, delignification rate of these two feedstocks must be compared along with measurement of the pH.

In order to rule out the effects of prehydrolysis on the pH of subsequent organosolv delignification, it must be compared to a feedstock with neutralising components removed. This is dealt with in Section 4.3.3 where a comparison is made between delignification of de-ashed and prehydrolysed feedstock.
3 Organosolv materials and methods

This chapter describes the materials and methods used for the organosolv pulping of willow and the pre-organosolv treatments. The preparation of feedstocks is described for *Salix alba* (for organosolv delignification in a 100ml reactor and subsequent examination of wood structure) and *Salix schwerinii*, (used for compositional analysis and delignification experiments). Two reactors are described and the method of operation is described for each set of experiments.

The methods of analysis are described for each set of experiments. These methods consist mainly of analysis of acid insoluble and acid soluble lignin by the Klason method, dry matter analysis of black liquor (organosolv liquor containing solubilised wood components) by dry solids measurement or dilution followed by separate dry solids measurement of precipitable and non-precipitable solids and UV visible absorbance measurements of black liquor using existing protocols.

### 3.1 Feedstock preparation

Each experiment using wood as a feedstock requires that a representative sample of wood is used each time. This is to ensure that process parameters can be examined without the influence of variation in feedstock. To do this, wood must be dried to sufficiently low moisture content that microbial degradation is inhibited and then bagged to prevent further water adsorption. Chipped dry wood was coned and quartered into equal aliquots after air drying to reduce random variation between the feedstock of each experiment.

#### 3.1.1 Re-precipitation experiments

Two-year-old stems (diameter ≈ 20mm, length ≈ 1m) of *Salix alba* (white willow) were harvested from a farm in Pukekoe, Auckland. They were chipped in an Arlee garden mulcher producing chips of dimensions approximately 10x5x1mm. The chipped wood was dried at 40°C and sieved by hand between two wire meshes of British test sieve aperture 2800μm and 4000μm. The dried and sieved portion of the wood chip was then
sealed inside a plastic bag, double bagged to prevent any change in moisture content and frozen at -20°C to reduce microbial degradation. A sample was dried at 105°C and the moisture content determined to be 9% w/w on a dry basis in accordance with National Renewable Energy Laboratory (NREL) biomass analysis protocols.

### 3.1.2 Autocatalysed, buffered and catalysed delignification

*Salix schwerinii* was used for further experiments because this species was identified as fast growing and a large sample was made available. It was grown at a willow farm in Wairoa, New Zealand. Two year old stems, of thickness approximately 30mm and length approximately 1m, were harvested in mid-winter. The willow stems were chipped in an Arlec garden mulcher and air dried to a moisture content of approximately 11%. Moisture content analysis was performed periodically during the period of experimentation to ensure the correct dry mass inputs. The approximate dimensions of the chips were 20x7x2mm.

#### 3.1.2.1 Autocatalysed delignification feedstock

In order to obtain two different size fractions, the dried wood chips were then sieved and the portion larger than 4.0mm mesh was retained. These large wood chips were coned and quartered and separated into two equal portions. One portion was ground in a Breville CG2B grinder.

Each portion was separated into 280g aliquots to be pulped in the organosolv reactor. An aliquot of each chip size was sieved and the weight average mean chipped size ($d_w$) was determined. The large wood chip was sieved using seven sieves of aperture ranging from 0.15mm to 9.5mm and had a weight average mean size of 8.2mm. The small wood chip was sieved using ten sieves of aperture ranging from 0.063mm to 4mm and had a weight average mean of 2.7mm. Chip size data is available in Appendix 1.

Four aliquots of 280g were prepared from the 8.2mm wood chips and four aliquots of 280g were prepared from the 2.7mm wood chips. This was done in order to verify that chip size had no effect on delignification rate. Chip size is not considered important as
discussed in Section 2.3.3. However, sufficient differences in chip size may not have been tested to make this conclusion for all wood chip or particle sizes.

### 3.1.2.2 Buffered and catalysed delignification feedstock

Chipped, dried *S. schwerinii* retained on a British test sieve aperture 2800μm was used for all further experiments. Each portion was separated into 280g aliquots to be pulped in the organosolv reactor.

### 3.1.2.3 Klason lignin analysis

Klason lignin analysis was performed using a modified version of the National Renewable Energy Laboratory (NREL) analytical procedures for lignin content determination [140]. A representative portion of the wood chip used in all experiments was ground to pass through a 2mm sieve in a Retsch SM100 grinder (similar to a wiley mill), exhaustively extracted in ethanol using soxhlet apparatus as described by Ehrman [141] and subjected to Klason lignin analysis in triplicate for pre-organosolv willow and duplicate for all treated willow samples. 0.2-0.3g of chipped sample was subjected to hydrolysis at 30°C in 3mL of 72% w/w H₂SO₄ for 1 hour followed by dilution to 4% H₂SO₄ (by washing into a schott bottle with 84mL deionised water) for dilute acid hydrolysis. The schott bottles were tightly sealed and heated in a convection oven at 121°C for one hour, cooled in the oven at 90°C for one hour and then allowed to cool to room temperature. Final cooling was accelerated by the use of a convective laboratory fan. The samples were then filtered through pre-weighed filter crucibles of porosity 3. The filtrate was subjected to UV visible spectroscopy for acid soluble lignin content. The absorbance at 320nm was recorded and acid soluble lignin (ASL) content determined using an absorbance of 11.4Lg⁻¹cm⁻¹ as suggested by Ramirez [142] for measuring the ASL of Poplar. The retentate was dried in the filter crucibles at 105°C for 8 hours and weighed, ashed in a muffle furnace and reweighed to determine the acid insoluble lignin (AIL) fraction. Table 3-1 shows the compositional analysis of *S. schwerinii* determined using this method.
Table 3-1. Untreated *Salix schwerinii* composition using the modified NREL protocol.

<table>
<thead>
<tr>
<th>Component</th>
<th>% (w/w)</th>
<th>σ (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol extractives</td>
<td>4.2%</td>
<td>0.17%</td>
</tr>
<tr>
<td>Water extractives (WE)</td>
<td>2.26%</td>
<td></td>
</tr>
<tr>
<td>Lignin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid soluble</td>
<td>5.98%</td>
<td>0.38%</td>
</tr>
<tr>
<td>Acid insoluble</td>
<td>20.65%</td>
<td>0.23%</td>
</tr>
<tr>
<td>Total</td>
<td>-------</td>
<td>26.63%</td>
</tr>
<tr>
<td>Ash</td>
<td>&lt;0.1%</td>
<td></td>
</tr>
<tr>
<td>Cellulose and hemicellulose (by difference)</td>
<td>66.9%</td>
<td></td>
</tr>
</tbody>
</table>

All organosolv and pre-organosolv treated willow was analysed using this procedure and total lignin content (TL) was taken as the sum of ASL and AIL.

A similar two-stage acid hydrolysis procedure was performed at the School of Biological Sciences (SBS) this time with quantification of individual polysaccharides. Only untreated, de-ashed and prehydrolysed willow was tested for polysaccharide content because the protocol was instigated close to the end of this research and quantification of all treated willow specimens was not practical due to time and budget constraints. The following procedure was used on willow samples after exhaustive soxhlet extraction using ethanol. The acid hydrolysis is based on TAPPI test methods.

The sample was ground in a Wiley mill to a size passing a 0.6mm sieve. 50mg was weighed into a glass hydrolysis tube and 1.0mL of 72% w/w H₂SO₄ was added. The tube was placed in a water bath at 30°C for 1 hour. 3mL of Milli Q water was added and the contents were transferred to a 50mL volumetric flask using 25mL water making a 0.5M H₂SO₄ solution. The flasks were placed in an autoclave at 121°C for 1 hour and then cooled. The solution was then made up to 50mL and filtered through pre-weighed glass filter crucibles of porosity 4. The filter crucibles were dried at 105°C and weighed to give acid insoluble lignin. Polysaccharides were measured by high performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD) using a
CarboPac PA20 column. The flow rate was 0.4mL/minute using the following solutions at each time interval (% by volume);

0 to 20 minutes - 80% water, 20% 5mM NaOH;

20 to 25 minutes - 50% 400mM NaOAc, 50% 400mM NaOH;

25 to 35 minutes - 50% water, 50% 400mM NaOH;

35 to 45 minutes - 80% water, 20% 5mM NaOH.

The HPAEC-PAD spectra are shown in Appendix 2.

Table 3-2 shows the composition, including hydrolysis sugars, of *S. schwerinii* using this protocol. The total lignin content is slightly higher than that determined by the modified NREL protocol. The modified NREL protocol resulted in much lower standard deviations of both ASL and AIL.
### Table 3-2. Untreated *S. schwerinii* composition using the School of Biological Sciences (SBS) protocol, University of Auckland.

<table>
<thead>
<tr>
<th>Untreated feedstock</th>
<th>% (w/w)</th>
<th>% (w/w)</th>
<th>σ (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin</td>
<td>29.9%</td>
<td>±</td>
<td>2.7%</td>
</tr>
<tr>
<td>---- ASL</td>
<td>6.3%</td>
<td>±</td>
<td>3.4%</td>
</tr>
<tr>
<td>---- AIL</td>
<td>23.5%</td>
<td>±</td>
<td>2.8%</td>
</tr>
<tr>
<td>Polysaccharides</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cellulose sugars</td>
<td>40.2%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---- Glucose</td>
<td>40.2%</td>
<td>±</td>
<td>1.5%</td>
</tr>
<tr>
<td>Hemicellulose sugars</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---- Xylose</td>
<td>15.8%</td>
<td>±</td>
<td>0.5%</td>
</tr>
<tr>
<td>---- Arabinose</td>
<td>0.7%</td>
<td>±</td>
<td>0.0%</td>
</tr>
<tr>
<td>---- Galactose</td>
<td>2.7%</td>
<td>±</td>
<td>0.3%</td>
</tr>
<tr>
<td>---- Mannose</td>
<td>2.0%</td>
<td>±</td>
<td>0.0%</td>
</tr>
<tr>
<td>Ethanol extractives</td>
<td>4.0%</td>
<td>±</td>
<td>0.2%</td>
</tr>
<tr>
<td>Water extractives</td>
<td>2.3%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ash</td>
<td>&lt;0.1%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>97.6%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.1.2.4  *De-ashing*

1kg (moisture content =9% d.b. giving a dry mass of 917g) of *S. Schwerinii* wood chips of size not passing 2.8mm was added to a 20L bucket. 15L of deionised water and 150mL of glacial acetic acid was added and stirred by hand. The reagents were allowed to soak for 3 days then the wood chip was poured onto a 0.5mm stainless steel mesh and washed with deionised water. This process was repeated with deionised water to allow all acetic acid to diffuse from the wood chip. The wood was then screened again, washed and dried at 45°C for 48 hours. The composition measured using the modified NREL protocol and SBS protocol are shown in Table 3-3 and Table 3-4 respectively. The reduction in solid mass during de-ashing was 3.2% w/w initial dry mass.
Table 3-3. De-ashed *S. schwerinii* composition by the modified NREL protocol.

<table>
<thead>
<tr>
<th>Component</th>
<th>% (w/w)</th>
<th>σ (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol extractives</td>
<td>2.39%</td>
<td>0.15%</td>
</tr>
<tr>
<td>Water extractives (WE)</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>Lignin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid soluble</td>
<td>6.40%</td>
<td>0.86%</td>
</tr>
<tr>
<td>Acid insoluble</td>
<td>21.85%</td>
<td>0.46%</td>
</tr>
<tr>
<td>Total</td>
<td>---------</td>
<td>28.25%</td>
</tr>
<tr>
<td>Ash</td>
<td>&lt;0.1%</td>
<td></td>
</tr>
<tr>
<td>Cellulose, hemicellulose and WE (by difference)</td>
<td>69.36%</td>
<td></td>
</tr>
</tbody>
</table>

Table 3-4. De-ashed *S. schwerinii* composition by the SBS protocol.

<table>
<thead>
<tr>
<th>De-ashed feedstock</th>
<th>% (w/w)</th>
<th>% (w/w)</th>
<th>σ (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin</td>
<td>32.7%</td>
<td>±</td>
<td>0.6%</td>
</tr>
<tr>
<td>----ASL</td>
<td>7.3%</td>
<td>±</td>
<td>1.9%</td>
</tr>
<tr>
<td>----AIL</td>
<td>25.4%</td>
<td>±</td>
<td>2.2%</td>
</tr>
<tr>
<td>Polysaccharides</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cellulose sugars</td>
<td>36.0%</td>
<td>±</td>
<td>1.1%</td>
</tr>
<tr>
<td>----Glucose</td>
<td>36.0%</td>
<td>±</td>
<td>1.1%</td>
</tr>
<tr>
<td>Hemicellulose sugars</td>
<td>22.5%</td>
<td>±</td>
<td>2.1%</td>
</tr>
<tr>
<td>----Xylose</td>
<td>15.0%</td>
<td>±</td>
<td>0.4%</td>
</tr>
<tr>
<td>----Arabinose</td>
<td>1.1%</td>
<td>±</td>
<td>0.6%</td>
</tr>
<tr>
<td>----Galactose</td>
<td>3.6%</td>
<td>±</td>
<td>1.0%</td>
</tr>
<tr>
<td>----Mannose</td>
<td>2.8%</td>
<td>±</td>
<td>0.6%</td>
</tr>
<tr>
<td>Ethanol extractives</td>
<td>2.4%</td>
<td>±</td>
<td>0.2%</td>
</tr>
<tr>
<td>Water extractives</td>
<td>n.d.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ash</td>
<td>&lt;0.1%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>93.6%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

n.d. = not determined
3.1.2.5 Prehydrolysis

Prehydrolysis was carried out using a 7L aluminium pressure cooker shown in Figure 3-1. 600g (moisture content =9% d.b. giving a dry mass of 550g) of *S. Schwerinii* wood chips of size not passing 2.8mm was added to the pressure cooker with 5L of 0.24% w/w (0.024M) H$_2$SO$_4$ in deionised water. The pressure cooker was brought up to 121°C on a hot plate and held at that temperature for 2 hours. The wood chips were then poured onto a 0.5mm stainless steel mesh and washed with deionised water. The process was repeated for 4 hours in 0.12% w/w (0.012M) H$_2$SO$_4$ then screened and washed. The wood chips were then screened and washed and treated again for 2 hours in deionised water at 121°C. The deionised water hydrolysis was repeated again to ensure that no H$_2$SO$_4$ remained. The wood was then screened, washed and dried at 45°C for 48 hours.

![Figure 3-1. 7L aluminium pressure cooker](image)

The composition measured using the modified NREL protocol and SBS protocol are shown in Table 3-5 and Table 3-6 respectively. One of the HPAEC-PAD results was discounted as an outlier. The sugar percentages of the prehydrolysed sample using the SBS protocol is the average of only two replicates. The reduction in solid mass during prehydrolysis was 15.3% w/w initial dry mass.
### Table 3-5. Prehydrolysed *S. schwerinii* composition by the modified NREL protocol.

<table>
<thead>
<tr>
<th>Component</th>
<th>% (w/w)</th>
<th>σ (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol extractives</td>
<td>1.71%</td>
<td>0.45%</td>
</tr>
<tr>
<td>Water extractives (WE)</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>Lignin</td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Acid soluble</em></td>
<td>2.95%</td>
<td>0.11%</td>
</tr>
<tr>
<td><em>Acid insoluble</em></td>
<td>28.79%</td>
<td>0.03%</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>--------</td>
<td>31.74%</td>
</tr>
<tr>
<td>Ash</td>
<td>&lt;0.1%</td>
<td></td>
</tr>
<tr>
<td>Cellulose, hemicellulose and WE (by difference)</td>
<td>66.6%</td>
<td></td>
</tr>
</tbody>
</table>

### Table 3-6. Prehydrolysed *S. schwerinii* composition by the SBS protocol.

<table>
<thead>
<tr>
<th>Prehydrolysed feedstock</th>
<th>% (w/w)</th>
<th>±</th>
<th>σ (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin</td>
<td>34.4%</td>
<td>±</td>
<td>0.9%</td>
</tr>
<tr>
<td>----ASL</td>
<td>5.3%</td>
<td>±</td>
<td>1.2%</td>
</tr>
<tr>
<td>----AIL</td>
<td>29.1%</td>
<td>±</td>
<td>1.8%</td>
</tr>
<tr>
<td>Polysaccharides</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cellulose sugars</td>
<td>34.8%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>----Glucose</td>
<td>34.8%</td>
<td>±</td>
<td>0.8%</td>
</tr>
<tr>
<td>Hemicellulose sugars</td>
<td>19.7%</td>
<td>±</td>
<td>0.7%</td>
</tr>
<tr>
<td>----Xylose</td>
<td>14.9%</td>
<td>±</td>
<td>0.4%</td>
</tr>
<tr>
<td>----Arabinose</td>
<td>0.2%</td>
<td>±</td>
<td>0.0%</td>
</tr>
<tr>
<td>----Galactose</td>
<td>2.0%</td>
<td>±</td>
<td>0.0%</td>
</tr>
<tr>
<td>----Mannose</td>
<td>2.6%</td>
<td>±</td>
<td>0.4%</td>
</tr>
<tr>
<td>Ethanol extractives</td>
<td>1.7%</td>
<td>±</td>
<td>0.5%</td>
</tr>
<tr>
<td>Water extractives</td>
<td>n.d.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ash</td>
<td>&lt;0.1%</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>90.6%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

n.d. = not determined
3.2 Organosolv pulping

Prepared and characterized feedstocks were used in a series of experiments using two different reactors, a small scale 100mL tube reactor, and a larger 3L packed bed reactor. Four sets of experiments were performed. Experiments were performed to investigate;

1. Lignin re-condensation using SEM,

2. Un-catalysed (auto-catalysed) organosolv pulping at different ethanol concentrations,

3. Buffered organosolv pulping at different ethanol concentrations and

4. Catalysed organosolv pulping with using pre-organosolv treated feedstock and measurement of pH.

3.2.1 Lignin re-precipitation experiments

A small scale reactor was used to prepare organosolv pre-treated wood for micro-structural analysis by scanning electron microscopy (SEM). Mass of wood solubilised was also investigated using this reactor and procedure. Full details of that work is published in the proceedings of the 5th Asia Pacific Conference on Sustainable Energy and Environmental Technologies [143].

3.2.1.1 Reactor

The pretreatment reactor shown in Figure 3-2 was designed and built for the purpose of carrying out these experiments. It consists of a 1” x 300mm long reaction tube (1) with an externally wound heating coil (2) connected to a Swagelok™ end-cap (3) with a welded port for a pressure transducer (4) and thermocouple (5). The other end of the tube is connected to a Swagelok™ 1” integral bonnet needle valve (6) connected to a 1” collection tube (7) of the same length as the reactor. The temperature of a thermocouple (8) wedged underneath the heating coil is controlled by a controller (9) regulating power output to the heating coil. This configuration facilitates the removal of solvent at
temperatures well above the boiling point of the solvent. A 1/4” integral bonnet needle valve (10) at the end of the collection tube is used to remove solvent after cooling in the collection tube. A support bridge (11) holds the pressure transducer and wires in place.

Figure 3-2. 100mL batch organosolv reactor.
3.2.1.2 Procedure

The reactor was loaded with 7.96g of the dried and frozen \textit{S. alba} chips and 83.5mL of 70\% ethanol. The reactor was sealed at all Swagelok™ fittings and both needle valves were closed. The temperature controller was set to the process temperature (180°C, 190°C, or 200°C) and the power was connected to the heating element. The reactor was mounted vertically on a swivel and agitation was provided during heat-up by inverting the reactor every minute to ensure that the process reached equilibrium quickly. Timing was started when the internal temperature, monitored on Picolog™, reached 5°C less than the selected process temperature. The time required for this to occur was 7 minutes ± 1 minute. At equilibrium, the temperature was controlled to within ±2°C of the selected temperature. The reaction was allowed to proceed for 80 or 100 minutes with periodic agitation by inverting the reactor ensuring an even temperature throughout. The conditions examined were;

- 80 minutes, 180°C, solvent separation at 180°C
- 100 minutes, 180°C, solvent separation at 180°C
- 100 minutes, 190°C, solvent separation at 190°C
- 100 minutes, 200°C, solvent separation at 200°C
- 100 minutes, 200°C, solvent separation at 40°C

At the end of the reaction time, the reactor was inverted and the Swagelok™ needle valve was opened to allow the solvent to drain into the collection tube without significant reduction in process pressure. Solvent was either removed to the collection tube at the process temperature or allowed to cool to 40°C before removal. A fine stainless steel mesh (12) positioned in the reactor against the valve, retains the solids fraction in the reaction vessel. The contents of the reactor and the collection tube were then cooled down to below the normal boiling point of the solvent (80°C) and the solvent was removed from the collection tube. The reactor was then filled with 83.5mL of wash water, then sealed and heated to ~110°C. The reactor was inverted several times over a
period of 30 seconds and the hot water was then removed using the same method as described for solvent removal. The solids are removed from the reaction tube by removing the Swagelok™ fittings at either end. The solvent, water wash and pretreated wood chips were then weighed, dried in a convection oven at 105°C and weighed again. The mass of solids retained in each fraction was calculated. A portion of the wood chips was freeze-dried and the microstructure analysed using scanning electron microscopy (SEM).

3.2.2 Packed bed pulping equipment

Following the analysis of liquid samples from the 100mL reactor it was apparent that a larger scale was required to obtain enough liquid sample for accurate analysis at several time-points throughout the reaction. A 3L packed bed reactor was designed and built for the purpose of regular liquor sampling. The reactor and its operation are described in detail.

3.2.2.1 Packed bed recycle reactor

Figure 3-3 shows schematically the packed bed reactor including the recycle loop (1), sample valve (2) and heater (3). The heater consists of electrical elements bound with conductive cement to a ¾” tube containing the circulating liquor. Temperature at the surface of the heater is controlled and the temperatures at the inlet (4) and outlet (5) of the reactor are recorded using K-type thermocouples connected to a data logger. A motor driving four propellers (6) inside a 2” section of the recycle loop circulates the solvent.
Figure 3-3. Organosolv reactor consisting of the vessel and external recycle loop with heating element and motor driven circulating pump.

Figure 3-4 shows a cross section of the packed bed reactor, which consists of a stainless steel pressure vessel, sealed with 2 rubber o-rings and bolted flanges. Liquid flows into the reactor through a ¾” inlet tube (4) at the top and out of the reactor through a 1” outlet (5) in the bottom. The other connections facilitate a pressure transducer (7), a 50 bar pressure relief valve (8) and two K-type thermocouples (9), (10) measuring temperature at the inlet, and outlet respectively. Vessel openings are Swagelok™ tapered thread to tube connectors. They are screwed into the 900lb blind flanges, which make the reactor ends. A stainless steel mesh basket holds the packed bed of wood chips in place (11). The reactor is charged with liquor and pressurized by nitrogen through a tee (12) in the inlet tube.

During operation, liquor is circulated counter-clockwise as shown in Figure 3-3. The four propellers forcing liquor through the recycle loop are driven by an electric motor and sealed with a PTFE rod seal supplied by SealJet New Zealand Limited (product #S19F). The heater consists of 6 electrical elements attached to the ¾” tube with heat conducting
cement, hose-clamps and insulation. Note that the total void volume of the reactor and accompanying tubing is approximately 3.2L. This allows for 250g dry wood and 3L of solution to fill the reactor.

![Figure 3-4. Cross-section of reaction vessel.](image)

### 3.2.2.2 Procedure

For each delignification run, an oven dry mass of 250g ±2g of *S. schwerinii* wood chips (moisture content of approximately 11% on a dry basis) was loaded into a stainless
steel mesh basket (11) and placed inside the 3L packed bed organosolv reactor. The reactor was then filled with 3L of aqueous ethanol solution and sealed. The circulating device was turned on and shortly thereafter the heater was turned on. Samples were taken from the sample collection valve (2) located at the lowest point in the recycle loop. After the heater was turned on, a 5mL sample was taken at times of t=0, 5, 10, 15, 20, 25, 30, 40, 50, 60, 90, 120, 150 and 180 minutes for autocatalysed delignifications and t=0, 5, 10,15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180 and 195 minutes for buffered delignifications.

3.2.2.3 Buffering pH

The same feedstock and procedure used for autocatalysed pulping was used for the buffered pulping runs. The buffer used was 7.5g/L sodium acetate and ~10mL/L acetic acid. The pH was then adjusted to pH 4 with sulphuric acid. 30% and 50% ethanol solutions were compared in these experiments. The pH of selected liquor samples was measured using a glass pH probe at 25°C ±1°C.

3.2.3 Analysis methods

Klason analysis has been described along with feedstock preparation. Here the analysis methods for determining the concentration of lignin and total solids dissolved in black liquor samples is described. The mass balance equation for converting these measured values into a wood lignin concentration at each sample time is described.

3.2.3.1 Liquor sample and treated wood analysis methods

The liquor samples of autocatalysed and buffered delignification were analysed gravimetrically. A 5mL portion of each sample was diluted four times with acidified water to fully precipitate the lignin. The palette was separated by centrifugation and decanting the supernatant into a pre-weighed aluminium dish. The lignin palette was re-dissolved in 70% ethanol and washed into a pre-weighed aluminium dish. The dishes were then dried in an oven at 105°C for at least 8 hours, cooled to room temperature in the presence of a desiccant and reweighed. The mass of precipitable lignin and water soluble solids (consisting mainly of sugars, hemicellulose fragments and low molecular
weight lignin) in 5mL of organosolv liquor was thus determined from the mass of the residue. The total solids concentration was verified by drying a 1mL black liquor sample and comparing it to the sum of precipitable and non-precipitable solids. In all cases the differences were found to be negligible.

The wood pulp was air dried and weighed then a 5-10g sample was weighed, dried at 105°C for at least eight hours and reweighed. The oven dry mass remaining in the pulp was thus determined. Another wood pulp sample from the same experiment was dried at 45°C for klason lignin analysis using the modified NREL protocol described in Section 3.1.2.3. The lignin content of delignified wood specimens is reported in Appendix 3. The total lignin content was used to scale the lignin content calculated from gravimetric analysis of the soluble solids. This corrects for low molecular weight lignin measured in the non-precipitable solids and xylose degradation products such as furfural measured in the precipitate.

3.2.3.2 Method of determining kinetic parameters

The kinetics of delignification depends on the concentration of lignin in the solid wood. Therefore it is necessary to convert the solvent dissolved solids concentrations measured from liquid samples and the initial and final klason lignin content and total dry mass into a corresponding wood lignin concentration.

Initially, Equation 3-1 is used to calculate the wood lignin content, L, at each sampling time in g/g dry wood.

\[
[L] = \frac{(TL_0 \cdot DM_0) - ([P] \cdot V)}{DM_0 - ([P] + [N]) \cdot V}
\]

Equation 3-1

where \(TL_0\)=total lignin content of untreated wood (g/g dry wood), \(DM_0\)=dry mass of untreated wood (g), \([P]\)=concentration of precipitable solids in liquor (g/L), \([N]\)=concentration of non-precipitable solids in the liquor (g/L) and \(V\)=volume of liquor in the reactor (L). This represents the mass of lignin in the starting material (\(TL_0, DM\))
less the precipitable solids dissolved ([P]V) divided by the dry mass (DM₀) less the total dissolved solids (([P]+[N])V). However, due to the discrepancy between [L] calculated from the liquor sample taken at the end of the reaction and the lignin content of the wood fiber after reaction, the values of [L] were scaled to the lignin content of the wood fiber after reaction. This was measured by the klason method described in Section 3.1.2.3. Results of this research have been published using Equation 3-1 [144].

A more accurate method of calculating wood lignin content is shown in Equation 3-2. The wood lignin content is calculated from the measured precipitable and non-precipitable concentration of the liquor by way of a mass balance. The wood lignin content, [L] (g/g dry wood), is calculated as the mass of unsolubilised lignin/mass of unsolubilised wood as shown in Equation 3-2.

$$[L] = \frac{TL₀ - (TL₀ - TL_f) \cdot ([P] + [N])}{(1 - DM_f/DM₀) \cdot ([P] + [N])}$$  

Equation 3-2

where TL₀=total lignin content of untreated wood, TL_f=total lignin content of organosolv treated wood (g/g, determined by the modified NREL protocol), DM₀=dry mass of untreated wood (g), DM_f=dry mass of organosolv treated wood (g), [P]=concentration of precipitable solids in liquor (g/L), [P]₀=the final concentration of precipitable solids in the liquor, [N]=concentration of non-precipitable solids in the liquor (g/L) and [N]₀=final concentration of non-precipitable solids in the liquor (g/L).

Another improvement over the method that has been published is the use of effective temperature rather than arithmetic average temperature as will be discussed in Section 4.2.1.

3.2.4 Organosolv pulping of de-ashed versus prehydrolysed feedstock

These experiments were performed to examine the differences in liquor pH and delignification rate brought about by the feedstock condition. They differ from previously described experiments because they are acid catalysed experiments. The liquor samples
are also analysed for lignin content using a different method. This was done to ensure they were comparable to literature using similar conditions [116]. Total solids concentration is analysed gravimetrically by drying at 105°C as it was in the previous experiments.

3.2.4.1 Procedure

The 3L packed bed reactor previously described in Section 3.2.2.1 was used for the delignification of de-ashed or prehydrolysed willow.

For the de-ashed feedstock delignifications, approximately 262g of de-ashed willow (moisture content = 4.8% d.b. giving a dry mass of 250g) was placed inside the packed bed reactor in the mesh basket. For the prehydrolysed feedstock delignifications, approximately 220g of prehydrolysed willow (moisture content = 4.4% d.b. giving a dry mass of 210g) was placed inside the packed bed reactor in the mesh basket. The difference in mass was to correct for the mass already removed by prehydrolysis. The reactor was filled with 3L of 70% ethanol in deionised water with an H₂SO₄ catalyst concentration of 0.08% w/w (0.007M). The reactor was sealed and the heater and circulation device started to bring the reactor and contents up to the desired temperature. 5mL samples were collected through the sample valve at t=0 and every 5 minutes for 120 minutes. At the end of 120 minutes, the heating element was turned off and the liquor was removed by opening the sample valve. The black liquor was cooled on removal by passing through a stainless steel coil immersed in an ice bath. The treated wood was removed after cooling and air dried before being analysed by soxhlet extraction and klensof lignin analysis as previously described.

Reactions were examined at inlet liquor temperatures of 170°C, 175°C and 180°C for each of de-ashed and prehydrolysed feedstock. The measurement at 175°C for each feedstock was replicated to give the standard deviation of data collected.

In addition to these conditions, the following delignifications were carried out according to the procedure above with the following alterations;

- Untreated feedstock (250g dry mass) at 180°C with 0.08% H₂SO₄ (0.007M) catalyst.
Untreated feedstock (250g dry mass) at 180°C with 0.04% H₂SO₄ (0.0035M) catalyst.

Untreated feedstock (250g dry mass) at 180°C with 0.08% H₂SO₄ catalyst and 2.0% v/v acetic acid added.

De-ashed feedstock (250g dry mass) at 180°C with 0.04% H₂SO₄ catalyst.

3.2.4.2 Product analysis methods

Treated wood was extracted in ethanol using soxhlet apparatus and analysed by the klason method previously described. Lignin content is reported on an extractives free basis.

Liquor samples were analysed using the method described in Gilarranz et al. [116]. A 30µL sample was dissolved in acetone and dried at 60°C in a vacuum oven for 24 hours. The dried sample was then dissolved in 5mL of 0.01M NaOH, diluted with 0.01M NaOH to make the absorbance fall within the range of 0.1-1.0AU and the dilution and absorbance at 280nm were measured. Lignin content of the pulp was calculated using Equation 3-2 using the absorbance measurements to calculate [P] and the klason method as described in Section 3.1.2.3 for initial and final total lignin content, TL₀ and TL₇ respectively.

Total dissolved solids mass concentration of the liquor was determined by pipetting 1mL of sample onto a pre-weighed plastic tray and drying in a convection oven at 45°C for a minimum of 24 hours. The tray before and after drying was weighed to the nearest 0.01mg. Total dissolved solids concentration was scaled to match the final dissolved solids concentration calculated from a mass balance of the input and output dry mass of wood.

pH of selected liquor samples (at least one every 15 minutes) was measured with a glass pH probe at room temperature (25°C ±1°C).
4 Organosolv results and discussion

This chapter is a discussion of the results obtained from organosolv pulping and the pre-organosolv treatments described in the materials and methods section. Further results on recovery of lignin and use of lignin prepared during these organosolv pulping experiments are discussed later in their respective self-contained chapters.

This chapter is separated into three sections on lignin re-condensation, effects of changing ethanol concentration and effects of feedstock condition for catalysed pulping. Section 4.1 is a micro-structural analysis using SEM identifying lignin re-condensed on the surface of wood under different autocatalysed organosolv treatment regimes.

The effects of changing ethanol concentration are then investigated in two parts. Unbuffered and buffered pulping is examined. The attempt to control pH is made. This proves difficult due to the effect of the activity of the hydronium ion in ethanol relative to water and the neutralising effect of biomass.

Finally, changes are made to the feedstock condition using de-ashing or prehydrolysis treatments followed by organosolv delignification. The difference in the polysaccharide content of these feedstocks is expected to have a significant effect on delignification rate. However, compositional effects of prehydrolysis may have been misunderstood in the literature.

4.1 Lignin re-precipitation

During organosolv pulping, lignin is made soluble in the solvent mixture. The soluble lignin can continue to react and may form a lignin that is no longer soluble in the solvent. When this occurs the lignin may drop out of solution and precipitate on the surface of (or indeed within) the wood structure. Re-condensation is a term referring to the re-polymerisation of lignin into a more resistant form and occurs during pulping at high temperatures and at low pH. The re-condensed lignin is more resistant to further dissolution than un-reacted lignin, as discussed in Section 2.3.2, and therefore its
occurrence results in a higher residual lignin content. The structures discussed in Section 4.1 are most likely the result of re-precipitation.

Figure 4-1 and Figure 4-2 are SEM images showing the structural changes in *S. alba* before and after pre-treatment in 70% ethanol at 200°C.

![Figure 4-1. Untreated *S. alba*.](image)

Figure 4-1 is an SEM image of untreated *S. alba* showing that the wood cells are intact. The cells are arranged tightly together and there is nothing deposited on their surface.
Figure 4-2 shows the surface of a *S. alba* wood chip that has been subjected to delignification at 200°C followed by removal of the solvent at 200°C using the apparatus and procedure described in Section 3.2.1. In contrast to untreated wood, string-like structures of diameter less than 0.1µm appear to have been peeled away from the outer surface of the cell. These structures may be cellulose micro-fibrils, which are typically 10-30nm in diameter. It is clear that the structure of the wood has been modified. Spherical structures are present that bear resemblance to those reported in the literature (reviewed in Section 2.3.2) and identified as precipitated lignin. Figure 4-3 and Figure 4-4 show *S. alba* extracted with 70% v/v ethanol at 180°C. The spherical structures are more visible due to the higher magnification and, by examining Figure 4-4, the size range of these spheres can be estimated at 0.2-1µm, which is of similar size to the structures observed by Xu et al. [111] when lignin was induced to re-precipitate on wood fibers.
Figure 4-3. SEM of willow treated at 180°C in 70% v/v ethanol for 80 minutes followed by ethanol removal at 180°C.

Figure 4-4. SEM of willow treated at 180°C in 70% v/v ethanol for 80 minutes followed by ethanol removal at 180°C. Willow fiber showing spheres of lignin of size range 0.2-1µm.
Figure 4-5. *S. alba* after organosolv treatment at 200°C in 70% v/v ethanol and cooling to 40°C before solvent removal.

Figure 4-5, shows the surface of chipped wood after 70% v/v ethanol treatment at 200°C followed by cooling to 40°C before separating solvent from the wood chip using the procedure described previously in Section 3.2.1.2. A layer has re-deposited on the surface of the wood chip. Presumably this occurred as a result of cooling the reaction medium before removing the solvent from contact with the wood as no such structure is present in the SEM image of wood chip after treatment in 70% v/v ethanol at 200°C for 100 minutes followed by removal of solvent at 200°C (see Figure 4-2). The components of wood that have solubilised that could make up this structure are hemicellulose sugars, degradation products of hemicellulose sugars, lignin or waxes. Extractives, which includes but is not entirely comprised of waxes, is typically 4% of willow dry mass. Sugars are easily solubilised by the hot water wash at 110°C following treatment. The structure must therefore be composed of a mixture of lignin and sugar degradation products.
This layer is likely to be a physical impediment to enzymes attaching to the wood fiber surface. Inhibition of enzymes by chemical or physical means is not verified by this SEM image. However, the difference observed between Figure 4-2 and Figure 4-5 suggests that allowing the solvent to cool in the presence of the treated wood allows at least some degree of lignin re-precipitation. Solvent should be removed at high temperature if clean fractionation of wood components is desired. This is in agreement with literature, which indicates that lignin removal rates are higher and lignin is of a significantly larger molecular weight if just a small flow rate is used in a flow through reactor rather than a batch reactor [19]. As reviewed in Section 2.3.2, cooling has been suggested as a cause of re-condensation in batch reactors.

The SEM images of *S. alba* treated at 180°C, 190°C and 200°C in 70% v/v ethanol for 100 minutes shown in Figure 4-6 shows the effect of temperature on the structure of wood. There is minimal difference in the structure between treatment at 180°C and 190°C (top and middle image in Figure 4-6) but at 200°C (bottom image of Figure 4-6) much more significant changes are observed. This illustrates the Arrhenius relationship that degradation of wood components has with temperature. At higher temperatures, both hemicellulose and lignin have higher reaction rates and this is observed in the micro-structural images as increased occurrence of wood cell and micro-fibril separation.

Observations on the microstructure of organosolv treated *S. alba* agree with current literature. Removal of solvent at pulping temperature has been proven beneficial. A batch reactor can be used while avoiding lignin re-precipitation due to a cooling period. This allows an examination of lignin reaction rates in batch reactors while avoiding erroneous lignin concentration measurements due to excessive precipitation of lignin by cooling.
Figure 4-6. Effect of process temperature on structure of willow during 70% v/v ethanol pulping for 100 minutes at 180°C, 190°C and 200°C.
4.2 Effects of solvent concentration

During the pulping process, the concentration of solvent (ethanol-water) has several effects on the rate of delignification, rate of hemicellulose conversion and degradation of soluble sugars into undesirable products such as furfural. Changing ethanol concentration may affect the solubility of lignin or polysaccharide hydrolysis products. It may also affect viscosity and hence penetration of solvent into the wood. Most importantly, the pH of the solution may change due to the lower activity of the H⁺ ion in ethanol compared to water. This section is concerned with the effect of changing ethanol concentration under two different pH conditions. The first is un-buffered, auto-catalysed pulping in which higher ethanol concentration results in a significantly higher pH. The second is buffered pulping in which the pH is buffered as close to 4.0 as possible and the effect of changing solvent concentration on delignification rate is examined in isolation. This is a novel approach, used to examine changing solvent concentration in isolation of pH changes, which usually accompany changes of solvent concentration.

4.2.1 Autocatalysed organosolv delignification

Figure 4-7 shows the lignin content calculated from Equation 3-2 versus time for each set of parameters (each plot is an average of data from each of two corresponding chip sizes, which showed no appreciable difference). Therefore the final lignin concentration for each run shown in Figure 4-7 is equal to the klason lignin content of the wood chip removed from the reactor. Figure 4-8 shows the dry mass of lignin and polysaccharide in untreated and organosolv treated wood using 4 different organosolv conditions. Note that the treated wood is analysed on an extractives free basis on the assumption that most or all of the extractives will be removed by high temperature ethanol pulping. This is necessary because an extractives reading may contain a high proportion of re-precipitated lignin re-dissolved by soxhlet extraction. A hot ethanol wash prior to soxhlet extraction would also dissolve some extractives if they are present, making an extractives reading superficial. Figure 4-8 shows the reduction of lignin content during each run as well as significant reduction in polysaccharides. The 35% v/v ethanol runs show a far greater removal of lignin from the pulp than 70% v/v ethanol runs.
at the same treatment temperature. This is caused by the lower pH in 35% v/v ethanol pulping. The temperature of liquor at the reactor inlet is noted on the legend.

Figure 4-7. Lignin concentration during autocatalysed pulping.

data is the average of small and large chip size runs
Due to the temperature difference between the inlet and outlet of the packed bed reactor, the arithmetic mean temperature is slightly inaccurate due to the Arrhenius relationship of reaction rate to temperature. Effective temperature, as described by Farid [145], is commonly referred to as virtual temperature in the pharmaceutical industry [146]. Figure 4-9 gives an example of the arithmetic average and effective temperature calculated from the inlet and outlet temperatures of the pulping at target inlet temperature of 185°C in 70% v/v ethanol. Equation 4-1 shows the method for obtaining effective temperature ($T_{	ext{eff}}$) from the inlet ($T_{\text{IN}}$) and outlet ($T_{\text{OUT}}$) temperatures. The integral was solved numerically using a MATLAB programme.

Figure 4-8. Mass of lignin and polysaccharides in wood before and after treatment.
The effective temperatures are slightly higher than the arithmetic mean temperatures.

\[ Teff = \frac{-E_a}{R} \ln \frac{T_{OUT} - T_{IN}}{e^{\frac{E_a}{RT}} - e^{\frac{E_a}{RT}}} \]

Equation 4-1

During the first 15 minutes of reaction, the reactor and contents are still heating up. Figure 4-10 shows the effective temperature of the reaction medium for each organosolv liquor condition. Effective temperature increases considerably and is not consistent between experiments during the heat-up period. For this reason the first 15 minutes of reaction is neglected and \( t=0 \) is set at the fourth sample. Figure 4-7 shows that little
reaction occurs in the first 15 minutes. Figure 4-10 also shows that effective temperature is increasing slowly after the heat-up period.

The activation energy used in the calculation of $T_{\text{eff}}$ was 89kJ/mol as this is the mean activation energy determined by Tirtowidjojo et al. [19] and Gilarranz et al. [116] for bulk delignification of hardwoods and falls well within the activation energy range for delignification of model lignin compounds.

Delignification is considered in the literature to follow pseudo first order kinetics [66] as described in Section 2.3.4. Therefore $k$ can be determined using the following equations:

$$\frac{dL}{dt} = -k[L],$$

Equation 4-2
which on integration gives Equation 4-3.

$$\ln\left(\frac{[L_0]}{[L]}\right) = k(t - t_0)$$

**Equation 4-3**

A plot of ln($L_0/L$) versus time will have a slope equal to $k$ during the bulk delignification phase. However, due to the slowly increasing temperature, the slope also increases with time as shown in Figure 4-11 and Figure 4-12. Figure 4-11 shows the plot of ln($L_0/L$) versus time for each inlet temperature setting at 35% ethanol concentration. Figure 4-12 shows the plot of ln($L_0/L$) for each temperature setting at 70% ethanol concentration. On each plot, a linear and 2nd order polynomial trend line are fitted to show that slope is increasing with time.

![Kinetic plot of delignification in 35% v/v ethanol.](image)

**Figure 4-11.** Kinetic plot of delignification in 35% v/v ethanol.
The plot for delignification at 185°C and 35% v/v ethanol concentration shows a transition to residual delignification as reported by Gilarranz et al. [116] and shown in Section 2.3.4. As discussed in the Section 2.3.3, residual delignification may be a result of a different lignin structure present in wood, lignin present in closer association with polysaccharides or an increase of lignin re-condensation, which produces a lignin more resistant to removal. The other conditions used here are not removing enough lignin to reach the residual phase. The treatment at 185°C and 35% v/v ethanol concentration has a transition to residual phase at a lignin concentration of 15.1% w/w. None of the other treatments reach this concentration so the effect of ethanol concentration or temperature on residual phase kinetics cannot be determined from these mild treatments. More severe delignification conditions result in a faster transition to residual phase kinetics as will be discussed in Section 4.3.4.

![Figure 4-12. Kinetic plot of delignification in 70% v/v ethanol.](image)
Figure 4-12 shows the delignification of willow in 70% v/v ethanol at both of the varying process temperatures. Delignification proceeds much slower in 70% v/v ethanol than in 35% v/v ethanol due to the differences in pH caused by the higher activity of the hydronium ion in water compared to that of ethanol. The inconsistency in concentration measurement seen at the start of delignification is due to the extent of reaction being comparable to the standard error of the measurements. At greater extent of delignification, seen in the later part of Figure 4-12, the errors are insignificant by comparison.

Because of the slow heat up time of the reactor and the temperature gradient inside the packed bed, the temperature that determines the rate constant is slightly different at each sample time during a single run. Therefore, at each sample time the rate constant, k, can be determined and associated with a different temperature. For each calculation of k, a new $t_0$ is selected. Where $t_0$ is the sampling time at which measurement is started and $L_0$ is the lignin concentration at $t_0$.

For example, $t_0$ is set to the fourth sample point and $\ln(L_0/L)$ is determined at the 4th, 5th, 6th and 7th sample points. The slope is then determined by linear regression. The slope of $\ln(L_0/L)$ versus time is equal to the rate constant, k, and $T$ is equal to the effective temperature at $t_0$. The next value of k is determined by setting $t_0$ to the 5th sample and $\ln(L_0/L)$ is determined at the 5th, 6th, 7th and 8th sample points. And the process is repeated until a k value has been calculated for each subsequent sample point.

A list of the effective temperatures and the k value at that temperature is shown in Table 4-1 and Table 4-2. $T_{\text{average}}$ is shown for comparison to $T_{\text{effective}}$. 
Table 4-1. Delignification k values measured at different times and temperatures in 35% v/v ethanol.

<table>
<thead>
<tr>
<th>t₀ (min)</th>
<th>T_inlet (°C)</th>
<th>T_outlet (°C)</th>
<th>T_effective (°C)</th>
<th>T_average (°C)</th>
<th>k (min⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>186.0</td>
<td>158.2</td>
<td>173.7</td>
<td>172.1</td>
<td>0.00649</td>
<td>0.99</td>
</tr>
<tr>
<td>5</td>
<td>184.7</td>
<td>162.3</td>
<td>174.5</td>
<td>173.5</td>
<td>0.00601</td>
<td>0.99</td>
</tr>
<tr>
<td>10</td>
<td>184.9</td>
<td>164.7</td>
<td>175.6</td>
<td>174.8</td>
<td>0.00705</td>
<td>0.99</td>
</tr>
<tr>
<td>15</td>
<td>185.0</td>
<td>166.6</td>
<td>176.5</td>
<td>175.8</td>
<td>0.00774</td>
<td>0.98</td>
</tr>
<tr>
<td>25</td>
<td>185.0</td>
<td>169.2</td>
<td>177.6</td>
<td>177.1</td>
<td>0.00844</td>
<td>0.99</td>
</tr>
<tr>
<td>35</td>
<td>185.1</td>
<td>171.3</td>
<td>178.6</td>
<td>178.2</td>
<td>0.00681</td>
<td>0.96</td>
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<td>45</td>
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<td>172.9</td>
<td>179.5</td>
<td>179.2</td>
<td>0.00513</td>
<td>0.93</td>
</tr>
<tr>
<td>75</td>
<td>185.3</td>
<td>175.9</td>
<td>180.8</td>
<td>180.6</td>
<td>0.00332</td>
<td>0.99</td>
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</table>

<table>
<thead>
<tr>
<th>t₀ (min)</th>
<th>T_inlet (°C)</th>
<th>T_outlet (°C)</th>
<th>T_effective (°C)</th>
<th>T_average (°C)</th>
<th>k (min⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>173.1</td>
<td>147.0</td>
<td>161.5</td>
<td>160.0</td>
<td>0.00315</td>
<td>1.00</td>
</tr>
<tr>
<td>5</td>
<td>171.1</td>
<td>150.0</td>
<td>161.5</td>
<td>160.6</td>
<td>0.00307</td>
<td>1.00</td>
</tr>
<tr>
<td>10</td>
<td>170.1</td>
<td>151.3</td>
<td>161.5</td>
<td>160.7</td>
<td>0.00288</td>
<td>1.00</td>
</tr>
<tr>
<td>15</td>
<td>169.8</td>
<td>152.3</td>
<td>161.7</td>
<td>161.1</td>
<td>0.00313</td>
<td>1.00</td>
</tr>
<tr>
<td>25</td>
<td>170.3</td>
<td>154.6</td>
<td>163.0</td>
<td>162.5</td>
<td>0.00369</td>
<td>0.99</td>
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<tr>
<td>35</td>
<td>170.4</td>
<td>156.5</td>
<td>163.9</td>
<td>163.5</td>
<td>0.00372</td>
<td>1.00</td>
</tr>
<tr>
<td>45</td>
<td>170.4</td>
<td>158.0</td>
<td>164.5</td>
<td>164.2</td>
<td>0.00393</td>
<td>0.99</td>
</tr>
<tr>
<td>75</td>
<td>170.2</td>
<td>161.2</td>
<td>165.9</td>
<td>165.7</td>
<td>0.00366</td>
<td>0.99</td>
</tr>
</tbody>
</table>
Table 4-2. Delignification k values measured at different times and temperatures in 70% v/v ethanol.

<table>
<thead>
<tr>
<th>t₀ (min)</th>
<th>T_inlet (°C)</th>
<th>T_outlet (°C)</th>
<th>T_effective (°C)</th>
<th>T_average (°C)</th>
<th>k (min⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>182.3</td>
<td>154.2</td>
<td>169.9</td>
<td>168.2</td>
<td>0.00166</td>
<td>0.98</td>
</tr>
<tr>
<td>5</td>
<td>183.8</td>
<td>160.5</td>
<td>173.3</td>
<td>172.2</td>
<td>0.0019</td>
<td>0.96</td>
</tr>
<tr>
<td>10</td>
<td>185.1</td>
<td>163.7</td>
<td>175.3</td>
<td>174.4</td>
<td>0.00169</td>
<td>0.94</td>
</tr>
<tr>
<td>15</td>
<td>185.2</td>
<td>166.0</td>
<td>176.3</td>
<td>175.6</td>
<td>0.00188</td>
<td>0.95</td>
</tr>
<tr>
<td>25</td>
<td>185.7</td>
<td>168.9</td>
<td>177.9</td>
<td>177.3</td>
<td>0.00221</td>
<td>0.94</td>
</tr>
<tr>
<td>35</td>
<td>185.4</td>
<td>170.6</td>
<td>178.4</td>
<td>178.0</td>
<td>0.00271</td>
<td>1.00</td>
</tr>
<tr>
<td>45</td>
<td>185.5</td>
<td>172.2</td>
<td>197.2</td>
<td>197.8</td>
<td>0.00279</td>
<td>1.00</td>
</tr>
<tr>
<td>75</td>
<td>185.5</td>
<td>175.3</td>
<td>180.6</td>
<td>180.4</td>
<td>0.00289</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Most k values obtained exhibit a high Pearson’s parameter. Any value with an R² value less than 0.60 is ignored. Also ignored is any value pertaining to the residual phase of delignification observed during pulping in 35% ethanol at 185°C. ln(k) versus 1/T_eff is plotted as shown in Figure 4-13. A good linear regression for 35% ethanol delignification is shown with an R² value of 0.98. The 70% ethanol delignification shows a linear regression with an R² value of only 0.82. It is expected that the method is more suitable for higher severity treatments where the rate of delignification is higher compared to the errors of concentration measurement. Table 4-3 shows the activation energies and
frequency factors calculated from the slope and intercept respectively. The activation energy for 70% ethanol delignification (79.5kJ/mol) is within the values of 79-118kJ/mol reported by Meshgini [126] and is comparable to activation energies determined by previous authors. 82.9kJ/mol was reported by Aravamuthan et al. [123] for auto-catalysed pulping of softwood using 70% v/v ethanol and 80.3kJ/mol by Tirtowidjojo et al. [19] for acid catalysed pulping of hardwood using 50% v/v ethanol. The activation energy for 35% ethanol delignification (95.7kJ/mol) agrees well with previously reported values such as that of Gilarranz et al. (98.4kJ/mol for acid pulping of hardwood using 50% w/w methanol) [116]. This method therefore gives an adequate estimate of activation energy without the need to perform Klason analysis on the solids fraction of many pulping experiments.

Figure 4-13. Linear plot of ln(k) versus 1/T_{eff} showing a linear regression with good correlation.

Table 4-3. Activation energy and frequency factor of delignification in 35% and 70% Ethanol.

<table>
<thead>
<tr>
<th>EtOH% v/v</th>
<th>E_a/R</th>
<th>E_a (kJ/mol)</th>
<th>ln(k_0)</th>
<th>k_0</th>
</tr>
</thead>
<tbody>
<tr>
<td>35%</td>
<td>11510</td>
<td>95.7</td>
<td>20.7</td>
<td>9.87E+08</td>
</tr>
<tr>
<td>70%</td>
<td>9560</td>
<td>79.5</td>
<td>15.2</td>
<td>3.84E+06</td>
</tr>
</tbody>
</table>
The activation energy for different ethanol concentrations is similar by comparison to the large range reported in the literature and reviewed in Section 2.3.4. The slightly lower activation energy for pulping using 70% v/v ethanol may be indicative of better solubility properties using 70% v/v ethanol at lower pulping temperatures or an effect of the different final pH of each pulping solution. However, greater control of these properties is required to confirm that ethanol concentration has any effect on activation energy. The literature indicates that it does not.

4.2.2 Buffered organosolv delignification

During the organosolv pretreatments examined in Section 4.2.1, the pH is not controlled. It was found that a delignification in 70% ethanol had a final liquor pH of approximately 4.8 whereas a 35% ethanol delignification had a final pH of approximately 4.0. The difference in delignification rate is brought about by a difference of pH and the effect of the ethanol concentration alone is masked. In order to show the effect of ethanol concentration, the pH must be controlled so that ethanol concentration is the only parameter that is changed.

![Figure 4-14. Temperature control during buffered pulping in 30% and 50% v/v ethanol.](image-url)
Figure 4-14 shows the average temperature of the packed bed during both 30% and 50% v/v ethanol pulping. The first 20 minutes of reaction is neglected as the heat-up period. Adequate control of the reaction temperature is demonstrated by the temperature data after the first 20 minutes of reaction.

![Figure 4-15. pH during buffered pulping in 30% and 50% v/v ethanol.](image)

Literature reports the effects of buffering organosolv liquor, but the effect of changing ethanol concentrations while maintaining pH has not been yet been studied. Controlling pH while changing ethanol concentration is complicated by the components of wood liberated during pulping. Acetic acid released by hemicellulose end chains lowers the pH while ash and protein neutralise acid, raising the pH. As can be seen from Figure 4-15, pH was not controlled as close as expected. The pH range during the sampling time was 3.6 to 3.8 for 30% v/v ethanol and 4.0 to 4.3 for 50% v/v ethanol. However, this is a suitable improvement considering that un-buffered pulping in 30% v/v versus 50% v/v ethanol results in a pH difference of more than 1 unit and that pH can drop from 7.5 to 4 during uncatalysed pulping in 50% v/v methanol as discussed in Section 2.3.5. The explanation for the difference in pH during these runs is that 50% v/v ethanol has a higher pH using this buffer system. Sulphuric acid was used to adjust the
pH of the buffer system. However, some of the sulphuric acid was neutralised by wood components. The feedstock should therefore have been de-ashed or prehydrolysed before attempting to control the pH.

Despite the small pH difference, there was minimal difference in the results obtained from the two pulping experiments. Figure 4-16 shows that there is no difference in mass of lignin remaining after 30% v/v ethanol pulping and 50% v/v ethanol pulping. Only a small difference is observed in the polysaccharide fraction of each pulp.

![Figure 4-16. Mass of wood components before and after pulping in 30% v/v and 50% v/v ethanol.](image)

The analysis of the mass dissolved in liquid samples is shown in Figure 4-17 and Figure 4-18. Figure 4-17 confirms that there is little or no difference in mass of lignin dissolved between the two concentrations compared during the entire pulping.
4 - Organosolv results and discussion

Figure 4-18 shows that 30% v/v ethanol pulping resulted in a faster removal of total solids. Previous research has shown that cellulose is recalcitrant to degradation during more severe conditions than these [147]. Section 2.3.6 describes how lignin and hemicellulose are depolymerised in significantly greater amounts than cellulose during the organosolv process. Since lignin removal was consistent between the two concentrations, a faster removal of hemicellulose must have occurred during 30% ethanol pulping. It is worthy of note that this did not result in a significantly faster rate of lignin removal or a lower final lignin concentration. Other researchers [122, 131] have indicated that removal of hemicellulose has facilitated lignin removal as discussed thoroughly in Section 2.3.6. It may be that removal of hemicellulose has an effect on the pH. When the pH is partially controlled as in the present work, the increase in delignification rate is minimal.

Figure 4-18 also indicates a discrepancy in the total solids measurement, which is more pronounced during 30% v/v ethanol pulping. The amount of total dissolved solids actually decreases after t=60 minutes and the final dissolved solids calculated from a mass balance analysis on the pulp, $TS_{mb}$, calculated by Equation 4-4 shows a higher concentration of solids.

$$TS_{mb} = \frac{DM_0 - DM_f}{V}$$

\textbf{Equation 4-4}

where $DM_0$ is the dry mass of wood input into the reactor (g), $DM_f$ is the dry mass of wood output from the reactor (g) and $V$ is the volume of liquor in the reactor (L).

One possible explanation for this is that sugars are being converted into volatile components such as furfural that evaporate during dry mass analysis resulting in a lower measured solids concentration than is present during the pulping run. According to Figure 4-17 the production of furfural does not appear to have caused a discrepancy in the measurement of precipitated lignin concentration. The final dissolved lignin
concentration calculated by a mass balance, $L_{mb}$, calculated by Equation 4-5 is close to the precipitate concentration.

$$L_{mb} = \frac{DM_0 \cdot TL_0 - DM_f \cdot TL_f}{V}$$

Equation 4-5

Where $TL_0$ is the total lignin content of the input wood (g/g dry wood) and $TL_f$ is the total lignin content of the output wood (g/g dry wood). Total lignin content is measured by the modified NREL protocol described in Section 3.1.2.3.

Figure 4-17. Mass of precipitate in liquor sample and final dissolved lignin based on a mass balance analysis of the pulp. Comparison of buffered 30% v/v and 50% v/v ethanol pulping.

Figure 4-17. Mass of precipitate in liquor sample and final dissolved lignin based on a mass balance analysis of the pulp. Comparison of buffered 30% v/v and 50% v/v ethanol pulping.
Figure 4-18. Mass of dissolved solids in liquor sample and final dissolved total solids based on a mass balance analysis of the pulp. Comparison of 30% v/v and 50% v/v ethanol pulping.

Due to the discrepancy with the total solids measurement, the kinetic plot of lignin concentration in the wood is calculated as the lignin mass remaining in wood, scaled to final lignin concentration, divided by the input mass of total dry solids rather than the total dry solids calculated from the liquor analysis at each sample time. Figure 4-19 shows the values of lignin concentration used for the kinetic plot.
4 - Organosolv results and discussion

Figure 4-19. Lignin remaining in pulp as a fraction of input total mass. Comparison of buffered pulping in 30% v/v and 50% v/v ethanol.

Figure 4-20. Kinetic plot of buffered pulping in 30% v/v and 50% v/v ethanol showing minimal difference in delignification rate.
Figure 4-20 is the kinetic plot showing a small difference in the $k$ value of each pulp. This difference can easily be attributed to the small difference in pH if we use methods of relating hydronium ion concentration to rate constant as discussed in Section 2.3.5. By using the model developed by Gilarranz et al. [116], the kinetic parameter can be adjusted for the different $H^+$ concentrations. According to Gilarranz et al., $k$ during bulk delignification is proportional to $[H^+]^{0.214}$.

$$k = [H^+]^{0.214}$$

$$k' = k_0 e^{\left(\frac{-E_a}{RT}\right)}$$

Equation 4-6

Table 4-4 shows the average $H^+$ ion concentration during the bulk phase for each pulping condition and the adjusted kinetic constant, $k'$. The pH range during the whole delignification is also shown to illustrate that pH did not change significantly during each delignification. During bulk delignification 30% v/v ethanol pulping has a pH 0.4 to 0.5 pH units lower than 50% v/v ethanol pulping. This is reflected in the bulk rate constant, $k$, being higher by 23% using 30% v/v ethanol. However, the difference between $k'$ (corrected using the data of Gilarranz et al. [116]) at each ethanol concentration is only 1.5%. The pH adjusted kinetic constant is almost the same for both 30% and 50% v/v ethanol buffered pulping meaning that changing only the ethanol concentration has no effect on the rate of lignin reaction assuming that this dependence on pH is correct.

<table>
<thead>
<tr>
<th>Ethanol % (v/v)</th>
<th>k (min⁻¹)</th>
<th>Average [H⁺] bulk phase</th>
<th>pH</th>
<th>$k' = k/\left[H^+\right]^{0.214}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.0130</td>
<td>0.0002014</td>
<td>3.7±0.1</td>
<td>0.0803</td>
</tr>
<tr>
<td>50</td>
<td>0.0106</td>
<td>0.0000725</td>
<td>4.2±0.2</td>
<td>0.0815</td>
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</tbody>
</table>

In theory, this means that lignin can be removed from lignocellulosic substrate with only 5% v/v ethanol or pure water. However, at sufficiently low ethanol concentrations,
lignin will precipitate significantly upon removal of the solvent and lignin will form a thick pasty precipitate that is difficult to recover. Yields of lignin from pure water delignifications were lower indicating that more lignin remains soluble after removal of liquor and re-precipitation of the lignin is occurring. It was noticed during the experiments using 30% v/v ethanol that lignin precipitated after removal of liquor from the reactor. This caused great inconvenience as the lignin had to be resolubilised for accurate analysis. For this reason, higher ethanol concentrations of 70% v/v are used in subsequent experiments.

There were no differences in the residual amount of lignin after pulping at each ethanol concentration and the small difference in bulk rate constant has proven to be a result of a failure to fully control the pH. However, there is a significant difference in the rate of polysaccharide hydrolysis and degradation of those hydrolysis products as shown in Figure 4-18 by the discrepancy between liquor samples and wood dry mass measurements. This may also be attributed to the pH differences but the effect of process parameters on the reaction of polysaccharides is outside the scope of this thesis. More in depth analysis regarding the fraction of hemicellulose and the specific carbohydrates comprising hemicellulose is required to draw definitive conclusions on the cause. As reviewed in Section 2.3.6, lower ethanol concentration results in greater removal of hemicellulose, but the cause is not identified. The lower ethanol concentration liquor may have a higher pH resulting in greater hemicellulose and lignin degradation. These experiments show that there is negligible difference in delignification rate between 30% v/v and 50% v/v ethanol pulping when pH is controlled.

It is also cited that too much acid catalyst results in high production of degradation products, excessive re-precipitation and loss of pulp yield [78, 110] as described in Section 2.3.5. Greater production of degradation products at lower pH is indicated by the drop in total solids measured after t=90 minutes. However, there is no difference observed in terms of lignin removal indicating that re-condensation rate is not affected by the small difference in pH or significant difference in ethanol concentration. It is clear that increasing the ethanol concentration from 30% v/v to 50% v/v has no effect on
delignification rate if pH can be controlled. Therefore a change in lignin solubility or mass transfer properties of the liquor did not affect bulk delignification rate.

### 4.3 Organosolv pulping of de-ashed versus prehydrolysed feedstock

In this section, feedstock condition is compared. The effects of de-ashing (described in Section 3.1.2.4) and prehydrolysis (described in Section 3.1.2.5) on composition are first considered and then a comparison of organosolv delignification of each feedstock is made. Comparisons are made between organosolv pulping of de-ashed and untreated feedstock. Finally, organosolv delignification of de-ashed feedstock is compared directly to prehydrolysed feedstock at three temperature levels. Such a comparison has not been made in the literature and is necessary in order to confirm the cause of increased organosolv delignification rates when prehydrolysis is applied.

The temperature levels are designated as low, mid and high temperature levels. This corresponds to the temperature at the inlet of the packed bed reactor being set at 170°C, 175°C and 180°C. The effective temperature is slightly lower than this due to the slow heat up of the reactor and temperature gradient inside the packed bed. Effective temperature, $T_{eff}$, is reported in tables and figures for the period relating to the measurement of bulk delignification rate constant. Figure 4-21 shows the effective temperature of all catalysed pulping experiments and shows good temperature control after the 10 minute heat-up period at each temperature level.

Previous experiments showed that low ethanol concentrations caused difficulty in analysis of organosolv liquor due to low solubility of lignin and unwanted precipitation. The reactor also operated more consistently using higher ethanol concentrations. For these reasons, 70% v/v ethanol was used in the remaining experiments.
pH is reported as a range during the whole run, from t=0 to 110 minutes, to show that fluctuation in pH was minimal. However, for an examination of corrected rate constant in Section 4.3.2, the mean hydronium ion concentrations are calculated from pH measurements taken during t=0 to 50 minutes, as this is the time for which bulk rate constant is calculated.

### 4.3.1 De-ashing and prehydrolysis

Measurements of the mass of solids remaining from each treatment are shown in Figure 4-22. De-ashing removed negligible amounts of both lignin and polysaccharide, while nearly half of the extractives (protein and waxes) were removed. Prehydrolysis by contrast removed 18% of the polysaccharide, 1.6% of the lignin and 57% of the extractives (the total mass reduction was 15% of the total dry mass). This compares well with Patel and Varshney [131] previously described in Section 2.3.6. It is unclear whether any differences were brought about by the size of the wood chip used. Although the penetration of ethanol into wood chip is sufficient that chip size does not affect delignification rate, hindered penetration of water and acid into the wood chips may have
reduced the efficacy of the hydrolysis treatment employed. Further research on prehydrolysis is warranted to determine the effect of chip size on polysaccharide removal.

![Figure 4-22. Mass input and output of de-ashing and prehydrolysis treatments.](image)

The appearance of the chipped willow was also altered considerably. De-ashed willow, shown in Figure 4-23A, remains white to light brown in colour whereas prehydrolysed willow is red-brown in colour as shown in Figure 4-23B.
Figure 4-23. De-ashed willow (A) and prehydrolysed willow (B).

4.3.2 De-ashed willow delignification

The de-ashing pretreatment was shown to be effective in suppressing the rise of pH during the delignification as shown in Figure 4-24. At the high temperature level (inlet temperature of 180°C) in 70% v/v ethanol, the average pH of de-ashed willow was approximately 0.45 units lower than for untreated willow at both the 0.04% w/w and 0.08% w/w H₂SO₄ catalyst levels. The pH remains closer to the target pH of 3 if de-ashed willow is used. Figure 4-24 shows that pH during delignification using untreated willow increases 0.95 pH units at the high acid loading and 1.3pH units at the low acid loading. For de-ashed willow delignification, the pH change is less than 0.5 pH units.
Due to the changes in pH and temperature during the first 10 minutes of these pulping experiments, the first 10 minutes is neglected. There is minimal reaction during this first 10 minutes as shown in Figure 4-25. The difference in pH is reflected in the kinetic plot of de-ashed willow and untreated willow. Figure 4-25 and Figure 4-26 show ln(L₀/L) versus time for 0.04% w/w H₂SO₄ and 0.08% w/w H₂SO₄ delignification respectively. In each case, delignification proceeds much faster for de-ashed willow than untreated willow. The pH range listed on the legend is for the whole experiment, neglecting the first 10 minutes.

Figure 4-24. pH of liquor samples from pulping at 180°C in 70% v/v ethanol.
Figure 4-25. Kinetic plot of willow delignification at 180°C in 70% v/v ethanol and 0.04% w/w H$_2$SO$_4$.

\[ y = 0.0186x \]
\[ R^2 = 0.9808 \]

\[ y = 0.0034x \]
\[ R^2 = 0.8226 \]

Figure 4-26. Kinetic plot of willow delignification at 180°C in 70% v/v ethanol and 0.08% w/w H$_2$SO$_4$.

\[ y = 0.0205x \]
\[ R^2 = 0.9169 \]

\[ y = 0.0099x \]
\[ R^2 = 0.9639 \]
The bulk rate constants of these 4 delignifications are adjusted for the pH during the bulk phase as shown in Table 4-5. The average \([H^+]\) and effective temperature are calculated from values pertaining to the bulk phase of delignification only, \(t=0\) to 50 minutes. During de-ashed willow delignification, the rate constant, \(k\), can be corrected using the method previously described in Section 2.3.5 using the exponent calculated by Gilarranz et al. [116] (where delignification rate constant is proportional to \([H^+]^{0.214}\)). For de-ashed willow delignification, the correction brings the rate constant at two different acid loadings to parity. However, for the delignification of untreated willow, this method of correcting rate constant performs poorly. Untreated willow pulped with 0.08% catalyst has considerably lower corrected rate constant, \(k'\), than de-ashed willow with 0.04% catalyst despite the almost identical liquor pH and reaction temperature. Other proposed relationships of \(k\) to \([H^+]\) also perform poorly such as a power law with an exponent of unity as discussed in Section 2.3.5.

Table 4-5. Bulk rate constant of untreated and de-ashed willow delignifications corrected for \([H^+]\).

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>(H_2SO_4) (w/w)</th>
<th>(T_{eff}) (°C)</th>
<th>(k) (min(^{-1}))</th>
<th>Average ([H^+])</th>
<th>pH range</th>
<th>(k') = (k/([H^+]^{0.214}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.04%</td>
<td>173.8</td>
<td>0.0034</td>
<td>0.000096</td>
<td>4.13±0.21</td>
<td>0.025</td>
</tr>
<tr>
<td>Untreated</td>
<td>0.08%</td>
<td>173.9</td>
<td>0.0099</td>
<td>0.000312</td>
<td>3.67±0.32</td>
<td>0.056</td>
</tr>
<tr>
<td>De-ashed</td>
<td>0.04%</td>
<td>174.5</td>
<td>0.0186</td>
<td>0.000277</td>
<td>3.63±0.21</td>
<td>0.107</td>
</tr>
<tr>
<td>De-ashed</td>
<td>0.08%</td>
<td>173.5</td>
<td>0.0205</td>
<td>0.000639</td>
<td>3.34±0.2</td>
<td>0.099</td>
</tr>
</tbody>
</table>

\(a^{pertaining\ to\ t=0-50\ minutes,\ b^{pertaining\ to\ t=0-110\ minutes}\)

The performance of the rate constant correction indicates that the penetration of \(H^+\) ions into the wood structure is hindered in untreated willow. That is to say, as pulping liquor diffuses into the structure of untreated wood the acid catalyst is neutralized by the ash and protein components. Therefore the pH of liquor in the wood chips is considerably higher than the pH of the bulk fluid. The good performance of the rate constant correction for de-ashed willow delignification suggests that a change in pH as liquor penetrates the wood chip does not occur to the same extent as for untreated willow. Instead, it appears that the measured pH of the liquor is representative of the pH throughout the wood chip. If the rate constant, \(k\), of the untreated willow delignifications and the exponent for
correcting the rate constant is assumed correct, the pH inside the wood chips where the reaction is occurring can be estimated. By adjusting the average $H^+$ concentration to give $k'$ the same as for the de-ashed experiments ($k' = 0.1$), the $H^+$ concentration of the reaction can be calculated. Delignification of untreated willow at $H_2SO_4$ loading of 0.04% w/w and 0.08% w/w corresponds to a lignin reaction rate at a pH of 6.9 and 4.7 respectively. These values are much higher than the measured pH’s during those experiments, which means that the pH of the liquor does not represent the pH where the reaction is occurring, within the wood chip.

The exponent used by Gilarranz et al. [116] for correcting the rate constant for pH performed well for buffered pulping of untreated willow as shown previously in Section 4.2.2. This is conducive to the supposition that $H^+$ ion penetration is responsible for higher delignification rates as the buffer reduces the effect of neutralising ash and protein components. The pH of buffered liquor diffusing into the wood structure would remain constant regardless of the effect of neutralising components. It should be noted that the exponent derived by Gilarranz et al. [116] works well with both buffered and de-ashed delignification data because the exponents were derived using buffered methanol-water solutions at a liquor-to-wood ratio of 50L/kg as described in Section 2.3.5. This would also result in negligible neutralization of liquor taking place as liquor penetrated the wood structure.

4.3.3 Comparison of de-ashed and prehydrolysed willow delignification

To my knowledge, there is no literature that compares de-ashed to prehydrolysed wood in terms of subsequent delignification rate. This is an important comparison because it is not known if removal of hemicellulose (resulting in accessibility of solvent to lignin) or removal of extractives and ash (resulting in lower pH) is responsible for the increased delignification rate of prehydrolysed feedstock compared to untreated feedstock.

The prehydrolysis treatment, like de-ashing, controlled pH effectively as shown by Figure 4-27 (henceforth, data pertaining to prehydrolysed willow will be indicated by
hollow markers and de-ashed willow by filled markers). pH values for prehydrolysed willow delignification are much lower than for untreated willow. At each temperature, the prehydrolysis controlled pH more effectively than de-ashing. During delignification of de-ashed willow there was a slight rise in pH over 110 minutes, whereas during delignification of prehydrolysed willow the pH was virtually constant. Untreated willow showed a significant rise in pH during the treatment.

The slight variation in the pH between experiments may be due to a number of things. Neutralisation may occur before the experiment is started and may depend on the porosity of the feedstock. There is likely to be slight variation in the liquor pH before contact with feedstock due to standard errors as each batch of liquor was prepared individually. Temperature may also have an effect on the rate of liquor neutralisation.

Figure 4-27. pH of liquor for delignification of willow in 70% v/v ethanol and 0.08% w/w H$_2$SO$_4$.

![Figure 4-27. pH of liquor for delignification of willow in 70% v/v ethanol and 0.08% w/w H$_2$SO$_4$.](image)
Figure 4-28 shows the percentage of lignin that has dissolved in the liquor as a percentage of the amount of lignin present in the feedstock during 70% v/v ethanol pulping at the low temperature level. There is virtually no difference between the amount of lignin dissolved from de-ashed compared to prehydrolysed willow at the low temperature level. Figure 4-29 shows a minimal difference in amount of lignin dissolved by organosolv pulping of de-ashed versus prehydrolysed willow at the mid temperature level. The error bars show the standard deviation calculated from the two replicates taken at this temperature level. Although the error bars overlap, it is clear that prehydrolysis shows no improvement over de-ashing when considering the percentage of lignin removed from willow. In fact, if there is any difference in lignin mass dissolved, the de-ashed willow performs slightly better than prehydrolysed. Figure 4-30 shows the same effect at the high temperature level.

![Figure 4-28](image)

**Figure 4-28.** % of lignin dissolved during pulping at the low temperature level, comparison of de-ashed and prehydrolysed willow delignification with 70% v/v ethanol and 0.08% w/w H$_2$SO$_4$. 

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101
Figure 4-29. % of lignin dissolved during pulping at the mid temperature level, comparison of de-ashed and prehydrolysed willow delignification with 70% v/v ethanol and 0.08% w/w H₂SO₄.

De-ashed, 169.9°C, pH 3.1±0.31

Prehydrolysed, 168.3°C, pH 3.02±0.06

standard deviation is for two delignification replicates
Figure 4-30. % of lignin dissolved during pulping at the high temperature level, comparison of untreated, de-ashed and prehydrolysed willow delignification with 70% v/v ethanol and 0.08% w/w $\text{H}_2\text{SO}_4$.

Also shown in Figure 4-30 are the untreated willow delignifications at this temperature and catalyst loading. Firstly, addition of 2% v/v acetic acid had no effect on the rate or extent of delignification of untreated willow. As was shown previously in Figure 4-24 and Figure 4-25, de-ashing gives an improvement in delignification kinetics and yield over untreated willow brought about by the lower pH of the liquor. The same improvement is observed for prehydrolysis of the willow, however, no improvement over de-ashing is observed.

Although the pH of most of the prehydrolysed willow delignifications was lower than the de-ashed willow delignifications, no appreciable difference in delignification is observed between these two pre-organosolv treatments. It has been shown by klason and mass balance analysis that prehydrolysis removes 18% of the polysaccharides present in
willow. However, this has no effect on the accessibility of solvent to lignin in the subsequent delignification by catalysed organosolv pulping. This is confirmed in Figure 4-31 showing the mass % (g/g dry untreated wood) of lignin, polysaccharide and extractives remaining after each stage of treatment. Both de-ashing and prehydrolysis show the same % of lignin remaining within the standard deviation shown for the delignification of each feedstock at the mid temperature level.

The only difference observed between delignification of de-ashed and prehydrolysed willow is the percentage polysaccharide remaining. This is where prehydrolysis shows a benefit. Figure 4-31 shows that prehydrolysed and organosolv pulped willow retains 37% of the initial mass as polysaccharide compared to 45% of initial mass for de-ashed and organosolv pulped willow. As shown in Figure 4-32 an analysis of the total solids...
dissolved during pulping shows that prehydrolysed willow gives only a slight improvement in total solids removal meaning that slightly more polysaccharide is removed by pulping prehydrolysed willow than de-ashed willow. Both de-ashed and prehydrolysed feedstock shows a vast improvement over untreated feedstock even with a lower pulping temperature. This is expected due to the lower pH resulting from a pre-organosolv treatment.

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**Figure 4-32.** Percentage total solids dissolved in 70% v/v ethanol. Mid temperature level with pre-organosolv treatment and high temperature level untreated.
It is important to note that 18% of the polysaccharide had already been removed from the feedstock by prehydrolysis and yet the total mass removed by the subsequent pulping was still as high as the pulping of de-ashed willow. It was expected that a feedstock reduced in polysaccharide content would undergo a slower dissolution of total solids because there was less hemicellulose available to react. The difference between the two wood fractionation regimes is made clear from the mass flow diagram shown in Figure 4-33. Values are in grams per 100 grams of dry feed.

Figure 4-33. Mass flows of willow components (g/100g feed) during either de-ashing or prehydrolysis and then pulping at the mid temperature level in 70% v/v ethanol with 0.08% w/w H2SO4.
De-ashing separates the willow feedstock into a liquid and solid fraction. As Figure 4-33 shows, the only component that is removed significantly in the liquid phase by de-ashing is extractives. The prehydrolysis step by contrast removes a significant amount of the polysaccharides (highlighted in Figure 4-33) as well as extractives in the hydrolysis liquor. The prehydrolysis step provides an extra stream of fractionated carbohydrates. This is confirmed by the mass flows in the subsequent pulping step. There is little difference in the components removed in the liquid phase by organosolv pulping of either feedstock. The amount of polysaccharides and lignin removed by the pulping step of each feedstock is nearly proportional to the mass of each that entered the pulping step. 83% and 77% of the lignin input into the organosolv step was solubilised from de-ashed and prehydrolysed willow respectively. For polysaccharides, the values are 34% and 36% of the input polysaccharide mass for de-ashed and prehydrolysed willow respectively.

4.3.3.1 Kinetic analysis based on single measurements of rate constant

Several attempts were made to determine activation energy for de-ashed and prehydrolysed organosolv pulping. However, this proved to be difficult due to the low repeatability of the dissolved lignin content measurements particularly at the high and low temperature levels, which were performed with only one replicate pulping experiment for each feedstock condition.

The kinetic plot for delignification of de-ashed willow in 70% v/v ethanol with 0.08% w/w H₂SO₄ at the low, mid and high temperature level (effective temperatures listed in the legend) is shown in Figure 4-34. At each temperature the bulk delignification phase shows good agreement with a linear trend line during the first 50 minutes of reaction. However, the data shows a low reliability at the later stage of delignification and a residual phase cannot be distinguished easily. Residual phase kinetics will be analysed in Section 4.3.4.
Figure 4-34. Kinetic plot of delignification of de-ashed willow at different temperatures.

Table 4-6. Kinetic data for delignification of de-ashed willow at three temperature levels.

<table>
<thead>
<tr>
<th>$T_{\text{eff}}$ (°C)</th>
<th>pH range $^b$</th>
<th>$1/T_{\text{eff}}$ ($°K^{-1}$)</th>
<th>$k$ (min$^{-1}$)</th>
<th>ln(k) $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>164.5 $^a$</td>
<td>3.11±0.26</td>
<td>0.002285</td>
<td>0.0110</td>
<td>-4.510</td>
</tr>
<tr>
<td>169.9</td>
<td>3.1±0.31</td>
<td>0.002257</td>
<td>0.0160</td>
<td>-4.134</td>
</tr>
<tr>
<td>173.5</td>
<td>3.34±0.2</td>
<td>0.002239</td>
<td>0.0205</td>
<td>-3.885</td>
</tr>
</tbody>
</table>

$^a$pertaining to $t=0$-50 minutes, $^b$pertaining to $t=0$-110 minutes

Table 4-6 shows the average packed bed temperature, pH and rate constants for delignification of de-ashed willow.
The kinetic plot for delignification of prehydrolysed willow in 70% v/v ethanol with 0.08% w/w H₂SO₄ at the low, mid and high level temperature (effective temperature shown in legend) is shown in Figure 4-35. The pH range shown on the legend is the average pH from t=0 to the end of the delignification.

![Kinetic plot of delignification of prehydrolysed willow at different temperatures.](image)

It is clear from the plot of delignification at the mid temperature level that the rate constant determined in this manner is subject to standard error. Most of the data points after the first 50 minutes are higher than the extended trend-line. An unusually slow heat up period and standard error may have contributed to the mid temperature delignification proceeding slower than the low temperature delignification. This could be explained by the zero point being an outlier. The kinetic plot must pass through the zero point, which
4 - Organosolv results and discussion

gives a higher weighting to that point. It may also be that the slow heat up period is still
influencing the data after the initial 10 minutes was removed from consideration.

Table 4-7 shows the effective temperature, average pH and rate constant during the
bulk phase of delignification of prehydrolysed willow.

Table 4-7. Kinetic data for delignification of prehydrolysed willow at 3 temperature levels.

<table>
<thead>
<tr>
<th>Teff (°C) a</th>
<th>pH range b</th>
<th>1/Teff (°K⁻¹) a</th>
<th>k (min⁻¹) a</th>
<th>ln(k) a</th>
</tr>
</thead>
<tbody>
<tr>
<td>165.5</td>
<td>3±0.04</td>
<td>0.002280</td>
<td>0.0101</td>
<td>-4.595</td>
</tr>
<tr>
<td>168.3</td>
<td>3.02±0.06</td>
<td>0.002265</td>
<td>0.0082</td>
<td>-4.804</td>
</tr>
<tr>
<td>174.0</td>
<td>3.34±0.2</td>
<td>0.002236</td>
<td>0.0169</td>
<td>-4.080</td>
</tr>
</tbody>
</table>

apertaining to t=0-50 minutes, bpertaining to t=0-110 minutes

Figure 4-36 shows the activation energy plot for bulk delignification of both de-
ashed and prehydrolysed willow.
The activation energies of delignification of de-ashed willow and prehydrolysed willow are calculated as shown in Table 4-8. The activation energies calculated from rate constant, k, are within the range (79-118kJ/mol) reported by Meshgini and Sarkanen [126]. However, the linear correlation of ln(k) with $1/T_{eff}$ is poor for prehydrolysed willow delignification.
4.3.3.2 Kinetic analysis using multiple zero points

In an attempt to obtain a more reliable correlation between $1/T_{eff}$ and $\ln(k)$ for the prehydrolysed willow delignification a method based on the procedure described in Section 4.2.1 was used. During each experimental run, the rate constant was calculated at four different time intervals and hence four different values of $t_0$, $L_0$ and $T_{eff}$. The method is as follows;

1. The first 25 minutes of reaction was neglected (instead of the first 10 minutes) to remove the influence of inconsistent heat up periods

2. $\ln(L_0/L)$ versus time was plotted for the zero point and the next 6 data points

3. Effective temperature was calculated from these 7 points

4. A single data point with value furthest from the trend-line is neglected

5. Rate constant, $k$, was calculated from the remaining points. Figure 4-37 shows an example of calculating a $k$ value based on $t_0=25$ minutes for each of the de-ashed willow delignifications.
Figure 4-37. Calculation of rate constant from 7 points after neglecting the first 25 minutes of reaction.

6. The above process was repeated, neglecting the first 30, 35 and 45 minutes so that four k and T_{eff} values are calculated for each delignification.

Each feedstock condition had four delignification experiments (1×low, 2×medium and 1×high temperature levels) giving a total of 16 k and T_{eff} for each feedstock condition with which to calculate activation energy. Table 4-9 and Table 4-10 show the calculated rate constants and effective temperatures at each of the four t_0 values for each experiment.
### Table 4-9. Kinetic constants and effective temperatures for delignification of de-ashed willow.

<table>
<thead>
<tr>
<th></th>
<th>De-ashed willow, low temp.</th>
<th>De-ashed willow, mid temp.1</th>
<th>De-ashed willow, mid temp. 2</th>
<th>De-ashed willow, high temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_0$ (minutes)</td>
<td>25</td>
<td>30</td>
<td>35</td>
<td>40</td>
</tr>
<tr>
<td>$k$ (min$^{-1}$)</td>
<td>0.0111</td>
<td>0.0116</td>
<td>0.0093</td>
<td>0.0100</td>
</tr>
<tr>
<td>$T_{\text{eff}}$ (°C)</td>
<td>166.4</td>
<td>166.6</td>
<td>166.9</td>
<td>167.1</td>
</tr>
<tr>
<td>$\ln(k)$</td>
<td>-4.501</td>
<td>-4.453</td>
<td>-4.682</td>
<td>-4.606</td>
</tr>
<tr>
<td>$1/T_{\text{eff}}$ (K$^{-1}$)</td>
<td>0.002275</td>
<td>0.002274</td>
<td>0.002273</td>
<td>0.002272</td>
</tr>
<tr>
<td>$t_0$ (minutes)</td>
<td>25</td>
<td>30</td>
<td>35</td>
<td>40</td>
</tr>
<tr>
<td>$k$ (min$^{-1}$)</td>
<td>0.0179</td>
<td>0.0147</td>
<td>0.0148</td>
<td>0.0101</td>
</tr>
<tr>
<td>$T_{\text{eff}}$ (°C)</td>
<td>171.7</td>
<td>171.9</td>
<td>172.1</td>
<td>172.2</td>
</tr>
<tr>
<td>$\ln(k)$</td>
<td>-4.021</td>
<td>-4.220</td>
<td>-4.216</td>
<td>-4.597</td>
</tr>
<tr>
<td>$1/T_{\text{eff}}$ (K$^{-1}$)</td>
<td>0.002248</td>
<td>0.002247</td>
<td>0.002246</td>
<td>0.002245</td>
</tr>
<tr>
<td>$t_0$ (minutes)</td>
<td>25</td>
<td>30</td>
<td>35</td>
<td>40</td>
</tr>
<tr>
<td>$k$ (min$^{-1}$)</td>
<td>0.0113</td>
<td>0.0102</td>
<td>0.0108</td>
<td>0.0114</td>
</tr>
<tr>
<td>$T_{\text{eff}}$ (°C)</td>
<td>171.3</td>
<td>171.7</td>
<td>172.0</td>
<td>172.2</td>
</tr>
<tr>
<td>$\ln(k)$</td>
<td>-4.480</td>
<td>-4.588</td>
<td>-4.527</td>
<td>-4.478</td>
</tr>
<tr>
<td>$1/T_{\text{eff}}$ (K$^{-1}$)</td>
<td>0.002250</td>
<td>0.002248</td>
<td>0.002247</td>
<td>0.002245</td>
</tr>
<tr>
<td>$t_0$ (minutes)</td>
<td>25</td>
<td>30</td>
<td>35</td>
<td>40</td>
</tr>
<tr>
<td>$k$ (min$^{-1}$)</td>
<td>0.0296</td>
<td>0.0163</td>
<td>0.0181</td>
<td>0.0127</td>
</tr>
<tr>
<td>$T_{\text{eff}}$ (°C)</td>
<td>176.1</td>
<td>176.4</td>
<td>176.7</td>
<td>177.0</td>
</tr>
<tr>
<td>$\ln(k)$</td>
<td>-3.520</td>
<td>-4.116</td>
<td>-4.011</td>
<td>-4.369</td>
</tr>
<tr>
<td>$1/T_{\text{eff}}$ (K$^{-1}$)</td>
<td>0.002226</td>
<td>0.002224</td>
<td>0.002223</td>
<td>0.002222</td>
</tr>
</tbody>
</table>
### Table 4-10. Kinetic constants and effective temperatures for delignification of prehydrolysed willow.

<table>
<thead>
<tr>
<th>Prehydrolysed willow, low temp.</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( t_0 ) (minutes)</td>
<td>25</td>
<td>30</td>
<td>35</td>
<td>40</td>
</tr>
<tr>
<td>( k ) (min(^{-1}))</td>
<td>0.0097</td>
<td>0.0117</td>
<td>0.0095</td>
<td>0.0112</td>
</tr>
<tr>
<td>( T_{\text{eff}} ) (°C)</td>
<td>167.1</td>
<td>167.3</td>
<td>167.5</td>
<td>167.6</td>
</tr>
<tr>
<td>( \ln(k) )</td>
<td>-4.631</td>
<td>-4.448</td>
<td>-4.654</td>
<td>-4.496</td>
</tr>
<tr>
<td>( 1/T_{\text{eff}} ) (K(^{-1}))</td>
<td>0.002271</td>
<td>0.002270</td>
<td>0.002269</td>
<td>0.002269</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Prehydrolysed willow, mid temp.1</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( t_0 ) (minutes)</td>
<td>25</td>
<td>30</td>
<td>35</td>
<td>40</td>
</tr>
<tr>
<td>( k ) (min(^{-1}))</td>
<td>0.0097</td>
<td>0.0132</td>
<td>0.0090</td>
<td>0.0121</td>
</tr>
<tr>
<td>( T_{\text{eff}} ) (°C)</td>
<td>171.2</td>
<td>171.7</td>
<td>171.9</td>
<td>172.1</td>
</tr>
<tr>
<td>( \ln(k) )</td>
<td>-4.638</td>
<td>-4.329</td>
<td>-4.709</td>
<td>-4.411</td>
</tr>
<tr>
<td>( 1/T_{\text{eff}} ) (K(^{-1}))</td>
<td>0.002250</td>
<td>0.002248</td>
<td>0.002247</td>
<td>0.002246</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Prehydrolysed willow, mid temp. 2</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( t_0 ) (minutes)</td>
<td>25</td>
<td>30</td>
<td>35</td>
<td>40</td>
</tr>
<tr>
<td>( k ) (min(^{-1}))</td>
<td>0.0072</td>
<td>0.0098</td>
<td>0.0103</td>
<td>0.0097</td>
</tr>
<tr>
<td>( T_{\text{eff}} ) (°C)</td>
<td>170.6</td>
<td>171.0</td>
<td>171.3</td>
<td>171.6</td>
</tr>
<tr>
<td>( \ln(k) )</td>
<td>-4.939</td>
<td>-4.624</td>
<td>-4.576</td>
<td>-4.636</td>
</tr>
<tr>
<td>( 1/T_{\text{eff}} ) (K(^{-1}))</td>
<td>0.002253</td>
<td>0.002251</td>
<td>0.002250</td>
<td>0.002248</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Prehydrolysed willow, high temp.</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( t_0 ) (minutes)</td>
<td>25</td>
<td>30</td>
<td>35</td>
<td>40</td>
</tr>
<tr>
<td>( k ) (min(^{-1}))</td>
<td>0.0155</td>
<td>0.0161</td>
<td>0.0178</td>
<td>0.0169</td>
</tr>
<tr>
<td>( T_{\text{eff}} ) (°C)</td>
<td>176.6</td>
<td>176.9</td>
<td>177.2</td>
<td>177.4</td>
</tr>
<tr>
<td>( \ln(k) )</td>
<td>-4.167</td>
<td>-4.127</td>
<td>-4.026</td>
<td>-4.082</td>
</tr>
<tr>
<td>( 1/T_{\text{eff}} ) (K(^{-1}))</td>
<td>0.002224</td>
<td>0.002222</td>
<td>0.002221</td>
<td>0.002220</td>
</tr>
</tbody>
</table>

A plot of \( \ln(k) \) versus \( 1/T_{\text{eff}} \) for organosolv delignification of each feedstock is shown in Figure 4-38. Table 4-11 gives the values of kinetic parameters calculated by this method. The activation energy is well within the range of values reported in the literature discussed in Section 2.3.4 and agrees well with the values obtained using similar conditions (Tirtowidjojo et al. [19] reported 80.3kJ/mol using de-ashed wood and acid catalysed methanol pulping).
The activation energy using each feedstock is different to that obtained by conventional means in Section 4.3.3.1. However, using either method, no significant difference can be observed between the pulping of de-ashed and prehydrolysed willow.

![Activation energy plot for delignification of de-ashed willow and prehydrolysed willow.](image)

**Figure 4-38. Activation energy plot for delignification of de-ashed willow and prehydrolysed willow.**

**Table 4-11. Activation energy and frequency factor for delignification of de-ashed willow and prehydrolysed willow.**

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>E&lt;sub&gt;d/R&lt;/sub&gt;</th>
<th>E&lt;sub&gt;a&lt;/sub&gt; (kJ/mol)</th>
<th>ln(k&lt;sub&gt;0&lt;/sub&gt;)</th>
<th>k&lt;sub&gt;0&lt;/sub&gt; (min&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>De-ashed</td>
<td>10463</td>
<td>87.0</td>
<td>19.2</td>
<td>2.14E+08</td>
</tr>
<tr>
<td>Prehydrolysed</td>
<td>10516</td>
<td>87.4</td>
<td>19.2</td>
<td>2.11E+08</td>
</tr>
</tbody>
</table>

Prehydrolysis is expected to result in a faster delignification than untreated feedstock. The cause has sometimes been attributed to greater accessibility of solvent due to the removal of hemicellulose. From this direct comparison of the organosolv delignification of de-ashed feedstock and prehydrolysed feedstock, no improvement was
observed in the rate of delignification. The faster delignification of both feedstocks compared to untreated willow may be due to the lower pH achieved during pulping. The lower pH is due to a removal of neutralising components during prehydrolysis.

The benefit of prehydrolysis is that it removes polysaccharide selectively without removing lignin. That process stream can then be treated as being uncontaminated with lignin. Another benefit of prehydrolysis is that it removes the neutralising components of wood and prevents the acid catalyst added to organosolv pulping liquor from being neutralised during pulping resulting in a lower pH and thus a higher reaction rate. De-ashing in 1% acetic acid at room temperature has the same effect on subsequent organosolv delignification rate. Under the organosolv condition studied, no evidence could be found that removal of part of the hemicellulose component has an effect on organosolv delignification rate.

4.3.4 Residual phase

One of the aims of this thesis was to determine the cause of the residual phase. Three options for the cause have been identified in Section 2.4. They are,

1. An equilibrium between the de-polymerisation and re-polymerisation of re-condensed lignin,

2. A change in mechanism from reaction to mass transfer controlled delignification, or

3. An association of lignin with polysaccharides that requires the dissolution of polysaccharides before lignin can be removed.

The examination of de-ashed versus prehydrolysed willow showed no evidence that polysaccharide interaction with lignin has any effect on delignification rate meaning that option 3 can be discounted. It is possible that lignin in association with the more recalcitrant portions of hemicellulose or with cellulose is preventing the ‘residual’ lignin from reacting. More severe prehydrolysis is required to rule out this possibility.
Option 2 is not supported by the results of buffered pulping using 30% v/v ethanol versus 50% v/v ethanol. The 50% v/v ethanol pulping should display improved mass transfer over 30% v/v ethanol due to ethanol having a lower viscosity than water. The 50% v/v ethanol has the greater penetration into wood and thus should result in lower residual lignin content. No improvement from 50% v/v ethanol pulping is seen. However, more replicates with greater solvent concentration difference and better control of pH is required to prove this definitively.

An examination of the lignin concentration at the precise onset of the residual phase will identify that option 1 is possible. It will also dispel the possibility of a residual lignin pre-existing in the wood as discussed in the literature (see § 2.3.3).

As reviewed in the literature, other researchers treat residual lignin as a separate species of lignin having a fixed proportion in any given feedstock. Under this assumption, exponential trend lines can be fitted to the residual phase only. Equation 4-3 can be rearranged to give,

$$[L_R] = [L_{0R}]e^{-k_R t}$$

Equation 4-7

where $L_R$ is the residual lignin content (g/g dry wood) at any time, $t$ (minutes), $L_{0R}$ is the initial residual lignin content (g/g dry wood) and $k_R$ is the first order rate constant of residual delignification (min$^{-1}$). Therefore, exponential trend lines can be used to indicate the initial amount of residual lignin, $L_{0R}$, and the rate constant of residual delignification, $k_R$. $L_{0R}$, is the intercept and $k_R$ is the slope of the lines shown in Figure 4-39.

Figure 4-39 shows delignification of de-ashed willow with the residual phase fitted with an exponential trend line (the axis is logarithmic). Lignin content is expressed in g/g dry wood input for simplicity. Figure 4-40 shows the delignification of prehydrolysed willow with the residual phase fitted with an exponential trend line. All other pulping experiments displaying a residual phase are shown in Figure 4-41. The heat-up period is neglected in each set of data.
Figure 4-39. De-ashed willow delignifications showing a transition to residual phase kinetics.

Figure 4-40. Prehydrolysed willow delignifications showing a transition to residual phase kinetics.
Figure 4-41. All other delignifications displaying a transition to residual phase kinetics.

Figure 4-39, Figure 4-40 and Figure 4-41 show that $L_{OR}$ changes considerably depending on the liquor conditions. This does not agree with the assumption that residual lignin has a fixed proportion in the untreated feedstock.

It appears from Figure 4-39 and Figure 4-40 that the lignin concentration at the transition to residual kinetics is dependant on the rate of bulk delignification. This is conducive to option 1 since different conditions can affect the rate constant of the forward and backward reaction differently resulting in a shift in equilibrium.

A faster lignin reaction is usually accompanied by faster hemicellulose reaction, which could affect the lignin-carbohydrate interaction (option 3). However, the extended removal of polysaccharides from prehydrolysed willow compared to de-ashed willow and the lack of any notable difference in the level of residual lignin between the two organosolv pulped feedstocks indicates that polysaccharide content has no effect on the lignin content at which the residual phase starts. Therefore, a model based on option 1, an equilibrium between forward and reverse reactions, will be developed.
4.3.4.1 A kinetic model for delignification

It is apparent from Figure 4-39 that a residual phase of delignification occurs at different lignin concentrations depending on the pulping conditions. Since the effects of mass transfer and lignin-hemicellulose interaction have been discounted, it is likely that a reversible reaction is occurring. A model is proposed in which ‘native’ lignin reacts to soluble lignin (reaction 1) and the reverse reaction converts soluble lignin to ‘native’ lignin (reaction 2).

$$\begin{align*}
L_N & \underset{k_2}{\overset{k_1}{\rightleftharpoons}} L_S \\
\end{align*}$$

Equation 4-8

The influence of polysaccharides can be discriminated against due to the comparison made between de-ashed and prehydrolysed willow delignification. Therefore the model is simplified by taking lignin content as a measure of mass per initial dry wood mass. The rate equation for this model assuming first order kinetics in both the forward and reverse reaction is shown in Equation 4-9.

$$\frac{dL_N}{dt} = -k_1[L_N] + k_2[L_S]$$

Equation 4-9

where $L_N$ is the natural lignin content (% g/g initial dry wood), $L_S$ is the soluble lignin concentration (g/L) calculated by Equation 4-10, $k_1$ and $k_2$ are the rate constants for the forward and backward reactions respectively.

$$[L_S] = ([L_{N0}] - [L_N])R_{WL}$$

Equation 4-10
where $[L_{N0}]$ is the initial lignin content of the wood (g/g) and $R_{WL}$ is the wood to liquor ratio (g/L). By letting $d[L_N]/dt=0$, Equation 4-9 and Equation 4-10 can be reduced to Equation 4-11 and the equilibrium constant, $K$, can be defined.

\[
\frac{k_2}{k_1} = \frac{L_{Neq}}{R_\mu (L_0 - L_{Neq})} = K
\]

Equation 4-11

\[
k_2 = K \cdot k_1
\]

Equation 4-12

Rearranging gives Equation 4-12 and now $L_s$ and $k_2$ can be substituted into Equation 4-9 assuming first order for the forward and reverse reactions. This gives Equation 4-13,

\[
\frac{dL_N}{dt} = -k_1[L_N] + k_1KR_{WL}([L_0] - [L_N])
\]

Equation 4-13

which can be integrated and rearranged to give Equation 4-14.

\[
[L_N] = \frac{L_0 e^{-k_1(1+KR_{WL})t} + KR_{WL}L_0}{1 + KR_{WL}}
\]

Equation 4-14

Equation 4-14 shows that this model cannot be fit to data showing an increase or decrease of lignin content during the residual phase. As time increases $L_N$ approaches $L_0KR_{WL}/(1+KR_{WL})$. Figure 4-42, Figure 4-43 and Figure 4-44 show the first order reversible model fit to the experimental data that displayed a transition to residual phase kinetics. Table 4-12 gives the value of $k_1$ and $k_2$ used to model each pulping experiment.
Figure 4-42. First order reversible model fit to pulping of de-ashed willow.

Figure 4-43. First order reversible model fit to pulping of prehydrolysed willow.
4 - Organosolv results and discussion

Figure 4-44. First order reversible model fit to other pulping experiments.

Table 4-12. Forward and reverse reaction rate constants for each pulping experiment fit with a reversible first order model.

<table>
<thead>
<tr>
<th>Feedstock and liquor conditions</th>
<th>( k_1 ) (min(^{-1}))</th>
<th>( k_2 ) ((10^{-5} \text{Lg}^{-1}\text{min}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>De-ashed, 0.04% H(_2)SO(_4) (high temp)</td>
<td>0.035</td>
<td>9.5</td>
</tr>
<tr>
<td>De-ashed, 0.08% H(_2)SO(_4) (low temp)</td>
<td>0.028</td>
<td>10.6</td>
</tr>
<tr>
<td>De-ashed, 0.08% H(_2)SO(_4) (mid temp)</td>
<td>0.036</td>
<td>10.9</td>
</tr>
<tr>
<td>De-ashed, 0.08% H(_2)SO(_4) (high temp)</td>
<td>0.046</td>
<td>8.9</td>
</tr>
<tr>
<td>Prehydrolysed, 0.08% H(_2)SO(_4) (low temp)</td>
<td>0.029</td>
<td>14.3</td>
</tr>
<tr>
<td>Prehydrolysed, 0.08% H(_2)SO(_4) (mid temp)</td>
<td>0.028</td>
<td>13.9</td>
</tr>
<tr>
<td>Prehydrolysed, 0.08% H(_2)SO(_4) (high temp)</td>
<td>0.034</td>
<td>12.3</td>
</tr>
<tr>
<td>Autocatalysed, 35%EtOH</td>
<td>0.018</td>
<td>8.2</td>
</tr>
<tr>
<td>Buffered, 30%EtOH</td>
<td>0.018</td>
<td>7.7</td>
</tr>
<tr>
<td>Buffered, 50%EtOH</td>
<td>0.013</td>
<td>5.8</td>
</tr>
<tr>
<td>Untreated, 0.08% H(_2)SO(_4) (high temp)</td>
<td>0.019</td>
<td>9.6</td>
</tr>
</tbody>
</table>
Table 4-12 shows that while $k_1$ generally increases with temperature during the similar de-ashed and prehydrolysed pulping experiments whereas no relationship between $k_2$ and temperature can be identified. This is in line with data reported in the literature, which indicates that delignification rate has higher dependence on temperature during the bulk phase than during the residual phase (see § 2.3.3).

The simple first order reversible reaction gives a reasonably good fit to all of the experimental data obtained. However, the model fails to explain three phenomena reported in the literature (see §§ 2.3.2 and 2.3.3);

1. In some literature data (and experimental data from the current work), lignin content does not ‘level off’ but continues on a downward trend during residual delignification.

2. Some literature data exhibits a minimum lignin content, after which the lignin content increases.

3. Literature data indicates the existence of three kinetic phases, initial, bulk and residual delignification.

The inability of the simple first order reversible model to explain these phenomena suggests that a more complex model is required to fully describe delignification kinetics. A finite element model was developed to investigate more complex delignification mechanisms.

### 4.3.4.2 A finite element model using MATLAB

A finite element model was developed, first to describe the simple reversible model, then to examine more complex models discussed in Section 4.3.4.3. In the simple reversible model, the reverse reaction may be first or second order with respect to $L_S$. Equation 4-15 is used to represent this.

\[
\frac{dL_N}{dt} = -k_1[L_N] + k_2[L_S]^q
\]

\textit{Equation 4-15}
where $\delta$ is the order of the reverse reaction (1 or 2). Equation 4-16 can be used to calculate the rate constant, $k_i$, where $i$ is 1 for the forward reaction and 2 for the reverse. The equation is derived from the Arrhenius relationship of rate constant to temperature and the dependence on $H^+$ concentration discussed in the literature (see § 2.3.5).

$$k_i = \left[H^+\right]^{\varepsilon_1} k_{0i} e^{\left(-\frac{E_{a_i}}{RT}\right)}$$

Equation 4-16

A time increment, $\Delta t$, of 0.1 minutes was selected and at each time increment, the rate constants, $k_i$, soluble lignin concentration, $L_S$, and $dL_N/dt$ were calculated from Equation 4-16, Equation 4-10 and Equation 4-15 respectively. $L_{Nt+\Delta t}$ was then calculated as $L_{Nt}(dL_N/dt)$. For all models and the activation energy for the forward reaction, $E_{a1}$, was 87kJ/mol as calculated from the delignification of de-ashed willow in Table 4-11 (§ 4.3.3.2). The other parameters, $\varepsilon_1$ and $\varepsilon_2$, $k_{01}$, $k_{02}$ and $E_{a2}$ were selected to give the lowest sum-squared-difference between the model and experimental data. Hence this is a curve fitting method designed only to establish if a model is capable of describing the reaction phenomena observed. An example of the MATLAB code for this finite difference model is available in Appendix 4.

Two dissimilar experimental runs were selected. These were the delignifications of de-ashed willow at an effective temperature during the whole run of 176°C with 0.04% w/w H$_2$SO$_4$ (pH=3.63±0.21) and the buffered delignification using 50% ethanol at an effective temperature of 178°C (pH=4.2±0.20).

At 1$^{st}$ order with respect to $L_S$ ($\delta=1$) the lowest sum squared difference obtained was 0.0013. The best fit, shown in Figure 4-45, was obtained with the following values $E_{a2}=20$kJ/mol, $k_{01}=1.6\times10^{11}$min$^{-1}$, $k_{02}=0.060$Lg$^{-1}$min$^{-1}$, $\varepsilon_1=0.73$ and $\varepsilon_2=0.16$. 

126
4 - Organosolv results and discussion

Figure 4-45. Best fit of simple reversible model that is 1\textsuperscript{st} order with respect to L\textsubscript{S}.

A model that is second order with respect to L\textsubscript{S} (\(\delta=2\)) gave a sum-squared-difference of 0.0011. The best data fit is shown in Figure 4-46. This is not a significant improvement over the 1\textsuperscript{st} order model.

Figure 4-46. Best fit of simple reversible model that is 2\textsuperscript{nd} order with respect to L\textsubscript{S}.
4.3.4.3 Alternative hypothetical models

The data obtained can be fit with a reversible model that is first order with respect to native lignin in the forward reaction and first or second order with respect to soluble lignin in the reverse reaction. However, this does not confirm that it is the reaction mechanism, it only fails to discount it.

Of particular interest is the tendency of the model towards an equilibrium. Literature reviewed in Section 2.3 indicates that lignin content continues to decrease during the residual phase or reaches a minimum and then increases. Also, the model may not be able to account for initial phase delignification reported by some researchers as described in Section 2.3.3. The data presented in this thesis does not exhibit an initial delignification phase. The initial phase may be masked by the heat-up period or not present at all.

An alternative model incorporates the re-condensation of soluble lignin to a more resistant species. This mechanism, suggested by Sarkannen, is described in Section 2.3.2.

\[
\begin{align*}
L_N \xrightleftharpoons[k_2]{k_1} & \quad L_S \\
L_s \xrightleftharpoons[k_4]{k_3} & \quad L_R
\end{align*}
\]

Equation 4-17

Re-condensation reactions to \( L_N \) or \( L_R \) (insoluble forms of lignin) are assumed to be second order with respect to \( L_S \) and reaction of native or re-condensed lignin to soluble lignin is assumed to be first order with respect to concentration of \( L_N \) or \( L_R \) respectively. This mechanism gives rise to Equation 4-18 and Equation 4-19.

\[
\frac{dL_N}{dt} = -k_1[L_N] + k_2[L_S]^2
\]

Equation 4-18
Equation 4-10 is used to determine $L_S$ and Equation 4-16 is used to determine the rate constants. Figure 4-47 shows the model fit to the same data shown in Figure 4-46. The model incorporating a re-condensation to a more recalcitrant structure of lignin gives a slightly better fit than the simple reverse model.

![Figure 4-47](image)

**Figure 4-47. Data fitted with model for dissolution and re-condensation to residual lignin.**

In addition, this reaction mechanism can be fitted to literature data shown in Section 2.3.2 that displays a minimum lignin content. Figure 4-48 shows the model fit to data from Parajo et al. [84]. The model fit in Figure 4-48 shows that the phenomena of increasing lignin content in the later stages of pulping can be explained by a re-condensation to more resistant forms of lignin.
4 - Organosolv results and discussion

This mathematical model still cannot account for an initial phase of delignification, nor does it account for a continually declining lignin content during the residual phase of delignification.

It should be noted that increasing the complexity of a model makes it easier to fit to experimental data. Therefore a model that represents the mechanism of delignification cannot been verified by simply fitting a model. However, the inability to fit a model is a means of rejecting the mechanism it describes.

It is clear that the mechanism is more complex than a simple reversible reaction with only native and soluble lignin as the species. The existence of lignin that is less reactive than native lignin (re-condensed lignin) accounts for an increase in lignin content during residual phase kinetics. However, different sizes and structures of soluble lignin are known and are reported in the literature (see § 2.3.1). Lignin may continue to react after solubilisation into smaller fragments that are not susceptible to re-condensation.

Figure 4-48. Model using re-condensed lignin fit to the data of Parajo et al. [84].
Figure 4-49. Data from literature fit with the $L_N$ to $L_S$ to $L_R$ reversible model.

Data generated from the work of Shatalov and Periera [115] shown in Section 2.3.3 clearly displays three phases of delignification. The reversible model with re-condensed lignin is first fitted to the data with a poor result as shown in Figure 4-49.

An alternative model is generated incorporating a second species of soluble lignin that does not re-condense as easily. This is represented as

$$
\begin{align*}
L_N & \xrightarrow{k_1} L_S \\
L_S & \xrightarrow{k_2} L_R \\
L_S & \xrightarrow{k_3} L_{SS}
\end{align*}
$$

Equation 4-20
where $L_{SS}$ represents a soluble form of lignin, that may be referred to as ‘super-soluble’, analogous to lower molecular weight lignin.

![Graph showing mass lignin per dry mass wood input (g/g) vs. time (minutes)](image)

**Figure 4-50. Model incorporating a second species of soluble lignin, $L_{SS}$.

The resulting model fit to data generated from the literature shows a vast improvement compared to the model containing one species of soluble lignin. Furthermore, this type of reaction mechanism could explain the lignin content of pulp not being affected by pulping in solvent with isolated lignin added to it as reported in the literature (Section 2.3.2). The lignin added before batch pulping by Tirtowidjojo et al. [19] may have been ‘super soluble’ lignin.

This mechanism can account for the kinetic phases of delignification and is based on logical ideas derived from the literature and experimental work performed here. However, to identify it as a true mechanism and obtain kinetic parameters for each reaction step requires further experiments designed to distinguish between the different species of lignin. This requires quantitative structural analysis of the lignin removed as well as the residual lignin. This is an area of future work.
5 Organosolv conclusions

SEM images have shown that there is benefit to removal of organosolv black liquor at elevated temperatures to reduce the incidence of lignin re-precipitation.

Based on the kinetic data obtained from autocatalysed pulping and from buffered pulping, ethanol concentration has no effect on the rate of lignin reaction and dissolution above ethanol concentrations of 30% v/v. It is only the pH difference inherent in differing ethanol concentrations that causes a change in the rate constant. The change in ethanol concentration, which would affect viscosity and surface tension, had minimal effect on delignification rate. The minimal difference can be attributed to the small difference in pH, which proved difficult to control even using a buffer.

Comparison of de-ashed versus prehydrolysed willow pulping has shown that prehydrolysis only affects delignification rate by removing neutralising components of the feedstock resulting in a more acidic organosolv pulping medium. Removal of hemicellulose does not increase the rate of delignification for the conditions tested. Prehydrolysis was shown to be a useful pre-organosolv treatment for the clean fractionation of wood components as it removes hemicellulose as well as extractives and ash that slow subsequent delignification without removal of lignin in the same liquid stream. Prehydrolysis can be used to effect cleaner fractionation and reduce the bulk volume of wood requiring organosolv treatment. This in turn reduces the volume of the organosolv reactor, which typically operates at high pressure and temperature and requires corrosion resistant materials of construction.

Previous authors have postulated that the removal of hemicellulose prior to organosolv delignification frees lignin to react more readily. No evidence of this has been found. A prehydrolysis step merely removes the neutralising components of wood, making the true pH of the reaction lower than it would be if prehydrolysis was not performed. This is evidenced by a comparison of prehydrolysed willow organosolv delignification with de-ashed willow organosolv delignification. Little difference is observed between the two pulping runs due to the steady control of the pH, which is made possible by the removal of neutralising components. Prehydrolysis also removed
some hemicellulose. This did not result in a faster rate of organosolv delignification compared to de-ashed willow delignification.

A mechanism for delignification has been proposed in which more than one species of insoluble lignin and more than one species of soluble lignin is present. While it is clear that lignin re-condenses to a structure of lignin that is more resistant to removal, the difficulty in distinguishing re-condensed lignin from native lignin makes determining kinetic parameters and order of reaction difficult. To confirm the mechanism, experiments will have to be designed to quantify residual lignin and the different molecular weights of lignin during pulping.
6 Lignin Recovery

Lignin is a potential raw material for the production of plastics, adhesives and resin additives [61]. Biorefining has been described as the separation and recovery of cellulose, hemicellulose and lignin as cleanly as possible [36]. While organosolv pulping produces a high quality lignin product, it is necessary to recover lignin from organosolv black liquor by precipitating the lignin. This can be done by either evaporating the ethanol or diluting it with acidified water. Simply boiling away the ethanol produces a hard amorphous form of lignin high in dissolved hemicellulose sugars. And evaporating by spray drying has a high capital cost and will require a high energy cost for subsequent ethanol recovery without solving the problem of contaminating lignin with hemicellulose derived products.

6.1 Background

Lignocellulosic material can be delignified as described in Section 2.3. In many processes the lignin concentration is increased by flashing to atmospheric pressure. Diluting black liquor with acidified water precipitates the lignin, which can then be centrifuged and recovered. Botello et al. [148] determined that greatest dilution and lowest pH resulted in the best lignin recovery yields although pH has a minimal effect.

Diluting black liquor with acidified water lowers the ethanol concentration and lowers the pH. This lowers the solubility of lignin in the solution (organosolv lignin is highly soluble in solvents or at high pH). When the lignin concentration exceeds the solubility of lignin, it forms a solid. The solubility of sugars in solution remains high. Lignin and hemicellulose fractions are therefore separated into solid and aqueous phases respectively. The problem is then to separate the precipitated lignin from the aqueous phase by any of the various unit operations for solid-liquid separation.

Centrifugation of precipitated lignin, as described in patents by Diebold et al. [90] and Lora et al. [149], has been met with aversion, perhaps due to high maintenance costs. Centrifugation of precipitated lignin is performed only after a slow preliminary settling step.
Filterability of precipitated ethylene glycol lignin was considered a problem due to the high viscosity of the solvent. Dilution, acid concentration and filtering temperature were studied. Liquor to acidified water ratio of 1:3 and filtering temperature of 50-60°C were the optimum conditions for high yield of lignin while maintaining adequate lignin properties [79].

Flotation is one method that requires low energy and low capital cost. It is recommended for particles that are hydrophobic and therefore repelled from the aqueous phase into the rising air bubbles. Lora and Glasser [61] report that organosolv lignins are typically water insoluble and very hydrophobic. While flotation of Kraft lignin is unsuccessful, as will be discussed in Section 6.1.1, the hydrophobic nature of organosolv lignin gives it an advantage over other lignin preparations.

6.1.1 Recovery of lignin by flotation

Foam fractionation of Kraft lignin is reported to be ineffective [150, 151]. However, foam flotation of Kraft lignin precipitated with aluminium salts can be effected with careful control of the pH [151]. Wang et al. [150] reports that foam fractionation of Kraft lignin without a precipitating agent or a collector results in only 27% lignin removal at the optimal superficial gas velocity. The addition of an alum precipitator (Al₂(SO₄)₃) prior to foam flotation gave only 12% lignin recovery. A collector was necessary to endow lignin-alum flocs with hydrophobic surfaces, allowing bubble adherence.

The hydrophobic nature of organosolv lignin makes flotation an ideal method of separation. However, turbulence after precipitation and flocculation of lignin may destroy the aggregates. Dissolved air flotation (DAF) has been identified by Rubio et al. [152] to eliminate destabilisation of aggregates when used for clarification of wastewater. Microbubbles are formed in DAF by the reduction in pressure of water pre-saturated with air. When the air saturated water is forced through an orifice or needle valve, bubbles in the size range 30-100μm are formed. These bubbles attach to flocs of particles in solution and the bubble and attached solids rise due to buoyancy. DAF is used extensively in minerals and wastewater processing [152, 153].
There are four mechanisms of particle-bubble attachment during DAF as shown in Figure 6-1. They are:

a) Particle-bubble collision and adhesion;

b) Bubble formation at particle surface;

c) Micro-bubble entrapment in aggregates;

d) Bubble entrainment by aggregates.

Collision efficiency has been shown to increase with increasing floc size, assuming consistent electric chemical properties of the bubble and the particle [154]. According to the trajectory model of Han [155], collision efficiency increases as floc size approaches the mean bubble size. Collision efficiency is low when particle size is much smaller than bubble size.
Increased pressure results in a greater number of bubbles and smaller average bubble diameter. Image analysis has shown that average bubble size is 71µm using saturation pressure of 29psi (2bar) and 32.4 µm using a saturation pressure of 73psi (5bar) [156]. Thus, higher pressure results in greater frequency of attachment and greater buoyancy.

Henry’s law dictates that the concentration of a dissolved gas in a liquid at equilibrium is proportional to the Henry’s law coefficient and the partial pressure of the gas. The Henry’s law coefficient decreases with increasing temperature resulting in lower gas solubility at higher temperatures [157]. Therefore, a higher temperature during gas saturation reduces the amount of gas dissolved and subsequently liberated upon decompression.

The use of dissolved air flotation DAF for the separation of ethanol pulping lignin from diluted black liquor is a novel approach to lignin recovery [158]. An examination of parameters important to dissolved air flotation of organosolv lignin is described in Sections 6.2 and 6.3. Factorial design of experiments is used to identify process parameters that are critical to the yield of lignin and clarification rate. Methods of experimental design described by Antony [159] are followed.

6.2 Materials and methods

The procedure for simultaneous precipitation and dissolved air flotation is described in Section 6.2.1. The fractional factorial design of experiments is described in Section 6.2.2.

6.2.1 Procedure

Black liquor for all experiments was produced by autocatalysed organosolv pulping of chipped S. schwerinii at 185°C for 3 hours using 70% v/v ethanol at a liquid: solid ratio of 11 as previously described in Section 3.2. In each experiment, black liquor was diluted in a falcon flask by 2, 3 or 7 times. The volume of black liquor diluted was 5, 10 or 13.3mL when using a water to black liquor ratio of 7, 3 or 2 respectively. This resulted in a final volume of 40mL for each experiment. Solutions were prepared from deionised
water containing each of the four combinations of 0 or 5mM of HCl and 0 or 10% ethanol. These solutions, intended to dilute the black liquor, were heated to the appropriate temperature using a water bath and saturated with gas by shaking in a sealed falcon tube, pressurised from a nitrogen cylinder to the desired pressure. On starting an experiment, the appropriate solution was removed from pressure, mixed with black liquor under one of two mixing regimes (designated by the ‘still phase’) and placed upright while a stop clock was simultaneously started. A photo record of the flotation process was made by taking frequent photos using a digital camera at a defined orientation to the falcon tube.

The mixing regime used is indicated by the ‘still phase’. If the still phase is water, the water is added to the falcon tube and then the black liquor is delivered into it using a syringe. If the stationary phase is labelled BL, the black liquor is first added to the falcon tube and the water is decanted into the black liquor.

Addition rate is defined as the volume of black liquor added divided by the time taken to perform the addition. Two addition rates are tested, 5mL/s and 10mL/s, using 10mL of black liquor. This corresponds to pushing the black liquor out of the syringe into the water evenly over 2 seconds and 1 second respectively. All trials, unless otherwise stated, were performed with an addition rate of 10mL/s.

In the second set of factorial experiments, the time elapsed between removing the nitrogen pressure from the water and addition of the black liquor was tested. This parameter is labelled as ‘time to addition’. Time to addition of 4 or 8 seconds was used in the second set of factorial experiments. In all other trials, the time to addition was 4 seconds.

6.2.1.1 Measurement of precipitate yield

Final flotation volume is defined as the volume that was occupied by the floating precipitate after at least 24 hours as shown in Figure 6-2. It was assumed that the equilibrium volume of lignin was proportional to its mass and therefore a measure of final yield.
To compare the yield at different water to black liquor ratio the final floated volume can be divided by the volume of black liquor diluted. This is defined as the ratio of final floated precipitate to black liquor (mL precipitate/mL black liquor).

This method is not precise and is therefore only used in the first block of experiments as a screening test for yield. Further yield measurements were based on filtered weight of precipitate by vacuum filtration using a Buchner funnel and filter paper.

6.2.1.2 Measurement of clarification time

50% clarification time was defined as the time elapsed between diluting the black liquor and 50% of the volume of the diluted liquor becoming clear as shown in Figure 6-3.
6.2.2 Experimental design

The first block of experiments was designed as a $2^{6-2}$ fractional factorial design to determine the effect of six parameters on both final flotation volume of lignin and 50% clarification time. In light of observations from the first block of experiments (see § 6.3.1), 3 further sets of experiments were designed as outlined in Sections 6.2.2.2 to 6.2.2.4. The temperature was examined without change of other parameter levels. Addition speed and nitrogen saturation pressure were examined in tandem. Finally, a second factorial block was designed to examine variables that may be affecting final yield. Yield was measured by dry mass of filtered precipitate.

6.2.2.1 First block of factorial designed experiments

The first block of trials is a $2^{6-2}$ fractional factorial design. Parameters and their value at each level are shown in Table 6-1. Table 6-2 shows the level of each parameter for 16 experiments, which were carried out in duplicate.
6.2.2.2 **Effect of temperature**

The temperature was studied in isolation using a water to black liquor ratio of 3, HCl concentration of 0mM, water as the still phase, a nitrogen pressure of 1barg and no ethanol in the water solution. Temperatures studied were 0, 5, 10, 15, 20, 25, 30, 35 and 40°C.
6.2.2.3 Effect of addition rate and nitrogen pressure

The effect of addition rate and nitrogen pressure on settling time was tested in order to show the effect of a fine dispersion of micro-bubbles during precipitation. A temperature of 20°C was used for all addition rate experiments. The levels of addition rate were 5mL/s and 10mL/s. The pressure levels were 1barg and 2barg. The H₂O:BL ratio was 3:1.

6.2.2.4 Second block of factorial designed experiments

A second set of factorial designed experiments was undertaken at constant water temperature to study effects of HCl concentration, water to liquor ratio, nitrogen pressures, black liquor temperature and time to addition. The design is a 2⁵-² fractional factorial design. The rate of addition was 10mL/s and the temperature was 20°C. Table 6-3 shows the value of high and low levels of each parameter. Table 6-4 shows the level of each parameter in each of 8 experiments, which were carried out in duplicate.

<p>| Table 6-3. Value of parameters for the second set of factorial designed experiments. |
|----------------------------------------|-----------------|----------------|----------------|----------------|</p>
<table>
<thead>
<tr>
<th>H₂O:BL               Time to add.</th>
<th>N₂ pressure</th>
<th>BL temp.</th>
<th>HCl Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low level            3             4s       0.3barg  20°C     1mM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High level           7             8s       1barg    25°C     5mM</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Table 6-4. Level of parameters for the second set of factorial designed experiments. |
|----------------------------------------|-----------------|----------------|----------------|
| run #               H₂O:BL | Time to add. | N₂ pressure | BL temp. | HCl Conc. |
|----------------------|-------------|-------------|----------|
| 1                    -1          -1           -1       +1       +1       |
| 2                    -1          -1           +1       +1       -1       |
| 3                    -1          +1           -1       -1       +1       |
| 4                    -1          +1           +1       -1       -1       |
| 5                    +1          -1           -1       -1       -1       |
| 6                    +1          -1           +1       -1       +1       |
| 7                    +1          +1           -1       +1       -1       |
| 8                    +1          +1           +1       +1       +1       |
In all experiments following the first set of factorial experiments, 50% clarification times and lignin yields by mass of filtered precipitate were measured. All experiments were performed in duplicates.

### 6.3 Results and discussion

Following the first set of experiments, it became apparent that temperature has a significant effect on both yield and clarification time. For this reason, Section 6.3.2 examines changing temperature while the other parameters remain the same. Effect of addition rate and nitrogen saturation pressure are discussed in Section 6.3.3. Results of the second block of factorial designed experiments are discussed in Section 6.3.4.

#### 6.3.1 First block of factorial designed experiments

Samples at 45°C water temperature resulted in a very fine precipitate, which settled very slowly if at all. Final floated volume at 45°C was 1.7mL versus 4.9mL at 20°C. The precipitate volume per volume of black liquor used is reported in Table 6-5.

Table 6-5 shows that greater final floated volume is achieved at high dilution, high HCl concentration, low temperature and low ethanol concentration. The still phase and nitrogen pressure did not have an effect on final floated volume.

<table>
<thead>
<tr>
<th>Level</th>
<th>H₂O:BL*</th>
<th>HCl Conc.</th>
<th>H₂O temp.</th>
<th>Still phase</th>
<th>N₂ pressure</th>
<th>EtOH conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>0.23</td>
<td>0.44</td>
<td>0.31</td>
<td>0.29</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>+1</td>
<td>0.36</td>
<td>0.14</td>
<td>0.27</td>
<td>0.30</td>
<td>0.20</td>
<td></td>
</tr>
</tbody>
</table>

*BBL=Black Liquor

At 45°C, accurate determination of 50% clarification time was not possible because an interface between the precipitate and aqueous phase was difficult to discern. If high temperature level trials are neglected, H₂O:BL ratio and ethanol concentration are confounded (all low H₂O:BL ratio trials had high ethanol concentration and all high H₂O:BL ratio trials had low ethanol concentration) and must be considered as a combined effect. Table 6-6 shows the remaining effects on 50% clarification time. The combined...
effect of low H₂O:BL ratio and high ethanol concentration has a faster clarification time. This may be due to incomplete precipitation at this condition, which is indicated by the low final floated volume shown in Table 6-5. For the other parameters, fastest clarification occurs at high HCl concentration, water as the still phase and high nitrogen pressure.

Table 6-6. 50% clarification time (minutes) for each parameter at low and high level.

<table>
<thead>
<tr>
<th>Level</th>
<th>H₂O:BL*</th>
<th>HCl Conc.</th>
<th>Still phase</th>
<th>N₂ pressure</th>
<th>EtOH conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>3.55</td>
<td>12.13</td>
<td>1.24</td>
<td>14.01</td>
<td>16.35</td>
</tr>
<tr>
<td>+1</td>
<td>16.35</td>
<td>7.76</td>
<td>18.35</td>
<td>5.89</td>
<td>3.55</td>
</tr>
</tbody>
</table>

*BL=Black Liquor

The still phase is the most significant parameter for clarification time and has little effect on final floated volume. It was also observed that the rate of addition of black liquor to water and the time between releasing the nitrogen pressure and adding the black liquor had to be carefully controlled to obtain repeatable results. An examination of these variables is discussed in Sections 6.3.3 and 6.3.4.

### 6.3.2 Effect of temperature

Temperature had a minor affect on yield below 20°C. Above 20°C, filtered yield declined as temperature increased. At 20°C, the settling time is short and the reduction in yield is only 3.5% of the maximum. This means that 20°C is a suitable temperature to examine the effects of other parameters. Temperature has a significant effect on clarification time as shown in Figure 6-4. 50% clarification time decreased with increasing temperature up until 35°C, after which it was impossible to discern a precipitate interface because most of the lignin formed a fine precipitate that did not destabilise. Figure 6-5 shows samples diluted at 30°C, 35°C and 40°C after 24 hours. At higher dilution temperature, the supernatant colour after 24 hours of settling was darker indicating that more lignin is present in a stable colloidal form.
Figure 6-4. Effect of temperature on clarification time and final filtered yield during dissolved air flotation of organosolv lignin.

Figure 6-5. Precipitates 24 hours after dilution. At 30°C (far left), an interface is visible. At 40°C (far right), no floated precipitate can be distinguished from the continuous phase.
As discussed in Section 6.1.1, flotation efficiency relies on particle-bubble collision and adhesion, bubble nucleation on particles, micro-bubble entrapment in aggregates and bubble entrainment by aggregates. At temperatures above 35°C, the precipitate formed is very fine and does not flocculate. For efficient particle-bubble adherence, particles must be of a similar size to bubbles as discussed in Section 6.1.1. A smaller size of precipitate also reduces the ability of aggregates to entrap or entrain a micro-bubble.

Temperature also affects rate of bubble nucleation and growth in two ways. Firstly, the concentration of nitrogen in water decreases with increasing temperature according to Henry’s law resulting in fewer bubbles of larger size. Larger bubbles have a greater volume to projected area ratio and therefore greater buoyancy. This would account for the faster clarification and decreasing yield with increasing temperature.

### 6.3.3 Effect of addition rate and nitrogen pressure

Figure 6-6 shows the 50% clarification time at two saturation pressures and two black liquor addition rates. The rising velocity depends on the presence of buoyant micro-bubbles attached to the precipitate. Black liquor addition rate and pressure are variables that determine the dispersion of micro-bubbles during precipitation of black liquor.

The high addition rate of 10mL/s results in faster clarification. The reason for this may be due to more aggressive mixing at the 10mL/s addition rate than the 5mL/s addition rate. The bubbles that had floated to the top of the tube after the release of pressure are re-distributed by greater turbulence at the faster addition rate. Also, lignin may agglomerate more due to the turbulent energy applied during faster mixing, resulting in larger floc size. At the 1barg pressure level, fewer micro-bubbles are nucleated to attach to precipitated lignin as it forms. Therefore the faster addition rate has a greater effect on clarification time. At the higher saturation pressure, the bubbles formed are smaller and more numerous as the literature reviewed in Section 6.1.1 suggests. The smaller bubbles do not rise as quickly and therefore the redistribution of micro-bubbles has less of an effect at 2barg than 1barg saturation pressure.
6.3.4 Second block of factorial designed experiments

Table 6-7 shows the 50% clarification time at each parameter level. Fastest clarification occurs at high H₂O:BL ratio, low time to addition, high nitrogen pressure and high HCl concentration. The effect of temperature was minimal as clarification is rapid at both 20°C and 25°C.

<table>
<thead>
<tr>
<th>level</th>
<th>H₂O:BL</th>
<th>Time to add.</th>
<th>N₂ pressure</th>
<th>BL temp.</th>
<th>HCl Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>1.59</td>
<td>1.17</td>
<td>1.49</td>
<td>1.26</td>
<td>1.44</td>
</tr>
<tr>
<td>+1</td>
<td>1.01</td>
<td>1.43</td>
<td>1.11</td>
<td>1.34</td>
<td>1.16</td>
</tr>
</tbody>
</table>

Increasing the pressure from 0.3barg to 1barg reduced the 50% clarification time by 0.4 minutes. This is expected due to increased bubble nucleation at higher saturation.
pressure and hence higher buoyancy. Slower clarification at the low level of H\_2O:BL ratio may be due to the larger volume of black liquor used resulting in flocs blocking each other from rising (steric hindrance).

<p>| Table 6-8. Yield of precipitate for each parameter at low and high level (mg lignin/mL black liquor). |
|-------------------------------------------------|-----------------------------------------------------------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>level</th>
<th>H_2O:BL</th>
<th>Time to add.</th>
<th>(N_2) pressure</th>
<th>BL temp.</th>
<th>HCl Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>14.9</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>14.9</td>
</tr>
<tr>
<td>+1</td>
<td>15.0</td>
<td>14.9</td>
<td>15.0</td>
<td>14.9</td>
<td>15.0</td>
</tr>
</tbody>
</table>

Table 6-8 shows that none of the variables examined had an effect on the filtered yield of lignin meaning that each condition in this block caused an equally high level of precipitation. This means that for adequate precipitation, acid concentration need not exceed 1mM, H\_2O:BL ratio need not exceed 3 and temperature need not be reduced below 25°C (higher temperature are favourable for faster clarification as shown in Section 6.3.2). The time to addition and saturation pressure were not expected to affect precipitation and no effect was observed.

From the delignification used for these recovery trials, 52% of the lignin was dissolved into the black liquor. From a mass balance, the concentration of lignin in the black liquor was estimated at 16.3mg/ml. This indicates a 92% recovery of dissolved lignin by precipitation, flotation and filtering. The total recovery yield is 48% (g lignin recovered/g lignin in wood).

### 6.3.5 Application of DAF to an industrial process

To apply dissolved air flotation of organosolv lignin in an industrial process, the addition of black liquor to nitrogen saturated water should be performed with turbulent addition of the black liquor into room temperature water with sufficient nitrogen saturation. It is critical that the final temperature of the diluted black liquor is below 35°C to avoid the formation of a fine precipitate. Black liquor from the organosolv process is typically at a temperature of 80-100°C after flashing at atmospheric pressure. The final temperature after dilution can be reduced in several ways:
1. Cooling of the black liquor either by heat exchanger or vacuum flashing prior to dilution.

2. Sub-cooling of the diluting water prior to dilution.

3. Increasing the water to black liquor ratio.

The third option is the most elegant and economical of these. However, the subsequent recovery of ethanol will be more energy intensive. This can be somewhat alleviated by distillation of the black liquor to the maximum lignin concentration before dilution. Also a concern is the higher throughput of water resulting in more difficult hemicellulose sugar recovery and waste water treatment.

### 6.4 Conclusions

Dissolved air flotation is an effective method of recovering organosolv lignin precipitate without the need for precipitating or collecting agents. Efficient flotation and good clarification of organosolv lignin occurs at temperatures below 35°C. Above 35°C, the precipitate formed does not flocculate and is too small to attach to micro-bubbles. Fastest flotation occurs when saturation pressure is high and black liquor-water mixing is rapid resulting in the redistribution of micro-bubbles during floc formation. Higher saturation pressure can reduce the effect of slow addition rate due to the formation of more bubbles of smaller size. Fastest flotation occurs at high water to black liquor ratio, high acidification of water and high nitrogen pressure. There is also faster clarification when black liquor is injected into water rather than water decanted into the black liquor.
7 Lignin use in polymers

Lignin is a highly cross-linked polymer synthesised by plant cells to provide rigidity and help with the transport of water. Its chemical structure bears similarity to a range of synthetic polymeric materials and as such is well suited as a natural, renewable replacement for some of the non-renewable chemicals used in polymer synthesis.

This chapter aims to prove the utility of lignin produced by the processing regimes discussed throughout Chapter 4. To do so, the lignin is incorporated by simple means into a common polymer product, phenol formaldehyde (PF) resin and the mechanical strength and curing kinetics are examined. First though, the possibilities of lignin use are reviewed and the existing literature on incorporating lignin into PF resin is examined to find a suitable method for resin synthesis. Throughout this chapter, PF resin that contains lignin is called lignin-PF resin.

7.1 Background

Conventional pulp and paper mills simply burn the lignin for its heat value. The value of lignin when used as a boiler fuel was estimated at US9c/kg in the year 1986 (US18c/kg in 2008) compared to a conservative estimate of US55c/kg (US108c/kg in 2008) if lignin is used for other products [160]. As a replacement for phenol in resin it had a potential value of US77c/kg [161] (US151c/kg in 2008). It is therefore important to the economics of bioethanol production to produce a high quality lignin product. Organosolv delignification is one such source of high quality, unmodified lignin containing many reactive side chains for further chemical modification [16, 61].

The reason for the slow industrialisation of materials containing lignin may be the chemical heterogeneity of lignin or the difficulty in incorporating its use into existing polymer manufacturing processes. Various applications for organosolv lignin have been implemented on an industrial scale but have not continued due to a lack of commercially available organosolv lignin [61]. Recent publications cite a sudden increase in the volume of research into lignin based polymers and an urgent need to produce renewable or
biodegradable polymers [162, 163]. This indicates that the perception of lignin is changing from low value boiler fuel to valuable chemical feedstock.

### 7.1.1 Lignin products

This section describes some of the recent research investigating high value uses for lignin. A wealth of polymer products have been developed in which lignin is shown to be beneficial to the functionality of the product it is incorporated into.

Lignin can be turned into hydrocarbons for addition to gasoline as shown by Thring et al. [164]. This required temperatures above 500°C and the highest yield of liquid product was 43% w/w consisting mainly of aromatic hydrocarbons. Toluene comprised 44% of the liquid product at a reaction temperature of 650°C using the zeolite catalyst HZSM-5. This is essentially using lignin for its heat value even though gasoline is considered a value added product. A use retaining the already cross-linked structure of lignin without the need for high temperature processing is logically favourable on an economic basis.

Organosolv lignin has been incorporated into inks, varnishes and paints with positive effects on viscosity and misting (a measure of the % of a material projecting into the atmosphere when a paint is transferred from a roll onto another surface at a given speed) with the addition of up to 10% w/w lignin. There were no negative side-effects of the addition apart from a brown discoloration, which was deemed irrelevant for most applications [165].

The hydrophobicity of polypropylene was reduced with increased addition of lignin up to 10% w/w. Kosikova et al. [166] investigated the addition of methanol organosolv lignin and liquid hot water extracted lignin from spruce and beech wood respectively into polypropylene films. Organosolv lignin retained the hydrophobic properties slightly better than liquid hot water lignin. The effect of adding lignin on tensile strength and elongation of the polypropylene was negligible.
Polyurethane films have been produced incorporating Alcell® lignin. Flexible but weak polyurethanes were produced at low lignin content. However, relatively tough polyurethane could be produced with lignin content from 15-25% w/w. Above 30% w/w lignin the polyurethanes were hard and brittle [167].

Increasing reactivity of lignin for oil palm fiber-polypropylene composites has been proven beneficial. Unmodified Alcell® lignin and Alcell® lignin modified with toluene diisocyanate were used as a coupling agent between polypropylene and empty fruit bunch fiber. The modified lignin composite showed improvements to mechanical properties as percentage lignin increased whereas the unmodified lignin resulted in a loss of mechanical strength with increased lignin addition [168]. Lignin modifications of this kind require an addition step for polymer synthesis.

Lignin has shown benefits as an additive in concrete. Nadif et al. [169] has applied sulphur free lignin to mortar and found that it improved the flow characteristics and reduced the amount of water required to achieve the desired flow. This has also shown improvements in concrete strength [170].

Other uses of lignin include; slow release nitrogenous fertiliser [171]; soy protein based plastics [172]; vinyl chloride-vinyl acetate copolymer blends [173]; hydroxypropyl lignin blends with poly methyl methacrylate or poly vinyl alcohol (PVA) [174, 175]; sorption active materials for environmental protection [176].

Stewart [162] considers the commercial application of lignins to phenolic resin inevitable given the move towards sustainable practices in the chemical industry and the increasing price of phenol. The size of the phenolics market and the economic attractiveness of utilising lignin for a phenol replacement justifies the large volume of research in this area. Section 7.1.2 examines research incorporating lignin into phenol formaldehyde (PF) resin.
7.1.2 Phenol formaldehyde resin and replacing phenol with lignin

Several authors have used lignin of different sources to produce phenol formaldehyde resin. PF resin can be synthesised as a novolac, which has a Formaldehyde (F):Phenol (P) ratio less than 1:1, cures under acidic conditions and requires a cross-linking agent. The other form of PF resin is a resole, which has a F:P ratio of typically 1.5:1, is synthesised under alkaline conditions and cures when heated. More research has been conducted on incorporating lignin into resoles than novolacs.

Phenol and formaldehyde react together by condensation to form a methylene bridge between phenol units at the ortho- and para- positions on the phenol aromatic ring. As phenol can react with three molecules of formaldehyde and formaldehyde can react with two molecules of phenol, resoles are capable of forming a highly cross-linked 3-D network polymer. Because lignin consists of phenyl-propanoid units, it is capable of reacting with formaldehyde in a similar manner to phenol. The similarity of lignin and phenol are shown in Figure 7-1.

![Figure 7-1. Structure of lignin and position of formaldehyde addition onto phenol. R= H or O-CH₃.](image-url)
7.1.2.1  **Lignin-PF resin synthesis**

Lignin can form methylene bridges when reacted with formaldehyde. In some cases, lignin is first reacted with formaldehyde (hydroxymethylation or methylolation) before phenol addition. The hydroxymethylene groups on lignin react with phenol to ensure that lignin is incorporated into the 3-D polymer network. Hydroxymethylated lignin is used as a precursor to PF resin synthesis by Benar et al. [177]. Addition of lignin has been proven to reduce synthesis time. Vazquez et al. [178] determined that methylolation does increase lignins reactivity in PF resin. Formaldehyde was shown to react with guaiacyl lignin at the C-5 position.

Gardner and McGinnis [179] have determined that the rate of formaldehyde addition to lignin is dependent on the reactive site availability on the lignin molecule. The rate of formaldehyde addition to phenol was faster than both kraft and steam explosion lignin even though the activation energy for the phenol reaction was higher. Kraft showed faster formaldehyde addition than steam explosion lignin. Peng et al. [180] gives the same conclusion for two types of lignosulphonate.

Phenolation is a modification to lignin whereby lignin is reacted with phenol in solution at 70°C. The benefit of phenolation has been shown by Cetin and Özmen [181]. PF resin with 20% phenol replaced with phenolated organosolv lignin hardened in only 1.3 minutes at 150°C, while 20% phenol replacement with non-phenolated organosolv lignin resulted in a hardening time of 3.5 minutes.

The phenolation of lignin for novolac production has been studied and similar to studies on resoles, 30-40% of phenol can be replaced by lignin with no detriment to rheological properties. Bagasse lignin was shown to give better resin properties than both rice straw and cotton stalk lignin. It appears that synthesis temperature and time has a significant effect on the properties and yield of resin produced [182].

Although current research indicates benefits to modification of lignin before incorporation into PF resin, the extra stage in polymer synthesis may be costly [183]. The
large market for phenolic resins compared to the currently low production of organosolv lignin suggests that simple addition of unmodified lignin at low phenol substitution levels is a logical step towards securing a market for organosolv lignin.

7.1.2.2 Determining curing activation energy by differential scanning calorimetry (DSC)

A method for determining activation energy of the PF resin curing reaction is discussed in this section. DSC is an analytical technique whereby a sample is heated in a pan and its temperature is measured with reference to an empty pan. Thus, differences in heat are observed corresponding to exothermic or endothermic reactions, change of state or sensible heating of the sample. Curing of PF resin is an exothermic reaction and therefore an exothermic peak is observed when the reaction is initiated by heating during DSC.

Activation energies of PF resin containing liquefied wood (liquefied by reaction at 180°C in phenol and oxalic acid) were determined by dynamic DSC. The activation energies were higher than pure PF resins but similar to lignin-PF resins. The reason was concluded to be the lower reactivity of lignin fragments compared to phenol. The method uses the Kissinger equation (Equation 7-1) to relate the DSC heating rate, temperature at exothermic peak maximum and the reaction kinetic parameters.

\[
\ln \left( \frac{\phi}{T_p^2} \right) = -\frac{E_a}{R} \cdot \frac{1}{T_p} + \ln \left( \frac{R \cdot A}{E_a} \right)
\]

where \( T_p \) is the temperature (K) at peak maximum of the DSC exotherm, \( \phi \) is the heating rate (K/s), \( E_a \) is the activation energy, \( R \) is the gas constant and \( A \) is a pre-exponential factor [184].

Alonso et al. [185] compares several dynamic DSC methods for determining kinetics of PF resins containing lignin. Some methods are reported to consistently overestimate kinetic parameters. However, for obtaining relative kinetic data this is not a drawback
and the methods require few experiments. One of the methods examined is the Doyle approximation as shown in Equation 7-2.

$$\log(\phi) = -2.315 - 0.4567 \left( \frac{E_a}{RT_p} \right) + \log\left( \frac{k_0 E_a}{R} \right) - \log(F(\alpha))$$

Equation 7-2

where $F(\alpha)$ is a constant, $T_p$ is the temperature (K) at peak maximum of the DSC exotherm, $\phi$ is the heating rate (K/s), $E_a$ is the activation energy, $R$ is the gas constant and $k_0$ is the frequency factor (s$^{-1}$).

Muller et al. [183] examines PF resin with lignin addition by first making a lignin prepolymer with hydroxymethylation and phenolation. PF resins containing kraft lignin or steam exploded lignin were compared to pure PF resin. DSC was used to compare activation energies of the resins with and without lignin added to resin with a lignin content of 36% to 41% (g/g of resin solids). A form of the Doyle equation is used by Muller et al. as shown in Equation 7-3.

$$E_a = -\frac{R}{0.457} \frac{\Delta \log \phi}{\Delta \frac{1}{T_p}}$$

Equation 7-3

where $R$ is the gas constant, $\Delta \log \phi$ is the change in log$\phi$ for three heating rates ($\phi$) and $\Delta 1/T_p$ is the change in inverse peak temperature of the final exotherm for each of those heating rates. This allows a simple Arrhenius plot of log$\phi$ versus $1/T_p$ giving a slope of $-0.457E_a/R$. Negligible difference was observed in the activation energy (93.5-98.9kJ/mol) and a shear test showed that strength of the resin containing lignin was slightly lower than a pure PF resin. Resin with steam exploded lignin had slightly lower shear strength than resin with kraft lignin [183].
This method has been proven reliable for the systems where there are multiple exotherms or unreliable baselines [186].

### 7.1.2.3 Lignin-PF resin strength

Lap joints are used to determine the adhesive strength of PF resins. Lap joint specimens consist of two wood veneer strips joined together by curing a resin between an overlapping section of the veneer strips. The specimens can then be subjected to a tensile test. Other strength measurement techniques are variations on lap joint testing. Lap joints prepared with resin containing phenolated or non-phenolated lignin showed comparable failure strength to pure PF resin [187]. The mechanical properties of particleboard using lignin-PF resin have also been investigated [188].

Khan et al. [189] initially produced a 1:1 by mass eucalyptus bark lignin:phenol derivative (LP) to synthesise lignin-PF resin of different lignin content. Adhesive strength increased up to a lignin substitution of 50% w/w. Using a 50% lignin substitution, F:LP ratio of 2.0 resulted in greater adhesive strength than 1.5, 2.5 and 3.0. A resin synthesis temperature of 80°C gave approximately the same strength as 90°C and greater strength than 60°C. In contrast to the increased strength noted by Khan et al., the cross-linking of phenol-formaldehyde and lignin has been shown to occur to a minimal extent at 20-30% replacement levels. At 40% the lignin deactivates the adhesive [190].

Senyo et al. [191] has found that organosolv lignin added to PF resin for wafer board and particleboard reduces emission of formaldehyde during hot pressing as much as 38% without reducing the strength.

The literature reports that PF resin strength may increase or decrease when lignin is added. This may depend on the synthesis methods, type of lignin and amount of phenol replaced. Lignin modifications may result in greater resin strength than unmodified lignin. However, the extra expense of the modification step, as discussed in Section 7.1.2.1, means that addition of unmodified lignin is preferable provided that strength is not compromised. Therefore, an attempt is made in Section 7.2 to synthesise lignin-PF resin with comparable strength to PF resin by simple addition of various isolated lignins.
7.1.3 Analysis of lignin

The suitability of lignin for various polymer feedstocks depends on the functional and macromolecular properties, which depend on the conditions of isolation. Oliet et al. [192] developed a model to predict the functional groups of lignin isolated using ethanol pulping at various times, temperatures and ethanol concentrations. Phenolic hydroxyl content, carbonyl content and molecular weight were all affected by changing any of the pulping parameters (time, temperature or ethanol concentration). Gel permeation chromatography (GPC, also referred to as size exclusion chromatography, SEC) was performed with a tetrahydrofuran mobile phase at 38°C oven temperature and polystyrene standards of known size were used for calibration. Conditions of 200°C and 30% w/w ethanol can achieve polydispersity ($M_w/M_n$, a measure of size range) of close to 1.0. The highest reported polydispersity was 2.7 at conditions of approximately 185°C and 55% w/w ethanol.

Xu et al. [193] examined the UV-vis absorption of lignin isolated under various conditions using organic acids and alcohols as pulping agents. Highest absorption was for aqueous alcohol indicating that it gave the highest purity. A characteristic region of absorption starting at 318nm was assigned to ferulic and p-coumaric acids. All of the lignin preparations displayed this region.

Several authors use either $^1$H or $^{13}$C nuclear magnetic resonance (NMR) to determine the relative proportions of structures present in lignin [193-195]. Ralph et al. [196] uses 2D $^{13}$C $^1$H correlation (edited-HSQC) spectra to quantify linkages between lignin by the relative volumes of NMR signal they produce. Considerable differences were observed between the 2-D NMR spectra of lignin from alfalfa plants and lignin from transgenic alfalfa. Peak in a 2-D NMR spectra can be assigned to different structures by the position. The amount of each structure can be determined relative to the other structures. The methoxyl group peak is often used as the reference. The ratio of guaiacyl to syringyl lignin ($G/S$) can also be determined. Some of the linkages in lignin that can be quantified are shown in Figure 7-2.
7 - Lignin use in polymers

Figure 7-2. Common linkages present in the structure of lignin.

2-D NMR, SEC and UV-vis absorbance are demonstrated by the literature as suitable methods of characterizing lignin and identifying differences between lignin preparations.

7.2 Materials and methods

This section describes the methods used to incorporate lignin into phenol formaldehyde (PF) resin. Lignin preparations from the various organosolv pulping conditions described in Chapter 4 are used. The lignin is isolated from organosolv black liquor by dilution and conventional centrifugation. It is then added to the phenol and formaldehyde mixture before resin synthesis as a direct replacement for phenol. Resin is synthesised and tested for curing properties and adhesive strength. PF resins with some portion of the phenol replaced by lignin (lignin-PF resin) were compared to PF resins without such replacement (pure PF resin). Each lignin preparation was then characterised to identify the cause of strength differences observed between lignin-PF resins.

Two sets of resins were produced. The first set was a screening test to examine what proportion of phenol could be replaced with lignin before the strength of resin is noticeably reduced (see § 7.2.1). The second set of resins were produced at a 20% w/w phenol replacement level using seven lignins isolated from ethanol-water pulping at
different conditions (see § 7.2.2). These resins were compared to pure PF resins synthesised by the same procedure.

7.2.1 Resin synthesis for screening replacement level and curing time

Screening tests were performed with lignin produced by pulping *S. schwerinii* in a 40L organosolv reactor described by Belanger et al. [6]. The process conditions used were 70% v/v ethanol, autocatalysed and unbuffered at 185°C. The larger reactor was used so that a large amount of uniform organosolv lignin could be produced.

Initial testing examined the percentage phenol replacement and curing time of lignin-PF resin synthesised by replacing 0%, 8%, 16%, 24% and 32% w/w of phenol with lignin.

**7.2.1.1 Resin synthesis procedure**

Lignin was dissolved in phenol at 50°C on a magnetically stirred hotplate, formaldehyde was added at F:P ratio of 1.8:1 and pH was adjusted to 10.5 by addition of 10M NaOH. The temperature was then adjusted to 70°C and viscosity was measured using a canon-fenske capillary tube viscometer 400 at 40°C ±1°C periodically until an elution time of 240s was achieved.

7.2.2 Resin synthesis for testing different lignins

Lignin-PF resins for examining the effect of organosolv process conditions were produced from *S. schwerinii* lignin prepared using the 3L packed bed reactor previously described. The lignins selected for characterisation and resin manufacture were isolated from the pulping runs with the conditions shown in Table 7-1.

All lignin samples were isolated from organosolv black liquor by dilution with 3:1 acidified water (1mM HCl) followed by centrifugation. The supernatant was discarded and the palette dried in a vacuum oven at 45°C. A sample of each lignin used for resin manufacture was analysed for klason lignin content. Moisture content was determined by
drying a sample at 105°C for at least 8 hours. 0.3-0.5g of lignin was weighed into a 100mL schott bottle and 87mL of 4% H₂SO₄ added. The schott bottles were sealed tightly and heated in a convection oven at 121°C for one hour followed by cooling to 90°C for one hour and then removed and allowed to cool to room temperature aided by a laboratory convective fan. The contents were filtered in pre-weighed filter crucibles with a 10µm filter pore size. The filter crucibles were dried at 105°C for at least 8 hours, removed to a desiccator to cool and re-weighed to determine acid insoluble lignin content. The filtrate was analysed for acid soluble lignin by UV visible spectrophotometry at 320nm. The total klason lignin content, acid insoluble lignin (AIL) and acid soluble lignin (ASL) is shown in Table 7-1. The standard deviation for AIL and ASL is 0.32% and 0.55% respectively.

Table 7-1. Lignin samples for analysis and resin synthesis: extraction conditions and klason lignin content.

<table>
<thead>
<tr>
<th>Label</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-organosolv treatment</td>
<td>None</td>
<td>None</td>
<td>PH</td>
<td>DA</td>
<td>DA</td>
<td>PH</td>
<td>None</td>
</tr>
<tr>
<td><strong>Organosolv pulping conditions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T_eff (°C)</td>
<td>177.4</td>
<td>176.6</td>
<td>176.3</td>
<td>176.4</td>
<td>166.7</td>
<td>167.3</td>
<td>174.5</td>
</tr>
<tr>
<td>Ethanol%</td>
<td>30</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>Final liquor pH</td>
<td>3.0</td>
<td>4.0</td>
<td>3.5</td>
<td>3.5</td>
<td>3.4</td>
<td>3.0</td>
<td>4.9</td>
</tr>
<tr>
<td>Time (minutes)</td>
<td>180</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>180</td>
</tr>
<tr>
<td><strong>Klason lignin analysis</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m.c.d.b.</td>
<td>2.5%</td>
<td>2.4%</td>
<td>2.5%</td>
<td>1.7%</td>
<td>2.1%</td>
<td>2.2%</td>
<td>3.3%</td>
</tr>
<tr>
<td>Total lignin (w/w)</td>
<td>99.6%</td>
<td>95.5%</td>
<td>97.2%</td>
<td>99.0%</td>
<td>95.5%</td>
<td>97.8%</td>
<td>95.6%*</td>
</tr>
<tr>
<td>Acid insoluble (AIL)</td>
<td>94.7%</td>
<td>90.8%</td>
<td>91.9%</td>
<td>92.8%</td>
<td>90.8%</td>
<td>94.0%</td>
<td>90.2%*</td>
</tr>
<tr>
<td>Acid soluble (ASL)</td>
<td>4.8%</td>
<td>4.7%</td>
<td>5.2%</td>
<td>6.2%</td>
<td>4.7%</td>
<td>3.8%</td>
<td>5.3%</td>
</tr>
</tbody>
</table>

PH = prehydrolysis, DA = de-ashing, *based on only one measurement
7.2.2.1 Resin synthesis procedure

16.54mL of 80% g/g phenol in methanol solution was added to 3.31g of either phenol crystals or lignin sample in a 100mL schott bottle. The lignin mass was corrected to neglect the moisture and carbohydrate content of each lignin sample. The percentage of phenol replaced by lignin was thus 20% g/g. 4mL of 10M NaOH was added followed by 25g of 37% formaldehyde solution giving formaldehyde to phenol molar ratio of 1.8:1. The mixture was stirred in a water bath at 50°C until the lignin dissolved. The mixture was then cooled to room temperature (21°C ±1°C) and the pH adjusted to 10.5 by addition of 10M NaOH.

The mixture was placed in a sand bath on a hot-plate set at 100°C and stirred magnetically. The temperature of the mixture was measured periodically using a k-type thermocouple and maintained at 70°C ±3°C to initiate the hydroxymethylation reaction.

The viscosity of the resin was measured periodically using a canon-fenske capillary tube viscometer 400 at 21°C ±1°C (a small sample was cooled in the viscometer by sitting in a water bath). When an elution time of more than 230s was achieved (corresponding to a viscosity of approximately 300mPa.s) the mixture was removed from the hot plate and rapidly cooled in an ice bath while magnetically stirred. The final viscosity of each resin was measured using a canon-fenske capillary tube viscometer 400 secured in a water bath at 25°C. Density of each resin was measured by weighing approximately 9mL of resin into a 10mL measuring cylinder and reading the net weight to within 1mg and volume to within 0.05mL.

Two lignin-PF resin replicates were prepared from each lignin preparation and three pure PF resin replicates were prepared. Resins were refrigerated at 4°C until tested.

7.2.3 Differential scanning calorimetry (DSC)

Differential scanning calorimetry was performed using a Shimadzu DSC-60. Dynamic DSC was performed on approximately 10mg of each resin in open aluminium pans using at least three different heating rates and a nitrogen flow rate of 20mL/minute. Heating rates were 5, 8, 10, 12, 13.3 and 20°C/minute.
7.2.4 Lap joint preparation and tensile testing

Lap joint samples were prepared using Rock maple veneer of 0.4mm thickness cut into 20x50mm strips. Each lap joint sample had an overlap of 4x20mm (the dimensions used by Cetin et al. [187] discussed in Section 7.1.2.3) and was made by applying resin liberally using a paint brush to the end 4mm of one side of a veneer strip and pressing the strip firmly by hand onto the other strip ensuring a 4x20mm overlap. The overlap section was marked lightly with a pencil line 4mm from the edge.

![Figure 7-3. Lap joint made from 0.6mm thick Rock maple veneer.](image)

Six replicate lap joints were made for each resin and pressed at the same time. Samples were cold pressed at 16kg/cm² for 20s and then heat pressed at 145°C at 25kg/cm² using a Carver model number 4332 heat press. Each resin was tested at heat pressing times of 120s and 480s. Pure PF resins, lignin A and lignin G containing resins were also tested with heat pressing times of 240s. One replicate of pure PF resin was also tested at 960s to show that an 480s curing time was sufficient for full cross linking of the resins. Lap joint samples were rapidly air cooled after removal from the heat press and stored in a plastic zip-locked bag at 4°C until testing was performed.

Lap joint samples were tested within 48 hours of pressing using an Instron #5567 tensometer. Samples were pre-tensioned to approximately 300N and tensile tested at a constant load rate of 250N/minute until failure. No lap joint specimens failed due to the pre-tension load.
7.2.5 Lignin characterisation

The samples shown in Table 7-1 were characterized by the methods described in this section.

Lignin was prepared from three more sources for comparison with the lignins used for resin synthesis. The first was prepared by acid hydrolyzing Lignin G (see Table 7-1). This is labeled as AILG (acid insoluble lignin G). The other two lignins were isolated from organosolv black liquor of uncatalysed pulping experiments. The pulping conditions for producing these lignins are listed in Table 7-2. Effective temperatures are calculated by neglecting the 20 minute heat-up period.

<table>
<thead>
<tr>
<th>Table 7-2. Lignin samples for analysis only.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AILG</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>Teff (°C)</td>
</tr>
<tr>
<td>Ethanol% (v/v)</td>
</tr>
<tr>
<td>Final liquor pH</td>
</tr>
<tr>
<td>Time (minutes)</td>
</tr>
</tbody>
</table>

*acid hydrolysis (4% w/w H$_2$SO$_4$) conditions used on Lignin G

Lignin samples were prepared by dilution of organosolv black liquor as described in Section 7.2.2. Each dried lignin precipitate was crushed into a powder and sealed in a plastic tube until analysed or used for resin manufacture. Lignin samples for analysis and resin manufacture were coned and quartered to make the sample uniform. The methods for lignin characterisation are described and lignin size, structure and UV absorbance of each lignin are compared.

7.2.5.1 UV visible spectrophotometry

A sample of each lignin (8-15mg) was dissolved in 0.01M NaOH and diluted to less than 1mg/mL. The UV visible spectrum of each lignin sample was measured using an Agilent UV spectrophotometer, model number 8453. Wavelengths of 200-800nm were measured in a quartz cuvette with a 1cm path length.
7.2.5.2 Size exclusion chromatography (SEC)

The gel permeation chromatography (GPC) system consisted of a Waters 515 HPLC pump, a Degassex DG-4400 in-line degasser connected to a series of three GPC columns (a Waters Styrogel HR6 column and two Polymer Labs PolyPore columns) with a PolyPore guard and 0.5μm in-line filter, a Rheodyne manual injector, and a Waters column oven. The eluent was THF at a flow rate of 1.0mL/min and injection volume was 200μl. All solutions were filtered through 0.45 μm syringe filters before injection. The columns and refractive index (RI) detector were maintained at 35°C. Data acquisition and processing were performed using the ASTRA 4 software (Wyatt Technologies Corporation). Ten polystyrene standards were run under the same conditions with polystyrene concentration of 2mg/mL. The standards were run in two sets of 5 standards each and a calibration curve was generated using the elution times. Lignin samples A to G and AILG were dissolved in tetrahydrofuran (THF) to a concentration of approximately 6 mg/mL. This was found to give a low intensity signal so the next samples, lignins X and Y, the lignin used for screening resin synthesis and a replicate of lignin A for comparison, were dissolved in THF to a concentration of 50mg/mL.

7.2.5.3 2-D nuclear magnetic resonance (2D NMR)

Approximately 25mg of each lignin sample was dissolved in 0.75mL of DMSO-d6 and placed in NMR 400 tubes. 2D $^{13}$C 1H correlation (edited-HSQC) spectra were acquired and quantified as described by Ralph et al. [196] on a DRX 400 MHz spectrometer (Bruker Biospin, Rheinstetten, Germany) equipped with an inverse 1H/broadband probe (broadband coil closest to the sample).

7.3 Results and discussion

The screening test for lignin-PF resins containing different % replacement of phenol with lignin was carried out to establish a sensible replacement level with which to test different lignin preparations. Section 7.3.1 gives the results of resin strength testing for the phenol replacement levels examined. Sensible hot pressing times for subsequent testing was also established.
Lignin-PF resins synthesised from lignin samples listed in Table 7-1 have been tested for curing activation energy and lap joint strength. The lap joint strength of each lignin-PF resin is compared to the pure PF resins and differences are examined statistically.

### 7.3.1 Screening tests

Screening tests were performed to examine the effects of % phenol replacement with lignin and hot pressing time on resin strength. Only one resin was produced for each level of phenol replacement and strength was measured using multiple lap joint specimens for each resin.

#### 7.3.1.1 Screening resin synthesis

The resins produced for screening phenol replacement level and pressing time all had a final viscosity of between 300 and 330mPa.s. The phenol replacement was 0%, 8%, 16% and 24% by weight. A 32% lignin-PF resin was produced but thickened too fast during synthesis and was not able to be tested. All resins containing lignin thickened faster than pure PF resin controls in agreement with literature discussed in Section 7.1.2.1.

#### 7.3.1.2 Lap joint strength testing

All of these resins were tested with lap joints cured using a pressing time of 120s and temperature of 145°C. The average failure load of lap joints prepared with each resin is shown in Figure 7-4. Error bars show the standard deviation of the five lap joint specimens tested for each resin. The failure loads of lap joints made with resins containing lignin are slightly higher than resin without lignin. At the 8% replacement level there is a clear improvement in strength over the pure PF resin. At higher replacement levels the difference is less clear and with only one resin preparation it is difficult to make conclusions with any certainty. Although the standard deviation of these measurements is high, the performance of lignin containing resins compares well with resin containing no lignin. The high standard deviation shown at the 24% lignin
replacement level may be an indication of lignin affecting curing properties of the resin, but it is clear that resin replicates are required in subsequent testing.

![Figure 7-4. Failure load of lap joints after heat-pressing for 120 seconds at 145°C.](image)

The 0% and 16% lignin resins were also tested with pressing times of 30, 60, 90, 180 and 240 seconds. Figure 7-5 shows strength versus pressing time of the 0% and 16% lignin containing samples. The error bars show standard deviation calculated from three lap joint failure load measurements at each time. Here the lignin containing resin appears to cure faster characterised by higher failure strength at the shorter pressing times. The failure strength of pure PF resin may still be increasing at the 240 second pressing time while the lignin-PF resin appears to have reached a maximum. Therefore it will be prudent to examine the strength of the subsequent set of resin preparations at longer pressing times.
Figure 7-5. Resin strength increase with time for pure PF and 16% lignin-PF resin.

Preliminary testing has shown that replicate resin preparations should be produced. A 16-24% w/w replacement level does not significantly reduce the strength compared to pure PF resin. For this reason a 20% w/w replacement level is selected for subsequent testing. In subsequent resin testing, a 120s hot pressing time was used to indicate the rate of the curing reaction. A 480s hot press time was also used to indicate the strength when the curing reaction is near completion.

7.3.2 Testing PF resins containing different lignins

Lignin-PF resins incorporating different lignin preparations at a 20% w/w phenol replacement level are examined in this section. Section 7.3.2.1 discusses the synthesis and physical properties of the resins. Activation energy and lap joints strength of each lignin-PF resin are compared to pure PF resins in Section 7.3.2.2 and 7.3.2.3 respectively.
7.3.2.1 Resin synthesis

For an examination of resin containing lignin extracted under different conditions, two replicate resin productions were prepared to smooth the variance caused by resin manufacture. Three pure PF resin replicates and two of each lignin-PF resin were produced using a phenol replacement of 20% w/w. The final viscosity and density of each resin replicate at 25°C is shown in Table 7-3. All resins had a final viscosity between 245mPa.s and 350mPa.s with the exception of lignin E1-PF resin, having a viscosity of 402mPa.s.

<table>
<thead>
<tr>
<th>Replicate #</th>
<th>% phenol replacement</th>
<th>Final viscosity at 25°C (mPa.s)</th>
<th>Density (g/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PF resin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0%</td>
<td>245</td>
<td>1.24</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>329</td>
<td>1.25</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>322</td>
<td>1.22</td>
</tr>
<tr>
<td>Lignin A</td>
<td>20%</td>
<td>258</td>
<td>1.21</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>324</td>
<td>1.22</td>
</tr>
<tr>
<td>Lignin B</td>
<td>20%</td>
<td>349</td>
<td>1.21</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>324</td>
<td>1.22</td>
</tr>
<tr>
<td>Lignin C</td>
<td>20%</td>
<td>328</td>
<td>1.22</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>318</td>
<td>1.23</td>
</tr>
<tr>
<td>Lignin D</td>
<td>20%</td>
<td>248</td>
<td>1.21</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>317</td>
<td>1.22</td>
</tr>
<tr>
<td>Lignin E</td>
<td>20%</td>
<td>402</td>
<td>1.22</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>280</td>
<td>1.22</td>
</tr>
<tr>
<td>Lignin F</td>
<td>20%</td>
<td>249</td>
<td>1.29</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>304</td>
<td>1.23</td>
</tr>
<tr>
<td>Lignin G</td>
<td>20%</td>
<td>252</td>
<td>1.21</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>322</td>
<td>1.22</td>
</tr>
</tbody>
</table>
There was no evidence that final viscosity affected resin strength as will be discussed in Section 7.3.2.3.

7.3.2.2 Curing kinetics by dynamic DSC

Dynamic DSC thermograms for heating rates of 5 to 20°C/minute for one of the pure PF resins are shown in Figure 7-6. Each heating rate shows an endothermic peak starting just after 100°C, which can be attributed to the evaporation of water and formaldehyde. Some thermograms showed several peaks occurring before the final exotherm (last peak), which was easily discernable in all thermograms. Exothermic peaks before the final exotherm can be attributed to exothermic addition of formaldehyde to phenol. Other exothermic and endothermic peaks observed in some samples can be attributed to changes in sample geometry during the curing process. The sample changes in shape and thermal properties considerably during the curing process. As discussed in Section 7.1.2 this method of determining activation energy is reliable despite multiple peaks and unsteady baselines. DSC thermograms of all data are shown in Appendix 7.

Figure 7-6. Dynamic DSC thermograms of pure PF resin 3.
Activation energy of PF resin and lignin-PF resin was determined using the same method described by Muller et al. [183] as discussed in Section 7.1.2. The spread of activation energies calculated by this method can be seen in Figure 7-7. Muller et al. reports an activation energy of 93.5kJ/mol for pure PF resin. The pure PF resin of the current work has an average activation energy of 84.5kJ/mol but a standard deviation (σ) of 24.8kJ/mol. All calculated activation energies fall within one standard deviation of the pure PF resin with the exception of pure PF resin 3 and lignin C1 resin.

If pure PF resin 3 is discounted as an outlier, all of the lignin-PF resins have higher activation energy than the two remaining pure PF resins. This is in line with literature reviewed in Section 7.1.2.2. However, due to the outliers and the poor agreement with literature values, this data is not reliable enough to confirm differences in curing kinetics.
Strength testing of resin containing different lignins

Figure 7-8 shows the average failure load at each hot pressing time for pure PF resin, lignin A-PF resin and lignin G-PF resin. Failure load at 120s hot pressing time is lower than at 480s confirming that at 120s the reaction is incomplete. The differences between failure load at 240s and 480s are small confirming that at 480s the reaction is near completion. Replicate 1 of pure PF resin was tested at 960s hot pressing time. The failure load did not increase from 480 to 960s.

Figure 7-8. Failure load of resins selected for testing at three hot pressing times.
The average failure load of each PF resin at 120s pressing time is given in descending order in Table 7-4. The significance of any difference in average failure load between a lignin containing resin and pure PF resin can be determined using a student’s t-test as described by Hayter [197] for two independent sample sets with different standard variance and different sample sizes. In this statistical significance test, \( t \) is calculated from Equation 7-4.

\[
t = \frac{\mu_1 - \mu_2}{\sqrt{\frac{\sigma_1^2}{n_1} + \frac{\sigma_2^2}{n_2}}}
\]

Equation 7-4

where \( \mu_1 \) and \( \mu_2 \) are the average failure load of pure PF resin and the lignin-PF resin respectively, \( \sigma_1 \) and \( \sigma_2 \) are the sample standard deviation of pure PF resin and the lignin-PF resin respectively, and \( n_1 \) and \( n_2 \) are the sample size of pure PF resin and the lignin-PF resin respectively (\( n_1=3, n_2=2 \)). Degrees of freedom (d.f.) is calculated from the Welch-Satterthwaite [198] equation (Equation 7-5).

\[
d.f. = \frac{\left(\frac{\sigma_1^2}{n_1} + \frac{\sigma_2^2}{n_2}\right)^2}{\frac{\sigma_1^4}{n_1(n_1-1)} + \frac{\sigma_2^4}{n_2(n_2-1)}}
\]

Equation 7-5

The critical value can be obtained from \( t \) distribution tables using d.f. and the level of certainty (95%). If \( t \) is greater than the critical value then the difference is considered to be significant.

The only observation that is statistically significant is that lignin G-PF resin has a lower failure load than pure PF resin at the 120s hot pressing time.
### Table 7-4. Failure load at the 120s hot pressing time and statistical significance.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Failure load, $\mu$ (N)</th>
<th>$\sigma$ (N)</th>
<th>t</th>
<th>d.f.</th>
<th>Critical value at $p=0.95$</th>
<th>Significant difference, Y/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin E</td>
<td>550</td>
<td>4</td>
<td>-1.67</td>
<td>2.1</td>
<td>2.81</td>
<td>N</td>
</tr>
<tr>
<td>Lignin C</td>
<td>531</td>
<td>33</td>
<td>-0.25</td>
<td>1.9</td>
<td>3.09</td>
<td>N</td>
</tr>
<tr>
<td>Lignin A</td>
<td>527</td>
<td>42</td>
<td>-0.08</td>
<td>1.6</td>
<td>3.87</td>
<td>N</td>
</tr>
<tr>
<td>Pure PF</td>
<td>524</td>
<td>27</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lignin D</td>
<td>516</td>
<td>59</td>
<td>0.19</td>
<td>1.3</td>
<td>4.84</td>
<td>N</td>
</tr>
<tr>
<td>Lignin F</td>
<td>503</td>
<td>81</td>
<td>0.35</td>
<td>1.2</td>
<td>5.48</td>
<td>N</td>
</tr>
<tr>
<td>Lignin B</td>
<td>483</td>
<td>61</td>
<td>0.90</td>
<td>1.3</td>
<td>4.93</td>
<td>N</td>
</tr>
<tr>
<td>Lignin G</td>
<td>445</td>
<td>24</td>
<td>3.43</td>
<td>2.5</td>
<td>2.46</td>
<td>Y</td>
</tr>
</tbody>
</table>

Only three of the resins were tested at the 240s hot pressing time. The statistical significance between each lignin-PF resin and the pure PF resin is shown in Table 7-5.

### Table 7-5. Failure load at the 240s hot pressing time and statistical significance.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Failure load, $\mu$ (N)</th>
<th>$\sigma$ (N)</th>
<th>t</th>
<th>d.f.</th>
<th>Critical value at $p=0.95$</th>
<th>Significant difference, Y/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PF</td>
<td>638</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lignin A</td>
<td>619</td>
<td>19</td>
<td>1.32</td>
<td>1.4</td>
<td>4.36</td>
<td>N</td>
</tr>
<tr>
<td>Lignin G</td>
<td>577</td>
<td>9</td>
<td>7.14</td>
<td>2.5</td>
<td>2.45</td>
<td>Y</td>
</tr>
</tbody>
</table>

Table 7-6 shows the failure load and statistical significance of each resin hot pressed for 480s. Lignin G-PF resin has a lower failure load than pure PF resin at each hot pressing time examined. This has been established at a 95% confidence level.
Table 7-6. Failure load at the 480s hot pressing time and statistical significance.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Failure load, $\mu$ (N)</th>
<th>$\sigma$ (N)</th>
<th>$t$</th>
<th>d.f.</th>
<th>Critical value at $p=0.95$</th>
<th>Significant difference, Y/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin E</td>
<td>678</td>
<td>28</td>
<td>-0.58</td>
<td>2.1</td>
<td>2.34</td>
<td>N</td>
</tr>
<tr>
<td>Pure PF</td>
<td>661</td>
<td>36</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lignin C</td>
<td>641</td>
<td>3</td>
<td>0.97</td>
<td>2.0</td>
<td>2.90</td>
<td>N</td>
</tr>
<tr>
<td>Lignin D</td>
<td>633</td>
<td>10</td>
<td>1.28</td>
<td>2.4</td>
<td>2.53</td>
<td>N</td>
</tr>
<tr>
<td>Lignin B</td>
<td>633</td>
<td>12</td>
<td>1.26</td>
<td>2.5</td>
<td>2.44</td>
<td>N</td>
</tr>
<tr>
<td>Lignin A</td>
<td>624</td>
<td>56</td>
<td>0.83</td>
<td>1.6</td>
<td>3.86</td>
<td>N</td>
</tr>
<tr>
<td>Lignin F</td>
<td>623</td>
<td>2</td>
<td>1.82</td>
<td>2.0</td>
<td>2.93</td>
<td>N</td>
</tr>
<tr>
<td>Lignin G</td>
<td>597</td>
<td>17</td>
<td>2.66</td>
<td>2.9</td>
<td>2.31</td>
<td>Y</td>
</tr>
</tbody>
</table>

Table 7-4 and Table 7-6 show that lignin E-PF resin has the highest average failure load at each 120s and 480s hot pressing time respectively. It was mentioned in Section 7.3.2.1 that a lignin E-PF resin replicate had a viscosity outside the accepted range. A relationship must be examined between viscosity and failure load to rule out the possibility that final viscosity is a significant variable.

Figure 7-9 shows viscosity and failure load of both replicates of lignin E-PF resin and all three replicates of pure PF resin. No viscosity-strength relationship can be confirmed from the control PF resin replicates or any of the other resins at either hot pressing time. Both pure PF resin and lignin E-PF resin exhibit high failure loads regardless of resin viscosity.
The failure load measurements have shown that 20% w/w replacement of phenol with lignin G has caused a reduction in strength of the resin. Section 7.3.3 will give a discussion of the differences between the lignins incorporated into resin and other lignins for general comparison.

### 7.3.3 Lignin characterisation

In this section the lignins are characterized in an attempt to explain the differences observed in Section 7.3.2.3 between the strength of each lignin-PF resin. The isolated lignins themselves were characterised to determine whether the organosolv process conditions had any effect on their UV absorbance spectra, structure and size. It appears that the SEC system used was not ideal as the lignins all had very low molecular weights.
In contrast, many linkages between molecules were observed using 2-D NMR and the degree of cross linking was correlated to the final pH of delignification.

7.3.3.1 *UV visible absorbance*

Figure 7-10 shows the UV spectra of the lignin preparations A to G and AILG (the acid insoluble lignin made from lignin G). The spectra have been normalised to the 220nm absorbance to account for slight differences in concentration. All of the spectra appear very similar except for lignin G, which has a lower absorbance at wavelengths from 240 to 265nm and above 310nm. Literature reviewed in Section 7.1.1 suggests that a region starting around 318nm can be attributed to *p*-coumaric and ferulic acids [193]. Lignin G was extracted under the mildest conditions of pH 4.9 and 70% v/v ethanol but had a longer treatment time of 180 minutes. The mild conditions of treatment may have suppressed the formation of those products resulting in a lower absorbance at wavelengths greater than 310nm. Figure 7-10 suggests that differences in lignin G chemical structure are responsible lignin G-PF resin having the lowest strength.
Figure 7-11. Comparison of absorbance of lignin A, lignin G and AILG.

Lignin A and AILG have absorbances at 280nm slightly lower than the other lignins. Figure 7-11 shows that AILG has a spectra that resembles lignin A more than lignin G. Lignin A was the only lignin extracted at the lower ethanol concentration of 30% v/v whereas all other lignins incorporated into resin were extracted using 70% v/v ethanol. AILG may have undergone the same changes to lignin structure during acid hydrolysis as lignin A during pulping at low pH (3.0) and low ethanol concentration.

7.3.3.2 2-D Nuclear magnetic resonance

The 2-D NMR spectra shown in Figure 7-12 shows the signal of C-H bonds present in the lignin structure. Using Bruker TopSpin™, positive signals indicating carbon atoms with single or triple hydrogen attachments are shown in dark blue while negative signals indicating carbon with double hydrogen attachment are shown in light blue (aqua). Figure 7-12 shows lignin Z from autocatalysed pulping in 70% v/v ethanol. These comparatively mild conditions result in a high number of the β-aryl-ether bonds between lignin phenylpropanoid units. Figure 7-13 shows the 2-D NMR spectra of lignin B from pulping under
acidic conditions. The smaller volume of the $\beta$-aryl-ether signal suggests that lignin B has undergone more severe cleavage of lignin linkages.

Figure 7-12. Lignin 2-D NMR spectra with signals of aliphatic C-H bonds labeled.

Figure 7-13. Labelled 2-D NMR spectra of lignin B.
The three lignin linkages discussed in Section 7.1.3 (Figure 7-2) can be quantified by calculating the volumes of the 2-D NMR signals. The $\alpha$ signal of $\beta$-aryl-ether structures is the most easily resolved and furthest from any possible overlapping signals. For this reason it is used for quantifying the number of $\beta$-aryl-ether linkages. The volumes of the O-Me peak and $\beta$-aryl-ether ($\alpha$) peak are calculated by integration using TopSpin™ and the ratio of $\alpha$ carbons to methoxyl carbons is calculated for comparison between spectra. The other signals used are the $\alpha$ signal of phenylecoumaran and the $\beta$ signal of resinol. The remaining spectra are available in Appendix 5. Other signals may be difficult to quantify due to overlapping signals from other structures. However, a high degree of ethanolysis is indicated by the $-\text{OCH}_2\text{H}_3$ signal in all 2-D NMR spectra.

**Table 7-7. Relative peak volumes of lignin structures by 2-D NMR.**

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>AILG</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>G/S</td>
<td>35%</td>
<td>41%</td>
<td>37%</td>
<td>54%</td>
<td>49%</td>
<td>49%</td>
<td>37%</td>
<td>31%</td>
<td>41%</td>
<td>43%</td>
</tr>
</tbody>
</table>

--- Linkages/O-Me

<table>
<thead>
<tr>
<th>Linkages/O-Me</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>AILG</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$-aryl-ethers</td>
<td>6.0%</td>
<td>5.6%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>2.0%</td>
<td>0.0%</td>
<td>12.2%</td>
<td>2.9%</td>
<td>10.7%</td>
<td>16.4%</td>
</tr>
<tr>
<td>Phenylecoumaran</td>
<td>0.5%</td>
<td>0.8%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>1.8%</td>
<td>1.3%</td>
</tr>
<tr>
<td>Resinol</td>
<td>6.4%</td>
<td>3.3%</td>
<td>2.1%</td>
<td>1.3%</td>
<td>2.8%</td>
<td>1.0%</td>
<td>3.2%</td>
<td>3.7%</td>
<td>4.5%</td>
<td>5.6%</td>
</tr>
<tr>
<td>Sum of links</td>
<td>12.9%</td>
<td>9.7%</td>
<td>2.1%</td>
<td>1.3%</td>
<td>4.8%</td>
<td>1.0%</td>
<td>15.4%</td>
<td>6.6%</td>
<td>17.0%</td>
<td>23.3%</td>
</tr>
</tbody>
</table>

Lignin G has the highest total links of the lignin incorporated into resin. The reduced strength of lignin G-PF resin may be due to greater proportion of lignin linkages. This result indicates that lignin monomers are more suitable for incorporation into lignin than lignin that is highly cross-linked. A greater range of lignins should be tested to verify this result.

The acid hydrolysis of lignin G (producing AILG) resulted in a large reduction in $\beta$-aryl-ether linkages as shown by Table 7-7. Resinol content appears to have increased.
from acid hydrolysis of lignin G. This may be due to a reduction in methoxyl content caused by the relatively strong acid treatment. Removal of methoxyl groups also makes 2-D NMR comparison between lignins difficult because the peaks of other structures are reported using the volume of the methoxyl peak as a reference.

Lignins D, E and F have high G/S ratios. This is expected to be linked to % of lignin removed as syringyl lignin is known to be more easily removed than guaiacyl lignin and pulping experiments resulting in high % of lignin removal would likely have extracted more guaiacyl lignin late in the reaction. Figure 7-14 indicates that there may be a slight correlation between the amount of lignin removed and the proportion of lignin that is G lignin.

![Figure 7-14. Extent of delignification versus % Guaiacyl/Syringyl lignin.](image)

Figure 7-15 shows the final pulping pH versus the sum of linkages identified by 2-D NMR. Higher pH results in lignin containing more linkages. Lignin G has the highest sum of links and the highest pulping pH of the lignin incorporated into resin. This suggests that low pH resulting in greater cleavage of lignin linkages is more favourable for producing lignin to be used in PF resin manufacture.
7.3.3.3 Size exclusion chromatography

All spectra were found to have a peak maximum at an elution volume corresponding to less than 360g/mol. Such low molecular weights were unexpected and size exclusion chromatography data has been excluded from this discussion. The raw data, peak separation and a method of estimating the number of links for correlation with NMR results is detailed in Appendix 6.

7.4 Conclusions

Lignins A to G were able to be incorporated into PF resin with a phenol substitution level of 20% w/w. All resin preparations, except lignin G, showed comparable lap joint strength using a curing temperature of 145°C and pressing times of 120 and 480 seconds. Further testing at a range of curing temperatures may be required to ensure these lignins can be used commercially.
The reason for the much lower strength of lignin G-PF resin may be due to differences in chemical structure. Lignin G had a significantly different UV absorbance spectra and the highest proportion of linkages between lignin units measured by NMR. Lignin monomers may be better for resin synthesis than highly cross-linked lignins.

A low pulping pH is responsible for the degradation of ether linkages in lignin. The low pH, low ethanol concentration and high pulping temperature resulting in lignin A caused chemical modification to lignin that was emulated by acid hydrolysis of a low severity pulping lignin (lignin G).
8 Summary of conclusions

The conclusions of Chapters 5, 6 and 7 are summarised here.

8.1 Organosolv pulping

It is ideal to separate black liquor from the wood substrate after organosolv delignification at elevated temperature. If the reaction medium is first cooled before liquor is removed, a high degree of lignin re-precipitation will occur. Precipitated lignin is visible on the surface of wood fibers using SEM and it is more prevalent when liquor is slowly cooled before removal.

From the kinetic data obtained in this work from uncatalysed pulping and from buffered pulping, ethanol concentration has a negligible effect on the rate of bulk delignification. It is only the pH difference inherent in differing ethanol concentrations that causes a change in the rate constant. A change in the solvent concentration, which would affect viscosity and surface tension of the liquor, had no effect on delignification rate. There was however noticeable difference in the rate of polysaccharide removal, which may be attributed to the slight pH differences.

Comparison of de-ashed versus prehydrolysed willow pulping has shown that prehydrolysis only affects delignification rate by removing neutralising components of the feedstock resulting in a more acidic organosolv pulping medium. Removal of hemicellulose did not increase the rate of delignification. Prehydrolysis is a useful pre-organosolv treatment for the clean fractionation of wood components as it removes hemicellulose as well as extractives and ash that slow subsequent delignification without removal of lignin in the same liquid stream. Prehydrolysis can be used to effect cleaner fractionation and reduce the bulk volume of wood requiring organosolv treatment. This in turn reduces the volume of the organosolv reactor, which typically operates at high pressure and temperature and requires corrosion resistant materials of construction.

Previous authors have postulated that the removal of hemicellulose prior to organosolv delignification frees lignin to react more readily. A comparison of feedstocks
with different hemicellulose content and similar acid neutralising capability has been performed and no evidence that hemicellulose removal causes faster delignification was observed. A prehydrolysis step removes the neutralising components of wood, resulting in a higher final pH than pulping of untreated feedstock. Organosolv delignification of de-ashed willow gave the same improvement of delignification rate over untreated willow. The similarity between pulping de-ashed and prehydrolysed willow may be due to the removal of neutralising components. Prehydrolysed willow, having less hemicellulose, did not delignify faster during organosolv pulping than de-ashed willow.

A mechanism for delignification consisting of two species of insoluble and two species of soluble lignin is proposed. This is based on the known behaviour of lignin and agrees well with literature and experimental results. However, to verify the mechanism requires well designed experiments obtaining kinetic parameters for each reaction.

### 8.2 Lignin recovery

Dissolved air flotation is an effective method of recovering organosolv lignin precipitate without precipitating or collecting agents. Efficient flotation of organosolv lignin occurs at temperatures below 35°C. Above 35°C, precipitated lignin does not flocculate and is too small to attach to micro-bubbles. Faster flotation occurs when saturation pressure is high or black liquor-water mixing is rapid resulting in redistribution of micro-bubbles during floc formation. Higher saturation pressure can reduce the effect of slow addition rate due to the formation of more bubbles of smaller size.

### 8.3 Lignin use in phenol formaldehyde resin

Replacing phenol at 20% w/w substitution level with lignin results in lignin-PF resins with comparable strength to pure PF resins. The weakest lignin-PF resin contained lignin with the highest degree of cross-linking and was produced from pulping under mild conditions relative to the other lignins.

A decrease in pulping pH results in fewer lignin linkages suggesting that low pH is preferable for the production of lignin suitable for PF resin manufacture.
9 Future recommendations

- It is clear from Section 4.1 that future research in the field of organosolv delignification should focus on the continuous or flow-through reactor configurations to avoid re-condensation and maximize lignin yields.

- Solvent concentration should be chosen solely with regard to lignin solubility and ease of lignin recovery since it does not affect the rate of bulk delignification provided pH is adjusted by changing the amount of acid catalyst employed.

- The effects of process conditions on the onset of residual delignification and the structure of the residual lignin should be examined. With more complete understanding it may be possible to reduce or virtually eliminate the occurrence of the residual phase.

- Due to the dependence of delignification kinetics on pH and the ability of biomass to neutralize acid catalysts, it is recommended that future research into acid catalysed organosolv pulping be conducted with feedstock that has undergone treatment to reduce its potential for neutralising the acid catalyst. Otherwise, any measurement of liquor acidity will be erroneous due to the changing pH of liquor exposed to the ash and protein components.

- Greater total polysaccharide removal was achieved by prehydrolysis followed by organosolv delignification. The prehydrolysis process should be further optimized to enhance overall hemicellulose removal and reduce subsequent organosolv treatment reactor volumes by removing a large portion of the biomass component.

- Further research is required to establish a delignification mechanism that can describe lignin behavior. The model proposed in Section 4.3.4.3 requires verification.

- The parameters important to dissolved air flotation of lignin have been identified. Future work in the field of lignin DAF may include optimization of the process
conditions for different solvent systems and optimization in a continuous recovery mode of operation.

- Future work in applying lignins to phenol formaldehyde resin should examine greater variation in lignin properties. A flow through reactor is capable of altering molecular weight of lignin extracted by varying flow rate as discussed in Section 2.3.1. An examination of the degree of cross-linking and the effect on resin properties should be undertaken.

- Further characterisation of lignin-PF resins is necessary. While the tests described in this thesis were simple and aimed at proving lignin to be equivalent to phenol, lignin is known to improve some of the properties of resin. Research providing proof of product enhancement may be required to convince industry use lignin as a phenol substitute. A range of curing temperatures must also be tested.
10 References


[49] Pan, XJ, Gilkes, N, Kadla, J, Pye, K, Saka, S, Gregg, D, Ehara, K, Xie, D, Lam, D, Saddler, J, *Bioconversion of hybrid poplar to ethanol and co-products using an*


[58] Shevchenko, SM, Chang, K, Robinson, J, Saddler, JN, Optimization of monosaccharide recovery by post-hydrolysis of the water-soluble hemicellulose


10 - References


# Appendix 1. Chip size analysis

<table>
<thead>
<tr>
<th>Aperture (mm)</th>
<th>Median Size, di (mm)</th>
<th>Mass particles retained (g)</th>
<th>Mass %</th>
<th>cumulative % passing</th>
<th>di(\times)mass %</th>
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<tbody>
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<td>0.063</td>
<td>0.1065</td>
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<td>0.5%</td>
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<td>0.000</td>
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<tr>
<td>0.15</td>
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<td>2.8%</td>
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<td>0.5</td>
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<td>0.85</td>
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<td>1.4</td>
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<td>1.7</td>
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<td>57.52</td>
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<td>0.462</td>
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<td>2.36</td>
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<td>3.4</td>
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<td>4</td>
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<td>94.2%</td>
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<td></td>
<td></td>
<td>252.83</td>
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<td>2.651</td>
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\(d_{15.87} = 1.5 \text{ mm}\)
\(d_{50} = 2.525 \text{ mm}\)
\(d_{84.13} = 3.65 \text{ mm}\)

![Cumulative % finer vs. Particle size (mm)](image-url)
### Appendix 1 - Chip size analysis

<table>
<thead>
<tr>
<th>Aperture (mm)</th>
<th>Median Size, $d_{50}$ (mm)</th>
<th>Mass particles retained (g)</th>
<th>Mass % passing</th>
<th>cumulative % finer</th>
<th>$d_{i} * m_{s}$ %</th>
</tr>
</thead>
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<td>0.925</td>
<td>0.17</td>
<td>0.1%</td>
<td>0</td>
<td>0.0005</td>
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<td>1.7</td>
<td>2.03</td>
<td>0.14</td>
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<td>0.0009</td>
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<td>2.36</td>
<td>2.58</td>
<td>0.31</td>
<td>0.1%</td>
<td>0.1%</td>
<td>0.0025</td>
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<td>4</td>
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<td>0.5%</td>
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<td>10.75</td>
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$d_{15.87} = 5.8$ mm

$d_{50} = 8.2$ mm
Appendix 2. HPAEC-PAD data

Shown here are the spectra of high performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD) and the summary of two stage acid hydrolysis of the untreated, de-ashed and prehydrolysed feedstocks. The procedure was performed at The School of Biological Sciences (SBS), University of Auckland.

<table>
<thead>
<tr>
<th>Residence time</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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<tbody>
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<td>1 Myo-inositol</td>
<td>1.467</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>2 Arabinose</td>
<td>6.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>3 Galactose</td>
<td>8.017</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>4 Glucose</td>
<td>9.15</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>5 Xylose</td>
<td>10.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 Mannose</td>
<td>11.467</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>7 Galacturonic Acid</td>
<td>25.667</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>8 Glucuronic Acid</td>
<td>26.017</td>
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<td></td>
</tr>
</tbody>
</table>

De-ashed 1:
Appendix 2 - HPAEC-PAD data

De-ashed 2:

De-ashed 3:
Appendix 2 - HPAEC-PAD data

Prehydrolysed 1:

Prehydrolysed 2:

Prehydrolysed 3:
Appendix 2 - HPAEC-PAD data

Untreated 1:

![Graph for Untreated 1]

Untreated 2:

![Graph for Untreated 2]

Untreated 3:

![Graph for Untreated 3]
## Compositional analysis.

<table>
<thead>
<tr>
<th></th>
<th>De-ashed</th>
<th>Prehydrolysed</th>
<th>Untreated</th>
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</thead>
<tbody>
<tr>
<td>Sample weight (mg)</td>
<td>79.2</td>
<td>69.9</td>
<td>64.2</td>
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</tbody>
</table>

### Dry mass of wood

<p>| | | | | | | |</p>
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<tr>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight tray (mg)</td>
<td>0.28568</td>
<td>0.44853</td>
<td>0.35988</td>
<td>0.24233</td>
<td>0.42496</td>
<td>0.37619</td>
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<tr>
<td>Weight tray + sample  (mg)</td>
<td>0.39769</td>
<td>0.52283</td>
<td>0.43999</td>
<td>0.3856</td>
<td>0.70338</td>
<td>0.5631</td>
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<tr>
<td>Weight after drying (mg)</td>
<td>0.39731</td>
<td>0.52263</td>
<td>0.4396</td>
<td>0.38503</td>
<td>0.70254</td>
<td>0.56264</td>
</tr>
<tr>
<td>% water on wet basis</td>
<td>0.3%</td>
<td>0.3%</td>
<td>0.5%</td>
<td>0.4%</td>
<td>0.3%</td>
<td>0.2%</td>
</tr>
<tr>
<td>Mean ± stdev (%)</td>
<td>0.30% ± 0.05%</td>
<td>0.44% ± 0.06%</td>
<td>0.27% ± 0.04%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% dry mass</td>
<td>99.7%</td>
<td>99.7%</td>
<td>99.7%</td>
<td>99.5%</td>
<td>99.5%</td>
<td>99.7%</td>
</tr>
</tbody>
</table>

### ASL

<p>| | | | | | | |</p>
<table>
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<tr>
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<tr>
<td>dilution</td>
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<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Abs poplar (L/gcm)</td>
<td>11.4</td>
<td>11.4</td>
<td>11.4</td>
<td>11.4</td>
<td>11.4</td>
<td>11.4</td>
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<tr>
<td>hydrolysate volume (mL)</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>mg</td>
<td>5.64</td>
<td>6.70</td>
<td>3.67</td>
<td>3.41</td>
<td>2.55</td>
<td>4.26</td>
</tr>
<tr>
<td>Dry mass sample (mg)</td>
<td>78.93</td>
<td>69.66</td>
<td>63.98</td>
<td>50.25</td>
<td>59.11</td>
<td>82.30</td>
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<tr>
<td>% ASL extractives free basis</td>
<td>7.2%</td>
<td>9.6%</td>
<td>5.7%</td>
<td>6.8%</td>
<td>4.3%</td>
<td>5.2%</td>
</tr>
</tbody>
</table>

### AIL

<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>sinter dry weight (g)</td>
<td>29.403</td>
<td>28.948</td>
<td>30.550</td>
<td>30.442</td>
<td>30.478</td>
<td>30.433</td>
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<tr>
<td>sinter + lignin dry weight (g)</td>
<td>29.425</td>
<td>28.964</td>
<td>30.567</td>
<td>30.456</td>
<td>30.496</td>
<td>30.458</td>
</tr>
<tr>
<td>Acid insoluble lignin (mg)</td>
<td>21.4</td>
<td>16.3</td>
<td>17.6</td>
<td>13.8</td>
<td>18</td>
<td>25.4</td>
</tr>
<tr>
<td>% AIL extractives free basis</td>
<td>27.1%</td>
<td>23.4%</td>
<td>27.5%</td>
<td>27.5%</td>
<td>30.5%</td>
<td>30.9%</td>
</tr>
</tbody>
</table>

### Extractives %

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<tbody>
<tr>
<td>ASL % on whole dry mass mean</td>
<td>7.0%</td>
<td>9.4%</td>
<td>5.6%</td>
<td>6.7%</td>
<td>4.2%</td>
<td>5.1%</td>
</tr>
<tr>
<td></td>
<td>7.3%</td>
<td>5.3%</td>
<td>6.3%</td>
<td>6.3%</td>
<td>6.3%</td>
<td>6.3%</td>
</tr>
<tr>
<td>st.dev.</td>
<td>± 1.92%</td>
<td>± 1.24%</td>
<td>± 3.43%</td>
<td>± 3.43%</td>
<td>± 3.43%</td>
<td>± 3.43%</td>
</tr>
<tr>
<td>AIL % on whole dry mass</td>
<td>26.5%</td>
<td>22.8%</td>
<td>26.8%</td>
<td>27.0%</td>
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<td></td>
<td>25.4%</td>
<td>29.1%</td>
<td>23.5%</td>
<td>23.5%</td>
<td>23.5%</td>
<td>23.5%</td>
</tr>
<tr>
<td>± 2.21%</td>
<td>± 1.83%</td>
<td>± 2.82%</td>
<td>± 2.82%</td>
<td>± 2.82%</td>
<td>± 2.82%</td>
<td>± 2.82%</td>
</tr>
</tbody>
</table>

### Total lignin on whole dry mass

<p>| | | | | | | |</p>
<table>
<thead>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total lignin on whole dry mass</td>
<td>33.4%</td>
<td>32.2%</td>
<td>32.4%</td>
<td>33.7%</td>
<td>34.2%</td>
<td>35.4%</td>
</tr>
<tr>
<td></td>
<td>32.7%</td>
<td>34.4%</td>
<td>29.9%</td>
<td>34.4%</td>
<td>34.4%</td>
<td>34.4%</td>
</tr>
<tr>
<td>± 0.65%</td>
<td>± 0.91%</td>
<td>± 2.73%</td>
<td>± 2.73%</td>
<td>± 2.73%</td>
<td>± 2.73%</td>
<td>± 2.73%</td>
</tr>
</tbody>
</table>
### Appendix 2 - HPAEC-PAD data

<table>
<thead>
<tr>
<th>Hydrolysis sugars</th>
<th>De-ashed</th>
<th>Prehydrolysed</th>
<th>Untreated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass in sample (mg)</td>
<td>outliers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arabinose</td>
<td>0.60</td>
<td>0.10</td>
<td>0.58</td>
</tr>
<tr>
<td>Galactose</td>
<td>0.85</td>
<td>0.23</td>
<td>0.75</td>
</tr>
<tr>
<td>Glucose</td>
<td>29.10</td>
<td>17.85</td>
<td>32.25</td>
</tr>
<tr>
<td>Xylose</td>
<td>12.48</td>
<td>7.75</td>
<td>12.85</td>
</tr>
<tr>
<td>Mannose</td>
<td>1.75</td>
<td>1.48</td>
<td>1.63</td>
</tr>
<tr>
<td>Galacturonic Acid</td>
<td>1.58</td>
<td>0.80</td>
<td>1.30</td>
</tr>
<tr>
<td>Glucuronic Acid</td>
<td>0.45</td>
<td>0.23</td>
<td>0.48</td>
</tr>
</tbody>
</table>

| Total sugars       | 46.80    | 28.43         | 49.83     |

| % on whole mass    |          |              |           |
| Arabinose          | 1%       | 0%           | 1%        |
| Galactose          | 1%       | 0%           | 1%        |
| Glucose            | 36%      | 35%          | 41%       |
| Xylose             | 15%      | 15%          | 16%       |
| Mannose            | 2%       | 3%           | 2%        |
| Galacturonic Acid  | 2%       | 2%           | 2%        |
| Glucuronic Acid    | 1%       | 0%           | 1%        |

| Total sugars       | 58%      | 56%          | 63%       |

| Hemicellulose sugars total | 21% | 20% | 22% |

<table>
<thead>
<tr>
<th>AVERAGES</th>
<th>De-ashed</th>
<th>Prehydrolysed</th>
<th>Untreated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arabinose</td>
<td>1.1% ± 0.6%</td>
<td>0.2% ± 0.0%</td>
<td>0.7% ± 0.0%</td>
</tr>
<tr>
<td>Galactose</td>
<td>1.5% ± 0.9%</td>
<td>0.5% ± 0.0%</td>
<td>1.0% ± 0.0%</td>
</tr>
<tr>
<td>Glucose</td>
<td>35.4% ± 1.1%</td>
<td>34.3% ± 0.8%</td>
<td>39.6% ± 1.5%</td>
</tr>
<tr>
<td>Xylose</td>
<td>15.0% ± 0.4%</td>
<td>14.9% ± 0.4%</td>
<td>15.8% ± 0.5%</td>
</tr>
<tr>
<td>Mannose</td>
<td>2.8% ± 0.6%</td>
<td>2.6% ± 0.4%</td>
<td>2.0% ± 0.0%</td>
</tr>
<tr>
<td>Galacturonic Acid</td>
<td>2.0% ± 0.2%</td>
<td>1.6% ± 0.0%</td>
<td>1.7% ± 0.3%</td>
</tr>
<tr>
<td>Glucuronic Acid</td>
<td>0.6% ± 0.0%</td>
<td>0.4% ± 0.0%</td>
<td>0.6% ± 0.1%</td>
</tr>
</tbody>
</table>

| Total sugars       | 58.5% ± 1.1% | 54.5% ± 1.6% | 61.4% ± 2.0% |

| hemicellulose sugars total | 22.5% ± 2.1% | 19.7% ± 0.7% | 21.2% ± 0.4% |
Appendix 3. Pulping conditions and final lignin content

This appendix gives the pulping conditions and lignin content of wood after treatment. The method used for determining lignin content is the modified NREL protocol described in Section 3.2.3.1.

<table>
<thead>
<tr>
<th>Ethanol concentration</th>
<th>35%</th>
<th>35%</th>
<th>35%</th>
<th>35%</th>
<th>70%</th>
<th>70%</th>
<th>70%</th>
<th>70%</th>
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</thead>
<tbody>
<tr>
<td>Reactor inlet temperature (°C)</td>
<td>170</td>
<td>170</td>
<td>185</td>
<td>185</td>
<td>170</td>
<td>170</td>
<td>185</td>
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</tr>
<tr>
<td>Time (minutes)</td>
<td>180</td>
<td>180</td>
<td>180</td>
<td>180</td>
<td>180</td>
<td>180</td>
<td>180</td>
<td>180</td>
</tr>
<tr>
<td>H₂SO₄ concentration (% w/w)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Final lignin content (% w/w dry wood)</td>
<td>14.90</td>
<td>14.74</td>
<td>11.20</td>
<td>10.96</td>
<td>21.09</td>
<td>19.68</td>
<td>16.25</td>
<td>17.33</td>
</tr>
<tr>
<td>σ (%)</td>
<td>0.51</td>
<td>0.08</td>
<td>0.09</td>
<td>0.60</td>
<td>0.25</td>
<td>0.39</td>
<td>0.65</td>
<td>0.53</td>
</tr>
<tr>
<td>Acid insoluble lignin (% AIL w/w dry wood)</td>
<td>13.63</td>
<td>13.02</td>
<td>10.70</td>
<td>9.82</td>
<td>17.80</td>
<td>15.62</td>
<td>14.13</td>
<td>15.78</td>
</tr>
<tr>
<td>σ (%)</td>
<td>0.22</td>
<td>0.02</td>
<td>0.05</td>
<td>0.30</td>
<td>0.25</td>
<td>0.28</td>
<td>0.58</td>
<td>0.73</td>
</tr>
<tr>
<td>Acid soluble lignin (% ASL w/w dry wood)</td>
<td>1.26</td>
<td>1.71</td>
<td>0.50</td>
<td>1.13</td>
<td>3.29</td>
<td>4.05</td>
<td>2.12</td>
<td>1.55</td>
</tr>
<tr>
<td>σ (%)</td>
<td>0.35</td>
<td>0.07</td>
<td>0.14</td>
<td>0.40</td>
<td>0.46</td>
<td>0.22</td>
<td>0.20</td>
<td>0.44</td>
</tr>
<tr>
<td>Input dry mass (g)</td>
<td>249</td>
<td>251</td>
<td>250</td>
<td>249</td>
<td>253</td>
<td>245</td>
<td>251</td>
<td>249</td>
</tr>
<tr>
<td>Output dry mass (g)</td>
<td>156.7</td>
<td>163.4</td>
<td>143.7</td>
<td>144.2</td>
<td>207.3</td>
<td>202.9</td>
<td>182.2</td>
<td>191.4</td>
</tr>
</tbody>
</table>
### Appendix 3 - Pulping conditions and final lignin content

#### Buffered pulping conditions and final lignin content

<table>
<thead>
<tr>
<th>Ethanol concentration (%)</th>
<th>30%</th>
<th>30%</th>
<th>50%</th>
<th>50%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor inlet temperature (°C)</td>
<td>180</td>
<td>180</td>
<td>180</td>
<td>180</td>
</tr>
<tr>
<td>Time (minutes)</td>
<td>180</td>
<td>195</td>
<td>180</td>
<td>195</td>
</tr>
<tr>
<td>H₂SO₄ concentration (% w/w)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

#### Acid catalysed pulping conditions and final lignin content

<table>
<thead>
<tr>
<th>Ethanol concentration (%)</th>
<th>70%</th>
<th>70%</th>
<th>70%</th>
<th>70%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor inlet temperature (°C)</td>
<td>180</td>
<td>180</td>
<td>180</td>
<td>180</td>
</tr>
<tr>
<td>Time (minutes)</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>H₂SO₄ concentration (% w/w)</td>
<td>0.04</td>
<td>0.08</td>
<td>0.08</td>
<td>0.04</td>
</tr>
</tbody>
</table>

#### Pre-organosolv treated feedstock pulping conditions and final lignin content

<table>
<thead>
<tr>
<th>Ethanol concentration (%)</th>
<th>70%</th>
<th>70%</th>
<th>70%</th>
<th>70%</th>
<th>70%</th>
<th>70%</th>
<th>70%</th>
<th>70%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor inlet temperature (°C)</td>
<td>170</td>
<td>170</td>
<td>175</td>
<td>175</td>
<td>175</td>
<td>175</td>
<td>180</td>
<td>180</td>
</tr>
<tr>
<td>Time (minutes)</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>H₂SO₄ concentration (% w/w)</td>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
</tr>
</tbody>
</table>

* DA=de-ashed, PH=prehydrolysed

---

220
Appendix 4. Mathematical model

In this appendix an example of the MATLAB code used to fit a mathematical model to experimental data is shown. The example given fits the following reaction mechanism to experiments performed in 70% v/v ethanol at pH of 3.3 and temperature of 176.5°C and 50% buffered ethanol at pH of 4.9 and temperature of 178°C.

\[
\begin{align*}
L_N & \rightleftharpoons \frac{k_1}{k_2} L_S \\
L_S & \rightleftharpoons \frac{k_3}{k_4} L_R \\
L_S & \rightleftharpoons \frac{k_5}{k_6} L_{SS}
\end{align*}
\]

%%%%%%%%%%%%%%%% reversible lignin reaction model
\texttt{clear all;}

%%%%%%%%%%%%%%%%RAW DATA%%%%%%%%%%%%%%%%%%%%%%%
\texttt{EXPERIMENTTIME1=[0,5,10,15,20,25,30,35,40,45,50,55,60,65,70,75,80,85,90,95,100,105,110];}
\texttt{AMC07=[0.252107954,0.219825054,0.185699478,0.163581321,0.147557097,0.136296225,0.116391547,0.09855042,0.086503401,0.069754225,0.066096808,0.058126384,0.063122956,0.055866457,0.047711296,0.046748571,0.047129077];}
\texttt{T1=273.15+176.5; pH1=3.3;}

\texttt{EXPERIMENTTIME2=[0,5,10,15,20,25,30,35,40,45,50,60,70,80,90,100,110,120,130,140,150,160,170,185];}
\texttt{buffer50=[0.256241386,0.235066285,0.227688336,0.208864902,0.202545386,0.194611673,0.182837504,0.175024802,0.158301469,0.154412957,0.144985896,0.139134436,0.11246794,0.099039408,0.090870063,0.084031861,0.084352547,0.076492397,0.08255145,0.073991074,0.067674964,0.065660022,0.07926533];}
\texttt{T2=273.15+178; pH2=4.15;}

\texttt{Vr=250/3; % g/L}
\texttt{dt=0.1; % minutes}
\texttt{WM=250; % g}
\texttt{t8=400; % minutes}
\texttt{points=t8/dt;}
\texttt{timevec=linspace(0,t8,points);}
Lvec=zeros(1,points);
Lsvec=zeros(1,points);
LRvec=zeros(1,points);
R=8.314;
ITER=100;
var=0.1;
currentlowest=100;

%%%data collection matrix
datacollect=zeros(21,ITER);

x1RT=1/(R*T1);
x2RT=1/(R*T2);

H1=10^((-1)*(pH1));
H2=10^((-1)*(pH2));

%rate data

%%%Dissolve natural
Ea1=87000; %J/mol %%%Activation energy
k01=1.08*10^10; %min^-1 %%%Frequency factor
pHexpb=0.45; %%%order wrt H+ ions
order1=1; %%%order wrt natural lignin content

%%%recon to residual
Ea3recon=97350;
k03recon=850;
pHexprecon=0;
order3res=0; %%%order wrt natural lignin content
order3tos=2; %%%order wrt soluble lignin concentration

%%%redissolve of residual
Ea4redis=56000;
k04redis=10;
pHexpredis=1;
order4tolar=1;

%%%recon to natural
Ea2=20000;
k02=0.0025;
pHexp2=0.14;
order2=0; %%%order wrt natural lignin content
order2s=2; %%%order wrt soluble lignin concentration

%%%rate constants for reaction of soluble to more soluble lignin
Ksolf=0.0015;
Ksolr=1.56;

%initialise lowest data set
lowestdata=[100,Ea1,k01,pHexpb,order1,Ea3recon,k03recon,pHexprecon,order3res,order3tos,Ea4redis,k04redis,pHexpredis,order4tolar,Ea2,k02,pHexp2 ,order2,order2s,Ksolf,Ksolr];
Appendix 4 - Mathematical model

%%%%%%%above variables same for each run
%%% now add some variance

for x=1:ITER

%%% CAN CHOOSE CONSTANTS to vary and find value with lowest
%%% sum-squared-difference

%%%Ea1=Ea1*(1+(randn)*var); %J/mol
k01=k01*(1+(randn)*var); %min-1
%pHexpb=pHexpb*(1+(randn)*var);
%order1=order1*(1+(randn)*var);

%Ea3recon=Ea3recon*(1+(randn)*var); %%%recon to residual
k03recon=k03recon*(1+(randn)*var);
%pHexprecon=pHexprecon*(1+(randn)*var);
%order3res=order3res*(1+(randn)*var);
%order3toLs=order3toLs*(1+(randn)*var);

%Ea4redis=Ea4redis*(1+(randn)*var); %%%redissolve of residual
k04redis=k04redis*(1+(randn)*var);
%pHexpredis=pHexpredis*(1+(randn)*var);
%order4toLr=order4toLr*(1+(randn)*var);

%Ea2=Ea2*(1+(randn)*var); %%%recon to natural
k02=k02*(1+(randn)*var);
%pHexp2=pHexp2*(1+(randn)*var);
%order2=order2*(1+(randn)*var);
%order2s=order2s*(1+(randn)*var);

Ksolf=Ksolf*(1+(randn)*var);
Ksolr=Ksolr*(1+(randn)*var);
%
%conditions specific to experiment1

L0=AMC07(1); %g/g
L=L0;
Ls=0;
LR=0;
Lsol=0;

k1=k01*(H1^pHexpb)*exp(-1*Ea1*x1RT);
krecon=k03recon*(H1^pHexprecon)*exp(-1*Ea3recon*x1RT);
kredis=k04redis*(H1^pHexpredis)*exp(-1*Ea4redis*x1RT);
k2=k02*(H1^pHexp2)*exp(-1*Ea2*x1RT);

for i=1:points
    dLbydt=-1*k1*L^order1+k2*(Ls)^order2s*L^order2;
    dLRbydt=krecon*L^order3res*(Ls)^order3toLs-kredis*LR^order4toLr;
    dLsolbydt=Ksolf*Ls^1-Ksolr*Lsol^1;
    L=L+dLbydt*dt;
    LR=LR+dLRbydt*dt;
    Lsol=Lsol+dLsolbydt*dt;
end
Appendix 4 - Mathematical model

```matlab
Lsol=Lsol+dLsolbydt;
Lvec(i)=L+LR;
Lsvec(i)=Ls;
LRvec(i)=LR;
Ls=(L0-L-LR-Lsol)*Vr;
end
modelpoints1=EXPERIMENTTIME1./dt+1;
G=length(modelpoints1);
for j=1:G
    A=modelpoints1(j);
    modelpoints1(j)=Lvec(A);
end;
B=AMC07-modelpoints1;
B=B.*B;
C=sum(B);
%%%%2222222222222222222%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%2222222
%conditions specific to experiment2
L0=buffer50(1); %g/g
L=L0;
Ls=0;
LR=0;
k1=k01*(H2^pHexpb)*exp(-1*Ea1*x2RT);
krecon=k03recon*(H2^pHexprecon)*exp(-1*Ea3recon*x2RT);
kredis=k04redis*(H2^pHexpredis)*exp(-1*Ea4redis*x2RT);
k2=k02*(H2^pHexp2)*exp(-1*Ea2*x2RT);
for i=1:points
    dLbydt=-1*k1*L^order1+k2*(Ls)^order2s*L^order2;
    dLRbydt=krecon*L^order3res*(Ls)^order3toLs-kredis*LR^order4toLr;
    L=L+dLbydt*dt;
    LR=LR+dLRbydt*dt;
    Lvec(i)=L+LR;
    Lsvec(i)=Ls;
    LRvec(i)=LR;
    Ls=(L0-L-LR)*Vr;
end
modelpoints2=EXPERIMENTTIME2./dt+1;
G=length(modelpoints2);
for j=1:G
    A=modelpoints2(j);
    modelpoints2(j)=Lvec(A);
end;
D=buffer50-modelpoints2;
D=D.*D;
E=sum(D);
F=E+C;
%%%%%find lowest sumsquaredifference
```
Appendix 4 - Mathematical model

```matlab
if F<currentlowest
    currentlowest=F;
end;

lowestdata=[F,Ea1,k01,pHexpb,order1,Ea3recon,k03recon,pHexprecon,order3res,order3toLs,Ea4redis,k04redis,pHexpredis,order4toLr,Ea2,k02,pHexp2,order2,order2s,Ksolf,Ksolr];
end;

%%%%%%%%%%%%%%%%%%
Put in best data and show graphs %%%%%

Ea1=lowestdata(2); % J/mol
k01=lowestdata(3); % min^-1
pHexpb=lowestdata(4);
order1=lowestdata(5);

Ea3recon=lowestdata(6); % recon to residual
k03recon=lowestdata(7);
pHexprecon=lowestdata(8);
order3res=lowestdata(9);
order3toLs=lowestdata(10);

Ea4redis=lowestdata(11); % redissolve of residual
k04redis=lowestdata(12);
pHexpredis=lowestdata(13);
order4toLr=lowestdata(14);

Ea2=lowestdata(15); % recon to natural
k02=lowestdata(16);
pHexp2=lowestdata(17);
order2=lowestdata(18);
order2s=lowestdata(19);

Ksolf=lowestdata(20);
Ksolr=lowestdata(21);
end;

% conditions specific to experiment 1

L0=AMC07(1); % g/g
L=L0;
Ls=0;
LR=0;
Lsol=0;

k1=k01*(H1^pHexpb)*exp(-1*Ea1*x1RT);
krecon=k03recon*(H1^pHexprecon)*exp(-1*Ea3recon*x1RT);
kredis=k04redis*(H1^pHexpredis)*exp(-1*Ea4redis*x1RT);
k2=k02*(H1^pHexp2)*exp(-1*Ea2*x1RT);

for i=1:points
    dLbydt=-1*k1*L^order1+k2*(Ls)^order2s*L^order2;
    dLRbydt=krecon*L^order3res*(Ls)^order3toLs-kredis*LR^order4toLr;
    dLsolbydt=Ksolf*Ls^1-Ksolr*Lsol^1;
    L=L+dLbydt*dt;
end;

```
Appendix 4 - Mathematical model

```
LR=LR+dLRbydt*dt;
Lsol=Lsol+dLsolbydt;
Lvec(i)=L+LR;
Lsvec(i)=Ls;
LRvec(i)=LR;
Ls=(L0-L-LR-Lsol)*Vr;
end

figure(3);
clf(3);
semilogy(EXPERIMENTTIME1,AMC07,'rd');
hold on;
semilogy(timevec,Lvec,'--r');
xlabel('Time (minutes)')
ylabel('mass lignin per dry mass wood input (g/g)')

modelpoints1=EXPERIMENTTIME1./dt+1;
G=length(modelpoints1);
for j=1:G
   A=modelpoints1(j);
   modelpoints1(j)=Lvec(A);
end;
B=AMC07-modelpoints1;
B=B.*B;
C=sum(B);

%%%%2222222222222222222%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%2222222222222222222
%conditions specific to experiment2
L0=buffer50(1); %g/g
L=L0;
Ls=0;
LR=0;
k1=k01*(H2^pHexpb)*exp(-1*Ea1*x2RT);
krecon=k03recon*(H2^pHexprecon)*exp(-1*Ea3recon*x2RT);
kredis=k04redis*(H2^pHexpredis)*exp(-1*Ea4redis*x2RT);
k2=k02*(H2^pHexp2)*exp(-1*Ea2*x2RT);

for i=1:points
   dLbydt=-1*k1*L^order1+k2*(Ls)^order2s*L^order2;
   dLRbydt=krecon*L^order3res*(Ls)^order3toLs-kredis*LR^order4toLr;
   dLsolbydt=Ksolf*Ls^1-Ksolr*Lsol^1;
   L=L+dLbydt*dt;
   LR=LR+dLRbydt*dt;
   Lsol=Lsol+dLsolbydt;
   Lvec(i)=L+LR;
   Lsvec(i)=Ls;
   LRvec(i)=LR;
   Ls=(L0-L-LR-Lsol)*Vr;
end

modelpoints2=EXPERIMENTTIME2./dt+1;
```
Appendix 4 - Mathematical model

G = length(modelpoints2);
for j = 1:G
    A = modelpoints2(j);
    modelpoints2(j) = Lvec(A);
end;

D = buffer50 - modelpoints2;
D = D .* D;
E = sum(D);
F = E + C;

SSQD = [C, E, F]
disp(k01)
disp(k02)
disp(k03recon)
disp(k04redis)
disp(Ksolf)
disp(Ksolr)

plot(EXPERIMENTTIME2, buffer50, 'ks');
plot(timevec, Lvec, '--k');
legend('De-ashed 0.04% sulphuric acid--experimental', 'De-ashed 0.04% sulphuric acid--model', 'Buffered, 50%EtOH--experimental', 'Buffered, 50%EtOH--model');
Appendix 5. 2-D NMR spectra

The peak volumes are integrated by SpinWorks™ and given as percentage of the volume of the largest peak. The largest peak was always the methoxyl peak for integrations of the aliphatic region and the S2/S6 peak for integrations of the aromatic region.

Lignin A
Appendix 5 - 2-D NMR spectra

Lignin B

![2-D NMR spectrum of Lignin B](image)

Lignin C

![2-D NMR spectrum of Lignin C](image)
Appendix 5 - 2-D NMR spectra

Lignin D

Lignin E
Appendix 5 - 2-D NMR spectra

Lignin F

Lignin G
Appendix 5 - 2-D NMR spectra

AILG

Lignin Y
Appendix 5 - 2-D NMR spectra

Lignin Z

50% ethanol buffered pulping
Appendix 5 - 2-D NMR spectra

50% ethanol buffered pulping

30% ethanol buffered pulping
Appendix 6. Size exclusion chromatography data

This appendix describes an attempt to correlate the size exclusion chromatography (SEC) chromatographs with the 2-D nuclear magnetic resonance (NMR) peak volumes. 2-D NMR gives the relative amount of linkages present in the lignin samples. The linkages/O-Me are calculated from the 2-D NMR spectra shown in Appendix 5. SEC gives the relative number of molecules with a given size. For each SEC chromatograph, the following procedure is performed;

1. Chromatographs are processed using the software Origin61™. Band resolution is performed using the Gaussian function to resolve a multi-component peak into component peaks.

2. Peaks with maximum intensity at elution volumes corresponding to less than 100g/mol are neglected.

3. Each peak area is divided by its molecular weight (corresponding mol weight at peak maximum) giving the relative number of moles.

4. The mol fraction is calculated.

5. The corresponding mol weight at peak maximum is divided by 190g/mol (the average mass of a lignin monomer assuming a G/S of 0.5) to give the approximate number of phenyl-propanoid monomers in the molecule.

6. The number of linkages is calculated as the number of phenyl-propanoid monomers minus one.

7. The expected links per O-Me is calculated as,

\[
\frac{\text{links}}{O-Me} = \frac{\sum_{i=1}^{n_{\text{peak}}} (\text{mol fraction})(\# \text{links})}{1.7(\text{mol fraction})(\# \text{monomers})}
\]
The factor 1.7 corresponds to the average number of methoxyl groups per monomer assuming a G/S of 0.5. The data obtained from this procedure are shown below.

Lignin A:
NMR results
\( \beta \)-aryl-ethers 6.0%
Phenylcoumaran 0.5%
Resinol 6.4%
Sum of links 12.9%

SEC results

<table>
<thead>
<tr>
<th>Peak</th>
<th>Elution V. (mL)</th>
<th>( M_i ) (g/mol)</th>
<th>Peak area</th>
<th>Area/( M_i ) fraction</th>
<th># monomers</th>
<th>linkages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30.20</td>
<td>208.15</td>
<td>0.127</td>
<td>0.001</td>
<td>1.1</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>30.78</td>
<td>131.31</td>
<td>0.003</td>
<td>0.000</td>
<td>0.7</td>
<td>-0.3</td>
</tr>
<tr>
<td>3</td>
<td>31.35</td>
<td>83.16</td>
<td>0.013</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>32.08</td>
<td>46.34</td>
<td>0.026</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ \text{Expected links/O-Me} = 0.041 \]
### Lignin A replicate: SEC results

<table>
<thead>
<tr>
<th>Peak</th>
<th>Elution V. (mL)</th>
<th>Mi (g/mol)</th>
<th>Peak area</th>
<th>Hi/Mi</th>
<th>mol fraction</th>
<th># monomers</th>
<th>linkage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>29.61</td>
<td>301.97</td>
<td>0.207</td>
<td>0.0007</td>
<td>28%</td>
<td>1.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Peak 2</td>
<td>30.22</td>
<td>184.61</td>
<td>0.234</td>
<td>0.0013</td>
<td>52%</td>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Peak 3</td>
<td>30.75</td>
<td>121.12</td>
<td>0.059</td>
<td>0.0005</td>
<td>20%</td>
<td>0.6</td>
<td>-0.4</td>
</tr>
<tr>
<td>Peak 4</td>
<td>31.35</td>
<td>74.88</td>
<td>0.207</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak 5</td>
<td>32.47</td>
<td>30.41</td>
<td>0.153</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>RI signal</th>
<th>Elution volume (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>27</td>
</tr>
<tr>
<td>0.05</td>
<td>28</td>
</tr>
<tr>
<td>0.10</td>
<td>29</td>
</tr>
<tr>
<td>0.15</td>
<td>30</td>
</tr>
<tr>
<td>0.20</td>
<td>31</td>
</tr>
<tr>
<td>0.25</td>
<td>32</td>
</tr>
</tbody>
</table>

Data: LIGNINA2_B
Model: Gauss
Chi^2/DoF = 1.7286E-6
R^2 = 0.99985
y0 0 ±0
xc1 29.61038 ±0.11212
w1 1.24847 ±0.05386
A1 0.20714 ±0.04948
xc2 30.22416 ±0.01268
w2 0.9788 ±0.06528
A2 0.23407 ±0.06197
xc3 30.74983 ±0.00836
w3 0.59468 ±0.02581
A3 0.65873 ±0.015
xc4 31.34953 ±0.01091
w4 0.8918 ±0.03293
xc5 32.47358 ±0.00817
w5 1.40072 ±0
A5 0.15298 ±0.00214

Expected links/O-Me 0.0402
Lignin B:
NMR results

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-aryl-ethers</td>
<td>5.6%</td>
</tr>
<tr>
<td>Phenylcoumaran</td>
<td>0.8%</td>
</tr>
<tr>
<td>Resinol</td>
<td>3.3%</td>
</tr>
<tr>
<td><strong>Sum of links</strong></td>
<td><strong>9.7%</strong></td>
</tr>
</tbody>
</table>

SEC results

<table>
<thead>
<tr>
<th>Peak</th>
<th>Elution V. (mL)</th>
<th>Mi (g/mol)</th>
<th>Peak area</th>
<th>Hi/Mi</th>
<th>mol fraction</th>
<th># monomers</th>
<th>linkages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28.93</td>
<td>576</td>
<td>0.028</td>
<td>0.00005</td>
<td>14%</td>
<td>3.0</td>
<td>2.0</td>
</tr>
<tr>
<td>2</td>
<td>29.58</td>
<td>342</td>
<td>0.011</td>
<td>0.00003</td>
<td>9%</td>
<td>1.8</td>
<td>0.8</td>
</tr>
<tr>
<td>3</td>
<td>30.12</td>
<td>222</td>
<td>0.057</td>
<td>0.00026</td>
<td>73%</td>
<td>1.2</td>
<td>0.2</td>
</tr>
<tr>
<td>4</td>
<td>30.82</td>
<td>127</td>
<td>0.002</td>
<td>0.00001</td>
<td>4%</td>
<td>0.7</td>
<td>-0.3</td>
</tr>
<tr>
<td>5</td>
<td>31.20</td>
<td>94</td>
<td></td>
<td>0.012</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>31.49</td>
<td>74</td>
<td></td>
<td>0.049</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Expected links/O-Me 0.1847
Appendix 6 - Size exclusion chromatography data

Lignin C:
NMR results
β-aryl-ethers 0.0%
Phenylcoumaran 0.0%
Resinol 2.1%
Sum of links 2.1%

SEC results

<table>
<thead>
<tr>
<th>Peak</th>
<th>Elution V. (mL)</th>
<th>Mi (g/mol)</th>
<th>Peak area</th>
<th>Hi/Mi</th>
<th>mol fraction</th>
<th># monomers</th>
<th>linkages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>28.52</td>
<td>796</td>
<td>0.006</td>
<td>7.5E-06</td>
<td>1%</td>
<td>4.2</td>
<td>3.2</td>
</tr>
<tr>
<td>Peak 2</td>
<td>29.78</td>
<td>292</td>
<td>0.071</td>
<td>2.4E-04</td>
<td>23%</td>
<td>1.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Peak 3</td>
<td>30.85</td>
<td>124</td>
<td>0.004</td>
<td>2.9E-05</td>
<td>3%</td>
<td>0.6</td>
<td>-0.4</td>
</tr>
<tr>
<td>Peak 4</td>
<td>30.54</td>
<td>159</td>
<td>0.127</td>
<td>8.0E-04</td>
<td>74%</td>
<td>0.8</td>
<td>-0.2</td>
</tr>
</tbody>
</table>

\[
0.208 \quad 1.1E-03 \quad 0.0047
\]

Expected links/O-Me
Appendix 6 - Size exclusion chromatography data

Lignin D:
NMR results
  β-aryl-ethers  0.0%
  Phenylcoumaran  0.0%
  Resinol  1.3%
  Sum of links  1.3%

SEC results

<table>
<thead>
<tr>
<th>Peak</th>
<th>Mi (g/mol)</th>
<th>Peak area</th>
<th>Hi/Mi</th>
<th>mol fraction</th>
<th># monomers</th>
<th>linkages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>28.46</td>
<td>0.0139</td>
<td>0.00002</td>
<td>2%</td>
<td>4.4</td>
<td>3.4</td>
</tr>
<tr>
<td>Peak 2</td>
<td>29.65</td>
<td>0.0913</td>
<td>0.00028</td>
<td>33%</td>
<td>1.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Peak 3</td>
<td>30.75</td>
<td>0.0045</td>
<td>0.00003</td>
<td>4%</td>
<td>0.7</td>
<td>-0.3</td>
</tr>
<tr>
<td>Peak 4</td>
<td>30.91</td>
<td>0.0630</td>
<td>0.00054</td>
<td>62%</td>
<td>0.6</td>
<td>-0.4</td>
</tr>
</tbody>
</table>

\[
\text{Expected links/O-Me} = 0.0234
\]

0.1726  0.00087

Data: AMC8_B
Model: Gauss
\[
\begin{align*}
\text{Chi}^2/\text{DoF} & = 2.1326E-7 \\
R^2 & = 0.99961 \\
y0 & = 0 \pm 0 \\
x_1 & = 28.46322 \pm 0.00895 \\
w_1 & = 0.84512 \pm 0.00982 \\
A_1 & = 0.01387 \pm 0.00049 \\
x_2 & = 29.65034 \pm 0.01301 \\
w_2 & = 1.2266 \pm 0.02052 \\
A_2 & = 0.09128 \pm 0.00739 \\
x_3 & = 30.74839 \pm 0.00003 \\
w_3 & = 0.61444 \pm 0.03249 \\
A_3 & = 0.00446 \pm 0.00004 \\
x_4 & = 30.91493 \pm 0.1281 \\
w_4 & = 1.90898 \pm 0.11683 \\
A_4 & = 0.06296 \pm 0.00045
\end{align*}
\]
Lignin E:
NMR results
\[ \beta\text{-aryl-ethers} \quad 2.0\% \]
\[ \text{Phenylcoumaran} \quad 0.0\% \]
\[ \text{Resinol} \quad 2.8\% \]

Sum of links \( 4.8\% \)

SEC results

<table>
<thead>
<tr>
<th>Peak</th>
<th>Elution V. (mL)</th>
<th>Mi (g/mol)</th>
<th>Peak Area</th>
<th>Area/Mi</th>
<th>Mol fraction</th>
<th># monomers</th>
<th>Linkages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28.43</td>
<td>855</td>
<td>0.0045</td>
<td>5.2E-06</td>
<td>1%</td>
<td>4.5</td>
<td>3.5</td>
</tr>
<tr>
<td>2</td>
<td>29.70</td>
<td>309</td>
<td>0.0354</td>
<td>1.1E-04</td>
<td>16%</td>
<td>1.6</td>
<td>0.6</td>
</tr>
<tr>
<td>3</td>
<td>30.89</td>
<td>120</td>
<td>0.0024</td>
<td>2.0E-05</td>
<td>3%</td>
<td>0.6</td>
<td>-0.4</td>
</tr>
<tr>
<td>4</td>
<td>30.42</td>
<td>174</td>
<td>0.0977</td>
<td>5.6E-04</td>
<td>80%</td>
<td>0.9</td>
<td>-0.1</td>
</tr>
</tbody>
</table>

\[ 0.1399 \quad 7.0E-04 \]

Expected links/O-Me \( 0.0262 \)
Appendix 6 - Size exclusion chromatography data

Lignin F:
NMR results
\( \beta \)-aryl-ethers 0.0%
Phenylcoumaran 0.0%
Resinol 1.0%
Sum of links 1.0%

SEC results

<table>
<thead>
<tr>
<th>Peak</th>
<th>Elution V. (mL)</th>
<th>Mi (g/mol)</th>
<th>Peak area</th>
<th>Hi/Mi</th>
<th>mol fraction</th>
<th># monomers</th>
<th>linkages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>28.373</td>
<td>897</td>
<td>0.011</td>
<td>1.2E-05</td>
<td>1%</td>
<td>4.7</td>
<td>3.7</td>
</tr>
<tr>
<td>Peak 2</td>
<td>29.619</td>
<td>331</td>
<td>0.100</td>
<td>3.0E-04</td>
<td>34%</td>
<td>1.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Peak 3</td>
<td>30.918</td>
<td>117</td>
<td>0.068</td>
<td>5.8E-04</td>
<td>65%</td>
<td>0.6</td>
<td>-0.4</td>
</tr>
</tbody>
</table>

0.179 9.0E-04

Expected links/O-Me 0.0255
Lignin G:
NMR results
\(\beta\)-aryl-ethers 12.2%
Phenylcoumaran 0.0%
Resinol 3.2%
Sum of links 15.4%

SEC results

<table>
<thead>
<tr>
<th>Elution V. (mL)</th>
<th>Mi (g/mol)</th>
<th>Peak area</th>
<th>Hi/Mi</th>
<th>mol fraction</th>
<th># monomers</th>
<th>linkages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>28.42</td>
<td>865</td>
<td>0.0031</td>
<td>3.6E-06 0%</td>
<td>4.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Peak 2</td>
<td>29.84</td>
<td>279</td>
<td>0.0208</td>
<td>7.4E-05 10%</td>
<td>1.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Peak 3</td>
<td>30.60</td>
<td>152</td>
<td>0.0022</td>
<td>1.5E-05 2%</td>
<td>0.8</td>
<td>-0.2</td>
</tr>
<tr>
<td>Peak 4</td>
<td>30.69</td>
<td>140</td>
<td>0.0929</td>
<td>6.6E-04 88%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

0.1190 7.5E-04

Expected links/O-Me 0.1867

***Note the unusually large peak at 140g/mol. It was ignored due to suspected interference from the THF elution.
Appendix 6 - Size exclusion chromatography data

AILG:
NMR results

<table>
<thead>
<tr>
<th>Compound</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-aryl-ethers</td>
<td>2.9%</td>
</tr>
<tr>
<td>Phenylcoumaran</td>
<td>0.0%</td>
</tr>
<tr>
<td>Resinol</td>
<td>3.7%</td>
</tr>
<tr>
<td><strong>Sum of links</strong></td>
<td><strong>6.6%</strong></td>
</tr>
</tbody>
</table>

SEC results

<table>
<thead>
<tr>
<th>Peak</th>
<th>Elution V. (mL)</th>
<th>Mi (g/mol)</th>
<th>Peak area</th>
<th>Hi/Mi</th>
<th>mol fraction</th>
<th># monomers</th>
<th>linkages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>30.18</td>
<td>212</td>
<td>0.0935</td>
<td>0.00044</td>
<td>97%</td>
<td>1.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Peak 2</td>
<td>30.77</td>
<td>132</td>
<td>0.0016</td>
<td>0.00001</td>
<td>3%</td>
<td>0.7</td>
<td>-0.3</td>
</tr>
<tr>
<td>Peak 3</td>
<td><strong>31.45</strong></td>
<td>77</td>
<td><strong>0.0234</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak 4</td>
<td>32.23</td>
<td>41</td>
<td>0.0063</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>0.1247</th>
<th>0.00045</th>
</tr>
</thead>
</table>

Expected links/O-Me 0.0511
Appendix 6 - Size exclusion chromatography data

Lignin Y:
NMR results

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-aryl-ethers</td>
<td>10.7%</td>
</tr>
<tr>
<td>Phenylcoumaran</td>
<td>1.8%</td>
</tr>
<tr>
<td>Resinol</td>
<td>4.5%</td>
</tr>
<tr>
<td><strong>Sum of links</strong></td>
<td><strong>17.0%</strong></td>
</tr>
</tbody>
</table>

SEC results

<table>
<thead>
<tr>
<th>Peak</th>
<th>Elution V. (mL)</th>
<th>Mi (g/mol)</th>
<th>Peak area</th>
<th>Area/Mi</th>
<th>mol fraction</th>
<th># monomers</th>
<th>linkages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>29.13</td>
<td>443</td>
<td>0.195</td>
<td>0.00044</td>
<td>19%</td>
<td>2.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Peak 2</td>
<td>29.95</td>
<td>229</td>
<td>0.280</td>
<td>0.00122</td>
<td>53%</td>
<td>1.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Peak 3</td>
<td>30.83</td>
<td>114</td>
<td>0.074</td>
<td>0.00065</td>
<td>28%</td>
<td>0.6</td>
<td>-0.4</td>
</tr>
<tr>
<td>Peak 4</td>
<td>31.53</td>
<td>65</td>
<td>0.083</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak 5</td>
<td>32.52</td>
<td>29</td>
<td>0.171</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Expected links/O-Me | 0.112 |

<table>
<thead>
<tr>
<th>Data: LIGNINX_B</th>
<th>Model: Gauss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chi^2/DoF</td>
<td>2.6438E-7</td>
</tr>
<tr>
<td>R^2</td>
<td>0.99997</td>
</tr>
<tr>
<td>y0</td>
<td>0 ±0</td>
</tr>
<tr>
<td>xc1</td>
<td>29.13164 ±0.02389</td>
</tr>
<tr>
<td>w1</td>
<td>1.16823 ±0.01457</td>
</tr>
<tr>
<td>A1</td>
<td>0.19471 ±0.01182</td>
</tr>
<tr>
<td>xc2</td>
<td>29.95409 ±0.01298</td>
</tr>
<tr>
<td>w2</td>
<td>1.06503 ±0.01425</td>
</tr>
<tr>
<td>A2</td>
<td>0.28045 ±0.01093</td>
</tr>
<tr>
<td>xc3</td>
<td>30.83037 ±0.00482</td>
</tr>
<tr>
<td>w3</td>
<td>0.73192 ±0.00871</td>
</tr>
<tr>
<td>A3</td>
<td>0.07434 ±0.0043</td>
</tr>
<tr>
<td>xc4</td>
<td>31.53217 ±0.0208</td>
</tr>
<tr>
<td>w4</td>
<td>1.01497 ±0.00723</td>
</tr>
<tr>
<td>A4</td>
<td>0.08261 ±0.0126</td>
</tr>
<tr>
<td>xc5</td>
<td>32.5205 ±0.1742</td>
</tr>
<tr>
<td>w5</td>
<td>2.70583 ±0.35849</td>
</tr>
<tr>
<td>A5</td>
<td>0.17123 ±0.02855</td>
</tr>
</tbody>
</table>
Appendix 6 - Size exclusion chromatography data

Lignin Z:
NMR results

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-aryl-ethers</td>
<td>16.4%</td>
</tr>
<tr>
<td>Phenylcoumaran</td>
<td>1.3%</td>
</tr>
<tr>
<td>Resinol</td>
<td>5.6%</td>
</tr>
<tr>
<td><strong>Sum of links</strong></td>
<td><strong>23.3%</strong></td>
</tr>
</tbody>
</table>

SEC results

<table>
<thead>
<tr>
<th>Peak</th>
<th>Elution V. (mL)</th>
<th>Mi (g/mol)</th>
<th>Peak area</th>
<th>Hi/Mi</th>
<th>mol fraction</th>
<th># monomers</th>
<th>linkages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29.01</td>
<td>488</td>
<td>0.254</td>
<td>0.00052</td>
<td>44%</td>
<td>2.5</td>
<td>1.5</td>
</tr>
<tr>
<td>2</td>
<td>29.77</td>
<td>265</td>
<td>0.060</td>
<td>0.00023</td>
<td>19%</td>
<td>1.4</td>
<td>0.4</td>
</tr>
<tr>
<td>3</td>
<td>30.38</td>
<td>163</td>
<td>0.071</td>
<td>0.00044</td>
<td>37%</td>
<td>0.8</td>
<td>-0.2</td>
</tr>
<tr>
<td>4</td>
<td>31.16</td>
<td>87</td>
<td>0.269</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>33.16</td>
<td>18</td>
<td>0.086</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Expected links/O-Me</th>
<th>0.241</th>
</tr>
</thead>
</table>
BioJoule Ltd Lignin:
SEC results

<table>
<thead>
<tr>
<th>Peak</th>
<th>Elution V. (mL)</th>
<th>Mi (g/mol)</th>
<th>Peak area</th>
<th>Hi/Mi fraction</th>
<th>mol fraction</th>
<th># monomers</th>
<th>linkages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>29.24</td>
<td>406</td>
<td>0.216</td>
<td>0.00053</td>
<td>38%</td>
<td>2.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Peak 2</td>
<td>30.02</td>
<td>218</td>
<td>0.132</td>
<td>0.00060</td>
<td>43%</td>
<td>1.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Peak 3</td>
<td>30.74</td>
<td>122</td>
<td>0.031</td>
<td>0.00025</td>
<td>18%</td>
<td>0.6</td>
<td>-0.4</td>
</tr>
<tr>
<td>Peak 4</td>
<td>31.16</td>
<td>87</td>
<td>0.119</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak 5</td>
<td>32.74</td>
<td>25</td>
<td>0.228</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Expected links/O-Me 0.174
Appendix 6 - Size exclusion chromatography data

Peak positions indicate lignins having molecular weight less than one lignin unit in size. This suggests the method of size exclusion chromatography was flawed.

<table>
<thead>
<tr>
<th></th>
<th>Sum of links by NMR</th>
<th>Expected links by SEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.129</td>
<td>0.03818832</td>
</tr>
<tr>
<td>A.replicate</td>
<td>0.129</td>
<td>0.037288113</td>
</tr>
<tr>
<td>B</td>
<td>0.097</td>
<td>0.182542593</td>
</tr>
<tr>
<td>C</td>
<td>0.021</td>
<td>0.001676783</td>
</tr>
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The method shows that an estimate of lignin linkages can be determined by SEC. Note that lignin G had an extra peak removed (at 140g/mol) due to suspected interference by the THF elution.
Appendix 7. DSC thermograms

The spectra shown in this appendix are dynamic DSC thermograms of resin samples. The legend indicates what heating rate and resin was used. The final peak temperature at maximum is used as the exotherm temperature, $T_p$.

The raw data obtained from these spectra are summarised below.

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<th>Heat rate, $\varphi$ (°C/min)</th>
<th>No lignin 1 $T_p$</th>
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$d\text{log}e/dT_p$ | -3986 | -3740 | -6211 | -4371 | -4142 | -5279 | -4180 |

$E_a$ (kJ/mol) | 73 | 68 | 113 | 80 | 75 | 96 | 76 |

Average $E_a$ (kJ/mol) | 85 | 77 | 86 |

$\sigma$ | 25 | 3 | 14 |
### Appendix 7 - DSC thermograms

<table>
<thead>
<tr>
<th>Heat rate, $\varphi$ ($^\circ$C/min)</th>
<th>Lignin C1</th>
<th>Lignin C2</th>
<th>Lignin D1</th>
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$E_a$ (kJ/mol) | -6159 | -4607 | -4813 | -4547 | -4788 | -4925 |

Average $E_a$ (kJ/mol) | 98 | 85 | 88 |

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$E_a$ (kJ/mol) | -4333 | -4505 | -4822 | -4950 |

Average $E_a$ (kJ/mol) | 80 | 89 |

| $\sigma$ | 2 | 2 |
Appendix 7 - DSC thermograms

[Graph showing DSC thermograms for various samples with temperatures and rates indicated]