

Catalytic hydrothermal liquefaction of industrial lignin to bio-oil

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1 **Abstract**

2 The negative implications of the world's current fossil fuel systems are driving researchers
3 to search for alternative energy resources. One of the alternative energy resources that has
4 received attention is renewable fuels produced from oils other than crude oil. However at
5 the moment, renewable fuels cannot compete with traditional fossil fuels due to
6 complications from the production process, lower energy contents and high costs
7 associated with the production. Therefore, if it is possible to improve on the process or even
8 the quality of the feed (bio-oil), an end product with the potential to compete with gasoline
9 or diesel may be produced. Bio-oil produced through hydrothermal liquefaction of non-
10 edible lignocellulosic waste could be the solution. However, the utilisation of bio-oil
11 produced by means of hydrothermal liquefaction as feedstock for biofuel production poses
12 challenges in terms of varying quality of the bio-oil. This can be attributed to the utilisation
13 of different types of biomass and the application of different reaction conditions during
14 hydrothermal liquefaction. This study was aimed at improving the quality of the bio-oil in
15 order to be more compatible with current processes and to improve the efficiency of the
16 renewable fuel production process.

17 In this study, bio-oil was produced from sodium lignosulphonate using ethanol as the
18 solvent and sodium hydroxide as a catalyst at varying process conditions such as reaction
19 temperature (240–320°C), residence time (20–80 min), and catalyst loading (2–6 mass%).
20 The feedstock, solvent and catalyst were mixed together and placed under anaerobic
21 conditions, using nitrogen, inside a hydrothermal liquefaction reactor for the selected time
22 and temperature to produce the bio-oil and other products. After which the products were
23 separated by venting the gas and washing the liquid product from the biochar with acetone
24 and a Büchner funnel. Rotary evaporation was used to obtain the bio-oil. The bio-oils'
25 properties and composition were determined using elemental analysis for the elemental
26 composition, Gel Permeation Chromatography (GPC) to determine the average molecular
27 weight and polydisperse index, Fourier Transform- Infrared spectroscopy (FTIR) to identify
28 functional groups present in the bio-oil, calorific values (CV) to determine the energy
29 content, Nuclear Magnetic Resonance spectroscopy (NMR) to assist in clarifying which
30 functional groups are present and Gas Chromatography coupled with mass spectrometry
31 (GC-MS) to determine which chemical compounds were present after hydrothermal
32 liquefaction.

33 The findings showed that the reaction variables affected the bio-oil's yield and quality. A
34 combined effect was also observed and measured with a severity factor. Residence time

had a larger effect on bio-oil yield at low temperatures, this could be seen in the variation of the severity factor from 5.42 to 6.03 at 240°C. As the reaction temperature increased however, residence time was less influential as seen when the severity factor variation decreases. To achieve higher yields of bio-oil, a higher catalyst loading (5 mass%) was advantageously combined with low temperatures (240°C) and longer residence times (40 min) as it increased the bio-oil yield (20.83 mass%) at the expense of gas production (11.04 mass%). For improved bio-oil quality, higher temperatures were required combined with lower catalyst loadings and shorter residence times. Longer residence times might have provided deeper depolymerisation but promoted repolymerisation; thus, increasing the number of heavy compounds that are present in the bio-oil as seen when the molecular weight and PDI increased from 198 g/mol and 1.8 at 60 min and 320°C to 342 g/mol and 2, respectively when the residence time was increased by 20 min. Shorter residence times produced a bio-oil with a larger diesel fraction (± 77 mass%), smaller molecular weights and less heavy compounds, with a high carbon recovery.

This study found that a change in reaction temperature had a larger effect than residence time on the quality and quantity of the bio-oil. It seemed as though temperature mostly encouraged decomposition and depolymerization, while residence time controlled the rate of repolymerization. However, it is important to consider the combined effect of the two variables. The loading of an alkali catalyst effected the process by enhancing the effects of reaction temperature and residence time while also decreasing the rate at which cracking reactions are taking place. However the rate of repolymerization was accelerated by the increase in catalyst loading. This study showed that due to the combined effect of the variables, the severity factors can be used as a design tool to predict the outcome of a process with different parameter requirements. It is recommended that more hydrogen-donating solvents and their effect on the bio-oil and Lignex® fractionation be investigated. This study also found that the produced bio-oil contained a large amount of compounds that may have pharmaceutical applications.

Keywords: bio-oil; hydrothermal liquefaction; lignosulphonate; severity factor

1 **Declaration of authorship**

2 I declare that this report is a presentation of my own original work. Whenever contributions
3 of others are involved, every effort was made to indicate this clearly, with due reference to
4 the literature.

5 No part of this work has been submitted in the past or is being submitted, for a degree or
6 examination at any other university or course.

7 Signed on this, 20th day of November 2021 in Pretoria.

8



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10 **D Bartlett**

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1	Table of contents	
2	Acknowledgements.....	i
3	Abstract	ii
4	Declaration of authorship	iv
5	List of figures	xi
6	List of tables	xvi
7	List of abbreviations	xix
8	Nomenclature	xx
9	1 Introduction.....	1
10	1.1 Background	1
11	1.2 Motivation	2
12	1.3 Research problem	4
13	1.4 Aim	4
14	1.5 Objectives.....	4
15	1.6 Scope	5
16	1.7 Dissertation outline	5
17	2 Literature Review.....	7
18	2.1 Renewable fuel.....	7
19	2.1.1 Background	7
20	2.1.2 Description of renewable fuel.....	7
21	2.1.2.1 First-generation biofuels	7
22	2.1.2.2 Second-generation biofuels	8
23	2.1.2.3 Third-generation biofuels	8
24	2.1.2.4 Fourth-generation biofuels	9
25	2.1.3 Production of biofuels from lignocellulosic materials	9
26	2.1.3.1 Bioethanol production	9
27	2.1.3.2 Bioethanol produced from corn	10
28	2.1.3.3 Bioethanol produced from sugarcane	10
29	2.1.3.4 Biochemical production of second-generation bioethanol	10

1	2.1.3.5 Biodiesel production	11
2	2.1.3.5.1 Thermal cracking.....	11
3	2.1.3.5.2 Micro-emulsion.....	11
4	2.1.3.5.3 Transesterification.....	12
5	2.1.4 Advantages of renewable fuel.....	12
6	2.1.5 Challenges of the biorefinery processes	12
7	2.2 Description of biomass	13
8	2.3 Lignin extraction and lignocellulosic biomass pre-treatment methods	15
9	2.3.1 Acidolysis of lignin	15
10	2.3.2 Alkaline hydrolysis of lignosulphonates.....	16
11	2.3.3 Cellulolytic enzyme lignin.....	16
12	2.3.4 Co-solvent enhanced lignocellulosic fractionation.....	17
13	2.3.5 Ionic liquid degradation of lignin.....	17
14	2.3.6 Kraft pulping process	17
15	2.3.7 Milled wood lignin	18
16	2.3.8 Organosolv pulping method	18
17	2.3.9 Sulphite pulping process.....	19
18	2.3.10 Sequential dissolution of lignin fractions	21
19	2.3.11 Steam explosion pre-treatment.....	21
20	2.4 Description of lignin	21
21	2.4.1 Chemical composition of lignin	22
22	2.4.2 Lignin bond types	23
23	2.4.3 Lignin properties	25
24	2.4.4 Lignin characterisation methods	25
25	2.4.5 Valuable products derived from lignin	28
26	2.5 Biomass conversion methods	29
27	2.6 Thermochemical conversion	29
28	2.6.1 Methods.....	29
29	2.6.2 Thermochemical conversion products.....	31

1	2.6.2.1	Biochar	31
2	2.6.2.2	Bio-oil	32
3	2.6.2.3	Biogas	32
4	2.7	Depolymerisation and conversion of lignin	33
5	2.7.1	Lignin conversion pathways.....	33
6	2.8	Bio-oil and its significance.....	33
7	2.8.1	Composition of bio-oil	34
8	2.8.2	Properties of bio-oil.....	35
9	2.8.2.1	The effect of temperature on bio-oil properties.....	37
10	2.8.2.2	The effect of residence time on bio-oil properties.....	38
11	2.8.2.3	The effect of catalyst loading on bio-oil properties	39
12	2.8.2.4	The effect of solvents on bio-oil properties.....	39
13	2.8.2.5	The combined effect of reaction parameters on the properties of bio-oil	
14		expressed as severity factors.....	39
15	2.8.3	Bio-oil applications.....	40
16	2.8.3.1	Bio-oil as an energy-rich fuel	41
17	2.8.3.2	Bio-oil as a high-value chemical source	42
18	2.8.4	Upgrading methods for bio-oil.....	43
19	3	Experimental methods	44
20	3.1	Materials.....	44
21	3.2	Methods.....	45
22	3.2.1	Phase 1: Sampling and preparation of Lignex®	45
23	3.2.2	Phase 2: Lignin fractionation.....	45
24	3.2.3	Phase 3: Hydrothermal liquefaction	47
25	3.2.3.1	Washing of reactor.....	47
26	3.2.3.2	Loading.....	47
27	3.2.3.3	Hydrothermal liquefaction procedure	47
28	3.2.3.4	Separation of bio-oil and biochar	48
29	3.2.3.5	Part 1: Catalyst comparison.....	48

1	3.2.3.6	Part 2: Investigating the effect of temperature and residence time.....	48
2	3.2.3.7	Part 3: Investigating the effect of catalyst loading	49
3	3.2.3.8	Part 4: Investigating the effect of different solvents.....	49
4	3.3	Analyses.....	50
5	3.3.1	Karl Fischer titration.....	50
6	3.3.2	Elemental analysis.....	50
7	3.3.3	GC-MS analysis.....	51
8	3.3.4	GPC analysis.....	51
9	3.3.5	NMR analysis	52
10	3.3.6	ICP-OES aqueous analysis	52
11	3.3.7	Proximate analysis.....	53
12	3.3.8	FTIR analysis.....	54
13	3.3.9	CV analysis	54
14	3.3.10	Rotary evaporator.....	55
15	4	Results and Discussion.....	56
16	4.1	Characterization of Lignex®.....	56
17	4.1.1	Introduction.....	56
18	4.1.2	Chemical properties.....	56
19	4.1.2.1	Major constituents	56
20	4.1.2.2	Elemental composition.....	57
21	4.1.2.3	Cation and anion content.....	57
22	4.1.2.4	Energy value.....	58
23	4.1.2.5	Molecular size distribution.....	58
24	4.1.2.6	FTIR analysis of Lignex®.....	59
25	4.1.2.7	NMR	62
26	4.1.3	Fractionation and characterisation of Lignex® feedstock	62
27	4.1.3.1	Hexane-soluble fraction	63
28	4.1.3.2	THF-soluble fraction	66
29	4.1.3.3	Acetone-soluble fraction	69

1	4.1.3.4	Ethanol-soluble fraction	71
2	4.1.3.5	Methanol-soluble fraction.....	73
3	4.2	The effect of different alkali catalysts on the bio-oil yield during HTL	79
4	4.3	The effect of liquefaction solvent on bio-oil yield and quality	80
5	4.3.1	The effect of liquefaction solvent on bio-oil yield	80
6	4.3.2	The effect of liquefaction solvent on bio-oil quality	80
7	4.3.2.1	The molecular weight distribution of the bio-oils.....	81
8	4.3.2.2	Effect of solvents on the chemical composition of the bio-oil.....	82
9	4.3.2.3	Functional groups of the bio-oil	83
10	4.3.2.4	Inorganic compounds present in the bio-oil.....	84
11	4.3.2.5	Elemental composition and energy contents of bio-oil	86
12	4.4	The effect of process variables on liquefaction product yields.....	89
13	4.4.1	The effect of reaction temperature on product yield	91
14	4.4.2	The effect of residence time on product yield.....	95
15	4.4.3	The effect of catalyst loading on product yield	99
16	4.5	The effect of process variables on liquefaction product quality	101
17	4.5.1	The effect of reaction temperature on product quality	101
18	4.5.1.1	Elemental composition of products	101
19	4.5.1.1.1	Elemental composition of bio-oil.....	101
20	4.5.1.1.2	Elemental composition of biochar.....	103
21	4.5.1.2	Energy content of products.....	106
22	4.5.1.2.1	Energy content of bio-oil.....	106
23	4.5.1.2.2	Energy content of biochar	107
24	4.5.1.3	Molecular weight distribution of bio-oils.....	108
25	4.5.1.4	Chemical composition of products	111
26	4.5.1.4.1	Boiling fractions of bio-oils.....	111
27	4.5.1.4.2	Functional and chemical groups of bio-oils.....	114
28	4.5.1.4.3	Interesting compounds found in bio-oils	117
29	4.5.1.4.4	Confirmation of chemical groups in bio-oils	120

1	4.5.1.4.5	Functional groups of biochars	121
2	4.5.2	The effect of residence time on product quality	122
3	4.5.2.1	Elemental composition of products	122
4	4.5.2.1.1	Elemental composition of bio-oil.....	122
5	4.5.2.1.2	Elemental composition of biochar.....	124
6	4.5.2.2	Energy content of products.....	126
7	4.5.2.2.1	Energy content of bio-oil.....	126
8	4.5.2.2.2	Energy content of biochar	127
9	4.5.2.3	Molecular weight distribution of bio-oils.....	127
10	4.5.2.4	Chemical composition of product.....	130
11	4.5.2.4.1	Boiling fractions of bio-oils.....	130
12	4.5.2.4.2	Functional and chemical groups of bio-oils.....	133
13	4.5.2.4.3	Confirmation of chemical groups in the bio-oils	135
14	4.5.2.4.4	Functional groups of biochars	135
15	4.5.3	The effect of catalyst loading on product quality	137
16	4.5.3.1	Elemental composition of products	137
17	4.5.3.1.1	Elemental composition of bio-oil.....	137
18	4.5.3.1.2	Elemental composition of biochar.....	138
19	4.5.3.2	Energy content of products.....	139
20	4.5.3.2.1	Energy content of bio-oil.....	139
21	4.5.3.2.2	Energy content of biochar	140
22	4.5.3.3	Molecular weight distribution of bio-oils.....	141
23	4.5.3.4	Chemical composition of products	142
24	4.5.3.4.1	Boiling fractions of bio-oils.....	142
25	4.5.3.4.2	Functional and chemical groups of bio-oils.....	144
26	4.5.3.4.3	Interesting compounds found in bio-oils	145
27	4.5.3.4.4	Confirmation of functional and chemical groups in bio-oils	146
28	4.5.3.4.5	Functional groups of biochars	146
29	5	Conclusions and Recommendations.....	147

1	5.1	Conclusions	147
2	5.1.1	Effect of reaction temperature and residence time on bio-oil.....	147
3	5.1.2	Effect of catalyst loading on bio-oil.....	148
4	5.2	Evaluation of objectives	148
5	5.3	Recommendations.....	148
6	6	References	150
7	7	Appendix A: Calculation methods and descriptions.....	156
8	7.1	Product yield calculation	156
9	7.2	Proximate analysis.....	156
10	7.3	Experimental error calculation	156
11	8	Appendix B: Additional data	158
12	8.1	From literature	158
13	8.2	Feedstock properties	159
14	8.3	Product yields	160
15	8.4	Quality analysis on bio-oils	165
16	9	Appendix C: Additional data for biochar	198
17	9.1	Biochar quality	198

18

19 List of figures

20	Fig. 1. The alkaline hydrolysis process of lignosulphonates (Aro & Fatehi, 2017)	16
21	Fig. 2. Reactions of the acidic sulphite pulping process on guaiacyl, adapted from Aro &	
22	Fatehi (2017)	19
23	Fig. 3. Reactions that occur on guaiacyl during the neutral sulphite pulping process,	
24	adapted from Aro & Fatehi (2017).....	20
25	Fig. 4 The molecular structure of lignin (Lu <i>et al.</i> , 2017).....	22
26	Fig. 5. Schematic representation of the structure of lignin including constituents and lignin-	
27	lignin linkages (Lupoi <i>et al.</i> , 2015).....	24
28	Fig. 6. NMR signal assignments for lignin (Lu <i>et al.</i> , 2017).....	26
29	Fig. 7. FTIR peak assignments of lignin samples (Lu <i>et al.</i> , 2017)	27
30	Fig. 8. Reaction mechanism of the HTL process, adapted from Gollakota <i>et al.</i> (2018) ...	31
31	Fig. 9. Conversion of biomass to biochar, (Lee <i>et al.</i> , 2017).....	31

1	Fig. 10. Karl Fischer titrator.....	50
2	Fig. 11. Elemental analyser.....	50
3	Fig. 12. A gas chromatography-mass spectrometry instrument.....	51
4	Fig. 13. Gel permeation chromatography instrument.....	51
5	Fig. 14. Furnace oven.....	53
6	Fig. 15. FTIR analysis equipment.....	54
7	Fig. 16. Calorific value analyser (BOMB calorimeter)	54
8	Fig. 17. Molecular weight distribution of raw Lignex®	59
9	Fig. 18. FTIR spectrum of raw Lignex®.....	61
10	Fig. 19. COSY NMR spectrum of Lignex®	62
11	Fig. 20. Mass fractions extracted with various organic solvents	63
12	Fig. 21. Chemical composition of the fraction extracted with hexane	64
13	Fig. 22. FTIR spectrum of fraction extracted with hexane	65
14	Fig. 23. NMR spectrum of the residue extracted with hexane	65
15	Fig. 24. Molecular weight distribution of residue extracted with THF	67
16	Fig. 25. Chemical composition of the fraction extracted with THF	67
17	Fig. 26. FTIR spectrum of residue extracted with THF	68
18	Fig. 27 . NMR spectrum of THF-soluble fraction	69
19	Fig. 28. FTIR spectrum of residue extracted with acetone	70
20	Fig. 29. NMR spectrum of the acetone-soluble fraction.....	70
21	Fig. 30. Molecular weight distribution of residue extracted with ethanol	72
22	Fig. 31. FTIR spectrum of residue extracted with ethanol	72
23	Fig. 32. NMR spectrum of residue extracted with ethanol	73
24	Fig. 33. Molecular mass distribution of the fraction extracted with methanol	74
25	Fig. 34. Chemical composition of the fraction extracted with methanol	75
26	Fig. 35. FTIR spectrum of the residue extracted with methanol.....	76
27	Fig. 36. NMR spectrum of the methanol-extracted fraction (Van der Merwe, 2020)	76
28	Fig. 37. Product yields from different catalysts	79
29	Fig. 38. Chemical groups of bio-oils produced in the presence of different solvents as	
30	analysed with GC-MS	83
31	Fig. 39. FTIR spectra of the bio-oils produced by the three pure solvents (Esterhuizen,	
32	2020)	84
33	Fig. 40. All HTL product yields	89
34	Fig. 41. Product yields with a residence time of 20 min.....	91
35	Fig. 42. Severity factor of products produced with a residence time of 20 min	92
36	Fig. 43. Product yields with a residence time of 80 min.....	93
37	Fig. 44. Severity factor of products formed with a residence time of 80 min	94

1	Fig. 45. HTL product yields with a reaction temperature of 260°C.....	96
2	Fig. 46. Severity factor of products formed at 260°C.....	96
3	Fig. 47. HTL product yields with a reaction temperature of 300°C.....	97
4	Fig. 48. Severity factor of products formed at 300°C.....	98
5	Fig. 49. HTL product yields with different catalyst loadings	99
6	Fig. 50. Effect of catalyst loading on product recoveries expressed as severity factors..	100
7	Fig. 51. Elemental composition of bio-oils formed with 20 min residence time	102
8	Fig. 52. Elemental composition of bio-oils produced with 80 min residence time.....	103
9	Fig. 53. Elemental composition of biochar produced with a short residence time (20 min)	
10		105
11	Fig. 54. Elemental composition of biochar produced with a long residence time (80 min)	
12		106
13	Fig. 55. Molecular weight distribution curve of bio-oils produced with a 20 min residence	
14	time.....	109
15	Fig. 56. Molecular weight distribution curve of bio-oils produced with an 80 min residence	
16	time.....	111
17	Fig. 57. Simulated distillation curve of bio-oils produced with a 20 min residence time ..	113
18	Fig. 58. Simulated distillation curve of bio-oils produced with a residence time of 80 min	
19		114
20	Fig. 59. Quantification of chemical groups that were present in bio-oils produced with a 20	
21	min residence time.....	115
22	Fig. 60. Quantification of chemical groups that are present in bio-oils produced with an 80	
23	min residence time.....	116
24	Fig. 61. Overlay of all the bio-oils' NMR DOSY spectrums	121
25	Fig. 62. Elemental composition of bio-oils formed at a low reaction temperature	123
26	Fig. 63. Elemental composition of bio-oils formed at a high reaction temperature	123
27	Fig. 64. Elemental composition of biochar produced with a low reaction temperature	124
28	Fig. 65. Elemental composition of bio-oils formed at a high reaction temperature	124
29	Fig. 66. Elemental composition of biochar produced with a high reaction temperature...	125
30	Fig. 67. Molecular weight distribution of bio-oils produced at a low temperature	129
31	Fig. 68. Molecular weight distribution of bio-oils produced at a high temperature.....	130
32	Fig. 69. Distillation curves of all bio-oils produced at a low temperature (260°C).....	131
33	Fig. 70. Distillation curves of all bio-oils produced at a high temperature (300°C)	132
34	Fig. 71. Quantification of chemical groups present in bio-oils produced at a low	
35	temperature	133
36	Fig. 72. Quantification of chemical groups present in bio-oils produced at a high	
37	temperature	134

1	Fig. 73. Elemental composition of bio-oils formed with various catalyst loadings	137
2	Fig. 74. Elemental composition of biochars formed with various catalyst loadings	139
3	Fig. 75. Molecular weight distribution curve of bio-oil produced with varying catalyst	
4	loading	142
5	Fig. 76. Simulated boiling curve of bio-oil produced with varied catalyst loading	143
6	Fig. 77. Quantification of chemical groups in bio-oils produced with various catalyst	
7	loadings	144
8	Fig. 78. Product yields with a residence time of 40 min (Dry ash-free)	160
9	Fig. 79. Severity factor of products formed with 40 min	160
10	Fig. 80. Product yields with a residence time of 60 min (dry ash-free)	161
11	Fig. 81. Severity factor of products formed with 60 min	161
12	Fig. 82. Product yields with a reaction temperature of 240°C (dry ash-free)	162
13	Fig. 83. Severity factor of products formed at 240°C	162
14	Fig. 84. Product yields with a reaction temperature of 280°C (dry ash-free)	163
15	Fig. 85. Severity factor of products formed at 280°C	163
16	Fig. 86. Product yields with a reaction temperature of 320°C (dry ash-free)	164
17	Fig. 87. Severity factor of products formed at 320°C	164
18	Fig. 88. Elemental composition of bio-oils formed with 40 min residence time	166
19	Fig. 89. Elemental composition of bio-oils formed with 60 min residence time	167
20	Fig. 90. Molecular weight distribution of bio-oils produced with 40 min residence time...	169
21	Fig. 91. Molecular weight distribution of bio-oils produced with 60 min residence time...	170
22	Fig. 92. Simulated distillation curve of bio-oils produced with a 40 min residence time ..	171
23	Fig. 93. Quantification of chemical groups that are present in bio-oils produced with a 40	
24	min residence time	172
25	Fig. 94. Simulated distillation curve of bio-oils produced with a 60 min residence time ..	172
26	Fig. 95. Quantification of chemical groups that are present in bio-oils produced with a 60	
27	min residence time	173
28	Fig. 96. FTIR spectra of bio-oils produced with a 20 min residence time	174
29	Fig. 97. FTIR spectra of bio-oils produced with a 40 min residence time	175
30	Fig. 98. FTIR spectra of bio-oils produced with a 60 min residence time	176
31	Fig. 99. FTIR spectra of bio-oils produced with an 80 min residence time	177
32	Fig. 100. HSQC NMR spectrums	178
33	Fig. 101. Enlargement of region A	178
34	Fig. 102. Overlay of all the bio-oils' NMR DOSY spectrums	178
35	Fig. 103. Enlargement of region B	179
36	Fig. 104. Enlargement of region C	179
37	Fig. 105. Elemental composition of bio-oils formed at 240°C reaction temperature	181

1	Fig. 106. Elemental composition of bio-oils formed at 280°C reaction temperature	181
2	Fig. 107. Elemental composition of bio-oils formed at 320°C reaction temperature	182
3	Fig. 108. Molecular weight distribution of bio-oils produced at 240°C.....	184
4	Fig. 109. Molecular weight distribution of bio-oils produced at 280°C.....	185
5	Fig. 110. Molecular weight distribution of bio-oils produced at 320°C.....	186
6	Fig. 111. Simulated distillation curve of bio-oils produced at 240°C.....	187
7	Fig. 112. Simulated distillation curve of bio-oils produced at 280°C	188
8	Fig. 113. Simulated distillation curve of bio-oils produced at 320°C	189
9	Fig. 114. Quantification of chemical groups that are present in bio-oils produced at 240°C	
10		189
11	Fig. 115. Quantification of chemical groups that are present in bio-oils produced at 280°C	
12		190
13	Fig. 116. Quantification of chemical groups that are present in bio-oils produced at 320°C	
14		190
15	Fig. 117. FTIR spectrum of all bio-oils produced at 240°C	191
16	Fig. 118. FTIR spectrum of all bio-oils produced at 260°C	192
17	Fig. 119. FTIR spectrum of all bio-oils produced at 280°C	193
18	Fig. 120. FTIR spectrum of all bio-oils produced at 300°C	194
19	Fig. 121. FTIR spectrum of all bio-oils produced at 320°C	195
20	Fig. 122. FTIR spectrum of all bio-oils produced with various catalyst loadings	197
21	Fig. 123. Elemental recovery through biochars produced with 40 min residence times ..	200
22	Fig. 124. Elemental recovery through biochars produced with 60 min residence times ..	201
23	Fig. 125. Elemental recovery through biochars produced at 240°C.....	203
24	Fig. 126. Elemental recovery through biochars produced at 280°C.....	204
25	Fig. 127. Elemental recovery through biochars produced at 320°C.....	205
26	Fig. 128. FTIR spectra of biochars produced with a 20 min residence time.....	207
27	Fig. 129. FTIR spectra of biochars produced with a 40 min residence time.....	208
28	Fig. 130. FTIR spectra of biochars produced with a 60 min residence time.....	209
29	Fig. 131. FTIR spectra of biochars produced with an 80 min residence time.....	210
30	Fig. 132. FTIR spectrum of all biochars produced at 240°C	211
31	Fig. 133. FTIR spectrum of all biochars produced at 260°C	212
32	Fig. 134. FTIR spectrum of all biochars produced at 280°C	213
33	Fig. 135. FTIR spectrum of all biochars produced at 300°C	214
34	Fig. 136. FTIR spectrum of all biochars produced at 320°C	215
35	Fig. 137. FTIR spectrum of all biochars produced with various catalyst loadings	217
36		

1 List of tables

2	Table 2-1. NMR signal assignments for lignin (Lu et al., 2017)	26
3	Table 2-2. FTIR peak assignments of lignin samples (Lu et al., 2017)	27
4	Table 3-1. Materials information.....	44
5	Table 3-2. Fractionation solvents and important properties	46
6	Table 4-1. Proximate results of Lignex®	56
7	Table 4-2. Elemental composition	57
8	Table 4-3. IC analysis of the raw Lignex®.....	57
9	Table 4-4. Molecular size distribution of Lignex®	59
10	Table 4-5. FTIR assignment of functional groups present in Lignex®	60
11	Table 4-6. GPC analysis of bio-oils produced with various pure solvents.....	81
12	Table 4-7. FTIR peaks and the corresponding functional groups (Esterhuizen, 2020).....	83
13	Table 4-8. Inorganic contents of bio-oil produced with various solvents	85
14	Table 4-9. Average moisture contents of bio-oils produced.....	85
15	Table 4-10. Elemental composition of bio-oils produced with different solvents	86
16	Table 4-11. Energy properties of the bio-oils.....	86
17	Table 4-12. Elemental ratios of bio-oils produced with various reaction temperatures....	101
18	Table 4-13. Elemental ratios of biochars produced with 20 min residence time.....	105
19	Table 4-14. CVs of bio-oils produced with a residence time of 20 min	107
20	Table 4-15. CVs of bio-oils produced with a residence time of 60 min	107
21	Table 4-16. CVs of biochars produced with a residence time of 20 min	108
22	Table 4-17. CVs of biochars produced with a residence time of 60 min	108
23	Table 4-18. GPC analysis of bio-oils produced with a residence time of 20 min.....	109
24	Table 4-19. GPC analysis of bio-oils produced with a residence time of 80 min.....	110
25	Table 4-20. Boiling ranges classification	112
26	Table 4-21. Boiling fractions' distribution of bio-oil compounds (20 min)	112
27	Table 4-22. Boiling fractions' distribution of bio-oil compounds (80 min)	114
28	Table 4-23. Elemental ratios of bio-oils produced with various residence times	122
29	Table 4-24. Elemental ratios of biochars produced with various residence times	125
30	Table 4-25. CVs of bio-oils produced with a low reaction temperature (260°C)	126
31	Table 4-26. CVs of bio-oils produced with a high reaction temperature (300°C).....	126
32	Table 4-27. CVs of biochars produced with a low reaction temperature (260°C).....	127
33	Table 4-28. Calorific values of biochars produced with a high reaction temperature	
34	(300°C)	127
35	Table 4-29. GPC analysis of bio-oils produced at a low temperature (260°C)	128
36	Table 4-30. GPC analysis of bio-oils produced at a high temperature (300°C).....	129

1	Table 4-31. Boiling fractions' distribution of bio-oil compounds at a low temperature	131
2	Table 4-32. Boiling fractions' distribution of bio-oil compounds at a high temperature....	131
3	Table 4-33. Elemental ratios of bio-oils produced with various catalyst loadings.....	138
4	Table 4-34. Elemental ratios of biochars produced with various catalyst loadings.....	139
5	Table 4-35. CVs of bio-oils produced with various catalyst loadings	140
6	Table 4-36. . CVs of biochars produced with various catalyst loadings	140
7	Table 4-37. GPC analysis of bio-oils produced with varying catalyst loading	141
8	Table 4-38. Boiling fractions' distribution of bio-oil compounds produced with various	
9	catalyst loadings	143
10	Table 8-1. NMR peak assignments	158
11	Table 8-2. Functional groups and structures identified within lignosulphonates (Rodríguez-	
12	Lucena <i>et al.</i> , 2009)	158
13	Table 8-3. Typical properties of standard bio-oil compared with fossil fuels (Sánchez-	
14	Borrego <i>et al.</i> , 2021)	159
15	Table 8-4. IC results of ashed Lignex® material.....	159
16	Table 8-5. Elemental ratios of bio-oils produced with various reaction temperatures	165
17	Table 8-6. Elemental composition of bio-oils produced with 20 min	165
18	Table 8-7. Elemental composition of bio-oils produced with 40 min	165
19	Table 8-8. Elemental composition of bio-oils produced with 60 min	166
20	Table 8-9. Elemental composition of bio-oils produced with 80 min	167
21	Table 8-10. CVs of bio-oils produced with a residence time of 40 min	167
22	Table 8-11. CVs of bio-oils produced with a residence time of 80 min	168
23	Table 8-12. GPC analysis of bio-oils produced with a residence time of 40 min.....	168
24	Table 8-13. GPC analysis of bio-oils produced with a residence time of 60 min.....	169
25	Table 8-14. Boiling fractions' distribution of bio-oil compounds (40 min)	170
26	Table 8-15. Boiling fractions' distribution of bio-oil compounds (60 min)	171
27	Table 8-16. Elemental ratios of bio-oils produced with various residence times	180
28	Table 8-17. Elemental ratios of bio-oils produced with various residence times (continued)	
29		180
30	Table 8-18. CVs of bio-oils produced with a low reaction temperature (240°C).....	182
31	Table 8-19. CVs of bio-oils produced with a medium reaction temperature (280°C).....	182
32	Table 8-20. CVs of bio-oils produced with a high reaction temperature (320°C).....	183
33	Table 8-21. GPC analysis of bio-oils produced at a low temperature (240°C)	183
34	Table 8-22. GPC analysis of bio-oils produced at a medium temperature (280°C).....	184
35	Table 8-23. GPC analysis of bio-oils produced at a high temperature (320°C).....	185
36	Table 8-24. Boiling fractions' distribution of bio-oil compounds (240°C)	186
37	Table 8-25. Boiling fractions' distribution of bio-oil compounds (280°C)	187

1	Table 8-26. Boiling fractions' distribution of bio-oil compounds (320°C)	188
2	Table 8-27 . Elemental composition of bio-oils produced at various catalyst loadings	196
3	Table 9-1. Proximate results of biochar produced with a 20 min reaction time	198
4	Table 9-2. Proximate results of biochar produced with a 40 min reaction time	198
5	Table 9-3. Proximate results of biochar produced with a 60 min reaction time	198
6	Table 9-4. Proximate results of biochar produced with an 80 min reaction time	199
7	Table 9-5. Proximate results of biochar produced with varying catalyst loading	199
8	Table 9-6. Elemental composition of biochar produced at a residence time of 20 min....	200
9	Table 9-7. Elemental composition of biochar produced at a residence time of 40 min....	200
10	Table 9-8. Elemental composition of biochar produced at a residence time of 60 min....	201
11	Table 9-9. Elemental composition of biochar produced at a residence time of 80 min....	201
12	Table 9-10. Energy content of biochars produced with a residence time of 40 min	202
13	Table 9-11. Energy content of biochars produced with a residence time of 60 min	202
14	Table 9-12. Elemental composition of biochar produced at 240°C	202
15	Table 9-13. Elemental composition of biochar produced at 280°C	203
16	Table 9-14. Elemental composition of biochar produced at 320°C	204
17	Table 9-15. Energy content of biochars produced at 240°C	205
18	Table 9-16. Energy content of biochars produced at 280°C	205
19	Table 9-17. Energy content of biochars produced at 320°C	206
20	Table 9-18. Elemental composition of biochars produced at various catalyst loadings...	216
21		
22		

1 **List of abbreviations**

CEL	cellulolytic enzyme lignin
CELF	co-solvent enhanced lignocellulosic fractionation
CV	calorific value
DOC	degree of carbonisation
Fig	Figure
FTIR	Fourier-transform infrared spectroscopy
GC-MS	gas chromatography coupled with mass spectrometry
GPC	gel permeation chromatography
HPLC	high-performance liquid chromatography
HTL	hydrothermal liquefaction
Mn	number average molecular weight
Mw	weight average molecular weight
MWL	milled wood lignin
NMR	nuclear magnetic resonance
PDI	polydispersity index
SANS	South African National Standards
THF	tetrahydrofuran

2

3

1 Nomenclature

Å	Angstrom
°C	degrees Celsius
cm	centimetre
cSt	centistokes
Da	Dalton (1Da=1 g/mol)
g	gram
h	hours
kg	kilogram
L	litre
M	molar
mass%	mass percentage
min	minute
MJ	megajoule
mL	millilitre
mm	millimetre
Nm	Newton-metre
Pa	Pascal
ppm	parts per million
rpm	revolutions per minute
µg	microgram
µm	micrometre

v/v volume to volume

% percent

1 Introduction

1.1 Background

Fossil fuels have been the world's main source of energy for decades, however, the resources are being depleted. These fuels are also a major contributor to environmental pollution and greenhouse gases, causing the need for an alternative resource to become more urgent (Gollakota *et al.*, 2018; Iroba *et al.*, 2014). Bioenergy already contributes at least 9% of the total global energy supply (Ahorsu *et al.*, 2018). In 2018, China, the United States of America, the European Union, and 29 other countries had set targets to have ethanol blended into gasoline (Ahorsu *et al.*, 2018; Valdivia *et al.*, 2016). Thus, it is of international importance that liquid biofuels be produced to blend with gasoline and diesel to ease the pressure on fossil fuel resources. The amount of pollution caused by fossil fuels could be significantly reduced by the use of biofuels such as biodiesel and bioethanol (Ahorsu *et al.*, 2018; Valdivia *et al.*, 2016). Converting lignocellulosic biomass into these biofuels and replacing fossil fuels is a promising option for the future (Ahorsu *et al.*, 2018; Kumar *et al.*, 2020a; Kumar *et al.*, 2020b).

Non-edible lignocellulosic biomass is a promising solution for the ongoing food vs energy debate and the concerns for the environment that accompanies the use of fossil fuels. Non-edible lignocellulosic biomass has great potential as a feedstock for biofuels and fine chemicals (Ahorsu *et al.*, 2018; Balan, 2014). Lignocellulosic materials are used for producing second-generation biofuels. When comparing biofuels with petroleum fuels, greenhouse gases can be reduced by 20–70% with the production and use of biofuels (Ahorsu *et al.*, 2018; Valdivia *et al.*, 2016). Lignocellulosic materials have a low cost and are the most abundant source of natural polymers (Meng *et al.*, 2019; Ramakoti *et al.*, 2019).

In 2017, of the 50–70 million tons of lignin that was produced per year, only 1–2% was used to produce value-added products, and thus lignin is a severely underutilised resource (Aro & Fatehi, 2017). While lignin is primarily being used for energy generation and pulping processes, less than 50% of lignin that is generated is being used for energy requirements. Thus, from an economic point of view, it is essential to find a way to utilise the rest. When considering these numbers, it is easy to deduce that it will be highly advantageous to the economy and environment to identify value-added products that can be manufactured from lignin (Aro & Fatehi, 2017; Meng *et al.*, 2019). However, the use of lignin as a feedstock for

biofuel production is limited by its complex structure and the variability of its composition for different biomass feedstock. A cost-effective pre-treatment is thus necessary to prepare lignin for conversion into biofuel products (Aro & Fatehi, 2017; Meng *et al.*, 2019). Unfortunately, the complex structure and high costs associated with pre-treatment methods of lignocellulosic biomass, render lignin-based biofuels more expensive to produce than fossil fuels. Research is therefore necessary to lower the cost of lignin-based biorefineries (Ahorsu *et al.*, 2018; Aro & Fatehi, 2017).

1.2 Motivation

Bio-oil is viewed to be the cleaner fuel when compared to traditional fossil fuels because lower levels of sulphur oxides and nitrogen oxides are released during the combustion of bio-oil (Kumar *et al.*, 2020b). However, bio-oil has lower calorific values (CVs) than fossil fuels, due to a lower carbon and hydrogen content. Bio-oil is also considered to be an inferior fuel to fossil fuels because of less suitable properties.

Bio-oil cannot directly replace fossil fuels, because of its higher oxygen content, lower hydrogen and carbon content, an acidic pH, and fractions with high boiling points compared to fossil fuel (Castello *et al.*, 2019; Kumar *et al.*, 2020a). Bio-oil usually has a water content of 15–30% that affects its heating and ignition properties and increases its pH. The higher oxygen content of bio-oil also affects its range of applications. Highly reactive oxygen compounds, such as aldehydes and carboxylic acids are responsible for the acidic pH of bio-oils, making bio-oils corrosive. These compounds can also affect the stability of bio-oil, resulting in challenges with storage. The changes in viscosity and the molecular weight are due to solid residues that are present in bio-oil. This further complicates its storage and transportation. Bio-oil also has a lower chemical and thermal stability when compared to fossil fuels due to these oxygenated compounds. The ash content is slightly higher in bio-oil which contributes to its corrosive nature. Inorganic compounds and metals that are present in bio-oil can also agglomerate, which can lead to the formation of a layer of sludge (Kumar *et al.*, 2020a).

Some of the problems associated with the characteristics of bio-oil can be remedied by upgrading the bio-oil (Castello *et al.*, 2019; Kumar *et al.*, 2020b). The physiochemical properties of bio-oil can be significantly improved with the help of numerous physical, chemical, thermal, and catalytic methods, allowing bio-oil to be utilised as a transportation fuel. Upgrading to improve the properties of bio-oil can be done either as a pre-treatment of

1 the feedstock or as a post-treatment of the bio-oil (Castello *et al.*, 2019; Kumar *et al.*,
2 2020a).

3 Bio-oil can be upgraded in-situ using a suitable catalyst by mixing the catalyst with the
4 lignocellulosic biomass during hydrothermal liquefaction (HTL) treatment. It has been
5 observed that the conversion of low energy-density oxygenated compounds into higher
6 energy-density hydrocarbon compounds is necessary to produce gasoline-like fuel from bio-
7 oil. The in-situ catalytic upgrading of bio-oil can help achieve higher feedstock conversions
8 and can help improve bio-oil properties (Kumar *et al.*, 2020a).

9 Catalytic HTL operating conditions, such as reaction temperature, biomass composition,
10 heating rate, residence time, catalyst to biomass ratio, and reactor type, can influence
11 overall conversion and bio-oil properties. It has been observed that higher temperatures
12 promote the formation of hydrocarbons and phenolic compounds. A higher catalyst-to-
13 biomass ratio can increase the formation of monocyclic and polycyclic aromatic
14 hydrocarbons. However, catalysts are susceptible to deactivation due to the formation of
15 coke (Kumar *et al.*, 2020a). One of the factors that affects the chemical composition of bio-
16 oil is biomass loading. As the solids loading increases so does the oligomeric sugar
17 concentration. Oligomeric sugars in bio-oil are unproductive as most of the microbes that
18 are used in fermentation cannot consume these sugars. These sugars therefore inhibit the
19 degradation of biomass (Balan, 2014).

20 Worldwide, the annual production of lignocellulosic biomass is roughly 200 gigatons. Thus
21 far, the operability of a plant for large-scale production of bio-oil from lignocellulosic biomass
22 has not been fully realised due to the challenges of an unperfected new technology and the
23 complexity and variability of its molecular nature (Iroba *et al.*, 2014; Valdivia *et al.*, 2016). It
24 is estimated that due to the cost of newer and uncertain technology, biofuel production is
25 more expensive than the production of fossil fuels. However, there is anticipation that the
26 costs will decrease as technology is improved (Balan, 2014).

27 Another factor that not only influences the quality and quantity of bio-oil, but also the cost
28 of production is the properties of the feedstock. To produce a bio-oil of sufficient quality and
29 quantity, an ideal feedstock with a carbon content of at least 48% and an ash content of 3%
30 or lower is preferred. The feedstock's properties should also be consistent and availability
31 should not be an obstacle (Ou, *et al.*, 2018).

1.3 Research problem

The production of renewable fuel from lignin is a viable option for the future, if processes are developed that will ensure effective energy conversion. However, lignin is rarely available in its pure form and its properties are highly dependent on the methods used to extract and purify it. The variation in the properties of lignin sources complicates the conversion of lignin into bio-oil and ultimately into biofuel. Before biofuel can be produced, it is important to use a bio-oil with suitable properties. Factors that influence the reaction mechanisms involved during the depolymerisation of lignin using HTL include feedstock characteristics, reactor loading, the catalyst systems used and reaction conditions, such as residence time, reactor temperature and pressure. Manipulating these factors could result in the production of a bio-oil with favourable properties that could easily be upgraded to high-value biofuel. High monomeric content, lower acidity, lower viscosity, lower ash content, and less high molecular weight components contribute to the quality of bio-oil. For pulping companies, such as Sappi, producing a waste product that contains mostly lignosulphonates and a relatively small amount of hemicellulose, it would be ideal to convert these lignosulphonates into a suitable bio-oil. It has not been seen that there has been any report on a study of how the different reaction parameters would affect a bio-oil produced from a sodium lignosulphonate as a feedstock, when it has been treated with a strong alkali catalyst. No evidence has been found of data collected and reported concerning the molecular weight, elemental composition, chemical composition or the energy content of bio-oil produced from this specific feedstock at different process conditions.

1.4 Aim

The role of several reaction conditions in the production of bio-oil produced specifically from sodium lignosulphonate, obtained from pulp and paper waste, have not been widely reported. The aim of this study is to investigate the effect of reaction temperature, residence time and catalyst loading as to its effect on the quality and quantity of bio-oil produced through hydrothermal liquefaction.

1.5 Objectives

- What is the chemical and physical characteristics of the lignosulphonate-rich feedstock in this study?

- When attempting the fractionation of the lignex® feedstock with different solvents through a process of sequential dissolution, what are the chemical properties of the lighter lignin fractions?
- What is the effect on the bio-oil yield when different alkali catalysts are used during the hydrothermal liquefaction production process?
- What is the effect on the produced bio-oil's yield and chemical properties if different solvents are used during the hydrothermal liquefaction production process?
- What is the effect of reaction temperature, residence time, and catalyst loading on the yield and properties of bio-oil produced from the Lignex® through hydrothermal liquefaction?

1.6 Scope

This study will focus on the effect of certain process conditions on the yield and properties of bio-oil produced through hydrothermal liquefaction. The reaction conditions that will be varied are reaction temperature (240 - 320°C), residence time (20 – 80 min) and catalyst loading (2 – 6 mass%). The extent of the effects will be measured by considering molecular weight distribution, chemical and elemental composition, energy content and product recovery.

1.7 Dissertation outline

Chapter 1 is an introduction to the topic of this dissertation. It highlights the problem that is being investigated, and motivates why this particular problem is of interest. It also outlines the goals and purpose of this study.

Chapter 2 is an in-depth study of existing literature to allow for a better understanding of the topic and past studies and theories. This chapter aids in identifying possible knowledge gaps and is a useful tool for comparing results, since it also presents information and findings from previous studies about biorefinery processes and lignin isolation, purification, and conversion techniques.

Chapter 3 is a complete list of the materials that were used in the experiments and gives a detailed account of the procedures and techniques used in each phase of the experimental investigation. All the analyses are also explained along with any standard procedures that were used.

- 1 Chapter 4 is a discussion of the outcome of the experiments and an interpretation of the
2 results of all the analyses that were reported in Chapter 3. It is also the chapter where
3 results are compared to the findings from previous studies that were discussed in Chapter
4 2.
- 5 Chapter 5 concludes with an explanation of what the outcomes of this study will mean for
6 the industry and future endeavours. It is also an evaluation of whether the goals of this study
7 were achieved.
- 8 The Reference List contains all publications that were used for information, data, and
9 guidance.
- 10 Appendix A contains step-by-step explanations of all analysis methods according to the
11 standard procedures that were used.
- 12 Appendix B contains any additional data, spectra, or graphs for bio-oil.
- 13 Appendix C contains additional data for biochar.

2 Literature Review

2.1 Renewable fuel

In order to understand the role and importance of bio-oil in the renewable and alternative energy industry, it is important to first investigate the types of renewable energy and how it is produced. Another aspect to consider is why renewable fuels can be advantageous and what challenges the world faces in the production of renewable fuels.

2.1.1 Background

Global biofuel production is increasing, with Europe being the leader in the production of biodiesel and with the United States of America being the leading producer of ethanol. Biodiesel and bioethanol are the two fuels with the most potential to replace diesel and gasoline, respectively. Recently, the production of biohydrogen has also attracted some attention due to its environmentally friendly by-product, water (H₂O) (Ahorsu *et al.*, 2018). The biorefineries for second-generation biofuels consist of four processes:

- Pre-treatment to expose the cellulose and hemicellulose in biomass for easy access; enzymatic hydrolysis to convert biomass into sugars through the use of suitable enzymes; fermentation to produce alcohol from the sugars (C₅ and C₆ monomers); and distillation to purify the liquid fuel (Valdivia *et al.*, 2016).
- Thermal cracking (Ahorsu *et al.*, 2018).
- Micro-emulsion (Gebremariam & Marchetti, 2017).
- Transesterification (Rodionova *et al.*, 2017; Sánchez-Borrego *et al.*, 2021).

In the case of converting biomass into biofuels, energy and valuable products in the biorefinery industry, all these processes still require technological improvements (Valdivia *et al.*, 2016).

2.1.2 Description of renewable fuel

2.1.2.1 First-generation biofuels

First-generation biofuels are ethanol and biodiesel produced from biomass that is more than often edible. The production of these biofuels depends mainly on biomass materials such

as corn and sugarcane (Ahorsu *et al.*, 2018; Rodionova *et al.*, 2017). Corn stover contains cellulose and hemicellulose and is pre-treated with hydrolysis methods. The production of first-generation bioethanol requires sugars, which are available after a saccharification step. If sugarcane is used the sugars are readily available, making the process simpler and less expensive (Ahorsu *et al.*, 2018).

First-generation biodiesel is produced from raw vegetable oils, derived from a variety of sources, such as soybean, palm oil, canola, sunflowers, animal fats, and used cooking oil (Ahorsu *et al.*, 2018; Rodionova *et al.*, 2017). Biodiesel's attraction is not only because it is derived from renewable resources, but also because of its environmental benefits. The production and use of biodiesel cause less air pollution due to its lower sulphur content, it is more biodegradable than fossil fuels, and the net atmospheric levels of carbon dioxide does not change due to the amount of carbon that was absorbed for photosynthesis during the feedstock's growth period. Biodiesel has a higher density, a larger cetane number, lower sulphur emissions, and a higher flashpoint than standard fossil diesel. The higher flashpoint means that biodiesel is less combustible making it a safer option when compared to petroleum diesel (Ahorsu *et al.*, 2018).

2.1.2.2 Second-generation biofuels

Lignocellulosic biomass is used as feedstock to produce second-generation biofuels. It is a realistic alternative to edible plants (Rodionova *et al.*, 2017; Valdivia *et al.*, 2016). Considering the significant amounts of cellulose and hemicellulose that are available, lignocellulosic biomass is a key source of sugars to be converted into ethanol (Ahorsu *et al.*, 2018). Another second-generation biofuel that has shown promise is bio-synthetic natural gas (bio syngas). It is a synthetic gas that is similar to natural gas. In terms of fuel equivalence, the yield for this biofuel is higher than it is for biodiesel or bioethanol. It is possible to blend second-generation biofuels and conventional fuels. This mixture can be used in combustion engines and particularly internal combustion engines. Some countries, such as Canada, China, and the European Union, have established national policies to blend biofuel with petroleum-based fuels (Ahorsu *et al.*, 2018).

2.1.2.3 Third-generation biofuels

These are fuels that are produced from algal biomass (Ahorsu *et al.*, 2018; Rodionova *et al.*, 2017). The biofuel produced from the algae depends on the lipid content of the algae. Algae is a potential feedstock, because they (Ahorsu *et al.*, 2018):

- Have a high lipid content (20–50%);
- Have high growth rates;
- Can grow in unfavourable conditions; and
- Are an economical feedstock option (high growth rates and low costs are associated with growth and harvesting).

The production of biodiesel from algae is 200 times more efficient than using traditional crops, because of algae's fast growth rate and the fast and easy harvesting process. Depending on the type of algae, harvesting can occur as soon as a few hours after cultivation. Microalgae do not require large or high quality agricultural land (Rodionova *et al.*, 2017).

2.1.2.4 Fourth-generation biofuels

These types of biofuels are created when solar energy is converted into solar biofuels by raw materials that are inexpensive, renewable, and widely available. Algae's and cyanobacteria's synthetic biology are used to produce photobiological solar biofuel or electrofuel. Fourth-generation biofuel is created by (Ahorsu *et al.*, 2018):

- Designing microorganisms that are photosynthetic; or
- Combining photovoltaics and principles of microbial fuel production; or
- Synthetic cell organelles, specifically tailored for the production of biofuels, and certain high-value chemical compounds.

2.1.3 Production of biofuels from lignocellulosic materials

2.1.3.1 Bioethanol production

This process depends greatly on which raw biomass is used as feedstock; it can be simplified into these steps (Ahorsu *et al.*, 2018):

1. Obtain or produce fermentable sugars;
2. Convert the sugars into ethanol through fermentation; and
3. Use processes such as distillation-rectification-dehydration to separate and purify the final product.

1 The process parameters must be modified for different feedstock and conversion methods
2 (Ahorsu *et al.*, 2018).

3 **2.1.3.2 Bioethanol produced from corn**

4 When corn stover is used as the feedstock, a pre-treatment is required to extract the natural
5 sugars or to make these sugars more accessible for fermentation processes. Usually, this
6 involves milling or grounding. Afterwards, enzymes and heat are added to convert the
7 sugars through hydrolysis. The sugars available for further processing depends on the type
8 of pre-treatment used. The fermentation process can be a batch, fed-batch, or continuous
9 process (Ahorsu *et al.*, 2018).

10 In batch fermentation, the hydrolysate, which contains sugars, nutrients, and other
11 ingredients, is added to a medium at the start of the fermentation process. With a fed-batch
12 process, one or more inputs are added during the progression of the fermentation process.
13 In a continuous process, the ingredients are continuously added to the process at a constant
14 flow rate, while the products are continuously removed from the fermentation reactors
15 (Ahorsu *et al.*, 2018).

16 The physical and chemical composition of corn makes this process more complex than
17 when sugarcane is used as a feedstock, but the volume of ethanol produced from corn is
18 five times higher than when sugarcane is used, although sugarcane produces ethanol with
19 higher productivity (Ahorsu *et al.*, 2018).

20 **2.1.3.3 Bioethanol produced from sugarcane**

21 Corn and sugarcane have similar fermentation and product recovery options, but the
22 approaches to release their sugars differ and they generate different by-products. With
23 sugarcane, the sugars can be directly extracted and the remaining bagasse can be burned
24 in boilers to provide much of the energy that is needed for the process (Ahorsu *et al.*, 2018).

25 **2.1.3.4 Biochemical production of second-generation bioethanol**

26 Bioethanol can be produced through a biochemical method, where enzymes and other
27 microorganisms convert the cellulose and hemicellulose to sugars before fermentation.
28 Biochemical processes (fermentation) occur at lower temperatures and lower reaction rates.
29 When bacteria consume the organic substrate in an anaerobic environment at 30–65°C it

is called anaerobic digestion. This fermentation process uses microorganisms to convert the sugars (available in the liquid phase) into recoverable products, mainly ethanol, but also other compounds with useful applications such as biopropanol and biobutanol. Biomethanol is another product but it is highly toxic and corrosive (Ahorsu *et al.*, 2018; Rodionova *et al.*, 2017).

2.1.3.5 Biodiesel production

Biodiesel is usually produced from animal fats or vegetable oils. These oils and animal fats are converted into fatty acid methyl esters. Biodiesel's chain length, energy density, and viscosity are similar to that of diesel derived from crude fossil oil. The esters in vegetable oils contain up to 11% more oxygen which accelerates its combustion more than that of hydrogen-based diesel. Among the world's top producers are Brazil, Germany, Belgium, Spain, and the USA. The four main processes for biodiesel production consist of thermal cracking, micro-emulsion, transesterification, and blending (Rodionova *et al.*, 2017; Sánchez-Borrego *et al.*, 2021)

According to Rodionova *et al.* (2017), biodiesel is important for several reasons:

- It is an affordable and local fuel for rural economies;
- It is a renewable and sustainable fuel source;
- Its production causes less toxic waste than fossil fuels;
- Most inputs and outputs are biodegradable;
- Biodiesel is more environmentally friendly; and
- It improves engine performance (Rodionova *et al.*, 2017).

2.1.3.5.1 Thermal cracking

Thermal cracking is also called pyrolysis. It is the thermal decomposition of biomass through heat and anaerobic conditions, sometimes with a catalyst. It provides high liquid-fraction yields that can have similarities to crude oil under certain conditions (Ahorsu *et al.*, 2018).

2.1.3.5.2 Micro-emulsion

Micro-emulsions are thermodynamically stable and isotropic dispersions of oil, water, and amphiphile. The components of biodiesel as a micro-emulsion include vegetable oil, fossil diesel, surfactant, alcohol, and cetane improver. Micro-emulsion yields a fuel with reduced

1 viscosity, increased cetane number, and better spray characteristics (Gebremariam &
2 Marchetti, 2017).

3 **2.1.3.5.3 Transesterification**

4 When fat or oil reacts with an alcohol group, glycerol and esters are formed. It is currently
5 the preferred method for manufacturing biodiesel because it gives a high yield with less
6 operational costs (Sánchez-Borrego *et al.*, 2021). Catalysts and ethanol or methanol can
7 facilitate this reaction (Ahorsu *et al.*, 2018; Rodionova *et al.*, 2017).

8 **2.1.4 Advantages of renewable fuel**

9 Currently, petroleum (crude oil) is the main feedstock source for the production of fuels.
10 However, due to its environmental impact and declining availability, the eyes of the world
11 are turning from petroleum to sustainable biofuels (Stedile *et al.*, 2019). Burning biodiesel
12 does not increase the net atmospheric levels of carbon dioxide and it causes less air
13 pollution. It is biodegradable and provides the opportunity to recycle waste oils. The
14 production of biodiesel creates less waste and is considered to be environmentally friendly
15 (Sánchez-Borrego *et al.*, 2021). It is also simple to manufacture and it gives unhindered
16 engine performance (Ahorsu *et al.*, 2018). One major advantage of the production and
17 search for renewable fuels is the advancements made in technological developments. New
18 processes have been developed and, in some cases, major improvements have been
19 made. These new developments include membrane reactors, microreactors, biological
20 reactors, microwave reactors, oscillatory flow reactors, centrifugal contractors, and reactive
21 distillation (Sánchez-Borrego *et al.*, 2021).

22 **2.1.5 Challenges of the biorefinery processes**

23 For a biorefinery plant to operate at maximum capacity, numerous challenges must be
24 overcome. First, the selected biomass must be sustainable; a few factors affect this
25 challenge. These factors include the environmental policies for the growing area, and the
26 type of bioenergy, biomass, processing methods and facilities that are available in the area.
27 The logistics of transporting biomass to refinery sites can also hinder the plant's
28 sustainability (Ahorsu *et al.*, 2018; Valdivia *et al.*, 2016).

29 Biomass diversity is a challenge as a plant can only treat a specific feedstock to generate
30 fuel with consistent properties. Developing a process that can treat a mixed feedstock would

eliminate most of the industry's challenges (Valdivia *et al.*, 2016). In countries such as Finland, Poland, and Estonia over 75% of renewable energy comes from wood, but the main drawbacks of wood are its high moisture content and low energy density (Wądrzyk *et al.*, 2019).

In the case of ethanol production, Ahorsu *et al.* (2018) expressed that the most important step is the pre-treatment. Its purpose is to depolymerise the cellulose and hemicellulose into glucose and xylose, respectively. The pre-treatment method can over-depolymerise or under-depolymerise, and oligosaccharides such as cellobiose and xylo-oligosaccharides will form. An over-depolymerisation will lead to lower yields of ethanol (Ahorsu *et al.*, 2018). The yield of the hydrolysis step can cause variation in the conversion efficiency (40–98%). It is affected by the biomass feedstock and the pre-treatment method. Enzymatic hydrolysis of lignocellulosic biomass has a low efficiency because it depends on the crystallinity of the cellulose, lignin and moisture content, available surface area, and degree of polymerisation. As lignocellulosic biomass composition is very inconsistent, the pre-treatment method requires thorough investigation before being applied to the industry. The biomass's composition affects the efficiency of biofuel production and the final energy content (Ahorsu *et al.*, 2018).

The current process that is used to produce biodiesel requires the addition of methanol, which is produced from fossil fuels. It has been stated that almost 35% of the energy required to manufacture biodiesel comes from fossil fuels and methanol accounts for about 10% of the feed for biodiesel, making biodiesel not entirely renewable (Ahorsu *et al.*, 2018).

The production of renewable fuels is still a very new technology; thus, the costs of production are still very high. To become economically feasible, the costs must be reduced. When using hydrodeoxygenation to upgrade bio-oil, there is a problem with coke formation that causes a very expensive catalyst to deactivate. It is suspected that sugars and aromatic components are mainly responsible for the deactivation of catalysts (Sánchez-Borrego *et al.*, 2021).

2.2 Description of biomass

After discussing the different aspects of renewable fuels and the challenges accompanying the production process, the feedstock for second generation fuels, biomass, will now be discussed. The use of lignocellulosic biomass for the production of renewable fuels, not only offers a possible solution to the food-vs-energy debate, but

could also reduce waste in some cases, such as using corn stover as the biomass feedstock.

The International Energy Agency defines biomass as any organic material that comes from a biogenic source and is readily available on a renewable basis. This includes animals, wood-based plants, agricultural crops, and organic waste from industrial and municipal sectors (Ahorsu *et al.*, 2018). Forestry and agricultural residues are the largest source of biomass (lignocellulosic biomass), generating approximately 200 billion tons per year. The abundance of this source makes it vital to find ways to effectively use it for the benefit of civilisation and the environment and also to prevent an accumulation of waste (Sánchez-Borrego *et al.*, 2021). Lignocellulosic biomass material consists of cellulose, hemicellulose, lignin, and a small amount of inorganic matter. The chemical composition and inorganic components are different for each plant (Ahorsu *et al.*, 2018; Aro & Fatehi, 2017). Each constituent has great potential for energy generation. Cellulose is a long-chain homopolymer that consists of D-glucose and repeating cellobiose units. Hemicellulose consists of short-branched chains grouped as polysaccharides. This constituent plays a vital role in the production of biofuels as it can make up to 35% of the biomass weight (Sánchez-Borrego *et al.*, 2021). After conversion, the composition of the product, the degree of decomposition and recalcitrance depend mostly on the compositional variations of the original biomass (Ahorsu *et al.*, 2018). The degree of decomposition difficulty of the three significant compounds is attributed to each compound's structural stability. The pyrolysis and hydrolysis of hemicellulose and cellulose produce more oil, while that of lignin contribute mostly to the production of biochar (Ahorsu *et al.*, 2018).

Woody biomass is viewed to be one of the most promising and significant resources. In many EU countries, wood is considered to be the single most important source of energy among all renewable resources (Wądrzyk *et al.*, 2019). Woody biomass is mostly made up of cellulose. The second most abundant aromatic biopolymer found in woody biomass is lignin – 15–40% of wood consists of lignin (Aro & Fatehi, 2017; Duan *et al.*, 2019). For biomass to be used for energy purposes it first has to comply with a few characteristics (Ahorsu *et al.*, 2018):

- Low energy input is required for cultivation;
- Low energy input is required during processing;
- High yields are required; and
- The cellulose and hemicellulose content must be high.

As it stands, popular lignocellulosic biomass applications, other than biofuel production, are electricity generation and producing syngas through gasification (Sánchez-Borrego *et al.*, 2021).

2.3 Lignin extraction and lignocellulosic biomass pre-treatment methods

In the previous section lignocellulosic biomass, its composition and contribution to renewable energy was discussed. However, cellulose and hemicellulose already have large scale applications such as in the paper pulping industry. The application of lignin has not been applied to such a large scale as mentioned in chapter 1. Before the application of lignin can be discussed, the different extraction and purifying methods for lignin should be discussed. These different methods with its resulting lignin fractions throw more light on specific high value applications for lignin.

Before lignin-based value-added products can be produced, the lignin should first be separated from its source. One of the greatest challenges of studying lignin is isolating the complete and unaltered molecule (Guerra *et al.*, 2006). Several different techniques exist to recover lignin and some will be discussed in this section (Aro & Fatehi, 2017; Ramakoti *et al.*, 2019). The sulphite and kraft pulping processes produce a waste product called black liquor that is the richest source of lignin, which means these processes are the most effective for separating lignin from wood (Aro & Fatehi, 2017; Lu *et al.*, 2017). Each technique produces lignin with different properties; so it is possible to obtain specific molecular weights and compositions by selecting a specific extraction method (Ramakoti *et al.*, 2019).

2.3.1 Acidolysis of lignin

This process involves the extraction of lignin using 1,4-dioxane, that contains hydrochloric acid, at room temperature. The extracted lignin is of high purity and is considered to be the most accurate representation of the original lignin structure. A drawback of this method is that the degradation of already liberated monosaccharides can lead to an overestimation of the degraded monosaccharides causing an inaccurate perception of the amount of polysaccharides. However, the resulting lignin has a phenolic group content higher than that of milled wood lignin (MWL). An increased syringyl-to-guaiacyl (S/G) ratio is also

1 observed. To increase the yield, a thioacidolysis process was developed by replacing water
2 with ethanethiol (Lu *et al.*, 2017).

3 **2.3.2 Alkaline hydrolysis of lignosulphonates**

4 Improving the low reactivity of lignin can be a vital tool before attempting to use the lignin.
5 Alkaline hydrolysis can accomplish this for lignosulphonates. The diagram depicted in Fig.
6 1 shows the process of alkaline hydrolysis and the purification of lignosulphonates. First,
7 lignosulphonates and water with a 1:10 weight ratio and 2 mass% sodium hydroxide are fed
8 to a reactor. The reaction occurs at 170°C, for 90 min with a pH of 12. The product is
9 recovered by drying. This process will decrease the molecular weight by a little more than
10 50% and increase the number of reactive sites by 55%. This process is easy to integrate
11 into any other existing process (Aro & Fatehi, 2017). By adding a pre-treatment step with
12 ammonia, a lignin recovery of above 65% can be achieved with more than 84% of
13 carbohydrate retention (Lu *et al.*, 2017).

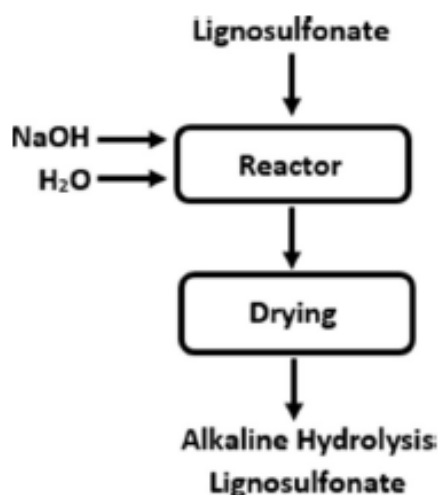


Fig. 1. The alkaline hydrolysis process of lignosulphonates (Aro & Fatehi, 2017)

14 **2.3.3 Cellulolytic enzyme lignin**

15 Cellulolytic enzyme lignin (CEL) was developed to improve the yield by extracting
16 enzymatically hydrolysed MWL residue. The residual carbohydrate content in the CEL
17 product is about 10–15 mass% of the initial MWL sample. The structure is similar to that of
18 the MWL; however, the CEL is a better representative of the entire lignin. Therefore, CEL
19 is commonly used for structural analysis of lignin. This method has a few advantages such
20 as milder conditions. However, the total yield remains relatively low (Lu *et al.*, 2017).

2.3.4 Co-solvent enhanced lignocellulosic fractionation

Co-solvent enhanced lignocellulosic fractionation (CELf) refers to a 'lignin-first' thermochemical approach where the use of miscible solutions such as tetrahydrofuran-water (THF-water) along with dilute acid is encouraged. This method can isolate a lignin product that is pure and has a low molecular weight from raw biomass. This method also makes it possible for a high recovery of sugars that are present in the biomass for converting them into ethanol, furfural, and 5-hydroxymethylfurfural (Meng *et al.*, 2019). During the pre-treatment of this method, 85–90% of the lignin can be dissolved into the co-solvent mixture. The product will precipitate once the THF is removed. The product obtained is ash-free and sugar-free. It is known as CELf lignin. Previous studies have shown that CELf lignin has a significantly reduced molecular weight compared to native lignin. It also has less competition for cross-condensation reactions. Ultimately, this method could be used as a tool to produce highly fractionated lignin (Meng *et al.*, 2019). This method is based on choosing two miscible fluids, one which is a lignin solvent and the other an anti-solvent. Thus changing the solvent/anti-solvent ratio by adding more anti-solvent or by removing the solvent, it is possible to obtain lignin fractions with the desired molecular weight and physico-chemical properties (Meng *et al.*, 2019).

2.3.5 Ionic liquid degradation of lignin

Some ionic liquids are capable of extracting lignin from certain wood sources with most of the lignin's structural features intact. Different ionic liquids can be used for selection purposes. This process is considered to be an environmentally friendly method due to relatively mild conditions and reagents recycling (Lu *et al.*, 2017).

2.3.6 Kraft pulping process

Kraft pulping technologies are used by most mills around the world, and therefore kraft lignin is easier to come by. Kraft lignin, along with soda and sulphite lignin, is the main technical lignin product produced through industrial processes (Aro & Fatehi, 2017; Lu *et al.*, 2017). NaOH and Na₂S are used to separate kraft lignin from wood. The kraft pulping process has fewer environmental concerns than the sulphite pulping process. Some studies have investigated the sulphonation of kraft lignin as kraft lignin is more readily available. Unmodified kraft lignin, separated from the black liquor of the kraft pulping process, is used to produce sulphonated kraft lignin. Carbon dioxide is added to the black liquor to reduce

the pH level from 13 to between 9 and 9.5. The acidification of the liquor converts ionic phenolic hydroxide groups, present in the lignin molecules, into their free forms which cause the precipitation of kraft lignin. Once the kraft lignin has been purified, it is sulphomethylated and becomes sulphonated lignin. This is done when kraft lignin reacts with sodium sulphite or sodium bisulphite and an aldehyde such as formaldehyde, at 100–160°C and a pH of 9 or higher for 4 hours. A weight ratio of sulphite to formaldehyde of 1.3:0.8 is preferred for this process. Too much sulphite will decrease the molecular weight of the product. This sulphonation reaction allows for the bonding of sulphonic acid groups to the aromatic rings of the lignin. This structure differs from the lignosulphonates that are produced with the sulphite pulping process (Aro & Fatehi, 2017).

Sulphonated kraft lignin is usually sold in the form of sodium or calcium salt. It is produced at a lower cost compared to some of the lignosulphonates that are produced through sulphite pulping methods (Aro & Fatehi, 2017).

2.3.7 Milled wood lignin

MWL is produced by using a neutral organic solvent under mild conditions to remove impurities from the milled particles of lignocellulosic biomass. This produces low-yield lignin with properties that are similar to the original sample (Lu *et al.*, 2017).

2.3.8 Organosolv pulping method

This method is a more traditional method which mainly targets the α -aryl ether bonds instead of the β -aryl ether bonds. This process is quite simple compared to the others and the solvents can be recycled, making this the most environmentally friendly and economical process (Ramakoti *et al.*, 2019). This method involves using a pure organic solvent. However, a mixed solvent with an organic acid can also be used. Frequently used acids include acetic acid, oxalic acid, and formic acid (Meng *et al.*, 2019; Ramakoti *et al.*, 2019). It can remove up to 50% of the lignin in biomass, with high purity (Lu *et al.*, 2017). This heterogeneous extracted lignin is known as organosolv lignin and is recognised for having a high phenolic content, a broad molecular weight distribution, and being highly soluble in a common solvent (Ramakoti *et al.*, 2019).

2.3.9 Sulphite pulping process

Lignin produced from this method is referred to as liginosulphonates. Liginosulphonates are produced with the aid of sulphurous acid or a sulphite salt that contains calcium, magnesium, ammonium, and sodium at varying pH levels. Usually, the pH levels are between 1 and 5. However, with a neutral sulphite pulping process, the pH will be between 5 and 7 (Aro & Fatehi, 2017). Liginosulphonates are produced by two key reactions which are sulphonation and hydrolysis; thus, they have more sulphur groups than kraft lignin and a higher degree of sulphonation. Liginosulphonates are water-soluble and anionically charged. Liginosulphonates can account for almost 90% of the total commercial lignin available in the market (Aro & Fatehi, 2017; Lu *et al.*, 2017).

There are several sulphite pulping processes which can be distinguished from one another by the different pH levels and the different sulphite salts that are used. The properties of the liginosulphonates produced will also vary due to the differences in process conditions and inputs (Aro & Fatehi, 2017).

Fig. 2 represents the sulphonation and hydrolysis reactions that occur during a typical sulphite pulping process at acidic pH levels. During the production of liginosulphonates, it is possible that a condensation reaction can occur between one molecule's benzylic carbon and another molecule's meta-carbon position on the aromatic ring. This reaction is caused

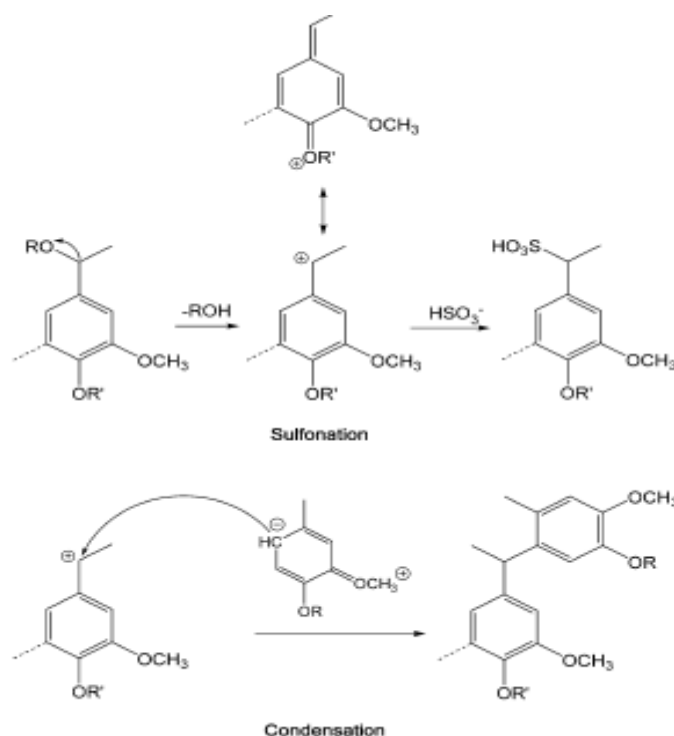


Fig. 2. Reactions of the acidic sulphite pulping process on guaiacyl, adapted from Aro & Fatehi (2017)

by the presence of the benzylic cation and as this reaction also occurs at the α position, it may inhibit the sulphonation reaction (Aro & Fatehi, 2017).

Fig. 3 shows the sulphonation reaction that occurs during the production of lignosulphonates by the use of a neutral sulphite pulping method (Aro & Fatehi, 2017). The reactions of neutral conditions differ from acidic conditions. During neutral conditions, hydrolysis only occurs with phenolic-type intermediates, and the sulphonation reaction is set in motion by the electron-withdrawing effect of adding the first sulphonic group (Aro & Fatehi, 2017). The methoxy group on the aromatic ring structures may differ as it depends which of lignin's subunits are present (Aro & Fatehi, 2017). The three main components of lignin are:

- p -hydroxyphenylpropene: which has no carbon-adjacent substitutions on the para-oxy group;
- guaiacyl: which has one carbon-adjacent substitution on the oxy group; and
- syringyl: where both carbon-adjacent atoms have been substituted to the oxy group (Aro & Fatehi, 2017).

The spent liquor contains lignosulphonates, hemicellulose, and residual chemicals from the pulping process. Lignosulphonates account for 50–80 mass% of the total solids present in the spent liquor. The hemicellulose content can be as high as 30 mass%, with organics accounting for more or less 10 mass% of the mixture (Aro & Fatehi, 2017).

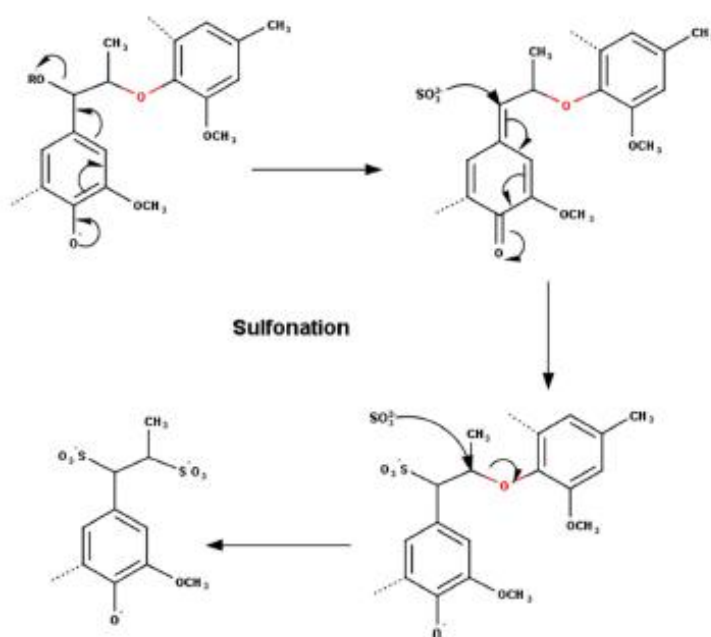


Fig. 3. Reactions that occur on guaiacyl during the neutral sulphite pulping process, adapted from Aro & Fatehi (2017)

2.3.10 Sequential dissolution of lignin fractions

The solvent fractional separation and the selective precipitation of lignin method can improve the quality of lignin and is successful when used to obtain a specific molecular weight and polydispersity. Fractionation methods can produce lignin with a very pure and homogeneous structure. The sequential dissolution technique is an efficient method to fractionate lignin resulting in several lignin samples with different molecular weights and varying phenolic acid content. FTIR analysis shows homogeneity in the fractionated lignin's chemical structure. All fractions obtained from different solvents are of high purity (Ramakoti *et al.*, 2019).

2.3.11 Steam explosion pre-treatment

Biomass has a complicated molecular structure that binds the different constituents such as cellulose and hemicellulose together. In most cases of producing valuable products, this structure of lignocellulosic biomass must first be broken down into simpler structures. The steam explosion method can be used as a pre-treatment to gain access to the different constituents by disaggregation and deconstruction of the original biomass matrix. A steam explosion occurs at relatively high pressures (5–11 bar) with very short residence times (5–10 min) and relatively low temperatures (140–180°C) with less than 50% mass loading of water. However, with this method, there is a significant risk that cellulose and hemicellulose will experience too much thermal degradation (Iroba *et al.*, 2014).

2.4 Description of lignin

After discussing the different types of lignin compounds, the following section will entail an investigation of the characteristics of pure lignin and the valuable products that can be produced from lignin-based products.

Lignin is one of the main components in lignocellulosic biomass (plant-based materials). It is a heterogeneous aromatic. It is a highly cross-linked macromolecule (Duan *et al.*, 2019; Guerra *et al.*, 2006). Lignin was considered to be a waste product of pulping processes (Lupoi *et al.*, 2015). Softwood contains 24–33 mass% lignin, while in hardwoods and grasses, lignin makes up 19–28 and 15–25 mass%, respectively (Lu *et al.*, 2017). It has been theorised that lignin has a molecular formula in the range of $C_{18}H_{24}O_{11}$ – $C_{40}H_{45}O_{18}$. Even though extensive research has been done, lignin is not fully understood because of its irregular and complex structure (Guerra *et al.*, 2006; Nam, 2013). Another factor that

contributes to the complexity of lignin is the fact that there is a significant variation in its structure depending on the type of lignocellulosic biomass and the degradation process. To use lignin effectively, its structural features are an important consideration (Lu *et al.*, 2017). An example of lignin's molecular structure can be seen in Fig. 4.

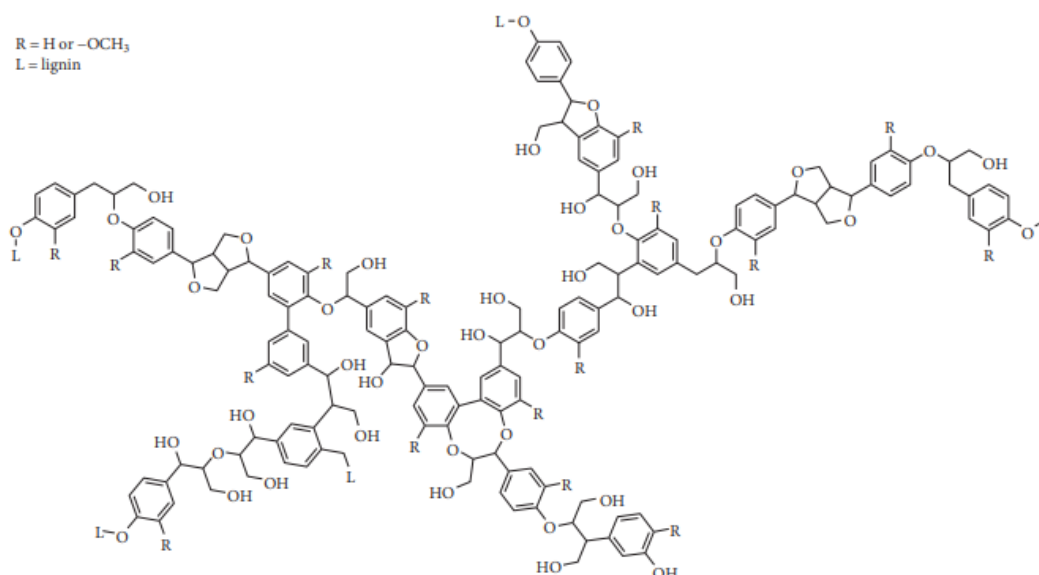


Fig. 4 The molecular structure of lignin (Lu *et al.*, 2017)

Lignin is mainly available in the form of technical lignin, usually as liginosulphonates, which are produced through chemical pulping processes such as sulphite and kraft. These two methods are responsible for the production of 90% of all technical lignin (Lu *et al.*, 2017; Nam, 2013). After purification, the product still contains a significant amount of sulphur. These liginosulphonates, although readily available, is not a true representation of the original lignin structure. The native lignin in lignocellulosic biomass undergoes significant structural changes during the sulphite and kraft pulping processes when linkages such as α -O-4 and β -O-4 are cleaved. It is important to note that liginosulphonates also contain large amounts of carbohydrates and sulphurous compounds as impurities (Lu *et al.*, 2017).

2.4.1 Chemical composition of lignin

As far as it is known, lignin is the largest natural source of aromatic compounds on earth (Aro & Fatehi, 2017). Despite differences, all types of lignin are complex, three-dimensional, biopolymers consisting of phenylpropanoids, linked through dehydrogenation reactions, that exist in a form that is bound to carbohydrates that do not include cellulose (Lupoi *et al.*, 2015; Nam, 2013). The lignin content consists of 30% aromatic (organic) carbon and is mainly composed of three primary functional compounds known as *p*-hydroxyphenyl (H),

1 guaiacyl (G) and syringyl (S) units. These units are derived from p-coumaryl, coniferyl and
2 sinapyl alcohol (Duan *et al.*, 2019; Lu *et al.*, 2017). Lignin has a variety of functional groups
3 which include carbonyl, methoxy, carboxyl and hydroxyl linked to aliphatic moieties and
4 aromatics. Free phenolic groups and condensing units are also usually present in lignin.
5 These groups can be present in different amounts which is why the chemical composition
6 and structure of lignin vary so greatly (Lu *et al.*, 2017; Lupoi *et al.*, 2015).

7 Lignosulphonates obtained from pulping processes contain large amounts of sulphur and
8 some hemicelluloses (Aro & Fatehi, 2017; Lu *et al.*, 2017). Hemicelluloses degrade much
9 easier than lignin and will release volatile components in the form of vapour during
10 degradation (Iroba *et al.*, 2014).

11 **2.4.2 Lignin bond types**

12 Lignin is a phenolic polymer and consists of three different phenyl monomers in varying
13 quantities (Aro & Fatehi, 2017; Ramakoti *et al.*, 2019). These phenyl monomers are linked
14 together mainly by ether and carbon bonds (Ramakoti *et al.*, 2019). Lignin consists primarily
15 of phenylpropane. The aromatic phenol monomers in lignin are an ideal source for
16 producing high value-added chemical compounds (Ahorsu *et al.*, 2018).

17 Lignin's structure consists of various functional groups. Condensed phenolic hydroxyl and
18 carboxylic acid groups can be present, especially in lignin, that has experienced some
19 degree of depolymerisation. These functional groups form tight interlinkage bonding, which
20 makes it challenging to extract lignin from its natural source (Guerra *et al.*, 2006; Ramakoti
21 *et al.*, 2019). There are numerous linkages present in a lignin molecule such as C-C or C-
22 O in different quantities (Lu *et al.*, 2017). The aromatic units of lignin are linked by numerous
23 non-phenolic aryl-glycerol- β -O-aryl ether units and other linkages like, β -5
24 (phenylcoumaran), β - β (resinol), β -O-4, 5-5 and α -O-4 which are all dibenzodioxocins. The
25 cleavage of aryl-alkyl ether bonds that are present in lignin forms smaller phenolic
26 monomeric compounds (Duan *et al.*, 2019; Guerra *et al.*, 2006). Lignin contains condensed
27 β -aryl ethers and dibenzodioxocins, which are resistant to depolymerisation caused by
28 mechanical action. Lignin is also covalently bonded to carbohydrates which consist of
29 benzyl-ethers, phenyl-glycosides and benzyl-esters (Guerra *et al.*, 2006). The most
30 common linkages in lignin are the β -O-4 links, which are relatively weak bonds. Thus, most

degradation processes usually target these links. The other linkages are stronger because of their complexity and greater difficulty to be cleaved (Lu *et al.*, 2017). Fig. 5 shows some of the most important bonds in lignin's structure.

The main problem with using lignin is its complex structure. Lignin tends to condense and form crosslinks with the hydroxyl reactive groups. Whenever lignin has two or more reactive hydroxyl groups, three-dimensional crosslinking will occur. The lignin obtained from a pulping process will already have experienced crosslinking (Nam, 2013).

Lignosulphonates have sulphonic acid groups attached to the aliphatic chain of lignin – 70–75% of the original lignin's hydroxyl groups become sulphonated during sulphite and kraft processes (Aro & Fatehi, 2017).

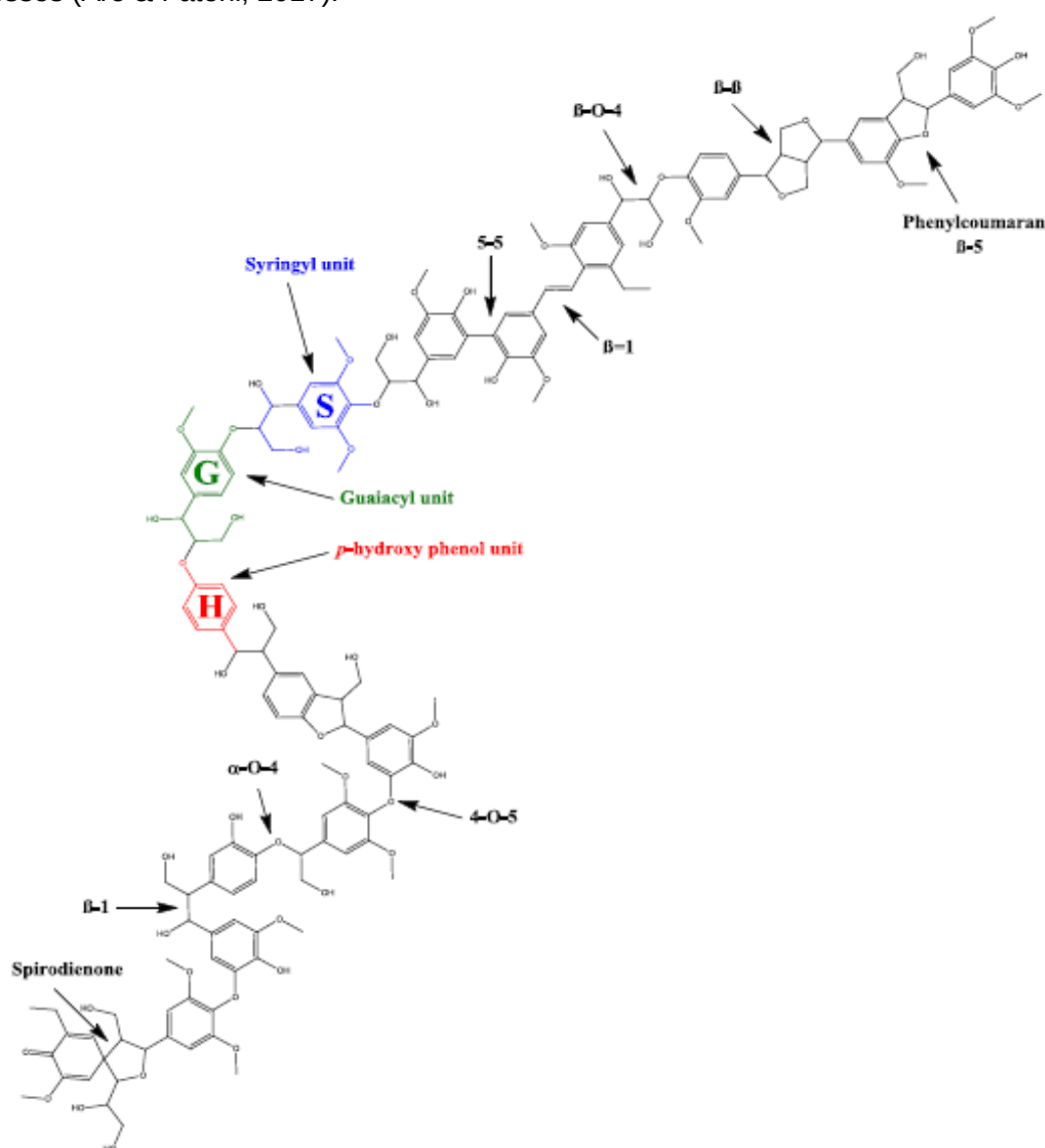


Fig. 5. Schematic representation of the structure of lignin including constituents and lignin-lignin linkages (Lupoi *et al.*, 2015)

2.4.3 Lignin properties

The properties and features of lignin depend heavily on the methods and conditions used during the extraction process and its chemical composition. The abundance of S, G and H units, and the functional groups that are present in the lignin structure, have a large influence on the physical and chemical properties of lignin (Lu *et al.*, 2017).

Properties such as reactivity and molecular weight distribution are highly dependent on the source of the lignocellulosic material and the solvent used for treatment (Ramakoti *et al.*, 2019). Lignin has a highly condensed, macromolecular structure which gives it a high chemical energy content, but a low reactivity (Ahorsu *et al.*, 2018; Aro & Fatehi, 2017). Lignin's reactivity depends on how frequently syringyl units appear in the structure (Yamada *et al.*, 2006). It is also known that lignin has very little to no thermal stability (Nam, 2013).

Lignosulphonates are reddish-brown and in some cases impossible to melt due to a lack of thermosetting properties (Nam, 2013). The structure can differ significantly due to the wide range of sulphite pulping process conditions. Typically, sodium lignosulphonates will have lower viscosities compared to calcium lignosulphonates, due to sodium having stronger electro-kinetic repulsive forces that increase repulsion. However, a greater viscosity is an indication of a larger molecular weight (Aro & Fatehi, 2017).

2.4.4 Lignin characterisation methods

The contents of bio-oil and its constituents, such as lignin, are usually analysed utilising GC-MS, NMR, FTIR, GPC and elemental analysis; however, the characterisation of lignin and bio-oil is not limited to these techniques or even the ones mentioned in this section (Duan *et al.*, 2019).

Near-infrared spectroscopy (NIR) is a method for obtaining quantitative information on chemical and physical properties. NIR is a rapid, non-destructive, and inexpensive method. It has been used to investigate lignin contents (Yamada *et al.*, 2006).

A popular lignin characterisation method, especially in the pulping industry is the determination of the acid-insoluble lignin (**Klason lignin**) and the acid-soluble lignin contents of a sample of biomass (Guerra *et al.*, 2006). An increase in acid-soluble lignin can be directly related to the decomposition of the lignin's molecular structure, while an increase in acid-insoluble lignin points to significant thermal degradation (Iroba *et al.*, 2014).

Spectroscopic techniques can deliver quantitative and qualitative information on lignin's functional groups, the linkages between constituents, and its degradation products. Various techniques can be applied, including FTIR spectroscopy, ultraviolet spectroscopy, NMR spectroscopy, and Raman spectroscopy. Several different NMR techniques exist, such as ^{31}P , ^1H , ^{13}C , ^{19}F and 2D NMR spectroscopy, that can provide quantitative and qualitative information. Raman spectroscopy is considered to be similar to FTIR spectroscopy. UV spectroscopy can be used to determine the content of acid-soluble lignin and its components, and also the purity of the isolated lignin. For characterising lignin, FTIR, ^{13}C and ^1H NMR spectroscopies are usually used, but recently ^{31}P NMR spectroscopy has gained popularity (Lu *et al.*, 2017).

NMR spectroscopy can provide comprehensive and precise qualitative and quantitative data on the linkages and composition of the lignin, like the ratios between H, G, and S units of lignin. NMR spectroscopy is also considered a non-invasive and non-destructive method for analysing samples (Lu *et al.*, 2017; Lupoi *et al.*, 2015). The most popular one-dimensional NMR techniques for analysing lignin are ^1H and ^{13}C while the two-dimensional technique most often used is the HSQC (heteronuclear single-quantum coherence). For a proton spectrum of lignin, the signal assignments are shown in Fig. 6 (Lu *et al.*, 2017). Quantitative ^{31}P NMR spectroscopy is very effective in providing information about the lignin's structure. ^{31}P NMR determines the number of different hydroxyl groups, such as carboxylic groups, aliphatic hydroxyls, condensed and uncondensed units, that contains phenolic hydroxyl groups. When aryl ether linkages are selectively cleaved, phenolic hydroxyls are released. By quantifying these phenolic hydroxyls, the number of aryl ethers can be determined. This will offer more information about condensed and uncondensed lignin units (Guerra *et al.*, 2006).

Table 2-1. NMR signal assignments for lignin (Lu *et al.*, 2017)

Chemical shift/ ppm	Assignments
9.7-9.9	Cinamaldehydes and benzaldehydes
6.7-7.1	Aromatic-H in guaiacyl
6.2-6.7	Aromatic-H in syringyl
5.8-6.2	Benzylic OH in β -O-4 and β -1
4.9-5.1	Carbohydrates
3.3-4.0	Methoxyl
3.0-3.1	H $_{\beta}$ in β -1
2.2-2.4	Phenolic OH

A more traditional and one of the most widely used techniques to characterise lignin is gas chromatography coupled with mass spectrometers to analyse biomass, bio-oil, and lignin.

This method focuses on detecting individual species to provide information about bond types, functional groups and the chemical state of the atoms (Lu *et al.*, 2017).

Determining functional groups with the use of FTIR is the most widely used technique for its accuracy and speed. It is a non-invasive and non-destructive technique. Fig. 7 provides a guide for the assignment of functional groups to peaks that can typically be observed in lignin samples (Lu *et al.*, 2017). FTIR can identify the structure and structural changes in lignosulphonates (Rodríguez-Lucena *et al.*, 2009).

Table 2-2. FTIR peak assignments of lignin samples (Lu *et al.*, 2017)

Wavenumber (cm ⁻¹)	Assignments	Functional groups and structures in lignin
3400-3600	V(O-H)	Free -OH
3100-3400	V(O-H)	Associated -OH
2820-2960	V(C-H)	-CH ₂ , -CH ₃
2920	V(C-H)	Carboxylic -OH
2650-2890	V(C-H)	Methyl group in methoxyl
1771	V(C=O)	Aromatic
1700-1750	V(C=O)	Unconjugated ketones, carbonyls, and ester groups
1722	V(C=O)	Aliphatic
1650-1680	V(C=O)	Conjugated ρ -substituent carbonyl and carboxyl
1500-1600, 1420-1430	V(aromatic skeletal)	Benzene ring
1450-1470, 1360-1370	V(C-H)	-CH ₂ , -CH ₃
1325-1330, 1230-1235	V(C-O)	Syringyl ring
1270-1275	V(C-O)	Guaiaacyl ring
1215	V(C-O)	Ether
1140-1145	V(C-H)	Guaiaacyl
1130	V(C-H)	Syringyl
1085-1090	V(C-O)	Secondary alcohol and aliphatic ether
1025-1035	V(C-O, C-H)	Aromatic ring and primary alcohol
750-860	V(C-H)	Aromatic ring

The FTIR peaks from 3200–3600 cm⁻¹ are typical of –OH stretching which indicates carboxylic acids, phenols, or alcohols. Between 950 and 1300 cm⁻¹, bands occur that indicates C-O and –OH stretching vibrations. Absorptions between 3000 and 2800 cm⁻¹ are due to C-H stretching vibrations in aliphatic groups. A peak at 1690 cm⁻¹ indicates carbonyl groups with C=O stretching which represent oxygenated compounds such as ketones, aldehydes, and carboxylic acids. C=C stretching bands in the range of 1670–1520 cm⁻¹ and the deformation vibrations at 700–900 cm⁻¹ are indications of unsaturated bonds such as aromatic rings (Wądrzyk *et al.*, 2019).

An important parameter for considering lignin as a source of renewable fuel is the CV. The CV of any biomass or any constituent thereof is an indication of the energy content. These values can be determined experimentally with an adiabatic bomb calorimeter or through

1 mathematical models that use the elemental and proximate results of the biomass (Iroba *et al.*, 2014).

3 The newest technique for analysing and imaging the chemical structure of lignin is confocal
4 Raman scattering microscopy and time-of-flight secondary ion mass spectrometry. As these
5 techniques are new, the availability is quite low because they have not been applied by
6 most scientific groups (Lu *et al.*, 2017).

7 **2.4.5 Valuable products derived from lignin**

8 The variety of functional groups in lignin allows for a wide range of applications, which
9 includes binders, emulsifiers, biofuel, resins, dyes, paints, synthetic floorings and other fine
10 chemicals (Lupoi *et al.*, 2015; Ramakoti *et al.*, 2019). Lignocellulosic biomass is the only
11 carbon-rich material on earth, besides fossils, that can be used as a renewable source to
12 produce transportation fuels and other chemicals, such as catechol, guaiacol, and phenol.
13 The high energy content of lignin/lignosulphonates/sulphonated lignin makes it ideal to be
14 used as a raw feedstock material for producing hydrogen in some biorefinery processes.

15 The high value-added chemical compounds made from lignin can be used to produce
16 bioplastics and bio-adhesives (Ahorsu *et al.*, 2018; Duan *et al.*, 2019). In pulping processes,
17 lignin can be used as a fuel source to generate electricity through the process of combustion
18 (Aro & Fatehi, 2017; Meng *et al.*, 2019). Lignin is also used in agrochemicals, fertilisers,
19 adsorbents, surfactants, rubber, and concrete additives. Efforts have been made to produce
20 thermoplastics from lignin that will have significant economic value (Lupoi *et al.*, 2015; Nam,
21 2013).

22 Lignosulphonates have unique properties, which makes them suitable for animal feed,
23 additives in oil drilling, and stabilisers in colloidal suspensions (Aro & Fatehi, 2017).
24 Lignosulphonates also have an affinity for forming iron (Fe) complexes making
25 lignosulphonates an excellent source to produce Fe chelates (Rodríguez-Lucena *et al.*,
26 2009).

27 The efficiency of these lignin-based products is determined by their molecular weight and
28 the degree of sulphonation. When these products are used in composites, some will have
29 increased hydrophilicity. However, in some cases, the products have to be desulphonated
30 before being used in composites. When the sulphur content in lignosulphonates is reduced
31 they can be used in storage batteries and synthetic resins. If the sulphonated lignin-based

products are to be used as flocculants, the products may first have to be cross-linked to ensure the increase of their molecular weight (Aro & Fatehi, 2017).

2.5 Biomass conversion methods

Since this study is focussed on converting biomass into products with high energy value it is important to consider the different techniques that can be used to accomplish this task. This section will also include a discussion on the different products that can be obtained and their applications.

Lignocellulosic biomass can be converted into energy sources or chemical products with biochemical and thermochemical conversion processes. Thermochemical conversion processes include transesterification and steam reforming (Gollakota *et al.*, 2018; Kambo & Dutta, 2015). Biochemical conversion methods for biomass are less popular as biomass's structure is naturally more resistant to enzymatic and microbial degradation, making it harder for a biochemical process to be economically and technically feasible. Thus it is a less attractive option (Iroba *et al.*, 2014).

2.6 Thermochemical conversion

Thermochemical conversion encompasses a wide range of applications and techniques. It is the most important method for the conversion of biomass into fuels and energy. It is defined as the controlled oxidation or heating of materials to generate energy products. The techniques used differ in temperature and oxidation range (Sánchez-Borrego *et al.*, 2021). Thermochemical conversion takes place at a faster rate and significantly higher temperature than biochemical conversion with a suitable catalyst. Thermochemical conversion processes occur under pressurised and anaerobic conditions (Gollakota *et al.*, 2018; Kambo & Dutta, 2015).

2.6.1 Methods

During **gasification**, the lignocellulosic biomass is kept at a temperature higher than 700°C, with oxygen at a limited level to produce syngas. Syngas can be used as a biofuel or to produce other fuels such as ethanol, isobutene, dimethyl ether, biomethanol, and other chemicals (Ahorsu *et al.*, 2018; Rodionova *et al.*, 2017). First, there is a drying step at temperatures up to 120°C to remove all moisture from the biomass. The next step is

devolatilisation which takes place at temperatures up to 350°C. When the volatiles are removed, char will start to form. The gasification of the char occurs at temperatures above 350°C (Sánchez-Borrego *et al.*, 2021).

Pyrolysis is where a medium range of temperatures (300–600°C) is used on an oxygen-deprived, dry biomass to convert the biomass into liquid pyrolytic oil (similar to crude oil), solid biochar, and syngas (Ahorsu *et al.*, 2018; Stedile *et al.*, 2019). Pyrolysis is an endothermic process, and thus its products usually have a high energy content and are heterogeneous. The largest fraction of the product consists of volatiles (syngas) (Sánchez-Borrego *et al.*, 2021).

Torrefaction is a thermal pre-treatment at low temperatures (200–300°C). It is designed to remove water and volatile compounds. The product is solid with a reduced oxygen content and increased energy content. It uses a very short residence time and is a softer version of pyrolysis. This carbonisation technique is less destructive to the molecular structure (Sánchez-Borrego *et al.*, 2021).

Direct combustion is used to generate heat using thermochemical processes. This is the oldest and most common method of conversion, where biomass is burned in an oxygen-rich environment (Ahorsu *et al.*, 2018).

HTL is used on wet biomass (Gollakota *et al.*, 2018). As wet biomass contains more than 30% moisture (Kambo & Dutta, 2015), no extra energy for drying or dewatering of the feedstock is needed (Elliott *et al.*, 2015). This process is the most effective when attempting to produce biochar (Kambo & Dutta, 2015). The low process temperatures, low tar yield, high energy efficiency, and its ability to process wet biomass are what makes HTL a promising option for biomass conversion (Gollakota *et al.*, 2018).

HTL forces complicated physical and chemical transformations of biomass under the conditions of relatively high temperatures and pressure. The chemical reactions taking place during HTL are strongly affected by the process parameters. Reactions that occur during HTL can cause significant energy densification to the biomass material (Wądrzyk *et al.*, 2019). During HTL, the biomass is degraded by hydrolysis, then dehydrogenation, dehydration, decarboxylation, and deoxygenation, into smaller compounds. Then chemicals are formed through repolymerisation (Gollakota *et al.*, 2018). Different sources have different defined temperatures for when HTL occurs, but mostly HTL occurs between 240–374°C under pressures of 4–22MPa (Kambo & Dutta, 2015; Wądrzyk *et al.*, 2019).

1 For a feedstock or renewable source such as waste cooking oil, the process of
 2 hydrotreatment is often applied as several studies have discovered that it is a promising
 3 and effective method to use if the goal is to deoxygenate the original biomass to eventually
 4 produce biodiesel. However, this process does have an H_2 requirement (additional solvent),
 5 which means that hydrotreating could be more costly than other available methods (Stedile
 6 *et al.*, 2019).

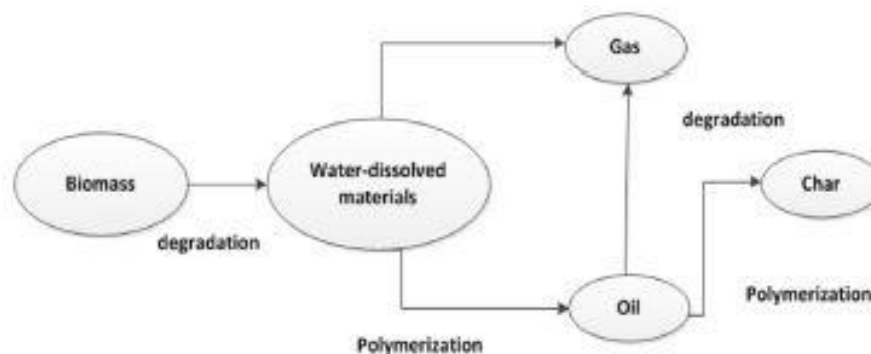


Fig. 8. Reaction mechanism of the HTL process, adapted from Gollakota *et al.* (2018)

7 2.6.2 Thermochemical conversion products

8 2.6.2.1 Biochar

9 A solid material, similar to charcoal, is produced by partially combusting carbonaceous
 10 organic matter, such as wood and plants (thermochemical conversion), in the absence of
 11 oxygen that prevents the complete combustion of the feedstock (Kambo & Dutta, 2015).
 12 Biochar is sometimes known as coke which can be an undesirable co-product (Stedile *et al.*, 2019)
 13 Biochar yields from organic feedstocks are usually in the range of 30 to 60 mass%
 14 at low temperatures (Qian *et al.*, 2015). Biochar usually has high carbon content and low
 15 oxygen content with an energy content of 26–30 MJ/kg, making it a potential competitor for
 16 coal in carbon sequestration. It can also contain high levels of inorganic compounds
 17 (Shrivastava *et al.*, 2021).

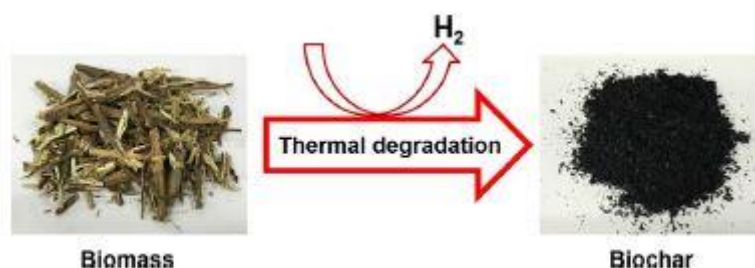


Fig. 9. Conversion of biomass to biochar, (Lee *et al.*, 2017)

2.6.2.2 Bio-oil

Bio-oil can be referred to as the liquid fraction or product of thermochemical conversion that has fuel-like characteristics. It is a complicated mixture of aliphatic hydrocarbons, oxygenated compounds, and aromatics (Stedile *et al.*, 2019). During HTL, the optimal temperature range for the production of bio-oil is 250–350°C (Wądrzyk *et al.*, 2019).

Wądrzyk *et al.* (2019) used pine wood to produce bio-oil through HTL. Nitrogen gas was used to remove all oxygen from the reactor and a starting pressure of 5 bar was used. The biomass loading was 10 mass% and the solvent used was distilled water. Dichloromethane (DCM) was used to extract the bio-oil from the post-reaction mixture. The products that were recovered included bio-oil, an aqueous phase containing dissolved polar organics, a volatile phase, and a solid residue. The process temperatures (250 and 350°C) and residence times (10, 20, 30 and 60 min) were varied. It was discovered that process temperature had a larger effect on the product yield than residence time. At a temperature of 250°C, solid residue had the highest yield due to the moderately deep decomposition of the raw biomass feedstock. However, with increasing residence time the solid residue yield decreased from 56 mass% to 47 mass% for 10 and 30 min, respectively. A reaction time of more than 30 min did not lead to any further decrease of the solid residue production. With these conditions, the bio-oil yield varied from 20–26 mass%. Residence time did have a small effect on the bio-oil and gas yield. This could be due to the decomposition of the wood towards components with lower molecular weight. At a higher temperature, the bio-oil yields were between 33–38 mass%. The highest yield was 38.4 mass% with only a 10 min residence time. Usually, bio-oils produced from wood-type biomass are in the range of 35–45 mass%. At a higher temperature, a longer residence time seemed to decrease the bio-oil yield, which can be explained as secondary reactions of unstable molecules converting bio-oils through repolymerisation towards the aromatic structure of the solids or through cracking into the gaseous phase (Wądrzyk *et al.*, 2019). Studies have shown that using woody biomass at high temperatures produces bio-oil yields of 35–55 mass% which have an energy content of 12.19–22.32 MJ/kg that consist mainly of phenol groups (Shrivastava *et al.*, 2021).

2.6.2.3 Biogas

During HTL, it is possible that intensive decarboxylation occurs due to a dominant contribution of carbon dioxide. It was noted that the gas yields were between 11.4–14.3

mass% (Wądrzyk *et al.*, 2019). Biogas is usually the non-condensable fraction of valuable products (Stedile *et al.*, 2019).

2.7 Depolymerisation and conversion of lignin

After discussing lignin and conversion pathways for biomass, this section focuses on how the method of HTL affects lignin.

Depolymerisation of lignin occurs through the cleavage of the uncondensed β -aryl ether linkages. The depolymerisation of these linkages can be accomplished through mechanical methods (Guerra *et al.*, 2006).

2.7.1 Lignin conversion pathways

Lignin can be converted into vanillin under milder conditions by decomposing the guaiacyl unit of lignin. Guaiacol is produced from lignin when subjected to hydrolysis and dealkylation (Wądrzyk *et al.*, 2019). By using liquefaction on lignin, the cleavage of aryl-alkyl ether bonds would form smaller phenolic monomer compounds. However, these smaller compounds are unstable and highly reactive and tend to undergo repolymerisation into char or oligomers (Duan *et al.*, 2019). When lignin is heated to 100°C, low molecular compounds are released as fumes and odours (Nam, 2013).

2.8 Bio-oil and its significance

For this study, it was necessary to first understand the concept of renewable fuels and how they can be produced, then lignin was discussed as a possible feedstock for the production of renewable fuels. However, lignin cannot be used directly as a feedstock. Lignin first has to be converted into a bio-oil through one of the conversion methods that was discussed in section 2.5 and 2.6. with the previous sections as background, this section focuses on the bio-oil.

Bio-oils are complex mixtures of various chemical compounds and just like petroleum crude oil, bio-oils consist mainly of hydrocarbons. The large number of compounds that are present in the bio-oils lead to more complicated methods of determining the properties of the specific bio-oil. As bio-oils are complicated mixtures of many different compounds, their significance should not be limited to transport fuel. Bio-oil can also be a source of various high-value chemicals. Bio-oil's properties and composition are highly dependent on the type

of biomass that is used as feedstock. Bio-oil can be divided into two main groups according to the biomass source:

- Lignocellulose; and
- Triglyceride (Stedile *et al.*, 2019).

Triglyceride sources include lipid biomass such as animal fats and vegetable oils (Stedile *et al.*, 2019).

2.8.1 Composition of bio-oil

Bio-oils derived from triglyceride biomass consist mostly of hydrocarbons and contain less oxygenated compounds than the bio-oils produced from lignocellulosic biomass (Stedile *et al.*, 2019). Studies have shown that compounds with larger carbon chains will be more likely to form when the reaction times are shorter as it is the faster route through a continuous pyrolysis reactor. The high content of light and renewable olefins in bio-oil may mean that bio-oil has the potential to be an important feedstock for the petrochemical industry (Stedile *et al.*, 2019).

In a study performed by Wądrzyk *et al.*, (2019), the elemental composition of bio-oil could be determined through elemental analysis. At the lower temperature, the carbon content of the bio-oils were significantly higher than in the raw feedstock (46.58 mass%) and seemed to vary between 58–63 mass%. It was also shown that the oxygen content (30–36 mass%) was lower than in the original wood (46.98 mass%). It was reported that a greater oxygen content in the biomass encouraged better reactivity.

The higher carbon content and lower oxygen content led to an increased higher heating value (23.26 MJ/kg) from the 18.57 MJ/kg of the raw wood. At the higher temperature, the bio-oils' carbon content ranged from 63–67 mass% with an oxygen content of 27–30 mass%. The CV improved to be between 26 to 28 MJ/kg (Wądrzyk *et al.*, 2019). It seemed as if an increase in both temperature and residence time had a positive effect.

A Van Krevelen plot was used by Wądrzyk *et al.* (2019) to represent the molar ratios of O/C and H/C of the bio-oils; both these molar ratios were significantly lower when compared to the feedstock, which would suggest that intensive deoxygenation reactions occur through dehydration or decarboxylation. These reactions produce water-soluble organics and carbon dioxide as a gas product.

When it comes to bio-oils, the FTIR spectra usually indicates the presence of phenols, aromatic carbons, and numerous oxygen-containing compounds, such as alcohols, ketones, esters, and aldehydes (Wądrzyk *et al.*, 2019).

GC-MS analyses have revealed that the main types of compounds in bio-oil are phenol, phenol derivatives, and oxygen-containing compounds. When compounds such as furfural and cyclic ketones are present in bio-oil it indicates the decomposition of cellulose and hemicellulose in the raw feedstock. When the feedstock contains lignin, vanillin will be present in bio-oil when produced under mild conditions. This is due to the decomposition of the guaiacyl unit of lignin. Vanillin concentrations will be higher when the temperatures are low and reaction times are longer. When higher temperatures are used the main compounds are usually guaiacol and derivatives of guaiacol. The formation of phenol is mostly contributed to the presence of lignin; however, phenol can also be produced from cellulose (Wądrzyk *et al.*, 2019). A few more compounds that can be found in bio-oil produced from lignin through HTL, are 2-methoxy-phenol, 2,6-dimethoxy-phenol, 4-ethyl-phenol, and 2-methoxy-4-ethyl-phenol (Duan *et al.*, 2019).

Alkali lignin will have an elemental composition of roughly 58.7% C, 5.6% H, 0.6% N, and 31.7% O with a CV of 25.4 MJ/kg (Duan *et al.*, 2019).

2.8.2 Properties of bio-oil

Bio-oils are known for having low thermal stability, and a high acidity, water and oxygen content; thus, having CVs lower than that of fossil fuels (Sánchez-Borrego *et al.*, 2021). Bio-oils are also highly viscous and possess an intense odour. Bio-oils produced through HTL usually has a dark colour with an appearance similar to heavy tar and crude petroleum. Bio-oils have a molecular mass range of 40–3000 g/mol. An estimation has been made that 41–57% of all compounds that are present in bio-oils will have a molecular mass of below 600 g/mol, which is in the range of the molecular mass of fuel oil distillates (Wądrzyk *et al.*, 2019).

An effective method to determine the properties of bio-oil is by constructing distillation curves. This is a method that is not usually applied to bio-oil, but it is a common method in the petroleum industry. Distillation curves can predict molecular weight, refractive index, and viscosity. By using the distillation curves along with a volatility measurement, it is possible to predict the thermochemical properties of complex mixtures such as petroleum and bio-oil. These curves have indicated in previous studies that the behaviour of bio-oil

and crude oil is very similar. The distillation curve method involves the plotting of the boiling temperatures against the cumulative distilled volume fraction of the specific mixture. It can predict properties such as:

- Volumetric average boiling point and mean average boiling point:
 - An oil mixture of various compounds will boil over a specific temperature range that will reflect each present individual compound's boiling point. Lower values will indicate lighter oils and higher values will suggest heavier oils.
- Watson characterisation factor (Kw):
 - This is a classification method for a variety of naphthenic, paraffinic, aromatic, or intermediate components in the oil. A Kw of 12.5 or higher indicates a hydrocarbon compound with a predominantly paraffinic nature. Lower values will suggest more aromatic or naphthenic components. A highly aromatic hydrocarbon will have a Kw value of 10.0 or less.
- Refractive index (RI):
 - RI is an input parameter for other relevant correlations within the refinery process.
- Molecular weight (Mw):
 - Molecular weight is usually an estimation of the petroleum fractions as crude oil consists of a complex mixture of hydrocarbons. Ranges of 70–200 are for lighter fractions while ranges of 200–600 indicate heavy fractions.
- Kinematic viscosity (Stedile *et al.*, 2019).

More important properties of bio-oils include the acid index and iodine index because these two properties influence the instability and corrosivity of the oils. The acid index, iodine index, and density cannot be determined from distillation curves but should be evaluated by different experimental methods or analyses (Stedile *et al.*, 2019).

If the goal is to use the bio-oil as a renewable fuel source one of the most important properties is the energy content expressed as CV. When it is not possible to analyse the CV of bio-oils, mathematical models and the elemental composition can be used to calculate these values (Demirbaş & Demirbaş, 2004). In previous studies, bio-oil produced from lignocellulosic biomass through pyrolysis had CVs between 17 MJ/kg and 28 MJ/kg (Shrivastava *et al.*, 2021).

The ideal fuel would contain no solids and no ash to prevent deposits, corrosion and high wear on fuel injectors and pumps. It is acceptable though for a fuel to have a solid content less than 0.25 mass%, so a bio-oil that already meets this requirement would be advantageous as there would be no need for filtering, and the renewable fuel produced from this oil would have little to no solids (Shrivastava *et al.*, 2021).

The degree of carbonisation (DOC) of the bio-oil can be determined by using the CV of the bio-oil and the CV of the original raw feedstock in the following equation (Iroba *et al.*, 2014):

$$DOC = \frac{CV_{product}}{CV_{feedstock}} \quad \text{Eq. 1}$$

2.8.2.1 The effect of temperature on bio-oil properties

The yields of liquid products such as bio-oil not only depend on the type of feedstock but also on temperature (Shrivastava *et al.*, 2021). Higher temperatures will lead to higher carbon content and increase in the bio-oil's CV. The higher temperature has been known to reduce the molar ratios of H/C and O/C. A decrease in the H/C ratio could encourage an increase in the number of aromatic compounds in bio-oil. A higher temperature and short residence times would reduce the intensity of carbonyl groups and C-O bonds that are present in bio-oils. For longer residence times, the intensity of methyl, methylene and hydroxyl groups are increased. This could be due to the re-arrangement of the phenol derivatives. Changing the reaction temperature will change the shape of the bio-oil's molecular distribution curve. However, it seems that when the temperature is increased, the smaller molecular mass components are converted into gas through cracking or they could repolymerise into bio-oil components that have larger molecular mass, especially with longer residence times. An increase in temperature will reduce the PDI due to cracking and depolymerisation. It will also lead to the production of more stable compounds. Higher temperatures assist in deeper decomposition of lignin (Wądrzyk *et al.*, 2019). The reaction temperature is the most important variable in any thermochemical conversion process. Increasing the reaction temperature will cause yields and CVs to decrease. Temperature also affects the DOC. As temperature increases, so will the DOC (Iroba *et al.*, 2014).

2.8.2.2 The effect of residence time on bio-oil properties

The effect of residence time on a bio-oil's composition is irregular. However, at low temperatures a relatively short residence time could increase the yield of bio-oil, while at high temperatures the longer the residence time, the more the bio-oil yield decreases. Reaction time does not cause a regular change in molecular ratios, but with lower temperatures, the residence time may have a larger effect than with high temperatures. At lower temperatures, the effect of residence time can be seen clearly on FTIR spectra. A shorter residence time will show more intensive bands that are assigned to oxygen compounds, especially those that contain hydroxyl and carbonyl groups. It seems like these groups are less stable when the residence time is longer. These compounds will break down with longer residence times and form simpler compounds. A longer residence time will also increase the intensity of bands representing C=C aromatic compounds and C-O stretching vibrations. This could mean that more phenols and phenol derivatives are being formed. It is believed that these phenols and their derivatives originate from lignin or wood carbohydrates. However, when the temperature is higher than 350°C, it is difficult to see if residence time has any effect at all. GPC analysis reveals that lower temperatures with longer residence times will cause the molar mass distribution curve to be more homogenous. With higher temperatures, residence time will not have a significant effect on the properties of bio-oil, except for a slight decrease of the heaviest compounds in the range of 700–2000 g/mol and a slight increase in the lighter components that are in the range of 130–350 g/mol. This can be attributed to the gradual depolymerisation and cracking reactions. An increase in residence time will reduce the PDI due to the above-mentioned reactions and produce more stable compounds. GC-MS analyses have revealed that the concentration of guaiacol should increase as residence time increases. After a residence time of 30 min, guaiacol has been known to partially decompose into phenol. If the reaction time is longer then more phenol derivatives can be formed. This could mean that deeper decomposition takes place at longer reaction times if combined with higher temperatures (Wądrzyk *et al.*, 2019). A longer residence time will promote the formation of lighter components in the bio-oil, which will lead to the bio-oils' profile changing from diesel to the gasoline range when a distillation curve is taken into account (Stedile *et al.*, 2019).

With longer residence times, the mass loss experienced during conversion processes can be attributed to less reactive components especially those present in hemicellulose, decomposing into volatiles and gases. This trend of mass loss has been reported by numerous studies (Iroba *et al.*, 2014).

2.8.2.3 The effect of catalyst loading on bio-oil properties

Compared to non-catalytic liquefaction reactions, catalytic liquefaction reactions seem to promote hydrodeoxygenation, hydrogenation, and deeper depolymerisation of bio-oils. Catalysts have been used for selective depolymerisation of lignin into valuable phenolic compounds. Catalysts have also been used to improve the yield of bio-oil. It has been known that certain catalysts can improve the bio-oil yield up to 88 mass%, depending on process variables. In the presence of a catalyst, the phenolic monomeric compounds' molecular weight can be lowered significantly. Some reductive catalysts can produce more aromatic rings to saturate the hydrocarbons and improve bio-oil yields. When reductive depolymerisation is applied the oil is likely to contain large amounts of phenolic monomers (Duan *et al.*, 2019; Lloyd & Wyman, 2005). Some previous studies have discovered that if there is ash present in the feedstock, the ash will act as a catalyst in the decomposition of biomass. Thus, to increase bio-oil yield it could be advantageous to first remove the ash from the feedstock. Previous studies have also shown that by increasing reaction temperature the process will favour the production of gas (Shrivastava *et al.*, 2021).

2.8.2.4 The effect of solvents on bio-oil properties

Solvents can affect the product yields as well as the monomer content of bio-oils. It has been found that solvents like 1,4-dioxane act only as solvents. Other solvents like ethanol and formic acids will become reactants and in-situ hydrogen donors (Duan *et al.*, 2019).

2.8.2.5 The combined effect of reaction parameters on the properties of bio-oil expressed as severity factors

Taking note of the overlapping effects of reaction temperature and residence time, one must consider the combined effect of the two process variables on the properties of bio-oil and how they can influence each other's effect on bio-oil properties. Previous studies, such as the one mentioned above which was done by Wądrzyk *et al.* (2019), expressed that with low temperatures the residence time had an effect on various bio-oil properties, but as the temperature increased, the effect of time became significantly less. Thus, an effective method to measure the combined effect on a specific property is through the use of a severity factor. Severity factors are a useful tool to measure the performance of a system that experiences effects from multiple variables. It can provide process conditions that will produce the highest yields utilising the least amount of energy, time, reactants, or catalysts.

Severity factors can assist in the optimisation of a process (Lloyd & Wyman, 2005). When the severity factors for different biomass sources are determined it becomes possible to compare the different types of lignocellulosic biomass (Iroba *et al.*, 2014). A combined severity parameter couples yield data and reaction conditions, such as temperature, residence time, and acid concentration to a single variable. The following equations define the severity factor:

$$R_0 = t \times \exp[(T_H - T_R)/14.75] \quad (\text{Lloyd \& Wyman, 2005}) \quad \text{Eq. 2}$$

With t = reaction time (min);
 T_H = hydrolysis temperature (°C);
 T_R = reference temperature (100°C)

$$\log CS = \log R_0 - pH \quad \begin{array}{l} \text{When the effect of acid is taken into account} \\ (\text{Lloyd \& Wyman, 2005}) \end{array} \quad \text{Eq. 3}$$

$$\text{Severity factor (SF)} = \log R_0 \quad (\text{Iroba et al., 2014}) \quad \text{Eq. 4}$$

This technique was also used in a study completed by Iroba *et al.* (2014) using steam explosion as a pre-treatment on lignocellulosic biomass (barley straw). In this study, the severity factor was used to combine the temperature and reaction time. It was noticed that the product of the steam explosion had an increased carbon content when the temperature and time were increased, and the hydrogen and oxygen content decreased. This allowed the CV of the product to increase as well (Iroba *et al.*, 2014). It has been noted that the severity factor for thermal conversion methods mostly depends on the combined effect of temperature and the moisture content of the biomass. However, increasing the temperature and time will also increase the severity factor. The study also showed that an increase in severity factor, caused the degree of polymerisation to decrease (Iroba *et al.*, 2014). Another advantage of employing the severity factor means that laboratory and experimental results can be directly converted to large-scale industrial applications (Iroba *et al.*, 2014).

2.8.3 Bio-oil applications

In recent years, bio-oils have been considered a potential source for renewable fuels and various chemicals. As the properties and compounds of bio-oil vary from the biomass and

production process used, there is a wide range of applications for bio-oil. Bio-oil can be used as a fuel, a source for the production of H_2 , or it can be seen as a rich source for value-added chemicals such as various aromatic compounds (Sánchez-Borrego *et al.*, 2021).

2.8.3.1 Bio-oil as an energy-rich fuel

It is well known that the overexploitation of the worldwide main energy source, fossil fuels, is resulting in depletion of energy sources, environmental destruction, and an increase in the fossil fuel price. There is also the challenge of most countries being dependent on imported fossil fuels which threaten worldwide economic stability and energy security. This is where alternative energy resources, such as wind, solar, hydroelectric, and biodiesel can alleviate the strain on the current fossil energy system (Sánchez-Borrego *et al.*, 2021).

Biodiesel is a fuel produced from bio-oil that is not only renewable but free of polycyclic aromatic hydrocarbons and sulphur compounds. Various oil resources are available which include waste cooking oils and other non-edible and edible oils. To produce biodiesel, the oils that are mostly used are waste cooking oils and palm oil. The reason this technology still needs to be further developed can be explained by comparing the properties of bio-oil to that of traditional gasoline and diesel. Bio-oils are known to have a higher acidity, lower energy content, lower thermal stability and a higher viscosity compared to petroleum diesel. The oxygen-related obstacles can be overcome by using hydrodeoxygenation processes. This will decrease the oxygen content, leading to an increase in thermal stability and the energy content of the fuel. However, this procedure is very expensive due to the necessity of a metal oxide catalyst that experiences rapid deactivation from coking and it also requires a certain amount of hydrogen that must be supplied from an external source. After hydrodeoxygenation, the upgraded bio-oil is rich in hydrocarbons, and can be applied as gasoline, aviation fuel, and naphtha. The bio-oil can also be fractionated and then used as an additive for any of these fuels. Unfortunately, the low viscosity of the bio-oil remains a major obstacle (Sánchez-Borrego *et al.*, 2021).

Bio-oil can be used for thermal energy plants and stationary electric power (Ahorsu *et al.*, 2018) or it can be co-fed to boilers and furnaces along with fossil fuels and burned directly. In regard to direct combustion, bio-oil has more advantages than heavy fossil fuels, simply because bio-oils will cause less air pollution due to their carbon neutrality and the release of less sulphurous and nitrous oxides into the atmosphere. Table 8-3 compares bio-oil with different fossil fuels. From this information, it can be assumed that bio-oil cannot be used

directly mostly due to bio-oil having a much lower viscosity and energy content, and a very high oxygen content. All the other properties of bio-oil indicate that boilers will have to be modified and redesigned before pure bio-oil can be used as fuel (Sánchez-Borrego *et al.*, 2021).

2.8.3.2 Bio-oil as a high-value chemical source

Bio-oil is a complex mixture that contains many different compounds including aromatics and other organic compounds. This unique chemical composition renders bio-oil an ideal source to harvest a variety of compounds from to produce fine chemicals that have great economic value. These compounds include aromatics such as phenols. Bio-oil also contains many organics that can be used to produce esters and acids. Compounds such as phenols can be used to produce a wide range of products; thus, making phenols very valuable and any source of phenols an invaluable asset. One of the applications for phenolics is the production of binders through crosslinking. Another high-value product that can be produced from bio-oil is hydrogen. Hydrogen can be seen as a valuable chemical or high-energy containing fuel (120.7 MJ/kg). When hydrogen combusts, the only waste that is produced is water, making it an environmentally friendly process.

Traditionally, electrodes are made from pitch, which is tar obtained from coal. However, during the pyrolysis of biomass, tar is also produced. This tar is called biopitch. It can be used to produce electrodes and one of the advantages of biopitch is its higher oxygen content (20 mass% instead of 2 mass% for traditional pitch). This higher oxygen content improves the softening point and increases the reactivity of the pitch material.

The high oxygen content in bio-oil promotes the production of solid products, making the process somewhat simpler. The low levels of sulphur and nitrogen in bio-oil make it a viable source to produce binders that can be used in asphalt.

Bio-oil production can be manipulated to produce pyroligneous acid (wood vinegar), which has biocide properties and can act as a potent pesticide that controls fungi growth.

Recently, some researchers have been successful in extracting polyurethane from bio-oil with ethyl acetate. The bio-polyurethane can be used to produce furniture, medicine, and insulation materials. Due to the huge environmental problem of plastic, lots of attention have been given to developing and producing biodegradable plastic. By fractionating bio-oil, chemicals have been produced which have the potential to be used in the production

process of various plastics. Researchers are in the process of developing this technology to be used industrially (Sánchez-Borrego *et al.*, 2021).

In the last few years, two main methods have been used to separate chemicals from bio-oil: distillation and solvent extraction. With distillation, it is possible to separate chemicals by using high temperatures and atmospheric pressure. Bio-oil has large amounts of reactive oxygen-containing organic compounds such as ketones, aromatics, and aldehydes, which tend to polymerise at high temperatures. To avoid undesired reactions, vacuum distillation should be used, which will also improve the efficiency and allow smaller molecules to be extracted before they polymerise into larger compounds. These compounds include hydroxyacetone and different types of acids, such as formic and acetic acid.

Solvent extraction of bio-oil is also used to separate chemical compounds. A wide range of solvents has been used for this extraction including, ketones, alkaline solutions, water, hexane, and many more. Different solvents can be used to extract different chemical compounds. For example, ethyl ether and 10 mass% caustic soda can be used to extract phenols; hydrochloric acid can also extract phenols (Sánchez-Borrego *et al.*, 2021).

2.8.4 Upgrading methods for bio-oil

Some bio-oils cannot be used in biorefinery processes while having unsuitable properties. The bio-oil may need to be upgraded to improve some of its properties. An acidity reduction or neutralisation can be done by using potassium or sodium hydroxide. The acidity of bio-oils is attributed to the presence of carboxylic acids; therefore, esterification can reduce its acidity. Hydrotreatment processes can reduce the olefins in bio-oil, while thermal cracking can remove most of the oxygen in bio-oil like CO and CO₂ (Stedile *et al.*, 2019).

The main challenges for upgrading are the reduction of high oxygen and moisture contents which are responsible for thermal instability and low energy content.

The storage, transportation and use of bio-oil in engines are complicated by thermal instability. However, hydrodeoxygenation can remedy these issues. This will change the properties and make it suitable for use as a high-value fuel in an internal combustion engine. It uses high operating temperatures and pressures to reduce the oxygen content of the bio-oil by selective cleaving of C-O bonds and increasing the C-C bonds to produce three products: aromatics, mixed alcohols, and fuel components (Sánchez-Borrego *et al.*, 2021).

3 Experimental methods

3.1 Materials

All materials and their specifications used in the different phases are specified in Table 3-1. Materials information . Phase 1 involves the mixing and sampling of the feedstock, Lignex®; while Phase 2 is the fractionation of the Lignex® into smaller fractions of lignin with the use of different solvents; and Phase 3 is when the Lignex® will undergo HTL with different catalysts, temperatures, residence times, catalyst loadings, and solvents to optimise the production of bio-oil.

Table 3-1. Materials information

Materials	Acquisition	Purity (%)
Lignex® (sodium lignosulphonate)	Sappi	N/A
Distilled water	Available in lab	100
Ethanol	Sigma-Aldrich	99.9
Tetrahydrofuran	Merck Chemicals	98
Hexane	Sigma-Aldrich	99.9
Acetone	Sigma-Aldrich	99.9
Methanol	Sigma-Aldrich	99.9
Acetone	Sigma-Aldrich	99.9
Calcium carbonate	Sigma-Aldrich	100
Hydrochloric acid	ACE Chemicals	32
Potassium hydroxide	Sigma-Aldrich	100
Sodium hydroxide	ACE Chemicals	100

3.2 Methods

3.2.1 Phase 1: Sampling and preparation of Lignex®

Lignex® was sampled using the coning and quartering sampling method according to the ASTM D6323-19 standard. The samples were dried overnight (at least 12 hours) at 40°C to ensure that the moisture content throughout the sample is uniform (Sjöström & Alén, 2013) until an amount of 10 kg was collected. The mass taken was an estimate of the amount of sample needed to do all the planned experiments and analyses. The samples were stored in airtight containers to prevent the Lignex® from absorbing any moisture from the air. Analysing and characterising of the Lignex® feedstock included:

- GPC;
- FTIR;
- NMR spectroscopy;
- Proximate analysis;
- Moisture content analysis;
- Calorific value analysis;
- Ion chromatography analysis (IC); and
- Elemental analysis.

The standards, methods and equipment used for the analyses are described in section 3.3.

3.2.2 Phase 2: Lignin fractionation

Phase 2 is part of characterising the Lignex®. A large thimble was weighed prior to the extraction step. Forty gram (40 g) of Lignex® was weighed into the thimble and 400 mL of solvent was added to the ball flask, followed by the assembling of the Soxhlet column. The heating mantle was turned on to allow the solvent to reach boiling point. The Soxhlet extraction process was continued overnight. After the extraction step, the Soxhlet column was taken apart and the solvent was transferred from the ball flask to the rotary flask of the rotary evaporator (rotovap) instrument. Almost all the solvent was evaporated under reduced pressure at a relatively low temperature of 40°C. A glass container was weighed, and the remaining solvent was poured into the glass container. The last bit of solvent was allowed to evaporate from the glass container in an oven at 60°C. After the evaporation of the solvent, the fraction was left in the oven to dry in the glass container at 60°C overnight. The fraction left in the container was weighed. The

Lignex® that was left in the thimble was placed back into the Soxhlet column with a new solvent and the entire process was repeated. After the last solvent, the thimble with the remaining solids (final fraction) was dried at 60°C and weighed. Each fraction was then analysed.

The solvents sequentially used in the Soxhlet extraction process and the analysis performed on the extracted lignin fractions are as follows:

- Solvents:
 - Hexane (Fraction 1);
 - THF (Fraction 2);
 - Acetone (Fraction 3);
 - Ethanol (Fraction 4);
 - Methanol (Fraction 5);
 - Fraction 6: Solids left in the thimble

Refer to section 3.1 for purities and source of solvents.

Table 3-2. Fractionation solvents and important properties

Step	Solvent	Boiling point (°C)	Relative polarity (Reichardt & Welton, 2010)	Hildebrand solubility parameter (Belmares <i>et al.</i> , 2004)
1	Hexane	69	0.009	14.9
2	Tetrahydrofuran	65-67	0.207	19.4
3	Acetone	56	0.355	20.0
4	Ethanol	78	0.654	26.6
5	Methanol	64.7	0.762	29.6

- Analyses:
 - GPC;
 - FTIR;
 - NMR spectroscopy;
 - Elemental analysis;
 - GC-MS; and

- 1 ○ Mass yields (determination of which is discussed in sections 3.2.3.3, 3.2.3.4
- 2 and 4.4)

3 **3.2.3 Phase 3: Hydrothermal liquefaction**

4 **3.2.3.1 Washing of reactor**

5 Before and after each experimental run, the reactor, the reactor sleeve, and the stirrer were
6 scrubbed with hot water and soap. Afterwards, the reactor, the sleeve and the stirrer were
7 washed thoroughly with acetone and allowed to dry, to prevent contamination.

8 **3.2.3.2 Loading**

9 A batch reactor with a total inner volume of 180 mL was used. A volume loading of 40%
10 was selected. Ethanol was chosen as the solvent. The biomass loading was chosen to be
11 30% and thus the solvent loading was 70%. A high biomass loading was desired to produce
12 enough product for analyses which was the highest biomass loading the reactor could
13 process without activating the pressure relief valve causing mass loss. This was determined
14 through trial and error. An alkali catalyst was used for the experiments.

15 **3.2.3.3 Hydrothermal liquefaction procedure**

16 Firstly, the clean reactor sleeve was weighed and both the catalyst and Lignex® were
17 weighed in the reactor sleeve. The sleeve was then inserted into the batch reactor. The
18 reactor was closed and sealed by tightening the bolts in a criss-cross pattern, with a torque
19 wrench using 60 Nm, 90 Nm, and 110 Nm, sequentially. Next, the reactor was filled with
20 nitrogen gas until the pressure inside the reactor was 50 bar. The air and nitrogen inside
21 the reactor were then vented and the purging was repeated three times. After the last purge,
22 the ethanol was injected into the reactor through an inlet valve. The reason for the injection
23 of ethanol after the purging was to prevent the loss of any ethanol that could have
24 evaporated during purging. The reactor was filled with nitrogen to a pressure of 5 bar. The
25 temperature in the reactor, before the heating process started, was noted. The stirrer was
26 turned on and so was the heating mantle, to have a relatively constant heating rate, until
27 the reactor reached the desired temperature. The reactor was kept at that temperature for
28 the selected residence time. The reactor was then allowed to cool down. The final
29 temperature and pressure were noted. The gas that had formed during the reaction was

then vented and the bolts of the reactor were loosened again in the criss-cross pattern. The sleeve was removed from the reactor and weighed to determine the amount of reactants that converted into gas.

3.2.3.4 Separation of bio-oil and biochar

A Büchner funnel was weighed along with a filter paper and the empty conical flask. Hydrochloric acid was added to the product mixture and mixed for 10 min to neutralise the alkali catalyst. The contents of the reactor sleeve were then emptied into the Büchner funnel to be filtered using a vacuum. The biochar was washed with 400 mL of acetone to ensure that the biochar was thoroughly washed. The Büchner funnel, containing the filter paper and the biochar, was placed into an oven to be dried at 60°C overnight. After the biochar has dried the Büchner funnel was weighed again to determine the conversion of the biochar. The solvent and acetone were transferred from the conical flask to a rotovap flask. The solvent and acetone were then evaporated almost completely under reduced pressure at 40°C. The entire volume was then poured into a glass container and dried for 6 hours at 60 °C in an oven. After drying, the oil was weighed and analysed. A Karl Fischer titration was performed to determine the moisture content of the bio-oil.

3.2.3.5 Part 1: Catalyst comparison

First, an experiment was completed with the loading that was mentioned in Section 3.2.3.2 and without an alkali catalyst. Then, three catalysts were compared to determine which gave the highest bio-oil yield. The loading of the solvent and Lignex® was used as explained in Section 3.2.3.2. The three catalysts that were compared were potassium hydroxide, sodium hydroxide and calcium carbonate. The conditions for these experiments were a temperature of 320°C with a starting pressure of 5 bar, a residence time of 20 min and a catalyst loading of 5 mass% of the biomass loading. After it was determined which catalyst gave the highest bio-oil yield, all other experiments were completed with just one catalyst. The proceeding of the experiments and the separations are explained in sections 3.2.3.3 and 3.2.3.4.

3.2.3.6 Part 2: Investigating the effect of temperature and residence time

The same loading was used as explained in Section 3.2.3.2. The effect of two variables was investigated by using the temperatures 240 °C, 260 °C, 280 °C, 300 °C and 320 °C. The

residence time was also changed between 20 min, 40 min, 60 min and 80 min. The starting pressure was kept constant at 5 bar for all experiments. The chosen catalyst was sodium hydroxide and the catalyst loading for all experiments was kept at a 5 mass% of the biomass loading. The proceeding of the experiments and the separations are explained in sections 3.2.3.3 and 3.2.3.4.

3.2.3.7 Part 3: Investigating the effect of catalyst loading

The optimum conditions for bio-oil yield and quality from the experiments in Part 2 were used to investigate the effect of alkali catalyst loading on the yield and quality of the bio-oil. Thus, the loading of the catalyst was varied between 2 to 6 mass%. The biomass loading was the same as explained in Section 3.2.3.2. The proceeding of the experiments and the separations are explained in sections 3.2.3.3 and 3.2.3.4.

3.2.3.8 Part 4: Investigating the effect of different solvents

Again, the loading was the same as in Section 3.2.3.2. The experiments were completed as described in Section 3.2.3.3. The solvents that were used were ethanol and THF. These solvents were used in ratios with distilled water. The ratios of solvent to water were 0.2, 0.4, 0.6, 0.8 and 1. As the solvent mixtures that were used contained water, the separation method described in Section 3.2.3.4 was not sufficient. Thus, to separate all the oils, the entire content of the reactor sleeve was emptied into a Büchner funnel with vacuum filtration. The liquid phase was filtrated from the biochar. The biochar was then washed with hexane to dissolve all non-polar oils that were trapped in the biochar pores. The hexane and aqueous phases did not mix due to the differences in polarity; they formed two layers in a separation funnel. The aqueous phase was the bottom layer because the density of the aqueous phase is greater than that of the hexane phase. The aqueous phase was then removed and stored, while the hexane phase was taken to the rotovap to remove the hexane, thus leaving the non-polar bio-oils. The biochar was then washed with acetone to dissolve all the polar oils in the biochar pores and to remove the remaining aqueous phase that was still trapped in the biochar's pores. The acetone phase was then taken to the rotovap to evaporate the acetone. The remaining liquid consisted of the aqueous phase and polar oils. The water was then evaporated by using a heating plate at 60°C until only the polar oils remained.

3.3 Analyses

3.3.1 Karl Fischer titration

The Karl Fischer titration method was used to determine the moisture content of the bio-oils. The analysis was conducted by using an 831 KF Coulometer and a 728 Stirrer from Metrohm.



Fig. 10. Karl Fischer titrator

3.3.2 Elemental analysis

For the elemental analyses, an Exeter Analytical, Inc. CE-440 Elemental Analyzer was used. An elemental analyser is used for the analysis of organic compounds such as oils and other petrochemical products to determine the carbon, hydrogen, nitrogen, oxygen, and sulphur content of the sample. The SANS 17247:2017 method was used as a standard for the duration of the elemental analyses (SABS, 2017).



Fig. 11. Elemental analyser

3.3.3 GC-MS analysis

The GC-MS analyses were conducted using Agilent Technologies' 7890A GC system and 5975C inert MSD system with a triple-axis detector. The GC-MS uses an Agilent J & W VF-5ht Ultimetel with helium as a carrier and operates at 35°C for 4 min, then 190°C for 5 min and then 420°C for 2 min. The sample was dissolved in acetonitrile before the analysis was started. The two methods that were used for this analysis are the NREL method (National Renewable Energy Laboratory), and, quantification of semi-volatile oxygenated components of pyrolysis bio-oil by gas chromatography/mass spectrometry. The GC-MS was used to qualitatively determine which chemical compounds were present in the bio-oil.



Fig. 12. A gas chromatography-mass spectrometry instrument

3.3.4 GPC analysis

The GPC analyses to characterise the feedstock and bio-oils' molecular mass size distribution were conducted using a GPC analyser consisting of a PerkinElmer's Flexar RI detector, a Flexar column and oven, a Flexar LC pump, a Flexar solvent manager, and a Flexar LC auto sampler. The GPC uses a solvent solution of 90 volume % DMSO (Dimethyl sulfoxide) and 10 volume % water with 0.05 mol/dm³ lithium bromide. The column consists of 2 Agilent technologies PolarGel-L 300 x 7.5 mm columns that are connected in series and operates at 55°C.



Fig. 13. Gel permeation chromatography instrument

3.3.5 NMR analysis

A Bruker 600 MHz Ultrashield Plus Avance III NMR spectrometer (Karlsruhe, Germany) was employed to record all spectra. A 2-channel direct observation broadband probe was employed to detect protons at 600 MHz (16 scans) and ^{13}C at 150 MHz (256 scans).

DOSY spectra were recorded utilising pulsed-field gradient spin echo NMR with the gradient set at 5–95% in 16 increments. The gradient was calibrated to the self-diffusion coefficient of chloroform at 298 K, $2.229 \times 10^{-9} \text{ m}^2/\text{s}$; p30 was set to 500–1,500 μs , and d20 to approximately 60 ms. The relaxation delay for all NMR measurements was set at 2 s. Topspin 3.6 (Bruker, Karlsruhe, Germany) was employed to operate the equipment and to process the data. The NMR was used to verify which functional groups were present in the bio-oil.

3.3.6 ICP-OES aqueous analysis

The inductively coupled plasma optical emission spectrometry (ICP-OES) analysis on the feedstock was conducted by an Agilent Technologies 725-ES ICP-OES with radial torch. The ICP-OES is based on the principle that atoms and ions can absorb energy to move electrons from the ground state to an excited state. The energy source is heat from an argon plasma that runs at 10,000 K. As an electron returns from a higher energy level to a lower energy level, it emits light of a very specific wavelength. The type of atom or ion and the energy levels the electron is moving between determines the wavelength of the emitted light and helps to determine the identity of the atom or ion. The amount of light released at each wavelength is proportional to the number of atoms or ions making the transition. The Beer Lambert law describes the relationship between light intensity and concentration of the element. This analyses method was used to determine the inorganic compounds in the raw feedstock.

3.3.7 Proximate analysis

First, an empty crucible with its lid was weighed. Its mass was known as m_1 ; 1 g of sample was added and the crucible with the lid and sample was weighed again (m_2). The crucible and the sample were placed in an oven without the lid, at 105°C, overnight. Then the crucible was allowed to cool in a desiccator and weighed again. The difference in mass was the moisture content that was calculated according to the SANS 5925:2007 method (SABS, 2007). The volatile matter was determined according to SANS 50:2011 (SABS, 2011). The crucible with its lid and sample was placed in a furnace at 900°C for 7 min. The crucible, lid, and sample were allowed to cool to be weighed again to determine the volatile matter ($m_{3,2}$). The ash content was determined according to SANS 131:2011 (SABS, 2011). Again, the entire crucible was placed into a furnace at 900°C overnight. The crucible was allowed to cool to be weighed ($m_{3,3}$). The fixed carbon content was calculated as the matter that remained in the crucible. The standards (SANS) are discussed in Appendix A. An industrial oven was used for the moisture content and a Carbolite Gero VMF 1000 furnace was used for the higher temperatures. The proximate analysis was used to determine the moisture, volatile, fixed carbon and ash content of the feedstock, biochar and some of the bio-oils.



Fig. 14. Furnace oven

1 **3.3.8 FTIR analysis**

2 FTIR analyses on the Lignex® feedstock, bio-oil, and biochar were conducted with the IR
3 Affinity 1 model infrared spectrometer. For solids, lithium bromide powder is used as a
4 background while for the bio-oils, acetone was used. The FTIR spectrums were used to
5 identify the functional groups present in the bio-oil and biochar.



Fig. 15. FTIR analysis equipment

6 **3.3.9 CV analysis**

7 The CVs of all the different samples of biochar and the Lignex® feedstock were determined
8 by an IKA C5003 control and IKA KV600 digital bomb calorimeter.

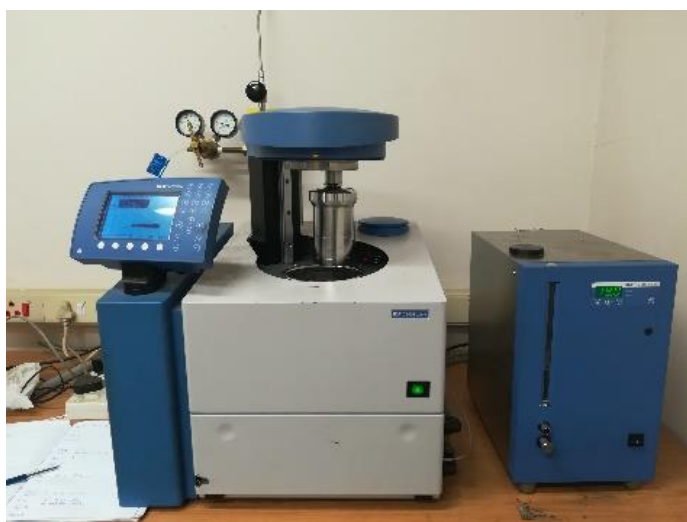


Fig. 16. Calorific value analyser (BOMB calorimeter)

1 **3.3.10 Rotary evaporator**

2 A Buchi Rotavapor R-100 was used in conjunction with a Buchi Interfacel-100, a Buchi
3 Vacuum pump V-100 and a Buchi Heating bath B-100. The cooling unit consisted of a
4 HAAKE DC30 and K20 which cooled to 5°C. The heating bath was set to 40°C and the
5 vacuum pump set to 200mbar. The rotation speed setting was set at 3.5. The rotary
6 evaporator was used to separate the bio-oil from the solvent.

4 Results and Discussion

4.1 Characterization of Lignex®

4.1.1 Introduction

Lignex® is a sodium lignosulphonate in the form of a fine powder with a reddish-brown colour and a slightly sweet odour. When Lignex® is exposed to the atmosphere for long periods it would absorb moisture from the air and become sticky. Lignex® is completely dissolvable in water.

4.1.2 Chemical properties

4.1.2.1 Major constituents

The proximate analysis was performed in triplicate and the average data is presented in Table 4-1 (SABS, 2007; SABS, 2011a). The data revealed that Lignex® contains very little moisture, which can be advantageous for pre-treatment methods as higher moisture contents can have a dampening effect on how successfully pre-treatment methods work. More than 53 mass% consists of volatiles which could indicate a large fraction of hemicelluloses and reactive components being present (Iroba *et al.*, 2014). The ash content of Lignex® is more than 30 % which can affect the acidity and contribute to lowering the energy value of Lignex®. According to the study completed by Ou *et al.*, 2018, the ash content of the Lignex is too high to qualify as an ideal feedstock for a biorefinery process.

Table 4-1. Proximate results of Lignex®

	#1 Mass%	#2 Mass%	#3 Mass%	Average (mass%)	Standard deviation
Moisture	2.90	2.93	2.82	2.88	0.06
Solids	97.10	97.07	97.18	97.12	0.06
Volatiles	53.64	53.40	52.64	53.23	0.52
Ash	33.18	32.44	32.47	32.70	0.42
Fixed carbon	10.28	10.99	11.07	10.78	0.44

4.1.2.2 Elemental composition

The elemental analysis was also repeated three times and the averages are displayed in Table 4-2. Lignex® contains relatively high amounts of sodium, sulphur, oxygen, and other elements that are represented by the % R-value (61.08 %). The nitrogen content is low which will be an advantage for the conversion to a high-energy product. With the use of upgrading and conversion methods, Lignex® could potentially be a source for high energy value products, such as biodiesel, hydrogen, and biopitch phenols that can be used for binders, esters, etc. Even though the ash content of the Lignex® might be too high, the carbon content looks promising for a feedstock (Ou *et al.*, 2018).

Table 4-2. Elemental composition

Element	Composition (%)
C	51.70 ± 0.01
H	5.89 ± 0.05
N	0.25 ± 1.05
O	42.16 ± 0.05

4.1.2.3 Cation and anion content

An IC analysis was conducted on raw Lignex® material. The results confirm the presence of components that would contribute to the high R-value. Table 4-3 displays the data of a 0.134 g raw Lignex® sample dissolved in 50 mL of water. The sample had a pH of 6.7. These results show high concentrations of sodium and sulphates confirming that raw Lignex® is indeed a sodium lignosulphonate.

Table 4-3. IC analysis of the raw Lignex®

Component	Composition (%)	Component	Composition (%)
F	ND	PO ₄	2.30
Cl	12.01	Na	82.25
NO ₂	ND	NH ₄	0.30
Br	0.04	K	11.66

NO ₃	0.15	Mg	2.20
SO ₄	26.40	Ca	2.70

*ND = Not detected

4.1.2.4 Energy value

Lignex® has a CV of 11.64 ± 1.48 MJ/kg. The relatively low energy content of Lignex® can be explained by the high oxygen content as seen in the results of the elemental and IC analyses. The relatively low carbon and hydrogen content as seen in Table 4-2 also contribute to the low energy value. If upgrading through catalytic HTL is successful the carbon and hydrogen content will increase while the oxygen content will decrease, which will allow for a higher CV to be obtained which is an indication of higher energy content.

4.1.2.5 Molecular size distribution

From the molecular weight data obtained through GPC analyses, displayed in Table 4-4, it can be assumed that Lignex® has a complex chemical structure with a large molecular weight. The PDI also shows that Lignex® contains many molecules that differ greatly in molecular weight. Sodium lignosulphonates usually have large molecular weights (Madad *et al.*, 2011), but pure sodium lignosulphonate that is available on the market has a molecular weight of 534.5 g/mol. This implies that Lignex® might have a heavily condensed structure and lots of impurities (Kim *et al.*, 2019). As can be seen in Fig. 17, Lignex® has a broad molecular weight distribution with three distinct peaks of which two are large, sharp peaks between 200 and 450 g/mol, and 450 and 800 g/mol, respectively. The peak with the highest intensity (Peak 1) represents very large molecules, but because this peak is narrow it suggests that there are only a small number of molecules that are this large and heavy. This peak might be indicative of lignosulphonate molecules or lignin degradation products. A broad peak (Peak 2) indicates larger and heavier molecules, but since this peak has a significantly lower intensity, it could mean that the molecules are smaller than those detected with Peak 1 molecules. The broader width of Peak 2 means that there are more molecules present in Lignex® that have a molecular weight between 800 and 2240 g/mol; these could be pure lignin or condensed lignin molecules. Peak 3 has a much lower intensity than the other two peaks, while also being narrow. This would mean this peak represents a smaller number of smaller molecules that are also lighter in molecular weight. This peak might be an indication of impurities detected by the GPC in the sodium lignosulphonate.

Three sections have been indicated in Fig. 17. If it is possible to fractionate or separate certain fractions of Lignex® according to molecular weight, it might be possible to identify exactly which types of compounds and molecules these peaks represent. In doing so, it might be possible to remove the impurities from the lignin molecules and thus purify the lignin. It might also be possible to break the lignin molecules into smaller chains of lignin with lighter molecular weights and a smaller distribution, making conversion into high-value products simpler and more predictable. This theory was attempted with the use of sequential dissolution with solvents such as hexane, THF, acetone, ethanol, and methanol. The findings are discussed in Section 4.1.3.

Table 4-4. Molecular size distribution of Lignex®

Material	Mw (g/mol)	Mn (g/mol)	PDI
Lignex®	2 468 ± 1	945 ± 1	2.6 ± 0.3

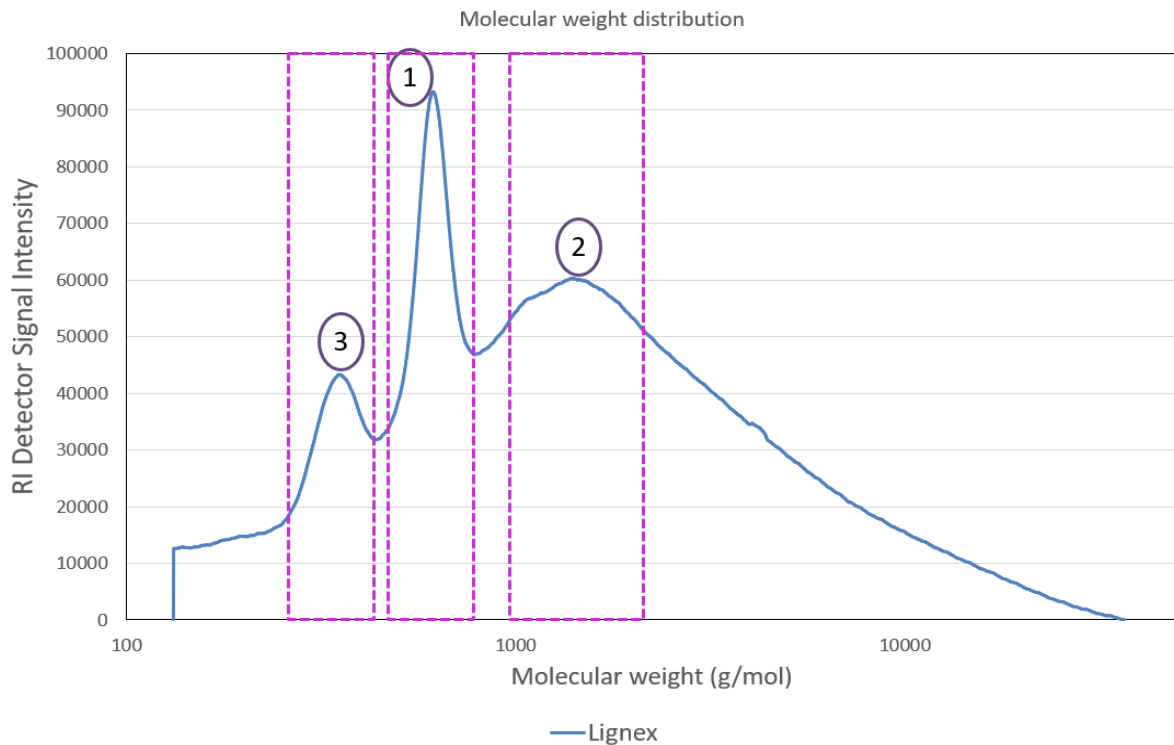


Fig. 17. Molecular weight distribution of raw Lignex®

4.1.2.6 FTIR analysis of Lignex®

The FTIR spectrum of Lignex® can be seen in Fig. 18. The assumption that the structure of Lignex® is complex is supported by this spectrum since it revealed the presence of

numerous functional groups. The peaks in the spectra were assigned to the different functional groups and can be seen in Table 4-5. The bands between 3700 and 3000 cm^{-1} were assigned to -OH stretching bands; however, Lu *et al.* (2017) divided the band into two sections where the stretch band between 3600 and 3400 cm^{-1} was assigned to free -OH groups and 3400–3100 cm^{-1} represented associated -OH groups, which according to Coates (2006) can be a terminal (vinyl) -CH group or the ammonium group that can be seen in Table 4-3 and Table 8-4 of the IC analysis. The sp^3 -hybridised C-H bonds in the range of 3000–2880 cm^{-1} indicate the presence of -CH, -CH₂ and -CH₃ groups as well as the possible presence of carboxylic groups (Esterhuizen, 2020; Lu *et al.*, 2017). The bends between 2320 and 2080 cm^{-1} most likely indicate the presence of the NO₃ that was detected by the IC analysis. According to Coates (2006), the bends between 1960 and 1830 cm^{-1} indicate the presence of aromatic combinations and five-membered rings. It could also indicate transition metal carbonyls; however, the IC results revealed a very low concentration of iron in the Lignex®; thus, it is unlikely that the iron would cause these prominent peaks. The C=O stretching between 1690 and 1630 cm^{-1} is representative of conjugated *p*-substituent carbonyl and/or carboxyl groups (Lu *et al.*, 2017). The peak at 1650–1540 cm^{-1} represents aromatic C=C stretches that indicate the presence of benzene rings. C=O bonds connected to aromatic compounds can be seen at the bend between 1540 and 1510 cm^{-1} . The sp^3 C-H bends between 1470 and 1450 cm^{-1} can be caused by -CH₂ and -CH₃ groups. More C-H groups can be seen between 1440 and 1400 cm^{-1} in the form of benzene rings. The C-O stretch that is represented by the bend at 1360 and 1320 cm^{-1} is indicative of syringyl rings and some others; it could also show the presence of sulphonates as supported by the IC results. Next, between 1280 and 1160 cm^{-1} , there is a peak of C-O stretches that could indicate either syringyl, guaiacyl, or phenol rings; however, with lignin compounds this peak would usually indicate an ether. Between 1140 and 1090 cm^{-1} there are stretching C-H bonds that indicate guaiacyl rings and cyclic ether bonds. The C-O and C-H bonds between 1080 and 1000 cm^{-1} indicate aromatic rings that are bonded to a primary alcohol. The small peak at 950–910 cm^{-1} is indicative of aromatic rings, probably like phenol and benzene. Lastly, there seems to be some rocking -CH bends which could indicate phenyl aromatic rings, of which some may contain sulphate ions (Coates, 2006).

Table 4-5. FTIR assignment of functional groups present in Lignex®

Wavenumber (cm^{-1})	Functional group
3700-3000	-OH stretch bands
3000-2880	Sp^3 - hybridised C-H bonds
2320-2080	Nitrates/ Alkynes $\text{C} \equiv \text{C}$

1960-1830	Aromatic combination rings
1690-1630	C=O stretching
1650-1540	Aromatic C=C stretch bands
1540-1510	C=O bonds
1470-1450	Sp ³ C-H bends
1440-1400	Aromatic C-H ring
1360-1320	C-O stretch bonds
1280-1160	C-O stretches
1140-1090	C-H stretch bonds
1080-1000	Aromatic C-O and C-H bonds
1000-800	Aromatic bonds (benzene and phenols)
800-520	Aromatic sp ² C-H bends

1

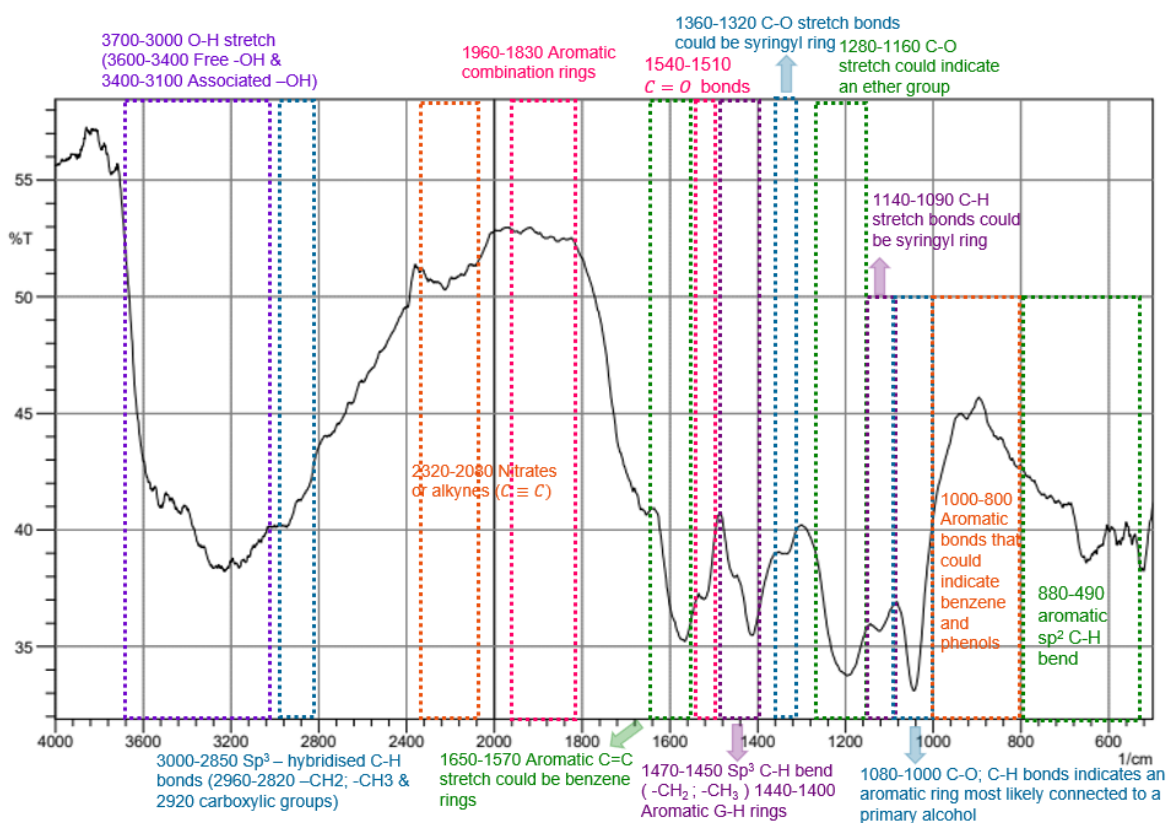


Fig. 18. FTIR spectrum of raw Lignex®

2

4.1.2.7 NMR

The NMR spectrum of the raw feedstock, Lignex®, can be seen in Fig. 19. According to this spectrum Lignex® contains S and G units, carbohydrates, ketones (a degradation product of hemicellulose and cellulose), and sulphonic groups. Structural bonds such as β -O-4, β - β , and β -5 were also present. The Lignex® also contains aromatic rings, methoxy groups and aliphatic oxygenated compounds.

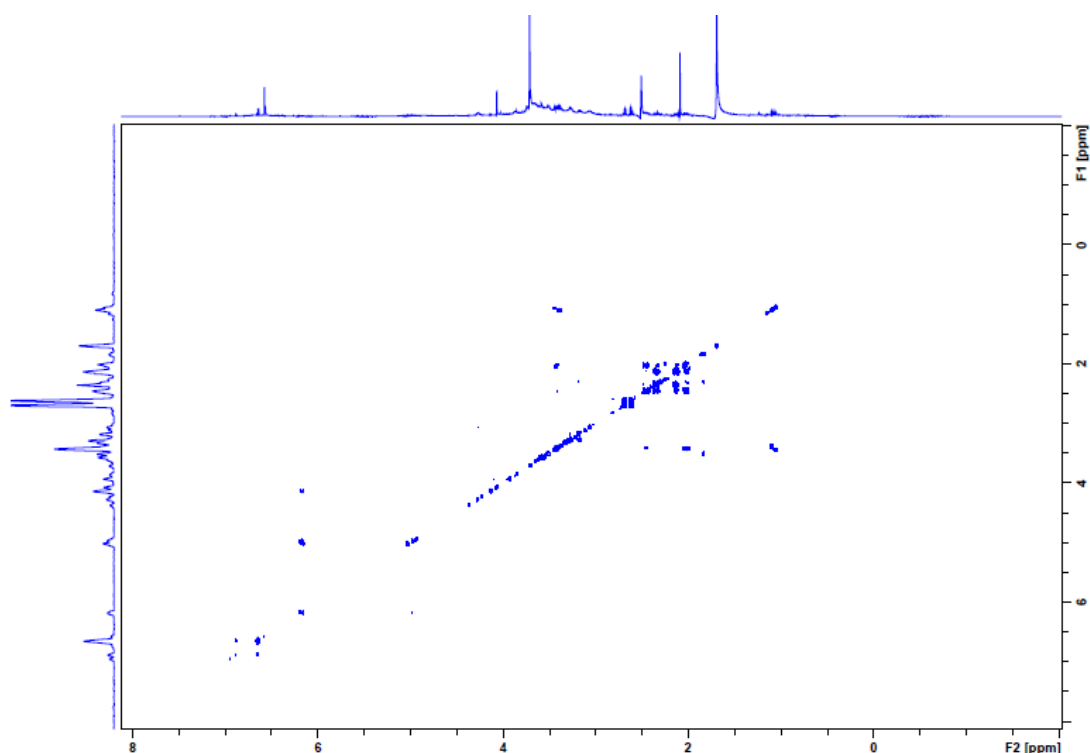


Fig. 19. COSY NMR spectrum of Lignex®

4.1.3 Fractionation and characterisation of Lignex® feedstock

Characterisation of the Lignex® revealed that it consisted not only of sodium liginosulphonate but also contained other impurities. An investigation was launched to attempt to separate these impurities or some parts of the lignin structure from the larger sodium liginosulphonate structure. This separation was attempted through sequential solvent dissolution (feedstock fractionation) as explained in Chapter 3. The fractionation of the feedstock was executed with a Soxhlet column, 40 g of Lignex® and 50 mL of solvent for 108 hours (after 108 hours there was no more significant gain in the yield). The solvents were chosen because of their Hildebrand solubility parameters. These solvents and their applicable properties are listed in experimental order.

1 In it can be seen that hexane is the least polar solvent while methanol is the most polar
 2 solvent. It was found that a higher Hildebrand solubility parameter allowed for a larger mass
 3 fraction to be extracted. The mass fraction extracted with each solvent is presented in Fig.
 4 20 with methanol which has the highest Hildebrand solubility parameter extracting the
 5 largest mass fraction (48.81 mass%).

6 Fig. 20 depicts the mass of the samples that were extracted from the Lignex® with five
 7 different solvents. The extraction was repeated four times and the averages are displayed
 8 in this figure. The insoluble fraction refers to the amount of Lignex® that could not be
 9 dissolved in these solvents.

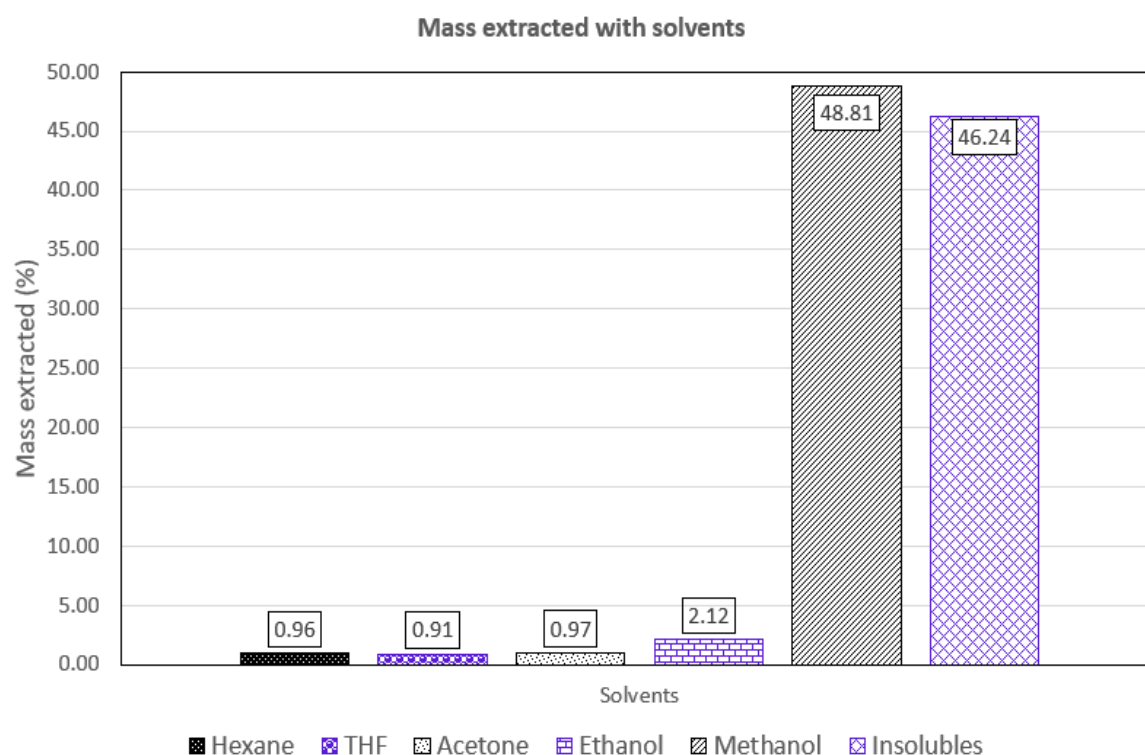


Fig. 20. Mass fractions extracted with various organic solvents

10

11 4.1.3.1 Hexane-soluble fraction

12 The solvent with the lowest Hildebrand solubility parameter, hexane, extracted one of the
 13 smallest fractions (0.96 %). GC-MS analysis of this fraction showed that hexane extracted
 14 alkanes, alkenes, alcohols, esters, and phenolics. These groups were semi quantitatively
 15 quantified by calculating the total peak area of each specific group as a percentage of the
 16 total peak area of the chromatogram from the raw GC-MS data. The alkanes and alkenes
 17 were the largest groups extracted with hexane and included compounds like hexadecane

and docosene. Anthracene was also present as an aromatic. This is believed to be because of the hexane's non-polar nature and ability to extract non-polar compounds. Fig. 21 shows the compounds that were present in the fraction that was extracted with hexane. It would seem that hexane extracted mostly impurities as lignin does not contain any alkane or alkene chemical groups. These impurities might originate from resins, waxes, fats and gums in the liginosulphonate. The phenolics that were extracted is believed to be a part of the original feedstock and was produced through degradation of lignin during the sulphite

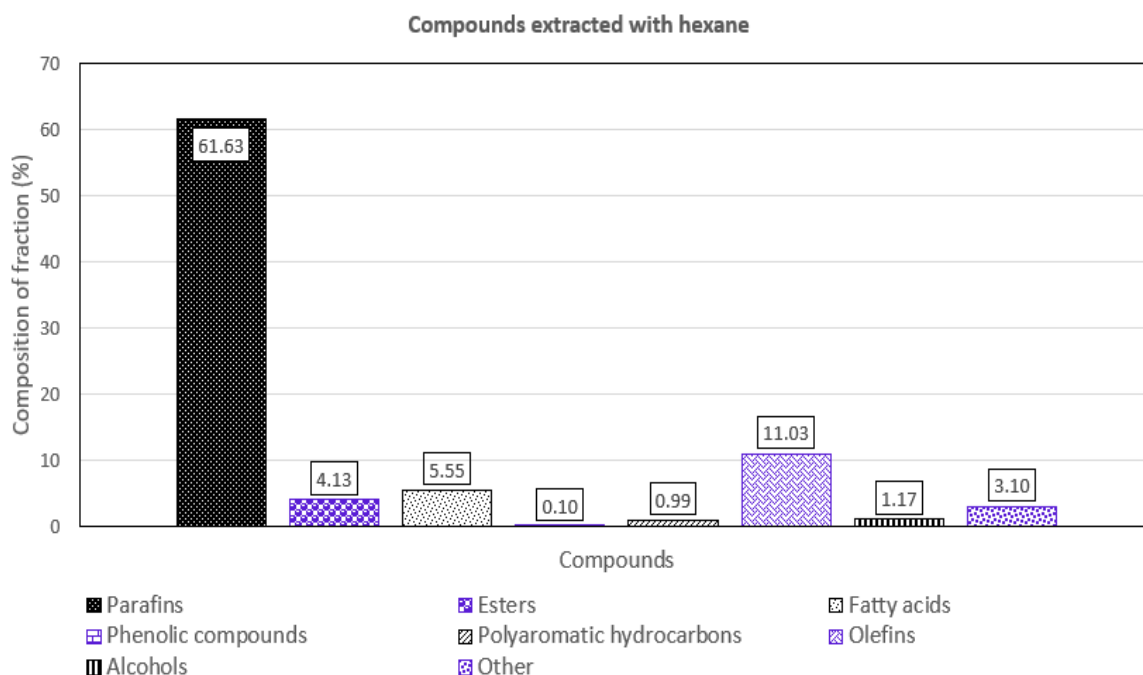


Fig. 21. Chemical composition of the fraction extracted with hexane

pulping process. The GC-MS detected two compounds that are represented in Fig. 21 by the 'Other' group. These two compounds are a nitrogen-containing aromatic called Dibenzo[b,e]7,8-diazabicyclo[2.2.2]octa-2,5-diene and a heterocyclic sulphur compound called 4,4'-Bis(tetrahydrothiopyran).

The FTIR spectrum showed the presence of C-H bonds, ketones, aromatic rings, and phenyl groups. The alkoxy and alkene groups were also visible on the spectrum. The first two peaks that were observed on the spectrum in Fig. 22 were at 2918 and 2850 cm^{-1} . These peaks represent the methylene, methoxy and methyl ether compounds that were also detected with GC-MS. The third peak was at 1710 cm^{-1} which represents carboxylic acids, like n-hexadecanoic and octadecanoic acid, which were detected by the GC-MS. The fourth peak marked in green represents C=O bonds that are present in esters like isopropyl myristate and methyl stearate. The fifth and sixth peaks marked with the red rectangle (roughly at 1360 cm^{-1} and 1305 cm^{-1}) were attributed to a phenolic compound (butylated hydroxytoluene) and an aromatic ring containing a nitrogen compound (dibenzo[b,e]7,8-

1 diazabicyclo[2.2.2]octa-2,5-diene), respectively. From 1200–1020 cm^{-1} , two sharp peaks
 2 can be seen that represent the alcohols. The intense peak at 980–940 cm^{-1} is believed to
 3 represent the heterocyclic sulphur compound, 4,4'-bis(tetrahydrothiopyran). From 800 cm^{-1}
 4 it is possible to see the vibrations caused by the presence of aromatic rings.

5

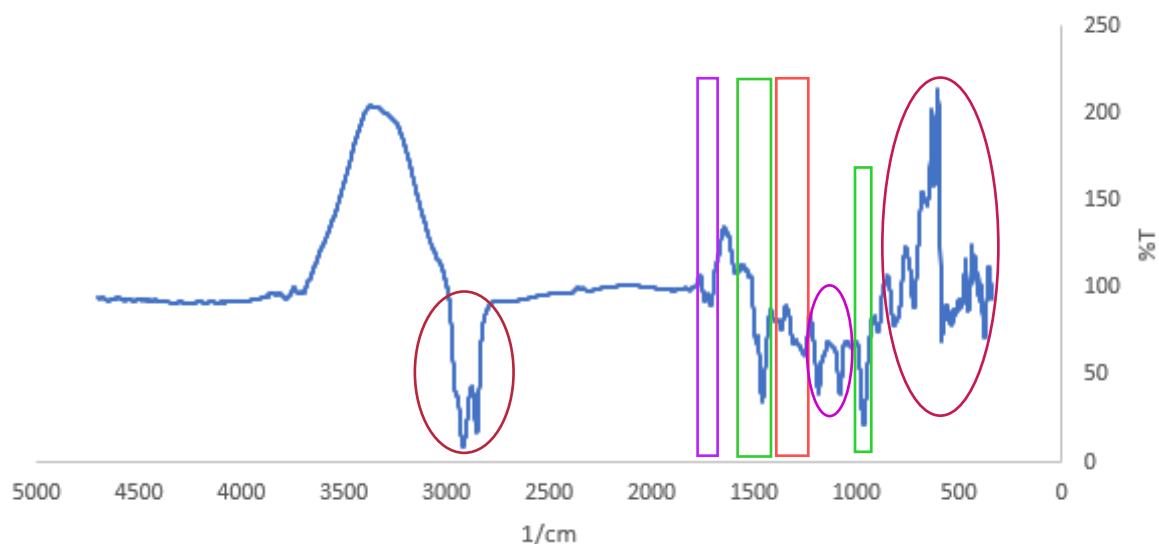


Fig. 22. FTIR spectrum of fraction extracted with hexane

6 The NMR spectrum depicted in Fig. 23 confirmed the presence of carboxylic acids, like n-
 7 hexadecanoic (1.2-1.3) and octadecanoic acid (2.5 ppm). It also showed the presence of
 8 aromatic compounds including phenols and heterocyclic compounds (6–8 ppm). Several

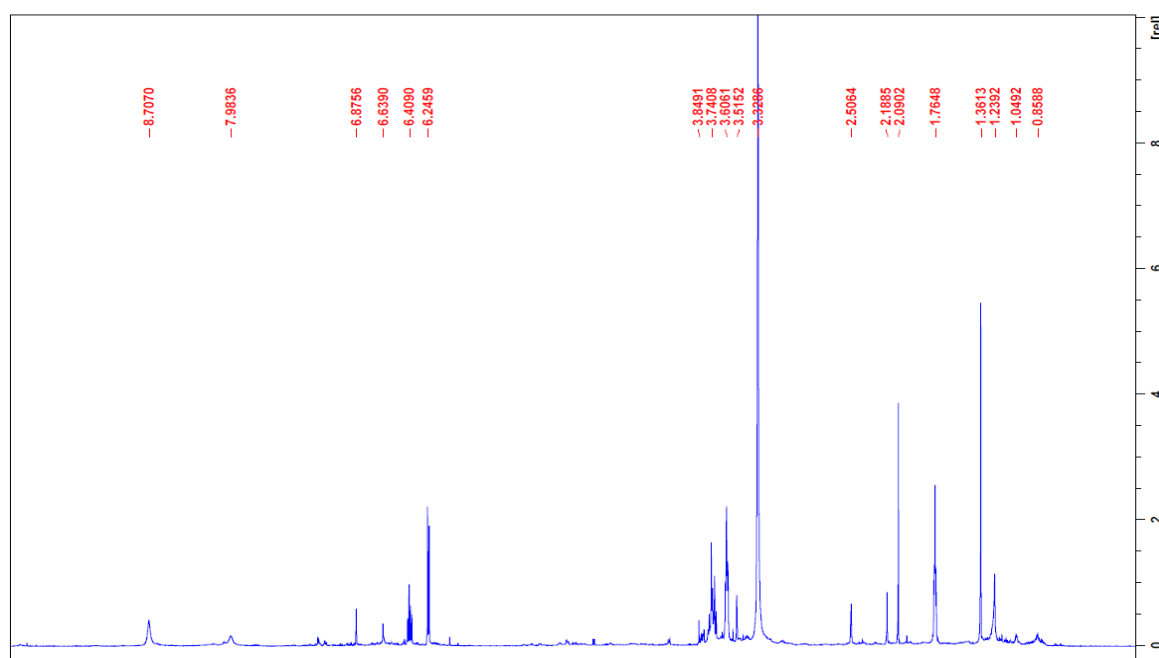


Fig. 23. NMR spectrum of the residue extracted with hexane

1 methoxy (alcohols and esters) groups were seen between 3.3 ppm and 4.0 ppm. Below 3
2 ppm the paraffins (alkanes, cyclo-alkanes, and branched alkanes) can be seen.

3 The residue that was extracted with hexane consisted of 78.65 mass% carbon, 13.17
4 mass% hydrogen, 0 mass% nitrogen and 8.64 mass% R-value. The high carbon content is
5 representative of all the alkanes and alkenes that were extracted, which also explains the
6 high hydrogen content. Even though hexane extracted a nitrogen-containing aromatic, it
7 can be concluded that it was a very small amount since the content was below the detection
8 limit of the elemental analysis. The residue's molecular weight could not be determined due
9 to the analysis producing inconsistent results.

10 It was concluded that the hexane only extracted compounds that were not bonded to the
11 sodium lignosulphonate, as there was no lignin, sodium or sulphonates detected during
12 analysis. The lignin degradation products such as phenols that were extracted were
13 removed from the lignin structure during the pulping process, which allowed the hexane to
14 easily extract the free phenolic compounds. The compounds that were extracted have come
15 from the cellulose and hemicellulose that were degraded during the sulphite pulping process
16 and the few aromatics and phenols that were detected were produced when smaller chains
17 of the lignin were degraded during the removal from the wood. It is believed that the
18 extraction of fatty acids from the feedstock could indicate the extraction of impurities such
19 as waxes and fats.

20 **4.1.3.2 THF-soluble fraction**

21 The second solvent, THF, only extracted 0.91 mass% of the original 40 g of Lignex®. The
22 data from the GPC analysis was used to plot the RI detector signal intensity vs molecular
23 weight (g/mol) of the residue. The THF-soluble residue stretched over a smaller area which
24 indicated a narrower distribution of its molecular weight range; thus, molecules with similar
25 molecular weights were extracted. This also means that THF extracted large and heavy
26 molecules. The THF fraction had a PDI of 1.4, a molecular weight of 895 g/mol and a Mn of
27 652 g/mol. The peak that was numbered as Peak 1 in Fig. 17, was suspected to represent
28 lignosulphonates or lignin degradation products. And in Fig. 24 this peak is seen to become
29 much more intense. This could indicate that the THF-extracted fraction mainly contained
30 lignosulphonates or decomposed lignin products and some lighter impurities.

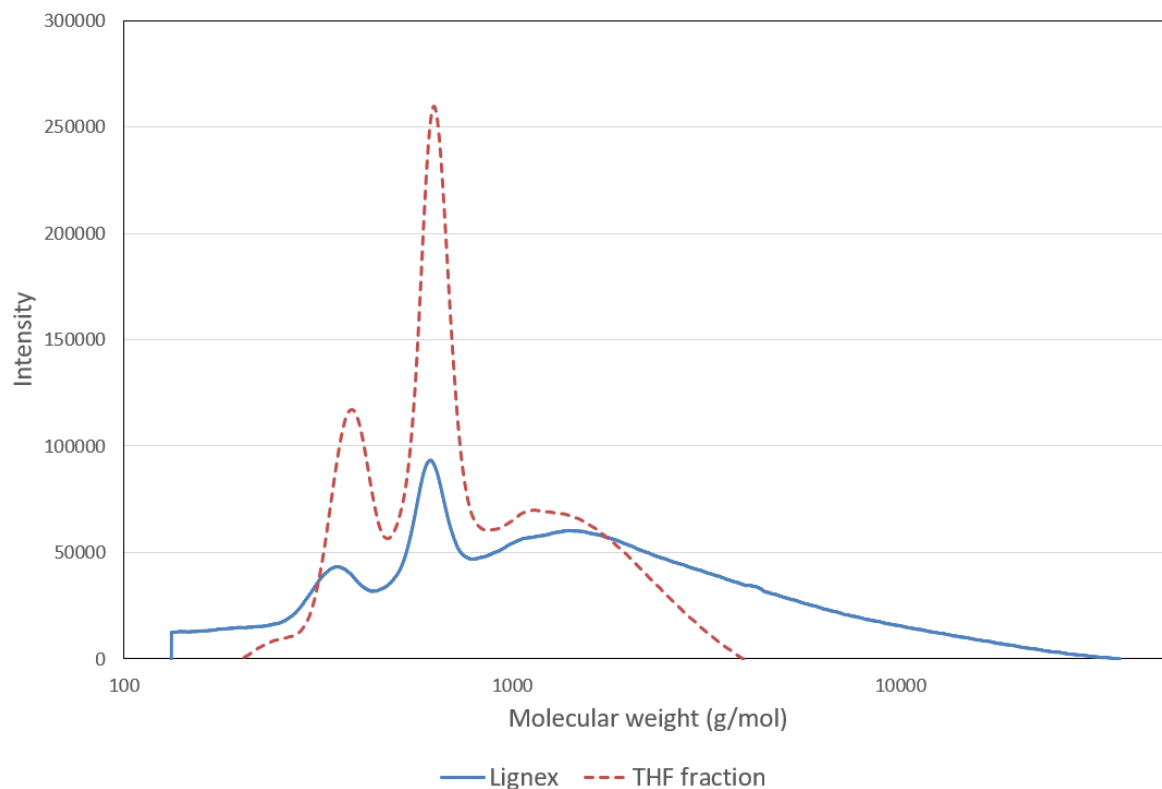


Fig. 24. Molecular weight distribution of residue extracted with THF

1

2 The GC-MS revealed that more than 88 mass% of the residue that was extracted with THF
 3 consisted of phenolic compounds. A small number of esters and ketones was present (with
 4 a certainty level of above 80%). This confirms the results of the GPC. THF mostly extracted

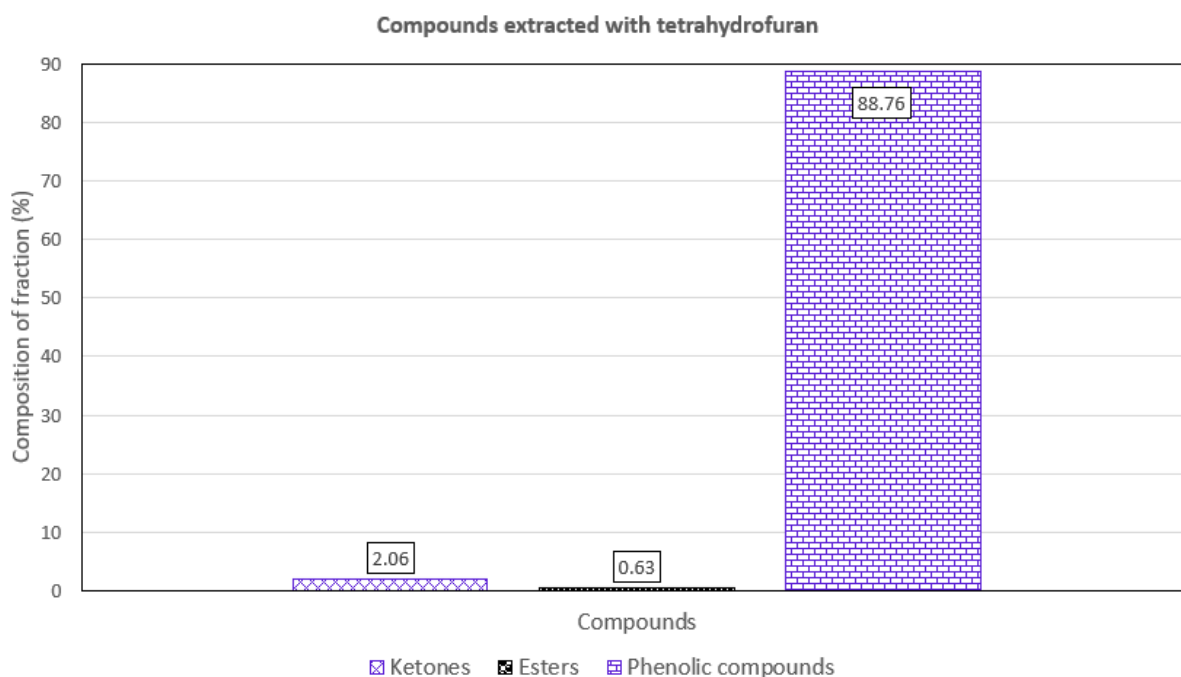


Fig. 25. Chemical composition of the fraction extracted with THF

phenolic compounds. Compounds like hexanedioic acid, bis(2-ethylhexyl) ester and 4,4'-ethylene bis(2,6-di-tert-butyl-phenol) (phenolic) were identified by the GC-MS. The increase in the extraction of aromatics can be explained by the polarity of the solvent. As THF has a significantly higher polarity than hexane, it would extract a combination of polar and non-polar compounds, with a much larger amount of polar compounds than the hexane could extract.

There is a significant difference between the FTIR spectrum of the hexane-extracted residue and the THF-extracted residue. Fig. 26 confirms the presence of -OH stretch groups and hybridised -CH_n bonds at $3000\text{--}2800\text{ cm}^{-1}$. The FTIR also detected carboxylic acids at 1700 cm^{-1} , esters at 1500 cm^{-1} , and phenols and aromatics at 1300 and below 800 cm^{-1} . Ketones were also detected between 1200 and 1100 cm^{-1} . The spectrum also indicates that there were several heavy molecules present in this THF-soluble fraction, because the GC-MS only detected phenols, ketones, and esters. This suggests that some molecules were too large for the GC-MS to detect.

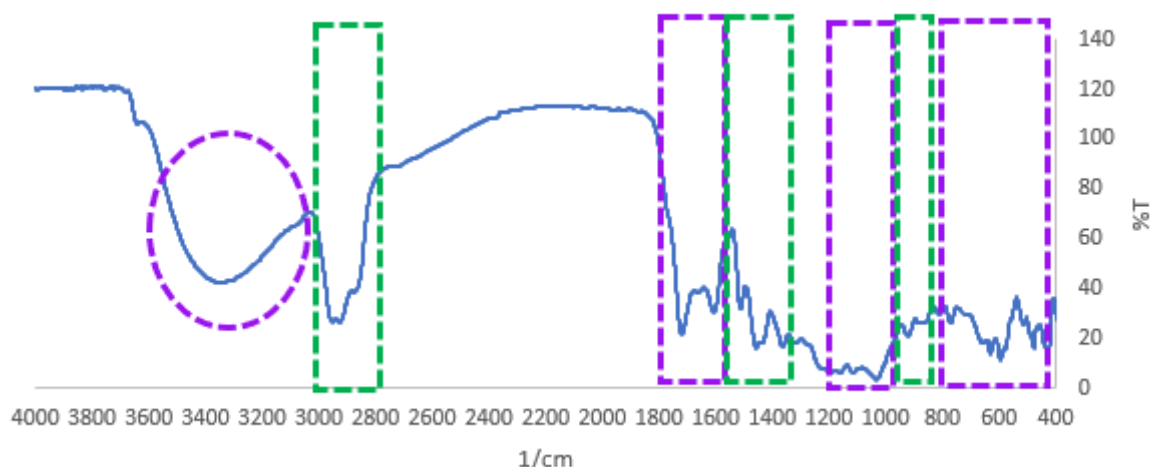


Fig. 26. FTIR spectrum of residue extracted with THF

The NMR spectrum only had a few peaks which reconfirm that the THF only extracted a few different groups of compounds. This spectrum also shows that aromatic rings and alkene compounds were present in the extracted mass. Alkenes were not detected by the GC-MS, but was also detected by the FTIR. This could mean that the alkenes which were extracted by THF are long-chained or larger molecules or highly branched molecules. Aromatic compounds were detected by the NMR at 6.8 ppm as well as ketones, carboxylic acids, and esters.

1

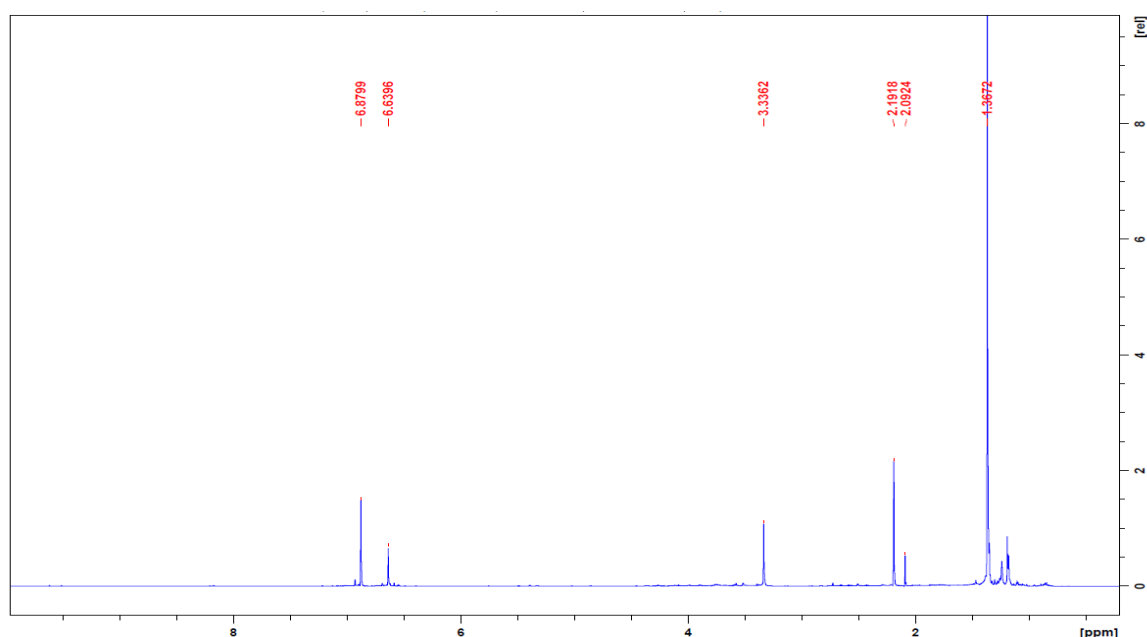


Fig. 27 . NMR spectrum of THF-soluble fraction

2 This extracted fraction's elemental composition shows a carbon content of 66.08 mass%, a
 3 hydrogen content of 9.58 mass%, and a 3.54 mass% for the R-value. No nitrogen was
 4 detected. Because THF is a more polar solvent than hexane, it can extract compounds that
 5 are somewhat polar, like compounds that include oxygen (Reichardt & Welton, 2010).

6 4.1.3.3 Acetone-soluble fraction

7 The solvent acetone was able to extract 0.97 % of the Lignex®. Consistent and reliable
 8 GPC results could not be obtained. The GC-MS only detected two compounds with high
 9 certainty, and both were phenolic compounds. This indicates that acetone either did not
 10 extract a lot of compounds or this fraction contained mostly molecules that were too large
 11 to be analysed by the GC-MS.

12 Fig. 28 is the FTIR spectrum of the fraction that was extracted with acetone as solvent. The
 13 -OH hydroxyl group can be seen between 3700 and 3000 cm^{-1} whereafter the hybridised -
 14 CH_n bonds can be seen. The peaks around 1700 cm^{-1} represents carboxylic groups and at
 15 1500 cm^{-1} the ester groups are presented as rather prominent. Furthermore, phenols and
 16 other aromatics were detected along with ketones.

1

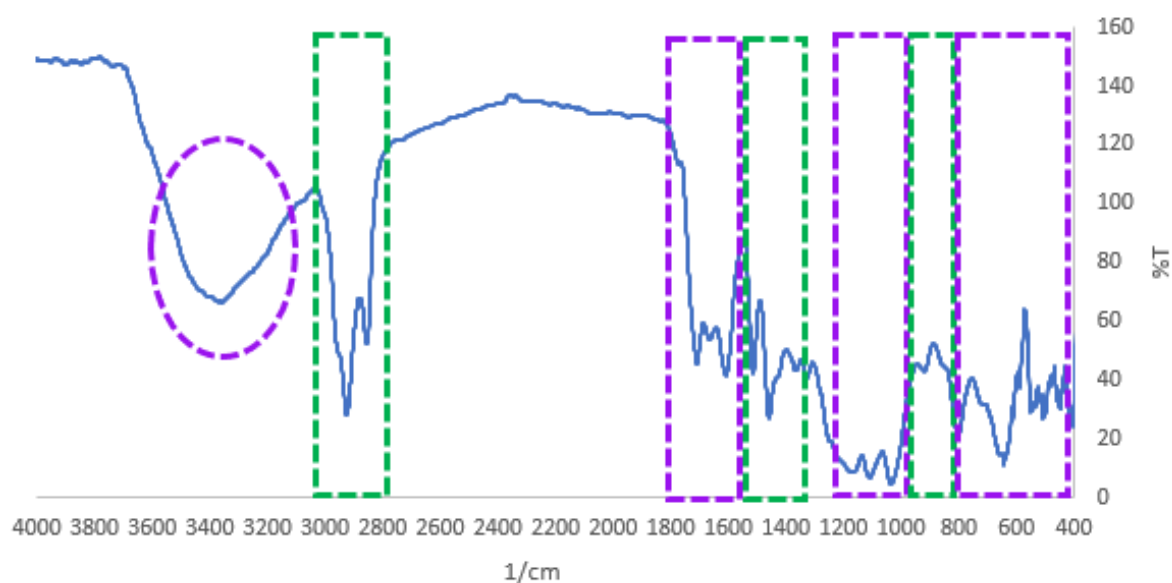


Fig. 28. FTIR spectrum of residue extracted with acetone

2 Comparing the NMR spectrum in Fig. 29 with the spectrum in Fig. 27 it is possible to see
 3 that acetone extracted more components; thus, it can be assumed that this fraction might
 4 have a high molecular weight due to the GC-MS not being able to detect most of the
 5 chemical compounds. The NMR showed that the compounds that were extracted with
 6 acetone included aromatic rings, alkenes, esters, hydroxyl groups, ketones, and carboxylic
 7 acids. It is possible that acetone extracted some of the smaller parts of lignin's structure.
 8 This can be seen in the peaks that are present in the lignin 'fingerprint' zone on the FTIR

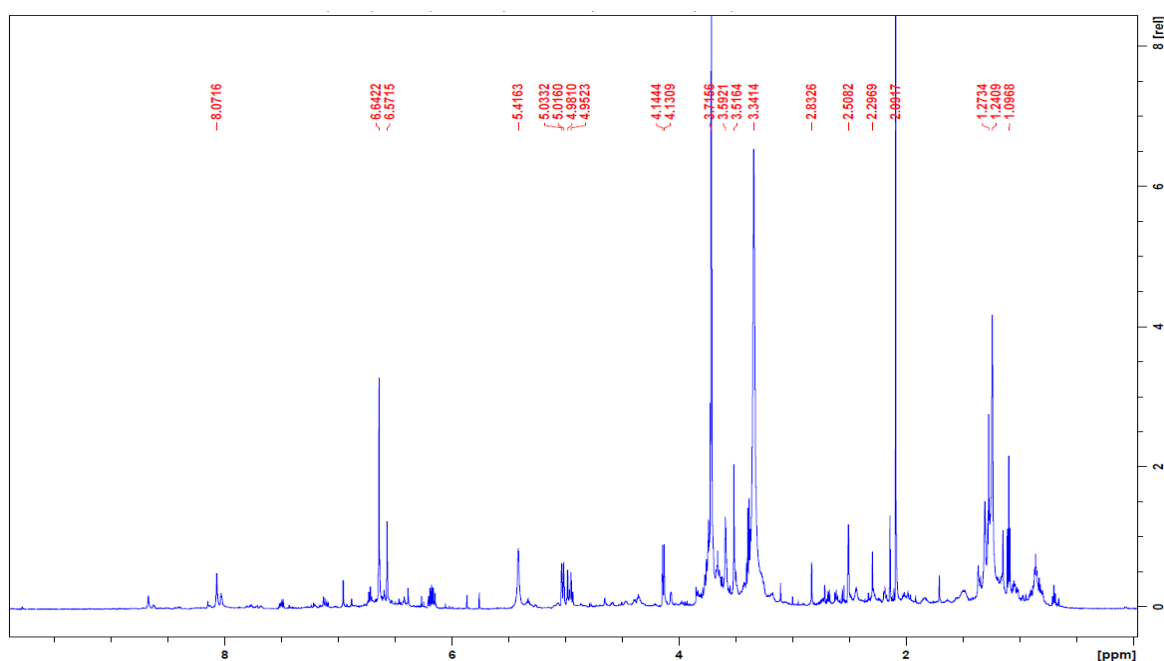


Fig. 29. NMR spectrum of the acetone-soluble fraction

spectrum. For example, from 1200 to 1000 cm^{-1} there are more peaks visible for acetone than with THF. Since acetone is more polar and have a higher hydrogen donor capability, it might have been able to break some of the weaker bonds of the lignin structure.

The elemental results once again indicated the absence of nitrogen in the acetone-extracted fraction and therefore no amide compounds could have been present. The carbon content was 53.08 mass% and the hydrogen content was 7.34 mass% with the % R-value at 41.91 mass% of the extracted fraction. The carbon content for the acetone-extracted fraction is lower than the carbon content for the THF-extracted fraction while the % R is higher. This could mean that most of the compounds that were extracted with acetone were either impurities, such as sulphur and sodium, or they consisted mainly of ketones and esters. Acetone is more polar than THF; therefore, it is expected that the number of oxygen-containing compounds would increase.

4.1.3.4 Ethanol-soluble fraction

A fraction of 2.12 mass% was extracted from the Lignex® with the use of ethanol as a solvent. The GPC results are presented in Fig. 30. It also seems that ethanol partially extracted the largest molecules in the Lignex® which could mean that a part of the lignin molecule chain in the Lignex® was fractionated and extracted. The PDI of the extracted fraction was 2.2 with the Mw as 2698 g/mol and Mn as 1233 g/mol.

With the GPC results alone, it is possible to deduce that more compounds were extracted with ethanol than with the previous solvents. The PDI shows that the ethanol extracted a slightly narrower range of molecules. However, mostly large molecules were extracted. This could mean that the ethanol can be used to selectively extract lignin while leaving behind most impurities. As mentioned above it was theorised that Peak 2 represents lignin and condensed lignin, and in Fig. 30, it was observed that this peak is larger than the others for the ethanol fraction, indicating that this fraction mostly consisted of lignin or condensed lignin.

The largest group that the GC-MS detected, consisted of phenolic compounds. Roughly 28 mass% of this fraction was phenols. This indicates a large presence of lignin degradation. It is believed that Peak 1 in Fig. 30 is representative of the lignin degradation products as well as some lignosulphonates. The increase in phenolic compounds that were extracted can be explained by considering that ethanol is significantly more polar than THF or hexane. This also shows that sodium lignosulphonate consists of mostly polar compounds and that

- 1 lignin has a relatively polar structure. The GC-MS were only able to detect some phenolic
- 2 compounds, because most of the molecules present in the fraction were very large and
- 3 heavy as can be seen from Fig. 30 and the high Mn.

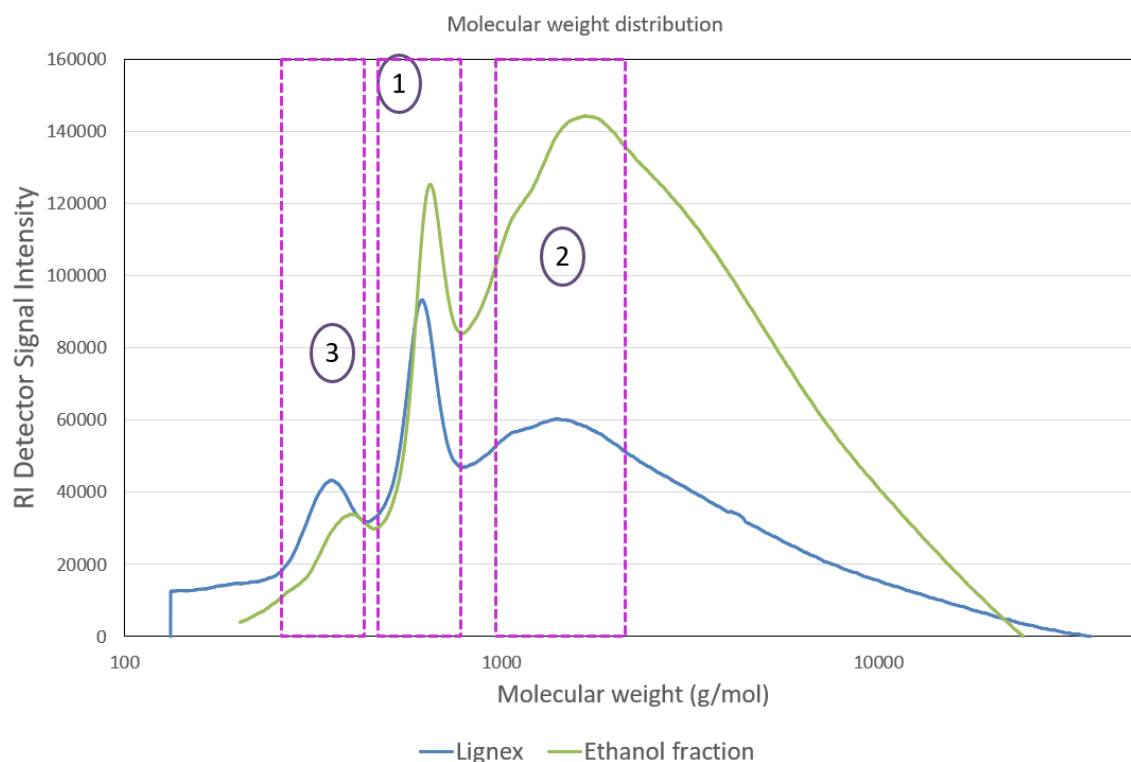


Fig. 30. Molecular weight distribution of residue extracted with ethanol

- 4 The presence of -OH stretch groups and hybridised -CH_n bonds can be seen in the FTIR
- 5 spectrum below. The FTIR also detected the presence of ketones, amides, carboxylic acids,
- 6 and esters. All of these compounds must have been large compounds as the GC-MS only
- 7 detected phenols which could be represented by the hydroxyl groups of the peaks seen
- 8 after 800 cm⁻¹. The blue circle at the lower end of the x-axis indicates the peaks visible in
- 9 the 'fingerprint' region where peaks indicative of lignin can be seen.

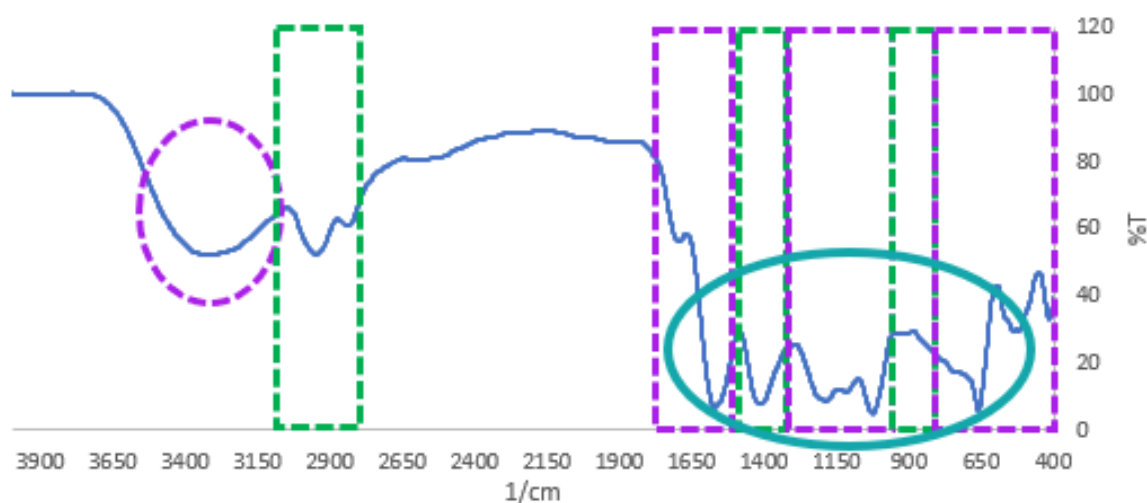


Fig. 31. FTIR spectrum of residue extracted with ethanol

- 1 The NMR spectrum for the ethanol-dissolvable fraction showed significantly less
- 2 compounds than what was expected, which led to the conclusion that most of the
- 3 compounds were insoluble in the solvent used as a medium for the NMR analysis. However,
- 4 a large peak was seen around 3.4 ppm which indicates the presence of alcohol and ester
- 5 groups. The second and largest peak can be seen at 1.0 ppm which represents $-CH_n$ bonds.
- 6 The smaller peaks can indicate ketones, carboxylic acids, amides, and hydroxyl groups.

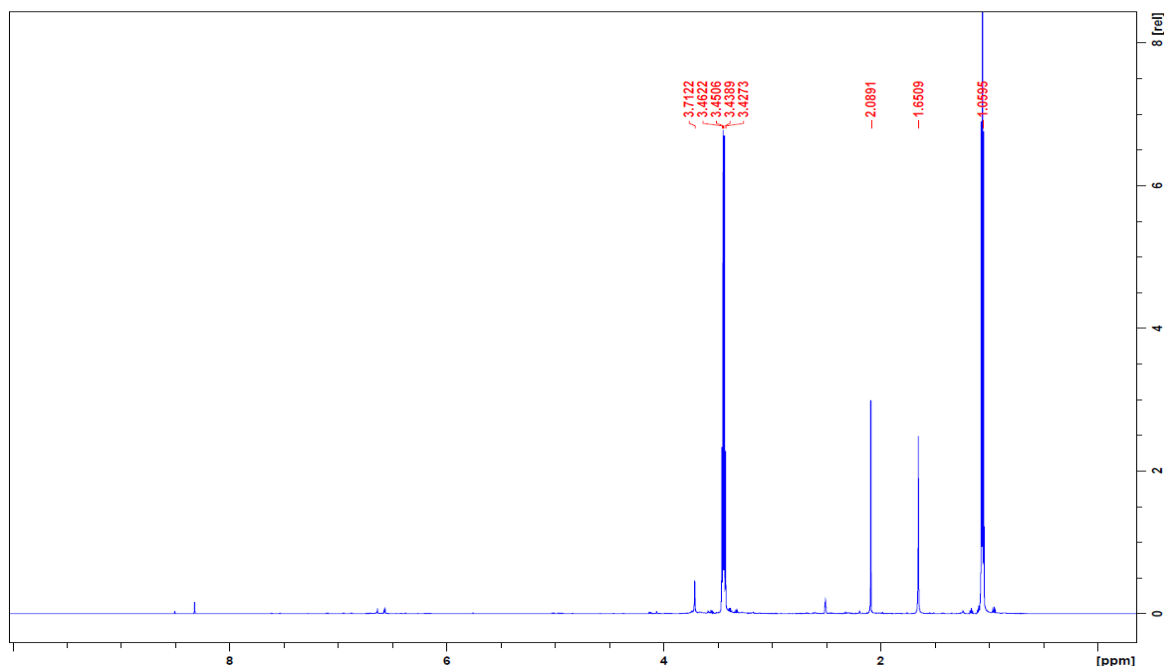


Fig. 32. NMR spectrum of residue extracted with ethanol

- 7 The elemental results showed a nitrogen content of 0.52 mass% which could confirm the
- 8 presence of amides in the form of 2-phenyl-5-methoxy-oxadiazol-1,3,4,6-nitro-2-
- 9 methylindole. The carbon content was 32.80 mass% and the hydrogen content 4.08
- 10 mass%; as ethanol's polarity is higher than that of acetone it can be expected that more
- 11 oxygen-containing compounds such as hydroxyl groups were extracted, as seen with the
- 12 increase of the % R-value (62.61 mass%).

13 4.1.3.5 Methanol-soluble fraction

- 14 The solvent, methanol, extracted the largest fraction (48.81%). This is due to the
- 15 combination of its high relative polarity and Hildebrand solubility parameter. Methanol
- 16 extracted more compounds from the Lignex® feedstock as is evident by the three new
- 17 peaks that appeared. The methanol distribution curve shifted drastically to the left, meaning
- 18 methanol extracted all the lighter components of the Lignex® which led to the high
- 19 extraction yield. The PDI of the methanol extracted fraction was 13.1 which is a very wide

distribution due to the lighter compounds with the Mw as 563 g/mol and the Mn measuring 43 g/mol. The Mw of 563 g/mol of the methanol fraction proves that the compounds which were extracted were significantly lighter than the compounds present in the original feedstock and the ones extracted by other solvents. The distribution curve showed three new peaks (peaks 4 and 5 and a small peak just before 100 g/mol). Peak 5 shows that some compounds that were extracted were relatively large molecules with molecular weights just above 10 g/mol, while Peak 4 represents relatively small molecules with molecular weights of roughly 50 g/mol. This might be an indication that methanol extracted volatile components from the sodium liginosulphonate structure as well as some impurities and polar liginosulphonates that were still structurally intact. Due to the presence of lighter components, it is suspected that the GC-MS could provide more data than for the previous solvent extractions.

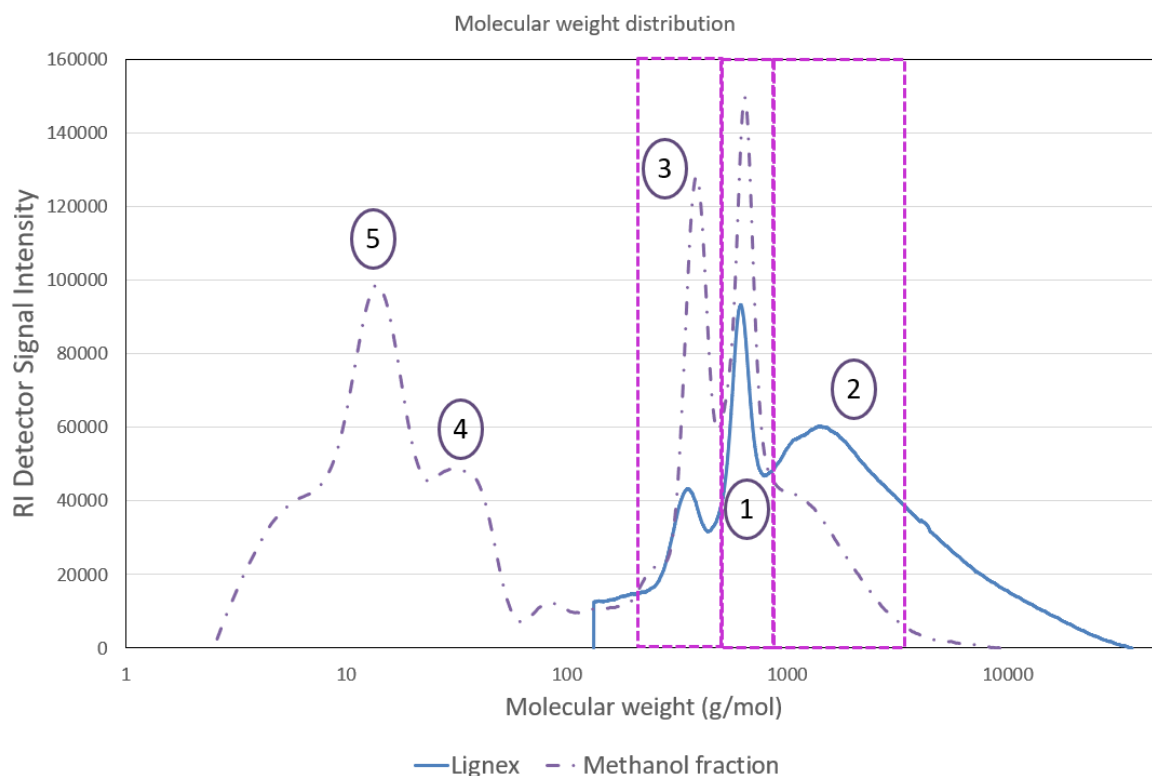


Fig. 33. Molecular mass distribution of the fraction extracted with methanol

GC-MS analysis of the fraction extracted with methanol indicated that with a certainty of 80 % most of the compounds that were extracted were phenolics (60.66 mass%), a small number of aromatic compounds (5.43 mass%) and 4 mass% of the fraction consisted of ketones. As methanol has a relatively high polarity and contains a hydroxyl chemical group, it was more likely to extract compounds with polar characteristics (Reichardt & Welton, 2010). This would explain the increased extraction of phenols, as they are polar aromatics (Widyawati *et al.*, 2014). The GC-MS results also showed that there was an amide group attached to the aromatic rings. Compounds like 2,6-dimethoxy phenol, 2,6-dimethoxy-4-(2-

propenyl) phenol, 3,4,5-trimethoxy phenol and 2-methoxy-4-(1-propenyl) phenol were identified with the GC-MS analysis. The high phenolic content explains why peaks 1 and 3 of Fig. 33 were significantly larger after methanol extraction. The GC-MS was unable to detect all the compounds that were present.

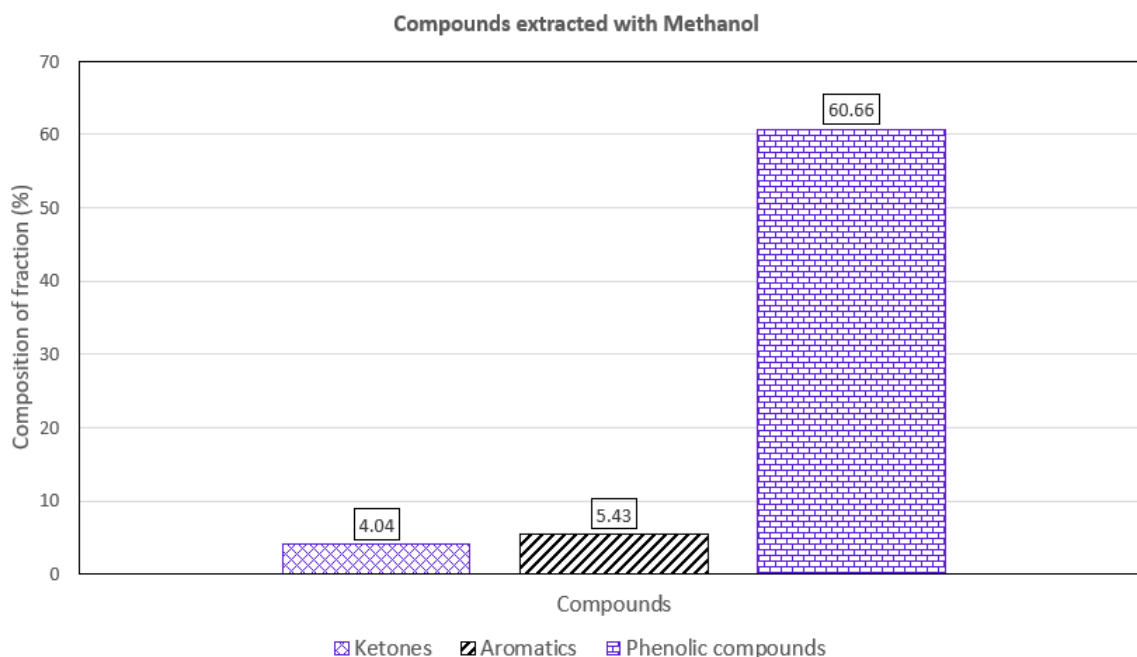


Fig. 34. Chemical composition of the fraction extracted with methanol

The FTIR spectrum of the fraction extracted with methanol can be seen in Fig. 35 and indicates the presence of hydroxyl groups, hybridised C-H bonds and carboxyl acid groups. Peaks representing esters were also detected and the peak between 1500 and 1450 cm^{-1} was attributed to the presence of aromatic rings. The smaller peaks between 1200 and 1000 cm^{-1} were attributed to the presence of ketones. The peaks after 1000 cm^{-1} were indicative of aromatic rings and phenols. The lignin peaks in the 'fingerprint' region could also be seen. The fractions extracted with acetone, ethanol, and methanol produced roughly the same shape for an FTIR spectrum, implying that the same groups were extracted. This would suggest that the feedstock, Lignex®, mostly consists of aromatics, phenols, esters, and ketones. Everything else, such as fatty acids, were extracted with hexane.

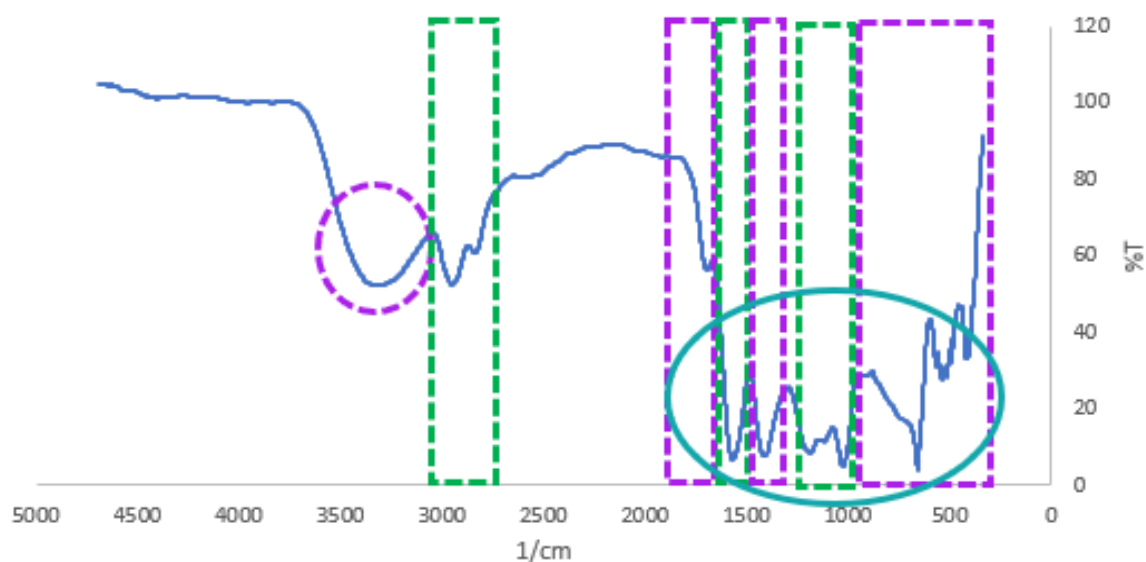


Fig. 35. FTIR spectrum of the residue extracted with methanol

1

2 The NMR spectrum can be seen in Fig. 36. The analysis identified fewer components from
 3 the methanol fraction than from the ethanol fraction. This can either mean that the methanol
 4 was responsible for the more selective extraction of compounds or that there were
 5 compounds that could not be dissolved in the required reagent for the NMR. Only hydroxyls,
 6 esters, ketones, and a small amount of aromatics could be identified on the NMR spectrum.

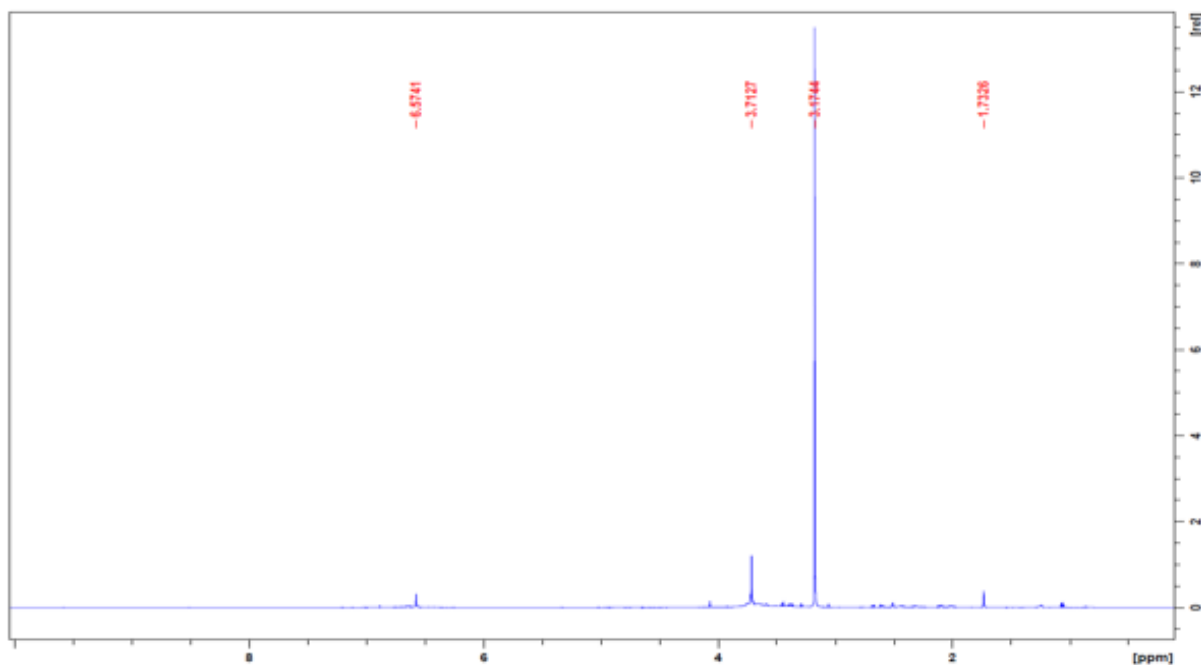


Fig. 36. NMR spectrum of the methanol-extracted fraction (Van der Merwe, 2020)

7

1 The elemental composition of the methanol-extracted fraction was 36.73 mass% of carbon,
2 7.34 mass% of hydrogen, 0 mass% of nitrogen and 56.28 mass% of the R-value. Methanol
3 is a polar solvent leading to the expectation that more oxygen atoms and hydroxyl
4 compounds would have been extracted. This confirms the results obtained from the GC-
5 MS that methanol extracted more compounds that contain hydroxyl groups, which was why
6 the phenol content increased significantly, although a smaller amount of oxygen was
7 extracted with methanol than with ethanol. The carbon and hydrogen content also improved
8 a bit. The NMR and elemental analysis did not reveal any amide groups that were present
9 while the GC-MS detected an aromatic ring, but included an amide group which no other
10 analysis detected. There was a large component with a heavy molecular mass detected by
11 the GPC, that was not detected by the GC-MS. This might have been the lignosulphonate
12 molecules.

13 To conclude, the hexane was unsuccessful at extracting any lignin from the Lignex®, but it
14 is suspected that hexane did extract, though in low quantities, impurities such as
15 pentadecane, 1-heptadecene, tritetracontane, and a few others from the Lignex®. THF
16 extracted almost the same small amount of mass from the 40 g of Lignex®. This fraction's
17 molecular weight was lowered and the THF was successful in extracting low concentrations
18 of lignin related aromatics. The THF-extract contained compounds such as butylated
19 hydroxytoluene, 2,6-bis(1,1-dimethyl ethyl) and 2,5-cyclohexadiene-1,4-dione. Like THF
20 and hexane, acetone also only extracted a small number of compounds from the Lignex®.
21 It seems that acetone also extracted lignin related aromatics just like the THF, but acetone
22 extracted these compounds in larger quantities. It was assumed that this fraction's
23 molecular weight and PDI were reduced as the molecular weight of all the compounds that
24 the GC-MS identified were lighter than the raw molecular weight of Lignex®. The 3,4,5-
25 trimethoxy phenol compound was extracted with acetone from the lignin polymer. Ethanol
26 extracted a larger amount of compounds from the Lignex® than the previous solvents. The
27 ethanol extract had a lower molecular weight and a lower PDI than Lignex®. The presence
28 of the hydroxyl group in ethanol allowed the ethanol to extract aromatic phenolics, which
29 was an advantage that the previous solvents did not have. Acetone extracted compounds
30 such as 3,4,5-trimethoxy phenol and 5-phenyl-1,3,4-oxadiazol-2-amine. Methanol's polarity
31 and Hildebrand solubility parameters led to a significantly larger amount of compounds
32 being extracted. Methanol extracted aromatic phenolics and aromatics derived from
33 hydroxyl-benzene. It is theorised that hexane and THF only extracted compounds that were
34 not directly bonded to the lignin structure, although both fractions mostly consisted of
35 phenols, ketones, esters, fatty acids, and olefins. Thus, hexane and THF seemed to mainly
36 extract compounds associated with cellulose and hemicellulose degradation. These

1 compounds most likely originated from the decomposition occurring during the pulping
2 process. As these compounds are not attached to the lignin's structure it can be assumed
3 that the phenols that were extracted were not attached to the lignin structure but was rather
4 a product of lignin degradation during the pulping process and so the solvents, hexane and
5 THF, did not cause any degradation of the lignin. This could explain why only two phenolic
6 compounds were detected in the acetone and ethanol fraction and no lighter compounds.
7 These solvents' increased polarity and solubility parameter caused a degree of degradation
8 of the lignin and so mostly phenols were present. Thus, because the methanol-extracted
9 fraction contained aromatic and phenolic compounds extracted from the lignin molecule
10 chain, it can be assumed that it caused more degradation to the lignin structure due to
11 having the highest polarity and solubility parameter compared to the other solvents. These
12 compounds included 3,4,5-trimethoxy phenol, 2-methoxy-4-(1-propenyl) phenol and 2,6-
13 dimethoxy phenol. When considering the GPC-generated molecular weight distribution of
14 methanol it was discovered that not only did methanol extract lignin fragments, but it
15 drastically changed the structure of the molecules, more than the other solvents did. It also
16 reduced the molecular weight and extracted compounds with very low molecular weights.
17 A contributing factor of the increased effect the solvents had on the fractionation of the
18 Lignex® could be the hydrogen-donating ability of the solvent. As the capacity to donate
19 hydrogen atoms increased so did the degradation of the Lignex® and the mass that was
20 extracted.

4.2 The effect of different alkali catalysts on the bio-oil yield during HTL

The first part of the HTL experiments involved testing three different alkali catalysts to see which would yield more bio-oil. The catalysts that were tested were calcium carbonate (CaCO_3), sodium hydroxide (NaOH) and potassium hydroxide (KOH). The graph in Fig. 37 was plotted with the data provided by the fourth-year student. From Fig. 37 it can be seen that the catalyst that promoted the production of bio-oil the most was sodium hydroxide (NaOH), with a yield of 9.57%. The experiment that was completed with sodium hydroxide also produced the lowest amount of biochar (67.12%), but the highest amount of gas. This could be due to sodium hydroxide promoting cracking reactions instead of repolymerisation. Thus, all further experiments proceeded with the use of sodium hydroxide as a catalyst.

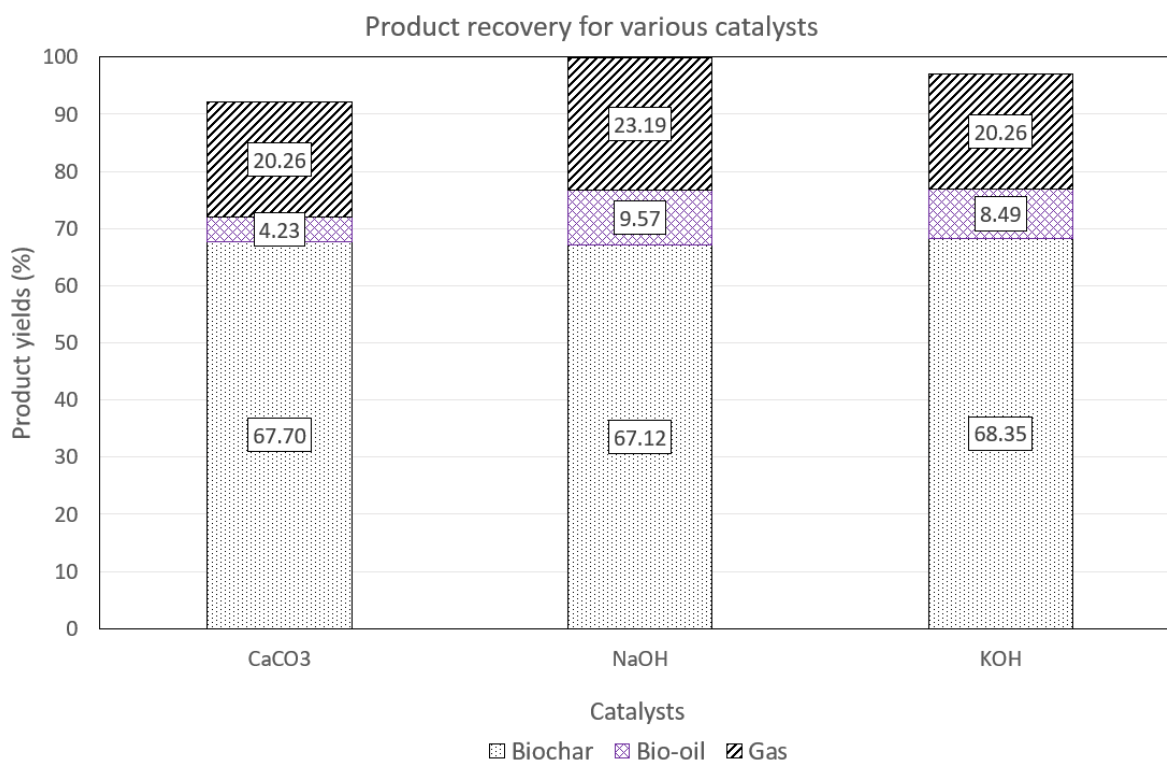


Fig. 37. Product yields from different catalysts

4.3 The effect of liquefaction solvent on bio-oil yield and quality

4.3.1 The effect of liquefaction solvent on bio-oil yield

The highest bio-oil yield was produced with water (± 50 mass%), while THF produced a bio-oil with the lowest yield (± 7 mass%). Ethanol produced a bio-oil with a yield of roughly 9 mass% which falls in between the other two solvents. The explanation for the bio-oil yields was contributed to the solvents' ability to donate hydrogen atoms. The presence of hydrogen will increase the cleavage of C-O and C-C bonds which will increase the bio-oil yield and its energy content. Water and ethanol are protic liquids, meaning liquids that act as hydrogen donors, while THF is an aprotic solvent, which means that THF is unable to donate hydrogen atoms. This could be the reason for the low yield of bio-oil that was obtained from using THF as a solvent. Ethanol was used at supercritical conditions which could lead to a higher degree of poly-condensation which could explain why the bio-oil's yield was significantly lower than that for the water solvent (Han *et al.*, 2019; Hu *et al.*, 2018).

The declining bio-oil yield as the solvent was switched from water to ethanol to THF could also be related to the solvent's relative polarity. Water has a relative polarity of 1 while ethanol's and THF's relative polarities are 0.65 and 0.21, respectively. It could be that most of the compounds that made up the bio-oil were polar and thus more compounds dissolved in the polar solvents, leading to a higher bio-oil yield when the solvent was extracted through evaporation. Since the Lignex® dissolves completely in water it can be assumed that the Lignex® consisted mostly of polar components. Another option to consider is the high organic content of the Lignex®. Salts can dissolve more easily in water than in THF; thus, the reason the bio-oil yield with water as a solvent was so much higher could be due to dissolved salts being extracted with the liquid phase.

4.3.2 The effect of liquefaction solvent on bio-oil quality

After the removal of acetone, used to wash the char product, through rotary evaporation, the product mix that was left were bio-oil and an aqueous phase. Emulsification had taken place and so the bio-oil could not be separated from the aqueous phase through physical separation methods. Thus, the mixture was placed into an oven at 60°C to evaporate the aqueous phase. For oils produced with pure ethanol or THF, the drying times were shorter because emulsification occurred at a lesser degree than with pure water as a solvent. However, for the bio-oil that experienced more emulsification, the longer drying times were

not the only challenge. The longer drying period combined with warmer conditions allowed more opportunity for the bio-oil to degrade and form species with higher molecular weights (Esterhuizen, 2020).

4.3.2.1 The molecular weight distribution of the bio-oils

The lowest molecular weight was achieved with ethanol as a solvent although the dispersion of the molecules did not change. The bio-oil produced with water as a solvent required a longer drying time, which might explain the large molecular weight. The longer time in a warmer atmosphere could have promoted a degree of repolymerisation. As this bio-oil's PDI was quite small in comparison to the raw feedstock and the bio-oil produced with ethanol, it could indicate that most of its compounds were large and heavy because the molecules were narrowly distributed.

The solvent, THF, produced a bio-oil that not only had low molecular weight but also a low PDI. This indicated that most of the THF-extracted bio-oil consisted of relatively small and light components. This might also suggest that larger polymers with heavier fractions would be more likely to form in a polar environment or when more hydrogen atoms are present.

For the ideal bio-oil, low molecular weight and small PDI are preferred, therefore it seems as though a bio-oil produced with THF as a solvent would be the best match for these criteria. It is clear from Table 4-6 that all the molecular weights of the bio-oils decreased, which confirms the depolymerisation of the feedstock.

Table 4-6. GPC analysis of bio-oils produced with various pure solvents

Solvent	Mw (g/mol)	Mn (g/mol)	PDI
Lignex®	2468	945	2.6
Water	604	427	1.4
Ethanol	252	97	2.6
THF	261	138	1.9

4.3.2.2 Effect of solvents on the chemical composition of the bio-oil

The main chemical groups that were present in the bio-oils were identified by GC-MS analyses and are presented in Fig. 38. The bio-oils obtained with pure ethanol as solvent, had a high presence of phenol and sulphur derivatives (included in the group named 'Others'). The group called 'Others' also included silicon derivatives, amides and alkanes. The ethanol produced a bio-oil that contained large amounts of ketones, benzene derivatives and phytosterols. It also had the largest amount of esters present. There were also high amounts of alkanes that were present in the bio-oil that could indicate the occurrence of deoxygenation reactions which were caused by ethanol's affinity for hydrogen donation (Hu *et al.*, 2018).

The high phenol content proves that lignin is a prominent source of phenolic compounds when the phenylpropane units are decomposed. This would also explain the presence of benzene and ketones (Cao *et al.*, 2016; Tian *et al.*, 2020).

Esterification reactions also occurred due to the reaction of the ethanol with the organic acids that were present in the feedstock. These reactions would lead to the presence of esters in the bio-oils (Zhao *et al.*, 2021). Bio-oil produced with water as the solvent did not show many compounds when analysed with the GC-MS. An explanation for this could be because most of the compounds that were present were too large and heavy for the GC-MS to detect. This substantiates the findings of the GPC, where the bio-oil produced with water had larger molecular weights. The solvent, THF, also yielded a bio-oil that consisted mostly of sulphur and phenol derivatives. Furthermore, this bio-oil had high amounts of sulphur derivatives, silicon derivatives (grouped as 'Others'), phenol derivatives and benzene derivatives as well as some phytosterols and ketones. The THF produced a bio-oil that contained the highest amount of ketones. The low amount of esters can be explained when considering the aprotic nature of THF and the absence of methoxy groups. The presence of sulphur derivatives could be attributed to sulphur groups in the Lignex® that were degraded during HTL.

The two solvents, ethanol and THF, produced bio-oils that differed significantly from each other in chemical composition. With ethanol, hydrogen ions are donated during HTL, which assists in the breaking of C-O bonds. This leads to deoxygenation and the formation of alkanes. Phenolic compounds, like guaiacol and syringol, were present in the bio-oils. For pure ethanol, the GC-MS detected 0.23 and 1.05 mass%, respectively (for guaiacol and syringol). For pure THF only 0.60 mass% syringol was detected. The phytosterol

- 1 compounds that the GC-MS detected in the bio-oils could be used for pharmaceutical
- 2 purposes (manufacturing of steroids) and cosmetics (several creams and lipsticks).

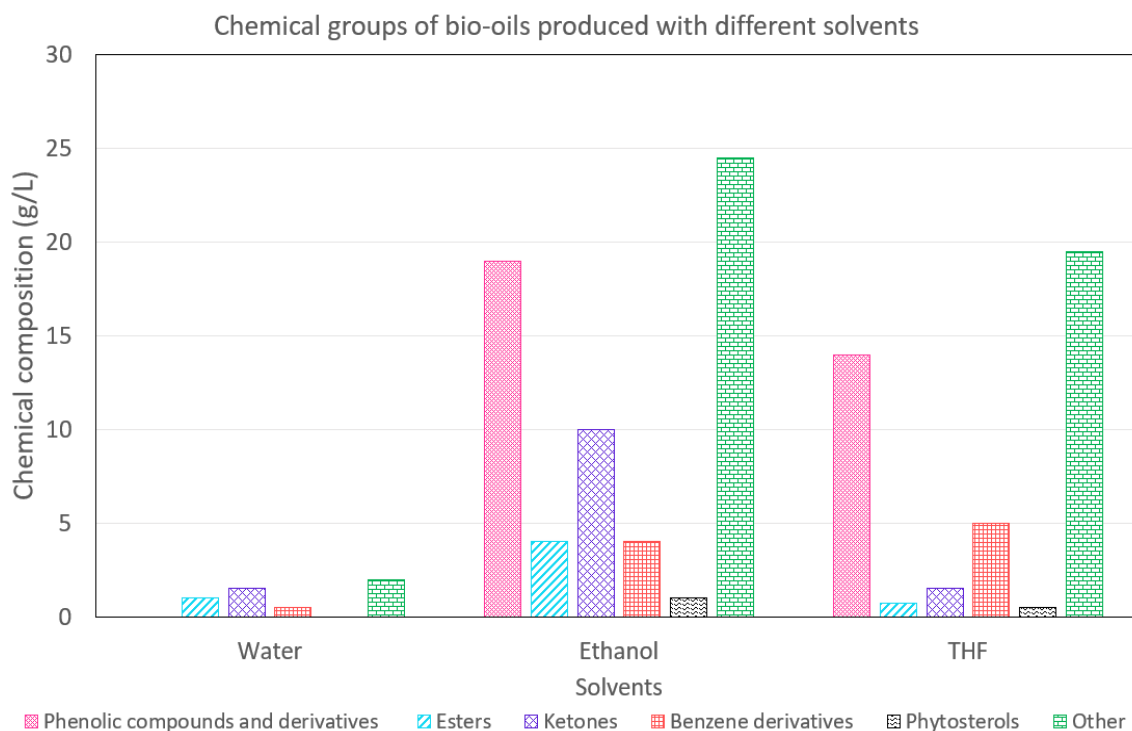


Fig. 38. Chemical groups of bio-oils produced in the presence of different solvents as analysed with GC-MS

4.3.2.3 Functional groups of the bio-oil

- 4 The effect of each solvent was investigated through FTIR analyses and the spectra are
- 5 presented in Fig. 39. By comparing the FTIR results of the bio-oils produced by the three
- 6 pure solvents the functional groups were assigned to the IR signals as follows:

7 Table 4-7. FTIR peaks and the corresponding functional groups (Esterhuizen, 2020)

Wavenumber (cm ⁻¹)	Functional group
3700-3000	O-H stretch
3000-2850	Sp ³ -hybridised C-H bonds
1700	C=O stretching
1650-1570	Aromatic C=C stretch
1500-1400	Sp ³ C-H bend
1280-1190	C-O stretch

880-490

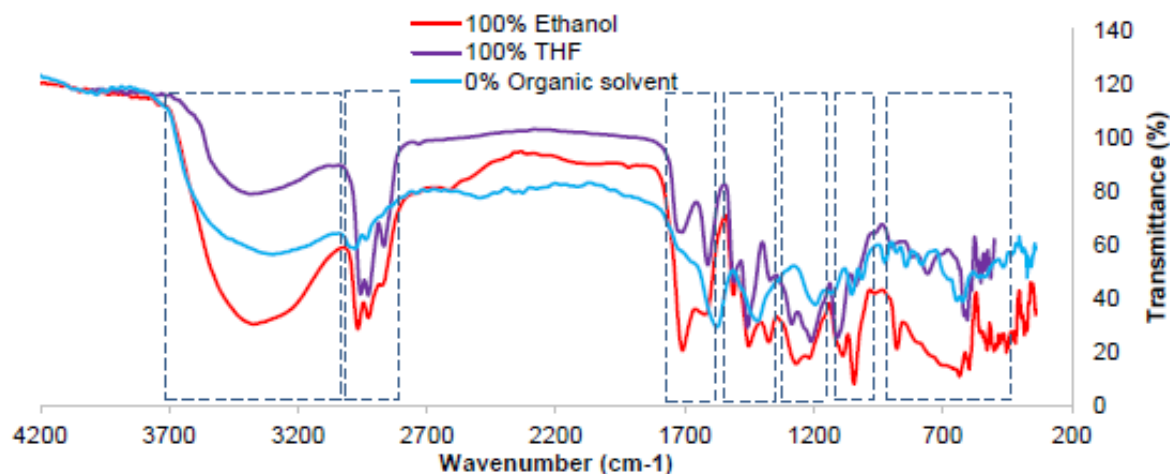
Aromatic sp^2 C-H bend

Fig. 39. FTIR spectra of the bio-oils produced by the three pure solvents (Esterhuizen, 2020)

Between 3700 and 3000 cm^{-1} the presence of O-H stretch bands were detected which could indicate alcohols, phenols, and water. It can be noted that this peak is significantly less prominent in the bio-oil produced with THF, while the bio-oil produced with ethanol's O-H peak is much larger than the bio-oil produced with water indicating more hydroxyl groups. This could be the larger amount of phenols that were present in the ethanol bio-oil. The peaks observed between 3000 and 2850 cm^{-1} is indicative of aliphatic groups. The bio-oil produced with pure ethanol has a prominent peak at 1700 cm^{-1} . The presence of this peak was ascribed to carbonyl groups, which could have been esters, acids, and ketones. This confirms the GC-MS results of high ester contents. However, the bio-oil produced with THF had a significantly more prominent peak indicating that this oil contained more aliphatic compounds. Aromatic compounds could be seen in the peaks between 1650 and 1570 cm^{-1} only for the ethanol and THF bio-oils. This supports previous conclusions drawn from the GC-MS. Furthermore, the peaks visible in the range of 1500–1400 cm^{-1} support the presence of aliphatic groups and the peaks between 1280 and 1190 cm^{-1} (C-O stretch) suggest that aliphatic alcohols, esters, and acids were present (Esterhuizen, 2020).

4.3.2.4 Inorganic compounds present in the bio-oil

The inorganic compounds present in the bio-oils were determined by dissolving the bio-oil in HCl and doing an ICP analysis on the samples. The following results were obtained:

1

Table 4-8. Inorganic contents of bio-oil produced with various solvents

Solvent	Ca	K	Mg	Na	S	Other	Total
Water	0.02	0.23	0.01	4.50	4.65	0.01	9.42
Ethanol	0.03	0.14	0.00	3.00	4.51	0.02	7.71
THF	0.03	0.00	0.02	0.42	1.24	0.03	1.73

2

*Contents expressed as mass%

3

These inorganic compounds would have contributed to the ash content of the bio-oil. The highest mass% of sulphur could be found in the bio-oil produced from pure water. The bio-oil produced with water as liquefaction solvent contained the most inorganic compounds. By using ethanol as a solvent instead of water, the total inorganic contents were reduced. This could be due to the relatively high solubility of the inorganic compounds in water compared to the organic solvents. It seems that THF is more successful at removing the inorganic compounds from the bio-oil. However, compared with ethanol as a solvent, the pure THF did not remove a lot of sulphur, although it removed more than the ethanol. When considering a bio-oil for the use of biofuel, the bio-oil's sulphur content must be as low as possible to prevent any harmful effects on the environment. Taking this into consideration, the bio-oil with the most suitable inorganic content would be the one produced from THF.

14

For a bio-oil to have a high energy value it is necessary that the moisture content also be as low as possible. The following moisture contents were determined with the use of coulometric Karl Fischer titration. As can be seen in Table 4-9, organic solvents produced bio-oils with less moisture. The lowest moisture content was achieved with ethanol as solvent. THF produced bio-oils with more moisture (33.69 mass%). Some of these values may include the unevaporated aqueous phase.

20

Table 4-9. Average moisture contents of bio-oils produced

Solvents	Average moisture (mass%)
Water	27.55
Ethanol	15.75
THF	33.69

4.3.2.5 Elemental composition and energy contents of bio-oil

The elemental composition of the bio-oils after drying is presented in Table 4-10. Ethanol was especially successful in lowering the oxygen content of the bio-oil, while also increasing the carbon and hydrogen content. However, the bio-oil produced with THF had the highest hydrogen content. The high moisture content could be the reason for the high hydrogen content.

Table 4-10. Elemental composition of bio-oils produced with different solvents

Solvents	Mass% C	Mass% H	Mass% N	Mass% Salts	Mass% O
Water	15.28	3.30	0.61	9.42	71.40
Ethanol	55.19	7.11	0.48	9.42	27.81
THF	51.79	7.22	0.36	1.73	38.91

The feedstock, Lignex®, combined with any solvent, produced bio-oils with less than 1 mass% nitrogen, which would be advantageous for biofuel production. High nitrogen content in fuel could form solids during the combustion process, which would not only affect the stability of the fuel but the longevity and operational efficiency of any engine, furnace, etc. As mentioned above, THF was also more successful with decreasing inorganics (salts) content in bio-oil. However, it was ethanol that achieved the lowest oxygen content. To know if these bio-oils do have suitable properties for energy purposes, the CV, along with the O/C and H/C ratios, should be inspected.

Table 4-11. Energy properties of the bio-oils

Solvent used to produce bio-oil	CV (MJ/ kg)	O/C ratio	H/C ratio
Water	0	3.51	2.57
Ethanol	23.91	0.38	1.54
THF	20.91	0.56	1.66

The CV for the raw Lignex® was 11.64 MJ/kg. Thus, the energy content was upgraded during the liquefaction process with ethanol and THF. The bio-oil produced with THF as a solvent probably experienced less deoxygenation compared to water as a solvent due to its

1 weak hydrogen-donating ability. However, the CV of the bio-oil produced with THF as a
2 solvent was higher than that of the bio-oil produced with water. It is believed that the high
3 inorganic content of the bio-oil produced with water was the reason for the significant
4 difference and the low CV. Unfortunately, even the highest CV obtained was still
5 significantly lower than that of standard diesel and biodiesel. For bio-oil produced from
6 Lignex® to compete with fossil fuels or even other biofuels, an extra upgrading step is
7 necessary. A deoxygenation step will probably make the largest difference.

8 The ideal O/C ratio for fuel should be close to 0 for the fuel to be of high quality. Even though
9 ethanol produced a bio-oil with the lowest O/C ratio, it was still higher than biodiesel; thus,
10 supporting the above-mentioned idea that a deoxygenation step is required to improve the
11 quality of the bio-oil. Some biodiesels' H/C ratios are 1.66, thus the bio-oils produced with
12 ethanol and even THF are in range, but the high oxygen content is a major hindrance.

13 It can be summarised that the organic solvent, ethanol, produced higher yields, probably
14 because of having a higher proton donor ability. The presence of organic solvents had a
15 significant effect on the quality of the bio-oil. It was discovered that in cases where the
16 aqueous phase and bio-oil could not be separated from each other like with water as a
17 solvent, the molecular weight and PDI increased. However, after drying to evaporate the
18 aqueous phase, the molecular weight and PDI decreased with the use of organic solvent.
19 This was attributed to less repolymerisation taking place because of the shorter time
20 required to remove the aqueous phase. It was discovered that pure water used as solvent
21 yielded the lowest PDI for bio-oil and the pure organic solvents produced bio-oils with the
22 lowest molecular weights.

23 The drying step also affected the PDI of the bio-oils by increasing it; thus, complicating the
24 determination of the most suitable solvent for molecular weight distribution. It can be
25 declared that as the molecular weight of all the bio-oils was lower than the raw Lignex®,
26 there occurred depolymerisation reactions during the HTL processes with the different
27 solvents.

28 The chemical composition of the bio-oils also experienced drastic changes due to the make-
29 up of the solvent – organic solvents had a positive effect on the chemical composition of
30 bio-oil as it decreased the sulphur and silicon content and increased monomer production.
31 The presence of phenol derivatives and aromatics also improved. Ethanol increased the
32 production of molecules with fewer oxygen atoms like alkanes. This low oxygen content is
33 a desired bio-oil property in the production of biofuels. Ethanol is a hydrogen donor that
34 promotes the breaking of C-O bonds and promotes deoxygenation, while THF produces

1 products with more components containing carbonyl groups. This means that due to
2 enhanced deoxygenation caused by organic solvents the bio-oil energy content improved
3 significantly.

4 The higher water fraction in the solvent mixtures caused lower heating values due to higher
5 moisture contents because of the difficulties with the drying step. Both organic solvents
6 helped to decrease the inorganics in the bio-oils and thus decreased the ash content.

7 Organic solvents had a positive impact on the production of bio-oil through HTL. Ethanol
8 was more successful at increasing the bio-oil yield while THF produced bio-oils with a few
9 improved properties such as a lower PDI; but unfortunately, THF was not as successful with
10 deoxygenation. Thus, by using ethanol as a pure solvent to increase the bio-oil's yield while
11 achieving a low molecular weight and oxygen content, other process parameters can be
12 manipulated to improve the quality and chemical properties of the bio-oil.

13

4.4 The effect of process variables on liquefaction product yields

The biochar was separated from the liquid and volatiles and washed with acetone. Then, the biochar was weighed after drying and so was the bio-oil. The aqueous phase was determined as the moisture present in the bio-oil after drying. The gas yield was determined by comparing the mass before the reaction with the total mass after the reaction. The yields were determined on a dry, ash-free basis. An average of 2.42 mass% of ash was assumed for the bio-oils, as not all ash contents could be determined through a proximate analysis (SABS, 2011b).



Fig. 40. All HTL product yields

In Fig. 40 all the product yields are presented in a single graph. The experimental error for the bio-oil yield equalled 8.73%, while the experimental errors for biochar and gas were 8.70 and 9.00%, respectively. By viewing the data from Fig. 40 along with the experimental errors, it was difficult to see an overall trend that would explain the effect of temperature and time on the product yields. Thus, the severity factor for the experiments was determined to provide some clarity on the combined effect of reaction temperature and residence time. The severity factor was determined by using the equation that was specified in the work of

1 Lloyd & Wyman (2005) and Iroba, *et al.* (2014). From this graph (Fig. 40) it is clear that the
2 average yield of the gas increased quite significantly by almost 10 mass% as the
3 temperature was increased from 240 to 320°C, while the bio-oil yield production decreased
4 with the increasing temperature.

5 As the feedstock, Lignex®), is a sodium lignosulphonate, it is known that the lignin will only
6 start to decompose or break apart at a temperature of 280°C or higher. Between this
7 temperature and 150°C, lignin will only condense through crosslinking molecules: a
8 structure quite difficult to break or penetrate (Nam, 2013). Thus, it is hypothesised that at
9 lower temperatures, from 240°C to just before 280°C, combined with lower residence times,
10 Lignex® will become soluble in the ethanol, thus yielding a larger amount of the liquid
11 product (bio-oil), and decreasing the solid residue (biochar), while little to no reactions will
12 occur.

13 However, as the temperature increases to above 280°C, both yields will decrease due to
14 the Lignex® bonds and molecules breaking apart and reacting. If the temperature increases
15 too much, repolymerisation and condensation reactions will be favoured which will increase
16 the yield of the solid product and form larger and heavier compounds.

17 The same can be said for an increase in residence time. As the residence time increases,
18 this will allow enough time for the breaking of lignin bonds at low temperatures (before
19 280°C), but it will also mean that the condensation and repolymerisation reactions will start
20 at lower temperatures. A longer reaction time will also allow the radicals that form at 240–
21 280°C to repolymerise and if the molecular compounds are weak or lighter, they will convert
22 to gas increasing the gas phase's yield. Thus, for each combination of variables, there will
23 be a point where depolymerisation and cracking reactions will decrease and
24 repolymerisation and condensation reactions will become dominant. This point will be
25 referred to as the turning point.

26 All of the mass that could not be accounted for was contributed to being lost as volatile
27 compounds as with previous studies, either during the solvent evaporation step with the
28 rotovap or during the drying step when the bio-oil was being dried in the oven at 60°C
29 (Shrivastava *et al.*, 2021).

30 To prove this hypothesis and prevent repeating explanations, the effect of temperature will
31 be discussed by using the data of one short residence time and one long residence time,
32 while the effect of residence time will be discussed with the data obtained at a low

1 temperature and a high temperature. All other data referred to can be found in the
2 appendices.

3 4.4.1 The effect of reaction temperature on product yield

4 The yield calculation can be found in appendix A.

5 To view the effect of temperature, a short residence time of 20 min and a long residence
6 time of 80 min will be discussed, while the data obtained for residence times of 40 and 60
7 min will be referred to as support for the statements made in this section.

8 For a short residence time of 20 min, the effect of a temperature increase on product yields
9 can be seen in Fig. 41. With an increasing temperature, the biochar yield increased from
10 74.97 ± 0.09 mass% at 240°C to 82.31 ± 0.09 mass% at 280°C , whereafter the yield
11 appeared to decrease as the temperature was increased to 320°C , producing a biochar
12 yield of 78.88 ± 0.09 mass%. The gas yield experienced an overall increase with the
13 increasing temperature but decreased again after 300°C . However, with the increasing
14 temperature, the bio-oil yield continued to decrease. The constant decrease of the bio-oil
15 yield was due to unstable lignin monomers that were either converted into secondary char
16 or residue through repolymerisation or converted into gas through cracking.

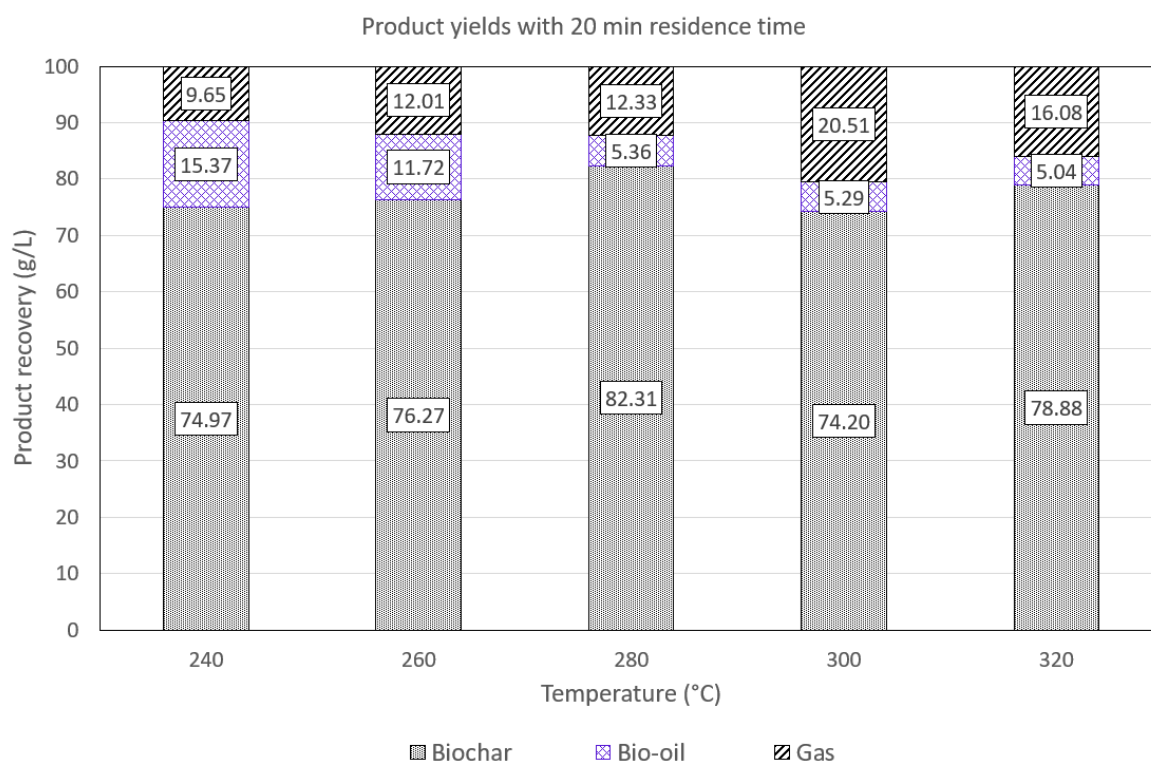


Fig. 41. Product yields with a residence time of 20 min

This indicates that at low temperatures, gas formation will be favoured over biochar and bio-oil production, which could be due to a few reactions occurring which formed radicals, which are lighter compounds that could be converted into the gas phase. The gas, however, decreased at 320°C when the biochar's yield suddenly increased. This indicates the occurrence of repolymerisation and condensation reactions, forming heavier and larger compounds that converted into solids.

Looking at the severity factor in Fig. 42 it is easier to see the relationship between the biochar and gas. At 280°C, as the one increased, the other decreased. With a short residence time like 20 min, repolymerisation occurred at 320°C and cleavage of the lignin bonds only started to occur at 280°C. Thus, 300°C will probably be the optimum temperature for bio-oil production. For a short residence time, a severity factor greater than 6.6 will not increase the bio-oil yield; thus, increasing the temperature for an increase in bio-oil yield will not be effective.

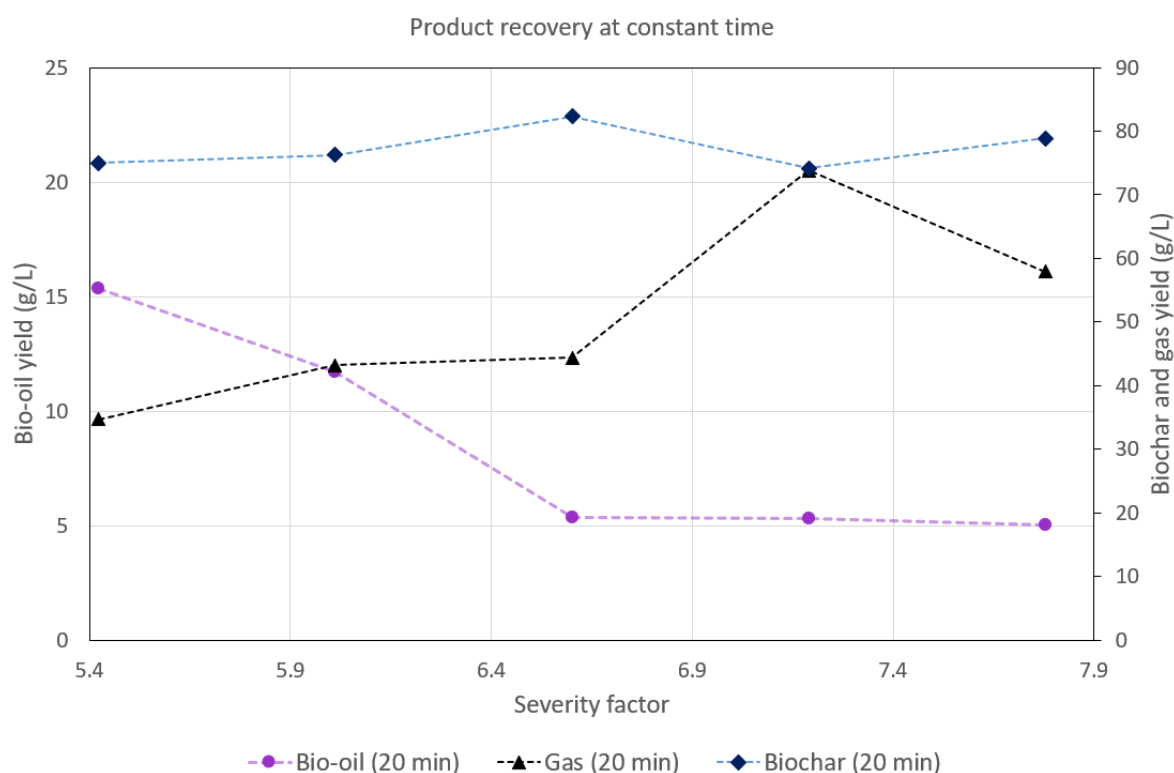


Fig. 42. Severity factor of products produced with a residence time of 20 min

For a longer residence time such as 80 min, the product yields are displayed in Fig. 43 and Fig. 44; the low temperatures encouraged radicals to repolymerise and condensation reactions to occur, which was why the biochar yield increased. The temperature increase caused the gas yield to increase through cracking reactions. At 280°C, both the bio-oil and gas yield increased at the expense of the biochar. This is believed to be due to the weaker bonds in the lignin structure breaking because of cracking reactions. Thus,

1 depolymerisation of heavy, solid molecules was occurring more thoroughly. When the
 2 temperature was increased the char and gas yield increased while the bio-oil drastically
 3 decreased; this was due to improved repolymerisation and cracking to form more stable
 4 molecules that converted to char or gas. When the temperature was increased to 300°C
 5 the char yield drastically decreased while all other products increased; this was due to lignin
 6 molecules and other large and heavy molecules depolymerising and cracking to form lighter
 7 and smaller molecules that converted to liquid or gas. Thus, at a relatively high temperature
 8 with a long residence time, deeper depolymerisation occurred. It seems that with a
 9 residence time of 80 min and a high temperature such as 320°C, mostly cracking reactions
 10 and some repolymerisation reactions occurred as the char and gas yields were favoured
 11 over the bio-oil yield.

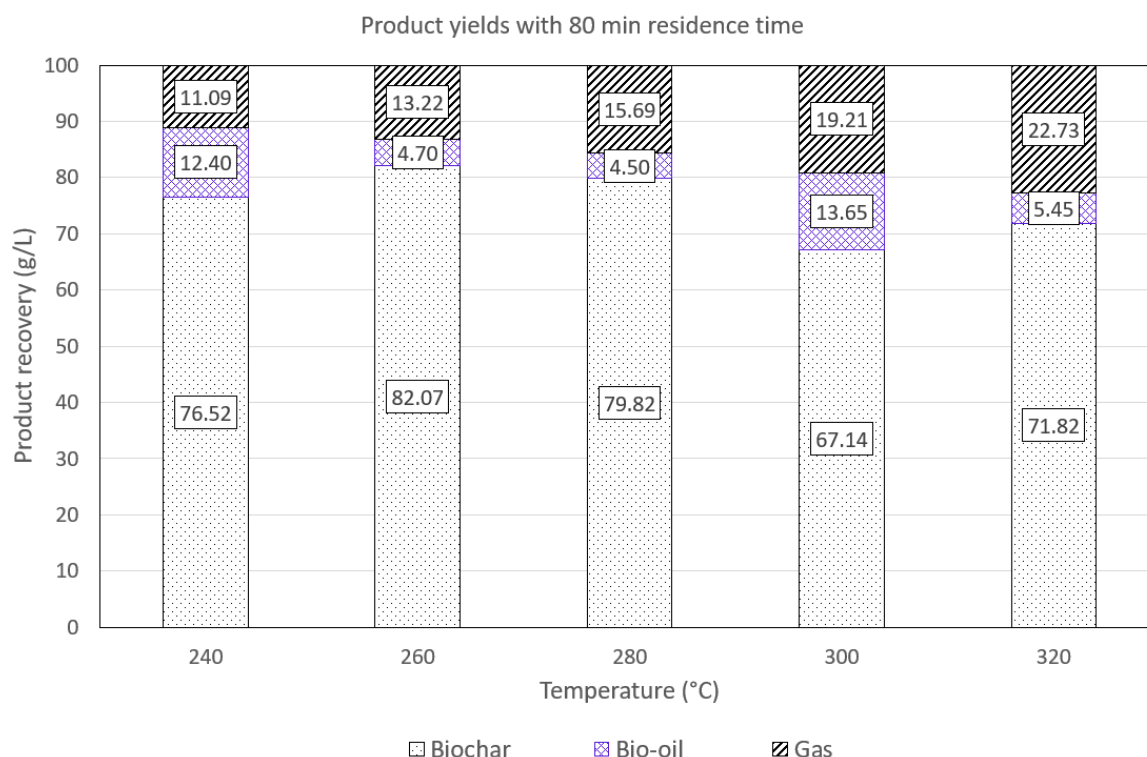


Fig. 43. Product yields with a residence time of 80 min

12 When viewing the severity factor in Fig. 44 and comparing it to the severity factor trend in
 13 Fig. 42, it is possible to see that the relationship between the biochar and bio-oil yields were
 14 stronger and inversely dependent on each other with longer residence times: as the one
 15 increased the other would decrease. Thus, at a relatively high temperature with a long
 16 residence time, extensive repolymerisation and cracking reactions will negatively influence
 17 the bio-oil yield since larger and heavier molecules will form. However, to achieve the
 18 highest possible yield of bio-oil (13.65 ± 0.09 mass%), a severity factor of 7.79 is required.
 19 As an example, instead of using 80 min and 300°C to achieve this yield, it is possible to

- 1 decrease the residence time to 40 min, but according to equation 1, a temperature of 310°C
- 2 should be adequate. For a temperature lower than 300°C, such as 290°C, a residence time
- 3 of almost 160 min will be required.

4

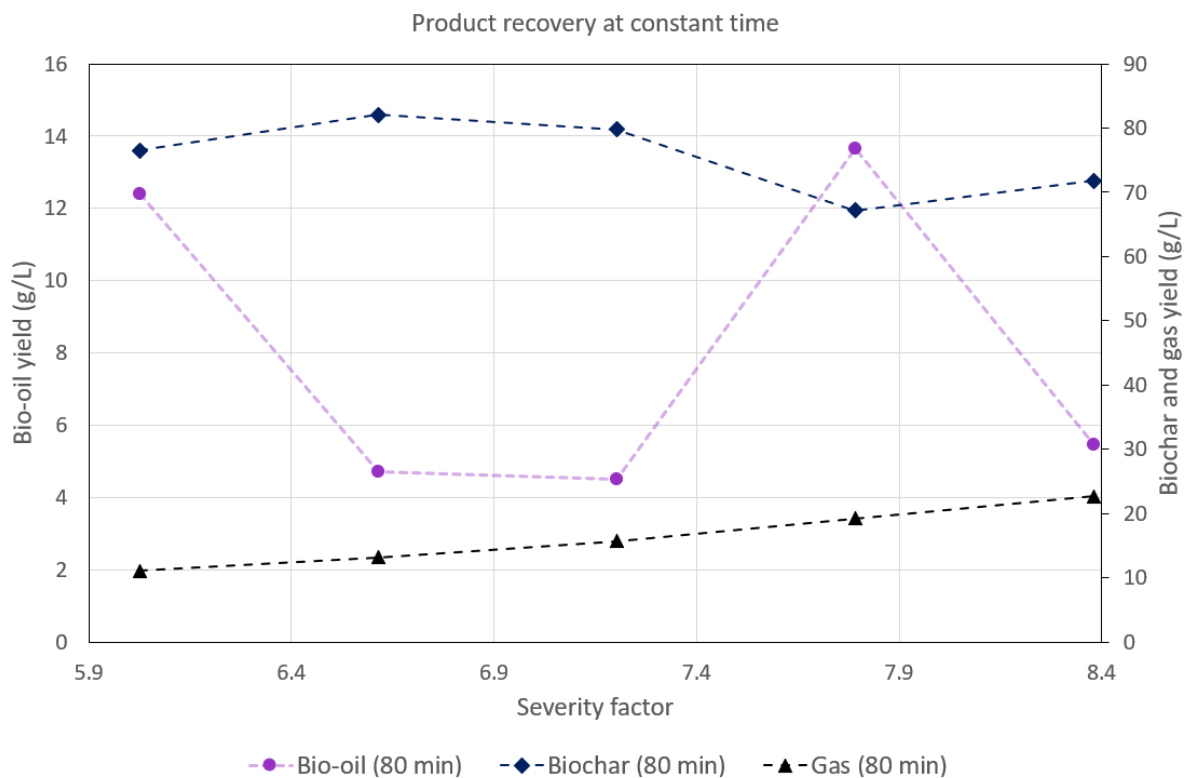


Fig. 44. Severity factor of products formed with a residence time of 80 min

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4.4.2 The effect of residence time on product yield

From the following data, it was proved that temperature had a more severe effect on yield than residence time, considering that the severity factor between different temperatures varied more than the severity factor between different residence times. At low temperatures, the residence time had a larger effect, but as the temperature increased, the difference in severity factor and the effect of residence time became even less. This trend was also confirmed by the Wądrzyk *et al.*, (2019) study. In this section, the product yields at a low temperature (260°C) and a high temperature (300°C) will be discussed. All yield data for the other temperatures can be found in Appendix B for reference.

At low temperatures, residence time had a decreasing effect on bio-oil yield and the formation of gaseous components was favoured over the formation of bio-oil and char, probably because no major reactions were occurring except the breaking of the weakest bonds in the molecules that were present. Any conversion or reaction at short residence times could have simply been the removal of the lightest impurities within the feedstock. By increasing the residence time, cracking reactions were encouraged, and thus the gas yield was increased by the addition of the lightest compounds. Repolymerisation and condensation reactions started to occur with very long residence times (80 min). The extended residence time allowed the opportunity for the lighter molecules in the gas phase and a small amount of dissolved lignin in the bio-oil to repolymerise into secondary char residue. As there was no significant gain in bio-oil content, it was believed that repolymerisation reactions were dominating. Fig. 46 demonstrates how an extended residence time could cause repolymerisation at much lower temperatures. The downward trend of the biochar up to 60 min residence time indicated deeper and more successful cracking and depolymerisation taking place.

At a temperature that was still relatively low, such as 280°C, where lignin started to decompose, it was possible to see how the bio-oil yield decreased due to the reactions occurring with the unreacted lignin molecules that dissolved in the bio-oil. The weaker bonds of these lignin molecules experienced cracking which increased the gas yield but as the residence time was increased more repolymerisation occurred producing large molecules that became a part of the solid phase; thus, increasing the biochar yield at the expense of the gas and bio-oil yield. Thus, longer reaction times at relatively low temperatures (240–280°C) promoted cracking reactions, but mostly the formation of heavier and larger molecules through repolymerisation reactions, which was also why the total recovery increased due to a reduced amount of volatiles being formed.

1

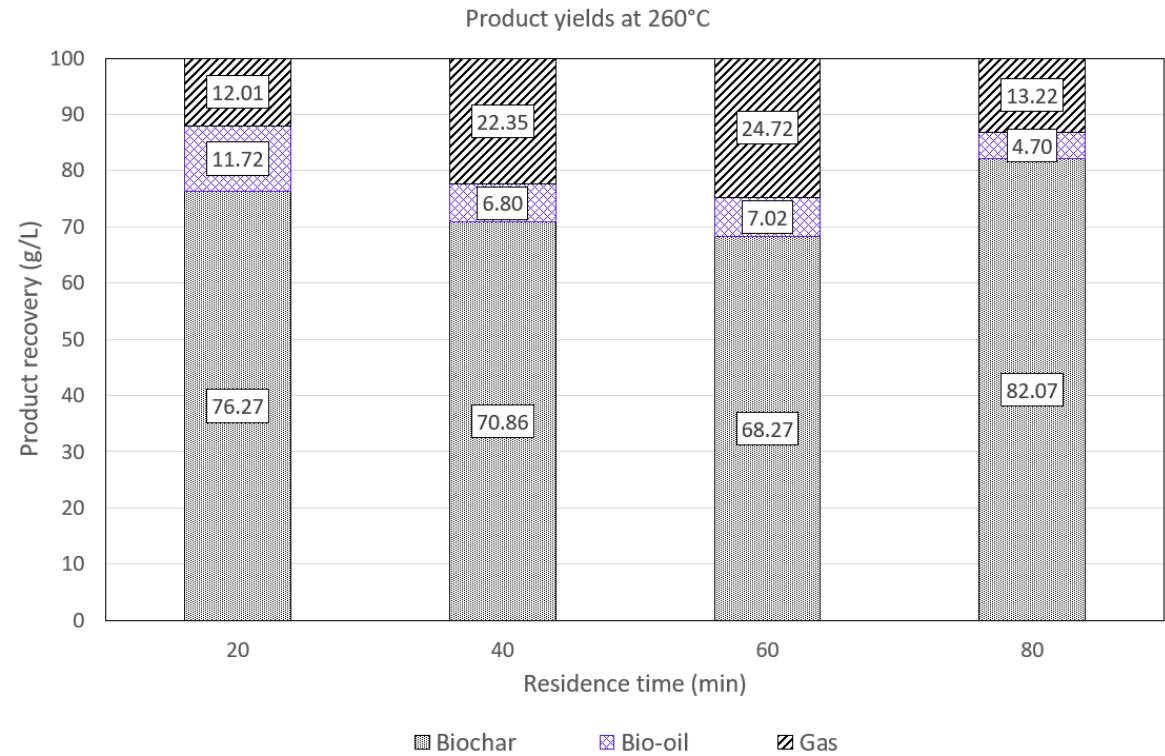


Fig. 45. HTL product yields with a reaction temperature of 260°C

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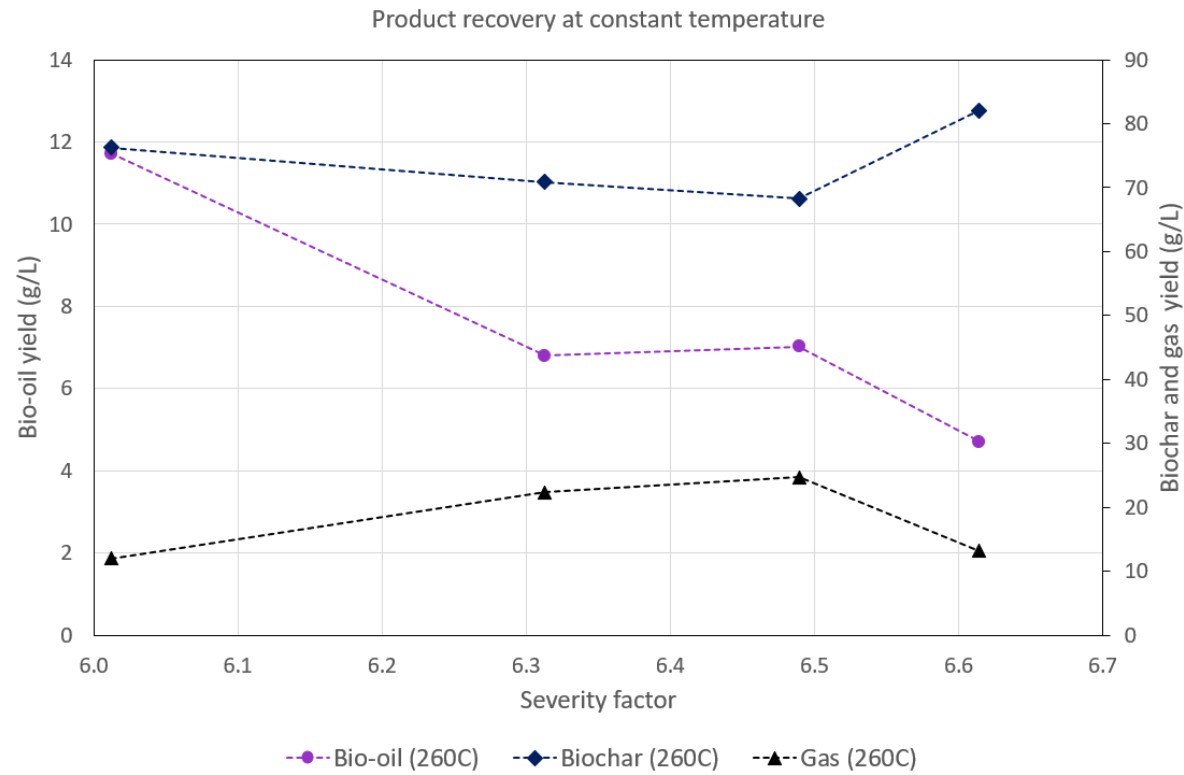


Fig. 46. Severity factor of products formed at 260°C

3

1 At high temperatures such as 300°C, depicted in Fig. 47 and Fig. 48, combined with short
 2 residence times (up to 40 min), the bio-oil and char yields increased at the expense of the
 3 gas through condensation and repolymerisation reaction. By increasing the residence time,
 4 the effect of cracking and depolymerisation can be seen, although it seems as if the cracking
 5 reactions were favoured as the char yield only slightly decreased between 40 and 60 min.
 6 When increasing the residence time even more to 80 min, the gas phase did not increase
 7 with a significant amount, indicating less cracking, while the bio-oil yield improved due to
 8 the char molecules depolymerising. This means that with high temperatures and long
 9 residence times, deeper depolymerisation took place which would increase the liquid phase
 10 yield at the expense of gas and biochar yields, until cracking reactions started to dominate.

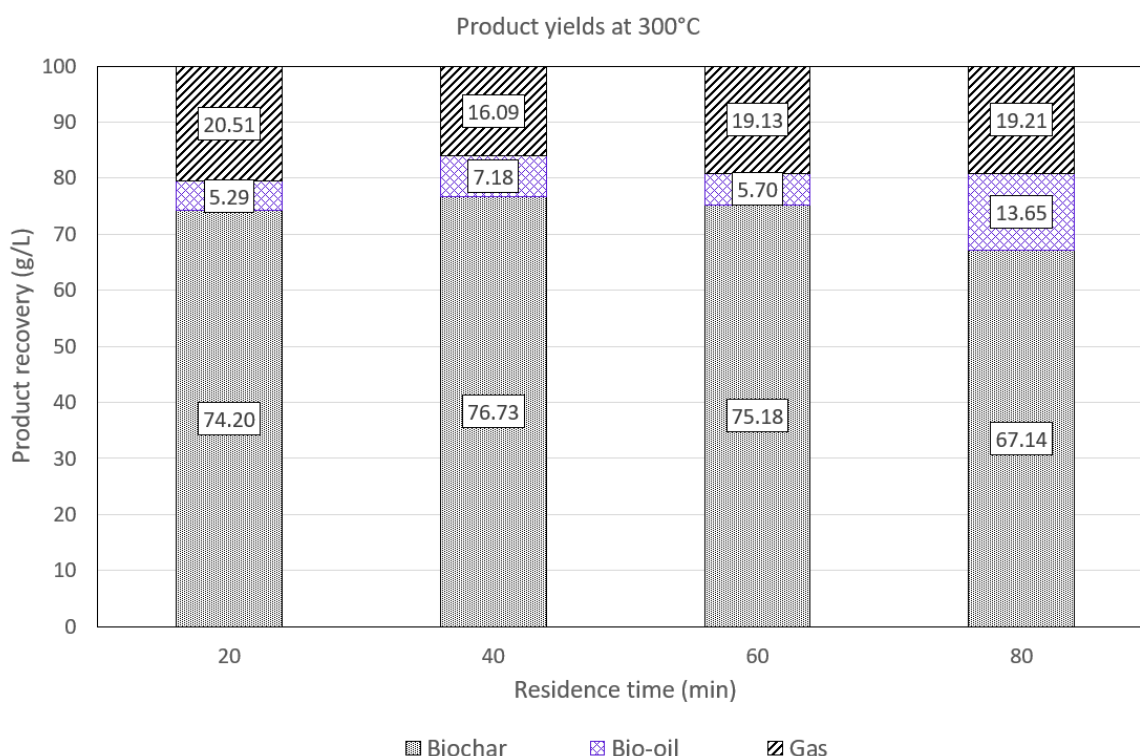


Fig. 47. HTL product yields with a reaction temperature of 300°C

11 The product yields at 320°C confirmed this trend. With the higher temperatures, the
 12 maximum bio-oil yield was achieved with shorter residence times. This implies that
 13 temperature controlled the extent of degradation, while residence time seemed to provide
 14 an opportunity for repolymerisation and restructuring.

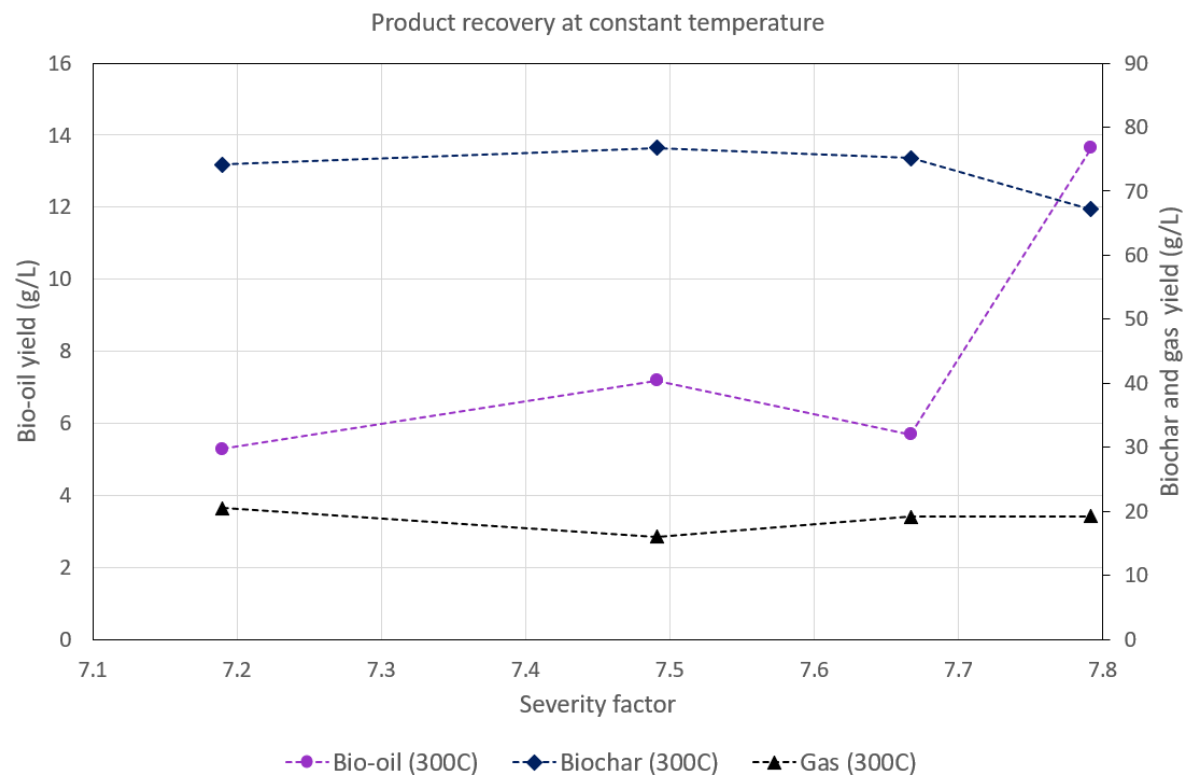


Fig. 48. Severity factor of products formed at 300°C

4.4.3 The effect of catalyst loading on product yield

As seen in Fig. 49, the presence of an alkali catalyst restricted and reduced cracking reactions, thereby decreasing the gas yield. The increased catalyst loading also led to improved depolymerisation which could be seen from the increase in bio-oil yield and decrease in biochar at 4 mass% loadings. However, the addition of catalysts also encouraged repolymerisation to occur faster, thus increasing the biochar yield. It can be assumed that the increase in catalyst loading not only reduced the gas fraction but improved the quality of the char and possibly the bio-oil. The reason for this statement comes from the gas and char yields having inversely dependent yields. The mass conversion between the two is connected; thus, whenever mass is lost from the gas phase it is converted to the solid phase by condensation. The increase in bio-oil yield can be explained as the depolymerisation of the weaker molecules in the char to become dissolved in the bio-oil. The 5 mass% sodium hydroxide yielded the lowest combined mass of biochar and gas with a high bio-oil yield.

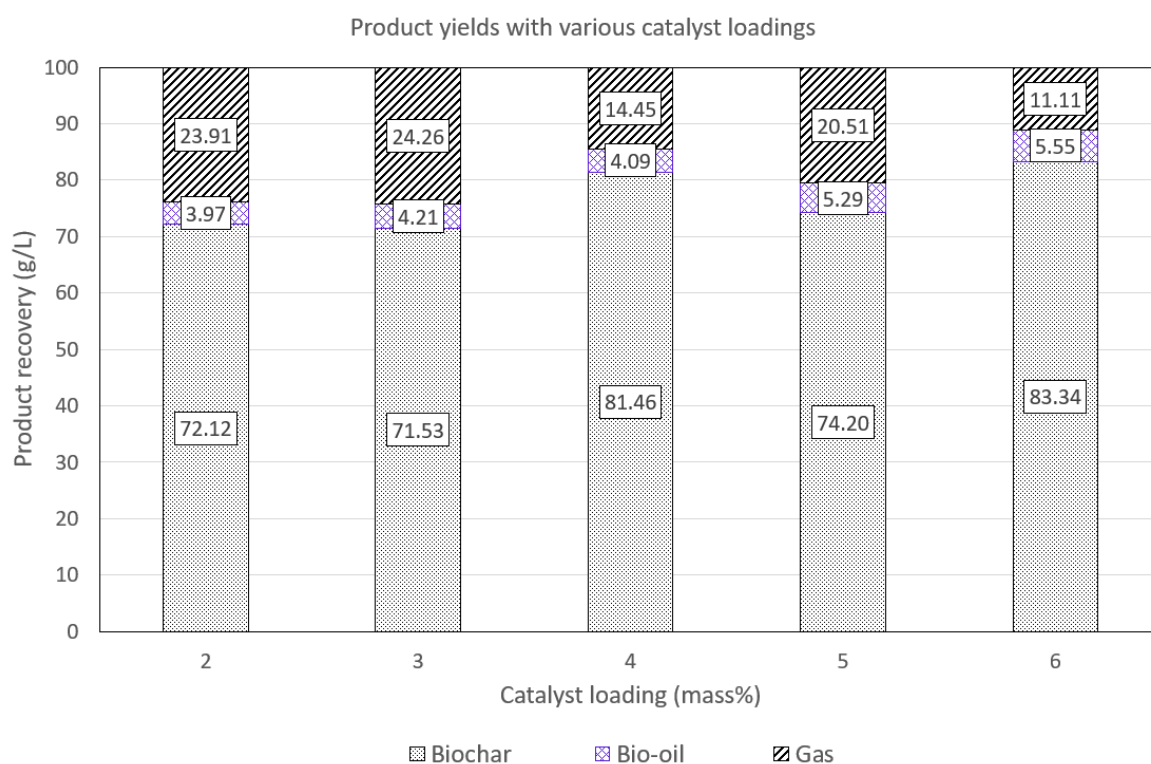


Fig. 49. HTL product yields with different catalyst loadings

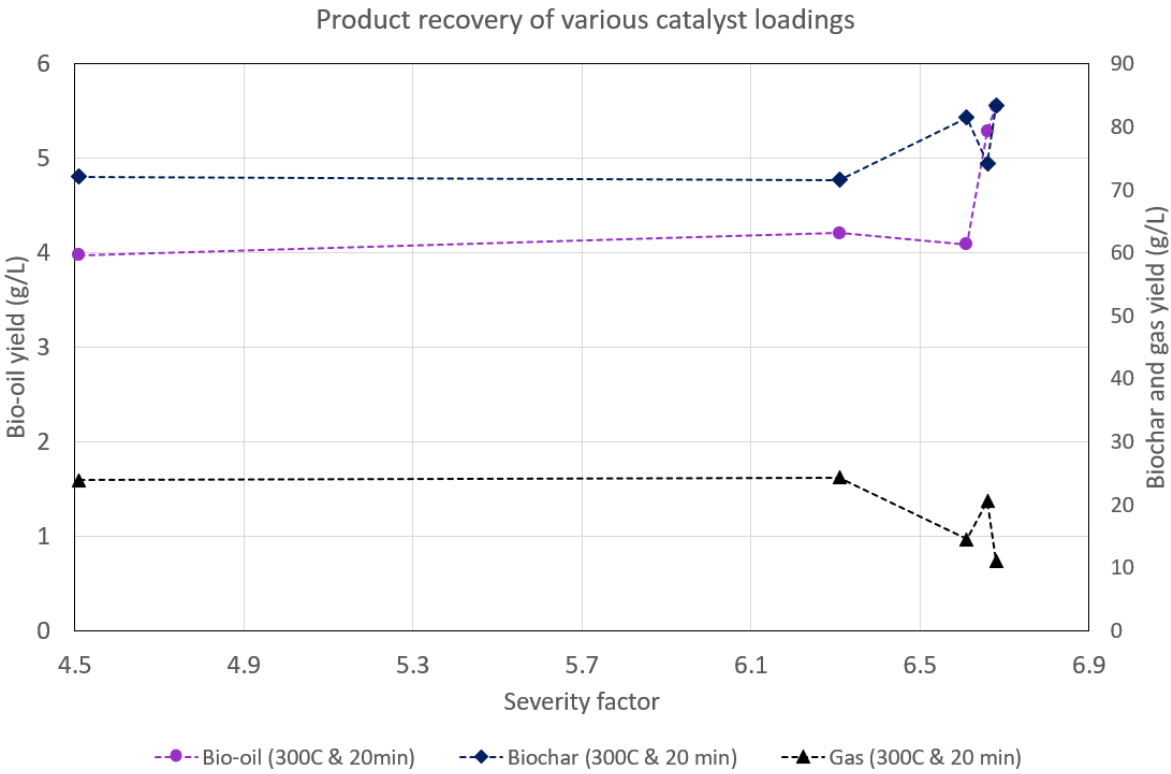


Fig. 50. Effect of catalyst loading on product recoveries expressed as severity factors

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4.5 The effect of process variables on liquefaction product quality

4.5.1 The effect of reaction temperature on product quality

4.5.1.1 Elemental composition of products

The elemental composition of each experiment's biochar and bio-oil was analysed and determined on the dry mass of the product. To determine the total elemental recovery for each experiment it was assumed that all gas produced during the reactions consisted of CO₂. As the experiments were conducted in a nitrogen atmosphere, the nitrogen recovery data was unreliable due to the absorption of nitrogen from this atmosphere. The % R represents mostly the oxygen content. The data obtained from the elemental analysis and the elemental balance calculations can be found in Appendix B.

4.5.1.1.1 Elemental composition of bio-oil

The elemental recovery for the bio-oils produced with a 20 min residence time is depicted in Fig. 51. As the temperature increased, less carbon was recovered with the lowest recovery at 280°C. It is believed that this loss of carbon and hydrogen was through the evaporation of volatiles (lighter components) during the separation processes, while the increase at 300°C is due to the repolymerisation of some lighter compounds into heavier molecules. Even though the total carbon recovery for the products produced at 20 min was above 70 mass%, the carbon recovered in the bio-oil was less than 25 mass%. For a short residence time, increasing the temperature would reduce the carbon, hydrogen, and oxygen content. For higher temperatures, it was possible to reduce the oxygen content to less than 2.5 mass% as seen in Fig. 51. Note that the carbon and hydrogen content may have decreased, but both were still roughly two times higher than that of the oxygen content. The lowest ratio is seen at 280°C as 1.6 and 1.8 for the carbon and hydrogen content, respectively; while the highest ratio is seen at 300°C as 3.0 for both carbon and hydrogen.

Table 4-12. Elemental ratios of bio-oils produced with various reaction temperatures

Temperature (°C)	Short residence time (20 min)		Long residence time (80 min)	
	O/C	H/C	O/C	H/C
240	0.46 ± 0.01	1.18 ± 0.00	0.33 ± 0.01	1.02 ± 0.00
260	0.49 ± 0.01	1.15 ± 0.00	0.70 ± 0.01	1.21 ± 0.00

280	0.61 ± 0.01	1.13 ± 0.00	0.51 ± 0.01	1.14 ± 0.00
300	0.34 ± 0.01	1.01 ± 0.00	0.91 ± 0.01	1.00 ± 0.00
320	0.48 ± 0.01	1.02 ± 0.00	1.12 ± 0.01	1.20 ± 0.00

1

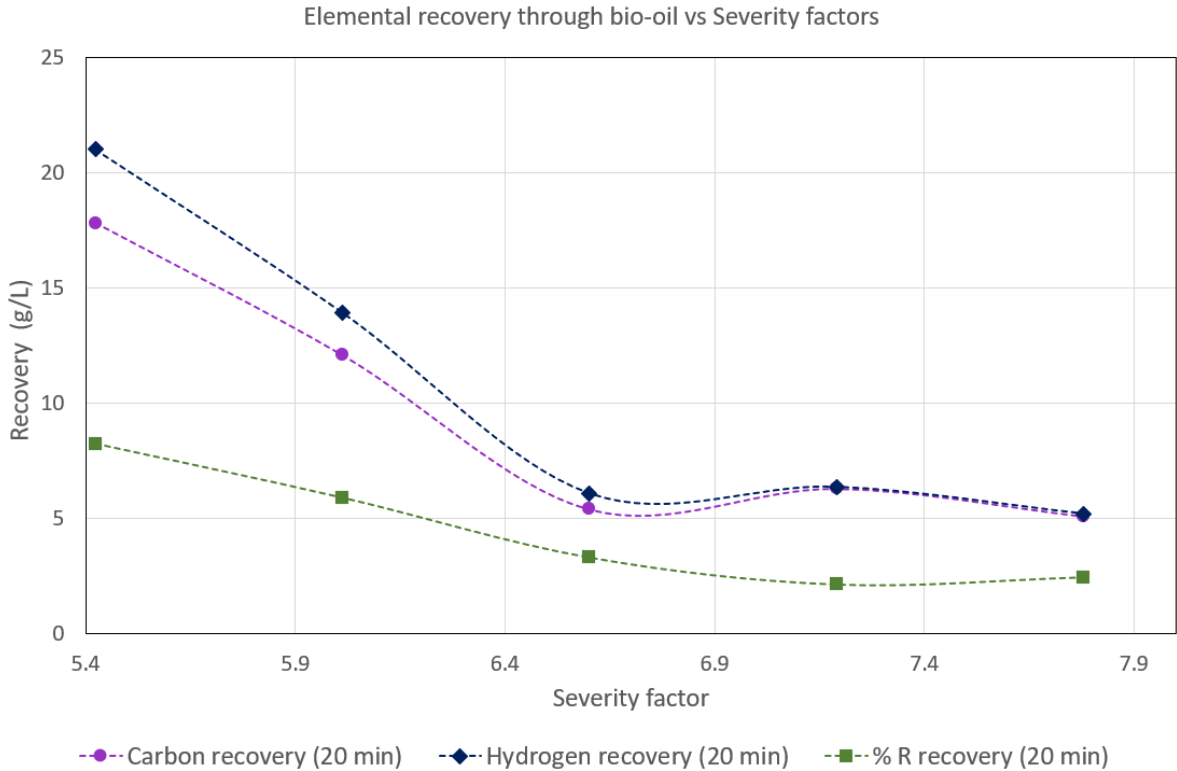


Fig. 51. Elemental composition of bio-oils formed with 20 min residence time

2 For longer residence times, Fig. 52 can be used as a guide. For a residence time of 80 min,
3 the total carbon recovery was above 80 mass%; however, for the bio-oil, the recovery was
4 less than 20 mass% for both carbon and hydrogen content, with the % R recovery below
5 10 mass%. As the temperature increased, the decrease in carbon and hydrogen content
6 was more drastic for the long residence times than for the short 20 min. This can be seen
7 as the ratio between carbon and oxygen recovery decreased from roughly 2.95 to 0.90 as
8 the temperature increased. For the ratio between hydrogen and oxygen, there was also a
9 visible decrease from 3.01 to 1.07 from low to high temperatures. With longer residence
10 times the gas fraction increased with temperature, which could explain the loss of carbon.
11 It can also be seen that long residence times combined with higher temperatures did not
12 encourage deoxygenation as much as short residence time – this could have been caused
13 by condensation and repolymerisation reactions. For both short and long residence times,
14 the hydrogen recovery was slightly higher than the carbon recovery, but as the temperature
15 increased they became equal. The higher hydrogen recovery was due to the molecular
16 structure of simple molecules (C_nH_{n+2}); thus, at a low temperature one can assume that the

- 1 bio-oil consisted mostly of long carbon chains with single bonds (fewer olefins and
- 2 aromatics) but as the temperature increased, more complex molecules formed (phenolics,
- 3 esters, ketones, etc.).
- 4 Another point to look at is the thermal instability of bio-oil. To increase bio-oil's thermal
- 5 stability the oxygen content must be reduced. Using a short residence time and by
- 6 increasing the temperature, the oxygen content could be reduced to below 3 mass% which
- 7 would ensure a bio-oil that is thermally more stable.

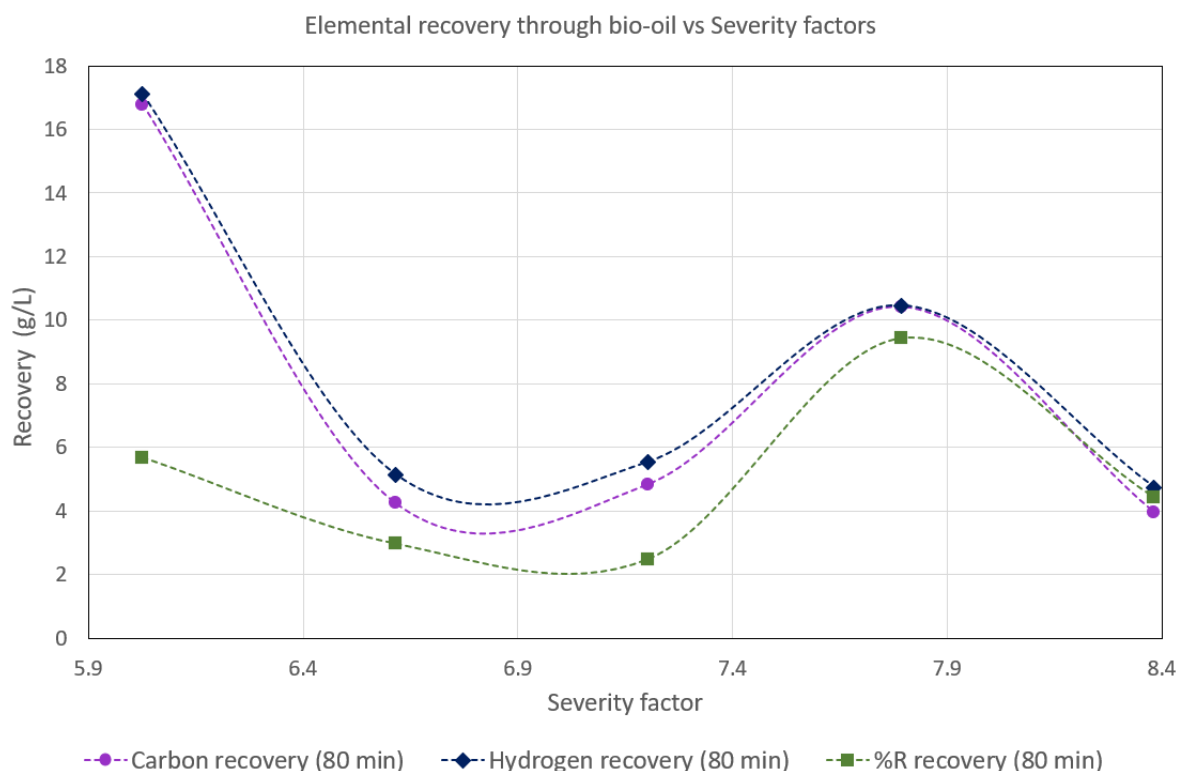


Fig. 52. Elemental composition of bio-oils produced with 80 min residence time

8 4.5.1.1.2 Elemental composition of biochar

- 9 As seen above with the bio-oils, the carbon and hydrogen recovery should follow the same
- 10 trend line. This is because of the chemical's carbon chain structure. Thus, when the carbon
- 11 recovery increases so must the hydrogen recovery. However, if the recovery does not follow
- 12 this trend (carbon increases, but hydrogen decreases) it could indicate the formation of
- 13 double and triple bonds in a chain. When this happens the molecules lose hydrogen atoms
- 14 that are replaced by other molecules (S, N, or Cl, etc.) or form more complicated, larger
- 15 molecules (double and triple bonds between carbon atoms). This seems to be a case for
- 16 the production of biochars from sodium lignosulphonate and ethanol with an alkali catalyst
- 17 with both a short and long residence time. However, with short residence times and low

temperatures, it was possible to achieve a relatively high hydrogen recovery (54–46 mass%), but the increase in temperature decreased the hydrogen content by almost half. This decrease in hydrogen content was not as drastic with longer residence times, mostly because the hydrogen recovery was not very high to start with (37.64 ± 0.34 mass% at 240°C). Both long and short residence times combined with high temperatures produced biochar with a hydrogen content of roughly 30.54 ± 0.34 and 30.45 ± 0.34 mass%, respectively. The carbon content of the biochar produced with short residence times was at its highest (66.79 ± 0.34 mass%) at the lowest temperature. As the temperature increased, the carbon content reduced and remained around 59 ± 0.31 mass%. The loss of carbon content proves depolymerisation of the molecules into smaller molecules that either dissolved in the bio-oil or experienced a phase change such as the production of CO_2 gas. The long residence time showed that temperature had an irregular effect on the carbon content, but ultimately improved the carbon content (72-65 mass%). The improvement and oscillation of the carbon content indicated the occurrence of repolymerisation of smaller, lighter molecules into larger, solid compounds. The oscillating results also showed that for each temperature there was a different turning point when the repolymerisation started; meaning that with 80 min at 260°C , repolymerisation reactions occurred for longer to result in the carbon content of 72.01 ± 0.31 mass%, while a temperature of 300°C indicated that depolymerisation went on for longer before repolymerisation started or that depolymerisation occurred again after repolymerisation to give a carbon content of 60.91 ± 0.31 mass% as can be seen in Table 9-6 to Table 9-9 found in the appendix for additional biochar data.

With a short residence time, a temperature increase assisted in the deoxygenation of the biochar. The % R dropped from 83.57 ± 0.14 to 71.41 ± 0.14 mass%, before repolymerisation occurred at 320°C and oxygen-containing compounds formed part of the solids again (80.23 mass %). The ratio of carbon-to-oxygen was below 1 for all temperatures and remained between 0.72 to 0.82, with no discernible trend, while the hydrogen-to-oxygen ratio was between 0.65 and 0.37, indicating a much larger oxygen fraction. For long residence times, increased temperature also aided in the deoxygenation of the biochar. The gas fraction increased with these temperatures so it can be assumed that the oxygen moved to the gas phase, although some joined the bio-oil as it experienced an increase in oxygen content. The bio-oil's oxygen content only increased with the two highest temperatures, indicating condensation reactions where oxygen joined the bio-oil after condensing out of the gas phase. The carbon-to-oxygen ratio varied less than with a short time (0.67-0.86) and the hydrogen-to-oxygen ratio was very low (0.43-0.37). The longer residence times

1 allowed more time for oxygenation and for salts to be incorporated into the biochar's
2 structure.

3 The significant difference between the carbon and hydrogen content for both long and short
4 times can be explained if the biochar contained molecules that had lots of double and triple
5 bonds with oxygen atoms, such as ketones, olefins, and aldehydes. This shows that with
6 longer residence times, these highly bonded molecules form even at low temperatures.
7 Thus, even when larger molecules experienced deeper depolymerisation there were also
8 more repolymerisation occurring simultaneously.

9 Table 4-13. Elemental ratios of biochars produced with 20 min residence time

Temperature (°C)	Short residence time (20 min)		Long residence time (80 min)	
	O/C	H/C	O/C	H/C
240	1.25 ± 0.00	0.81 ± 0.01	1.48 ± 0.00	0.64 ± 0.01
260	1.32 ± 0.00	0.77 ± 0.01	1.16 ± 0.00	0.50± 0.01
280	1.33 ± 0.00	0.55 ± 0.01	1.17 ± 0.00	0.44± 0.01
300	1.21 ± 0.00	0.63 ± 0.01	1.19 ± 0.00	0.49± 0.01
320	1.37 ± 0.00	0.52 ± 0.01	1.22 ± 0.00	0.47± 0.01

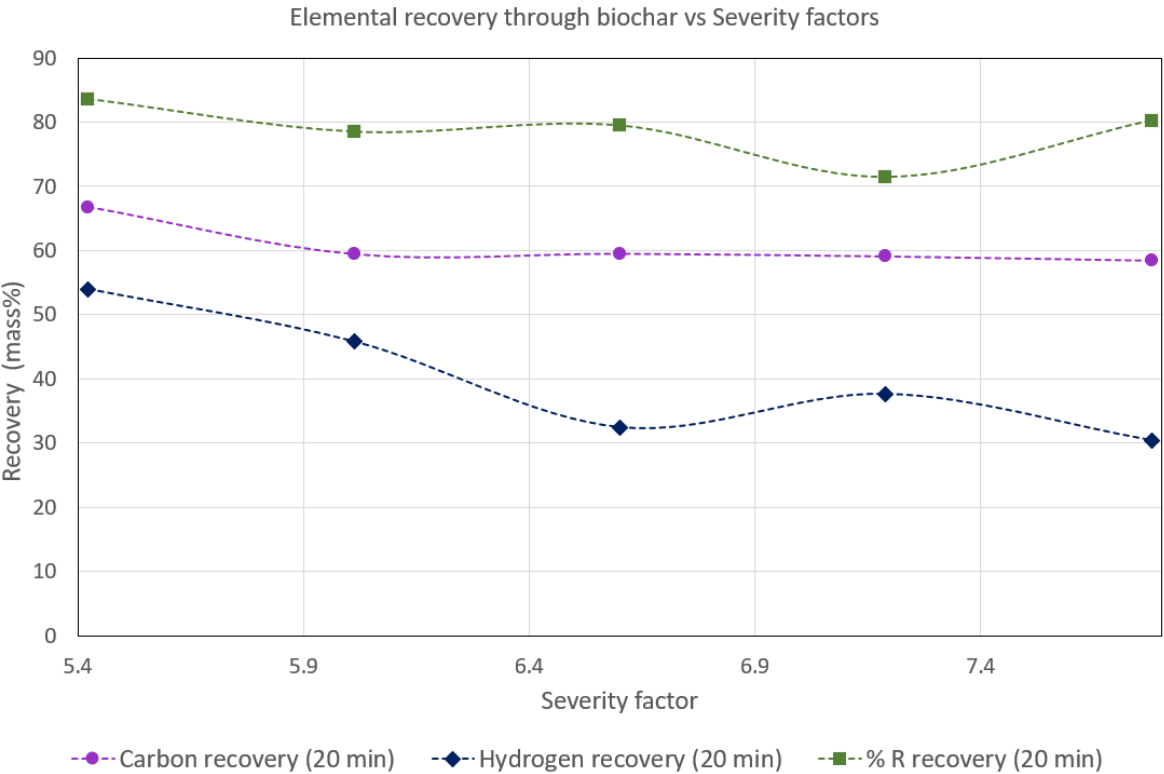


Fig. 53. Elemental composition of biochar produced with a short residence time (20 min)

1

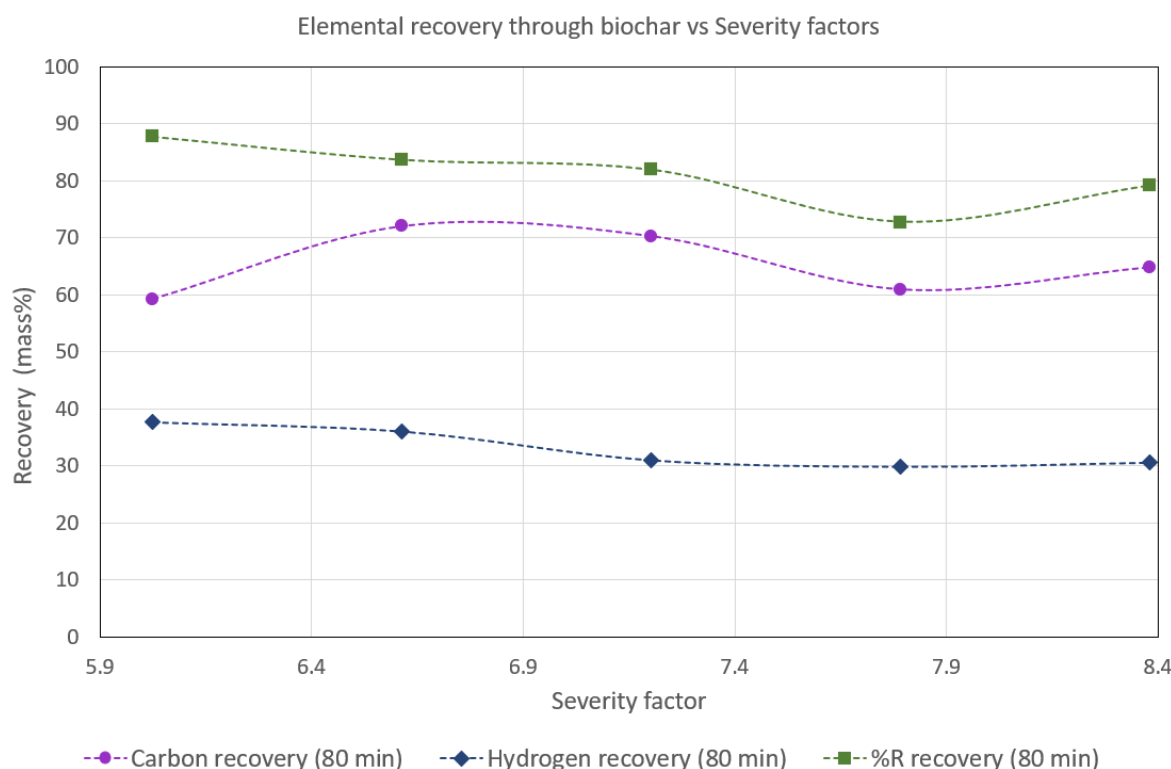


Fig. 54. Elemental composition of biochar produced with a long residence time (80 min)

2 4.5.1.2 Energy content of products

3 4.5.1.2.1 Energy content of bio-oil

4 The CVs for the bio-oils produced with 20 min residence time at 300 and 320°C could not
 5 be determined due to a too small sample. From the available data, the HTL process
 6 improved the energy content of the bio-oil to 25.70 ± 1.48 MJ/kg; however, as the
 7 temperature increased from 240–280°C the CVs decreased. This can be explained by the
 8 decrease in carbon content that was seen in Fig. 51. To have a high energy content a bio-
 9 oil must have a high carbon content and a low oxygen content. However, at a short
 10 residence time, the increased temperature, decreased both the oxygen and carbon content,
 11 and in doing so the CV of the bio-oil also decreased.

12 Increasing temperature at longer residence time also lowered the CVs of the bio-oils. This
 13 decrease was not as significant as with the lower residence times but might be explained
 14 from Fig. 52 where it shows that the carbon and oxygen did not differ by much. The energy
 15 content of the oils was still a significant improvement from the feedstock.

1

Table 4-14. CVs of bio-oils produced with a residence time of 20 min

Temperature	CV (MJ/kg)	DOC
Lignex®	11.64 ± 1.48	-
240°C	25.70 ± 1.48	2.21
260°C	24.66 ± 1.48	2.12
280°C	16.77 ± 1.48	1.44
300°C	ND	-
320°C	ND	-

2

3

Table 4-15. CVs of bio-oils produced with a residence time of 60 min

Temperature	CV (MJ/kg)	DOC
Lignex®	11.64 ± 1.48	-
240°C	22.54 ± 1.48	1.94
260°C	21.12 ± 1.48	1.81
280°C	19.35 ± 1.48	1.66
300°C	19.18 ± 1.48	1.65
320°C	17.93 ± 1.48	1.54

4

5 4.5.1.2.2 Energy content of biochar

6 The low CVs of the biochar are proof that its quality was very low and the HTL process was
7 ineffective in improving the quality of the biochar. According to the World Nuclear
8 Association, the biochar produced from Lignex® through HTL has an energy content a little
9 lower than that of lignite or brown coal (less than 17 MJ/kg). There was no improvement in
10 the biochar's energy content for longer residence times either. The increase in temperature
11 at longer residence times even decreased the biochar's CV to below the feedstock's CV.
12 The low CV of the biochars was caused by the very high oxygen content combined with the
13 low hydrogen and carbon content.

14

1

Table 4-16. CVs of biochars produced with a residence time of 20 min

Temperature	CV (MJ/kg)	DOC
Lignex®	11.64 ± 1.48	-
240°C	13.05 ± 1.48	1.12
260°C	12.95 ± 1.48	1.11
280°C	13.64 ± 1.48	1.17
300°C	12.53 ± 1.48	1.07
320°C	13.27 ± 1.48	1.14

2

3

Table 4-17. CVs of biochars produced with a residence time of 60 min

Temperature	CV (MJ/kg)	DOC
Lignex®	11.64 ± 1.48	-
240°C	10.16 ± 1.48	0.87
260°C	11.23 ± 1.48	0.96
280°C	10.49 ± 1.48	0.90
300°C	11.67 ± 1.48	1.00
320°C	13.11 ± 1.48	1.13

4 4.5.1.3 Molecular weight distribution of bio-oils

5 For both short and long residence times, it was possible to see that increasing temperature
6 had a significant effect on the depolymerisation of the sodium lignosulphonate (Lignex®)
7 compounds. The molecular weight data for the 20 min experiments can be seen in Table
8 4-18. Based on the Mw and Mn columns, the successful depolymerisation of Lignex® is
9 clear. A reduction in molecular weight also implies a reduction in viscosity, thus a
10 temperature increase can decrease the bio-oils viscosity, as was shown in the study by
11 Wądrzyk *et al.*, (2019). The data for the 320°C clearly shows the repolymerisation as the
12 molecular weight increased. However, the PDI stayed relatively the same, meaning that the
13 broadness of the molecular weight distribution did not change. Fig. 55 shows that the
14 broadness for all temperatures was about the same. This constant PDI indicates that even
15 though the larger structures changed through depolymerisation into smaller pieces that had
16 about the same molecular weight, there were very few reactions taking place during HTL.

1

Table 4-18. GPC analysis of bio-oils produced with a residence time of 20 min

Temperature	Mw (g/mol)	Mn (g/mol)	PDI
Lignex®	2468 ± 1	945 ± 1	2.6 ± 0.3
240°C	767 ± 1	313 ± 1	2.5 ± 0.3
260°C	683 ± 1	260 ± 1	2.6 ± 0.3
280°C	402 ± 1	167 ± 1	2.4 ± 0.3
300°C	384 ± 1	162 ± 1	2.4 ± 0.3
320°C	395 ± 1	154 ± 1	2.6 ± 0.3

2

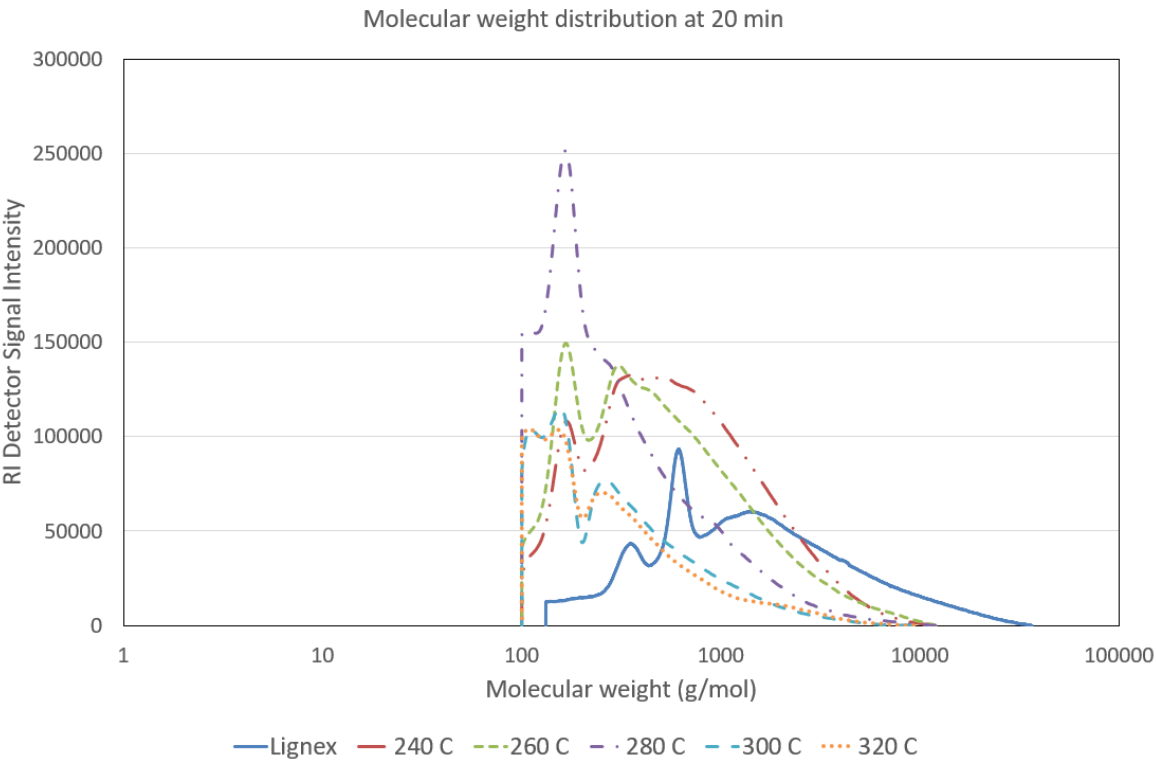


Fig. 55. Molecular weight distribution curve of bio-oils produced with a 20 min residence time

3

With a longer residence time, a temperature increase will have a more significant effect on the depolymerisation of the molecules as can be seen in Fig. 56. With a long residence time (80 min) it was possible to decrease the Mw from 2468 ± 1 to 345 ± 1 g/mol and the Mn from 945 ± 1 to 172 ± 1 g/mol. The broadness of the molecular weight also decreased to 2.0 ± 0.3. However, the lowest PDI of 1.7 ± 0.3 was achieved at 280°C with 60 min. The decrease in PDI, Mw and Mn shows that with an increase in temperature at longer residence times, deeper and more extensive depolymerisation of the Lignex® could take place. It also means that the viscosity of the bio-oils had decreased. By comparing the results in Table

10

4-19 with the results of the 60 min residence time in Appendix B, it was revealed that the molecular weight and PDI for 80 min were larger than what was achieved at 60 min; it can be assumed that the extra 20 min added to the residence time, gave the smaller molecules more time to form bonds and repolymerise into somewhat larger structures. Even though the molecular weight was larger than the molecular weights of the bio-oils that were produced at 20 min, it was still a significant improvement of the raw Lignex® feedstock.

The decreased Mw, Mn, and PDI prove that the HTL process was successful in breaking apart the large polymers present in the Lignex® into smaller monomers. By increasing the temperature, depolymerisation could occur more effectively and the number of monomers could be increased. However, the specific combination of the selected time and temperature was of extreme importance, as increasing both too much could have forced the process beyond the turning point where more repolymerisation than depolymerisation would have taken place. The results from the molecular weight distribution can also explain the decreasing CVs of the bio-oil. The decrease in molecular weight means that the long chains of polymers were broken into shorter chains of monomers. This would also decrease the CV because the carbon chains were getting shorter each time the temperature was increased. For the short residence times, the breaking or depolymerisation of long chains was not as advanced yet which explains why the CVs of the shorter residence times were so much higher than the CVs for the longer residence times. The bio-oil produced with short residence times still contained a larger number of long-chained, carbon-based molecules (polymers). This was why the CVs of the bio-oils produced at 260 and 280°C differed so significantly, because there was a significant increase in depolymerisation, probably due to the lignin molecules decomposing at 280°C. For the longer residence time, the depolymerisation was very effective in decreasing the molecular weight even at low temperatures.

Table 4-19. GPC analysis of bio-oils produced with a residence time of 80 min

Temperature	Mw	Mn	PDI
Lignex®	2468 ± 1	945 ± 1	2.6 ± 0.3
240°C	506 ± 1	210 ± 1	2.4 ± 0.3
260°C	953 ± 1	250 ± 1	3.8 ± 0.3
280°C	351 ± 1	186 ± 1	1.9 ± 0.3
300°C	385 ± 1	176 ± 1	2.2 ± 0.3

320°C

345 ± 1

172 ± 1

2.0 ± 0.3

1

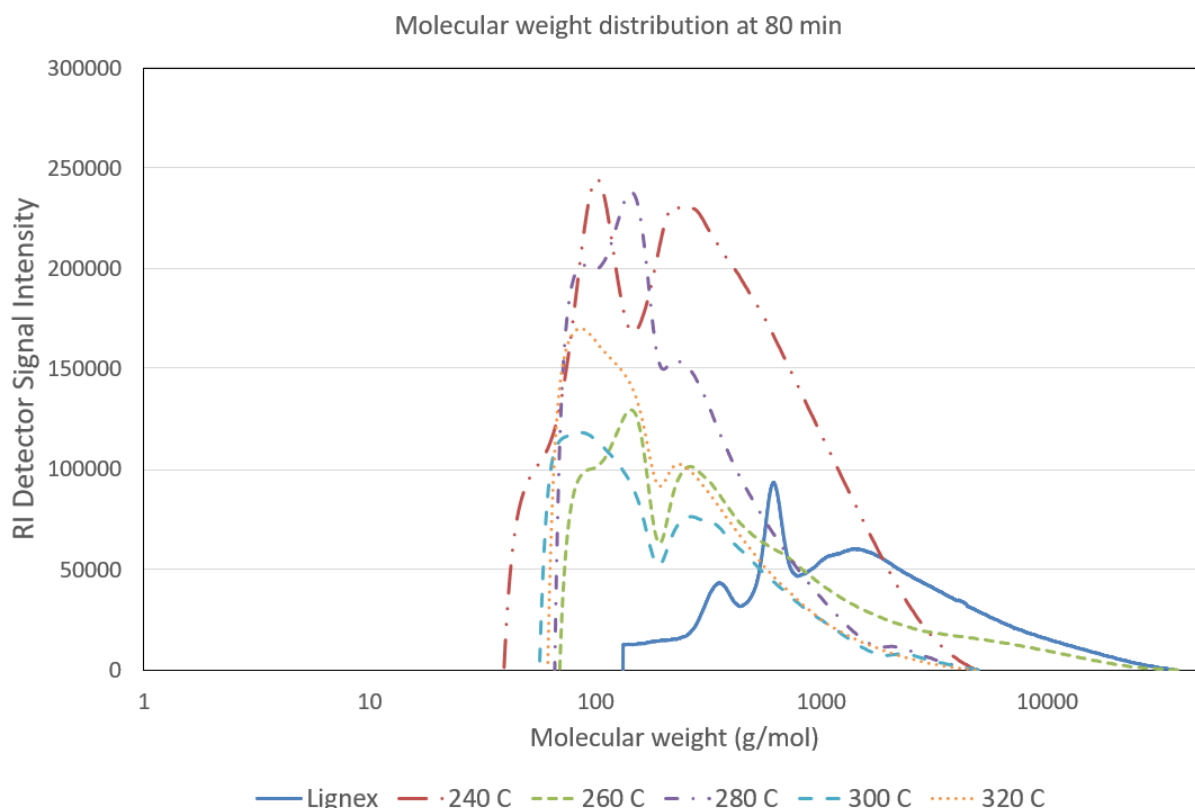


Fig. 56. Molecular weight distribution curve of bio-oils produced with an 80 min residence time

2 4.5.1.4 Chemical composition of products

3 4.5.1.4.1 Boiling fractions of bio-oils

4 Thus far it has been clear that the bio-oils are complex mixtures that consist of different
 5 compounds with different molecular weights. The molecular weight distribution data
 6 revealed that increasing the temperature would encourage the depolymerisation of
 7 polymers into lighter smaller chains. To see how these compounds with different boiling
 8 points and molecular weights are distributed, simulated distillation curves were created to
 9 depict the different factions within the bio-oil. Simulated distillation curves were compiled
 10 using a modified method based on the ASTM D7213 Standard Test Method for Boiling
 11 Range Distribution of Petroleum Distillates. The compounds were detected with the use of
 12 a GC-MS analysis and were then classified according to their boiling points and according
 13 to the number of carbon atoms in the molecular chain and their accompanying residence
 14 times (Stedile *et al.*, 2019). C₁₀ C₂₁, C₂₃, C₂₇, C₂₉, C₃₂ and C₃₆ n alkanes with known boiling

points were used as calibration standards. However, the heavier components present in the bio-oil with boiling points above 500 °C could not be detected by the GC-MS. The boiling ranges are:

Table 4-20. Boiling ranges classification

Boiling range	Groups
30-150°C	Naphtha
150-240°C	Kerosene
240-370°C	Diesel boiling range
370°C and higher	Heavy fractions

To be able to see how each fraction changed with an increase in temperature at a short residence time the data was quantified and is presented in Table 4-21 and Fig. 57. The information obtained from the boiling range distribution curves supports the previous results. As the temperature increased, so did the efficiency of the depolymerisation reactions. This statement is supported by the increasing size of the diesel boiling fraction, while the size of the heavy fraction decreased significantly. The increase in the diesel boiling fraction was also quite large. This demonstrates how the long and heavy chains were depolymerised into shorter and lighter chains. By increasing the temperature, the light kerosene fraction dropped to 15.58 ± 1.71 mass%. As the temperature increased, the diesel boiling fraction increased to 77.73 ± 0.08 mass% at 320°C while the heavy fraction continued to decrease from 38.25 ± 0.37 to 6.67 ± 0.37 mass%.

Table 4-21. Boiling fractions' distribution of bio-oil compounds (20 min)

Compound fractions (%)	240°C	260°C	280°C	300°C	320°C
Naphtha	0	0	0	0	0
Kerosene (± 1.71)	32.48	5.52	5.32	14.64	15.58
Diesel boiling (± 0.08)	28.45	58.08	75.92	71.78	77.73
Heavy fraction (± 0.37)	38.25	36.00	18.71	12.54	6.67

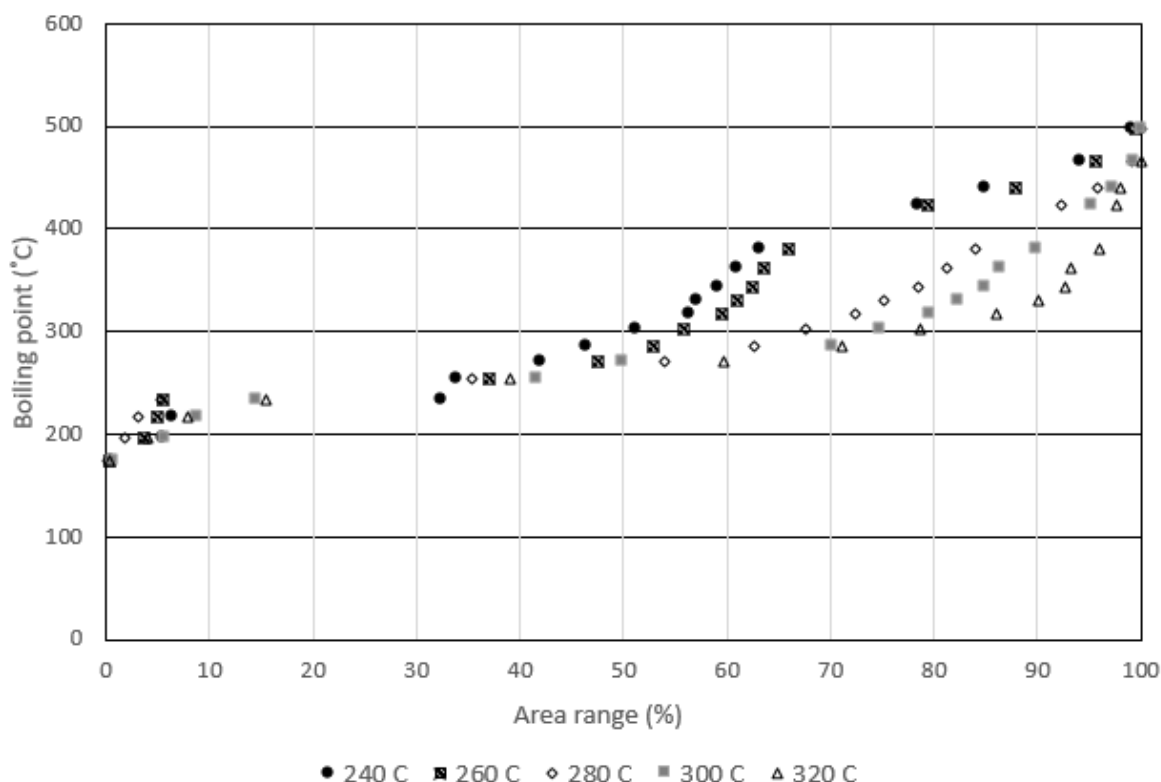


Fig. 57. Simulated distillation curve of bio-oils produced with a 20 min residence time

1

2 When the residence time was made longer, the boiling range of the bio-oil was more widely
 3 distributed across the area instead of being more clustered, as seen in Fig. 57, which would
 4 drastically change the size of the fractions. When comparing the data in Table 4-21 with
 5 Table 4-22, the distribution of the fractions differed significantly. With a long residence time,
 6 the lighter fractions (kerosene and diesel) increased drastically at low temperatures (260
 7 and 280°C), reaching 9.64 ± 1.71 and 76.12 ± 0.08 mass% at 280°C, respectively. While
 8 the lighter fractions increased the heavy fraction decreased to 14.17 ± 0.37 mass% at 280°C.
 9 This proves that depolymerisation occurs at much lower temperatures than with short
 10 residence times. It also shows that the turning point for 80 min where repolymerisation starts
 11 to dominate is between 280 and 300°C. This was seen when the kerosene and diesel
 12 fraction decreased while the heavy fraction increased. This once again reinforces the
 13 statement that with longer residence times, the increase in temperature would favour
 14 repolymerisation reactions.

1
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Table 4-22. Boiling fractions' distribution of bio-oil compounds (80 min)

Compound fractions (%)	240°C	260°C	280°C	300°C	320°C
Naphtha	0	0	0	0	0
Kerosene (± 1.71)	7.95	7.56	9.64	4.52	7.26
Diesel Boiling (± 0.08)	46.43	74.36	76.12	70.76	65.27
Heavy fraction (± 0.37)	41.78	17.96	14.17	24.65	27.36

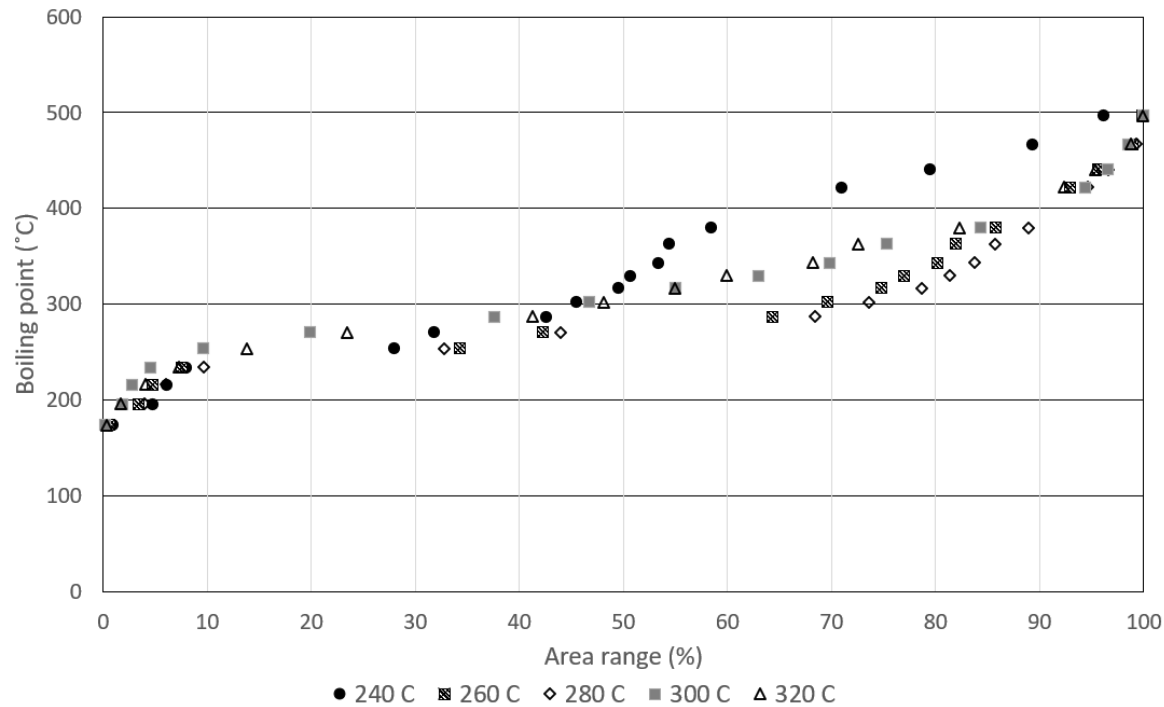


Fig. 58. Simulated distillation curve of bio-oils produced with a residence time of 80 min

3 **4.5.1.4.2 Functional and chemical groups of bio-oils**

4 The sample preparation for the FTIR analyses of the bio-oils was conducted by dissolving
5 roughly 0.02 g of bio-oil in 3 mL of acetone. The entire mixture was then transferred to the
6 FTIR's plate used for liquids and the acetone was allowed to evaporate at room temperature
7 until the oil on the plate was completely dry.

1 To classify the functional groups of the bio-oils the FTIR spectra will be used to identify the
 2 groups while the GC-MS analyses will be used to quantify the changes in these groups. The
 3 FTIR spectra are shown in Appendix B to allow a sufficient size of the figure to ensure the
 4 visibility of all details. Fig. 96 shows the spectra of all the bio-oils produced with 20 min and
 5 5 mass% catalyst loading. From Fig. 96 the peaks that were identified included -OH
 6 stretches, -CH, -CH₂, -CH₃ and possible carboxylic groups. Aromatic compounds, benzene
 7 rings, C=O bonds, phenols, and C-O stretch bonds were identified. The GC-MS was
 8 successful in identifying the individual compounds. The quantification of the groups was
 9 only completed for those the GC-MS identified with a quality of 75 or higher.

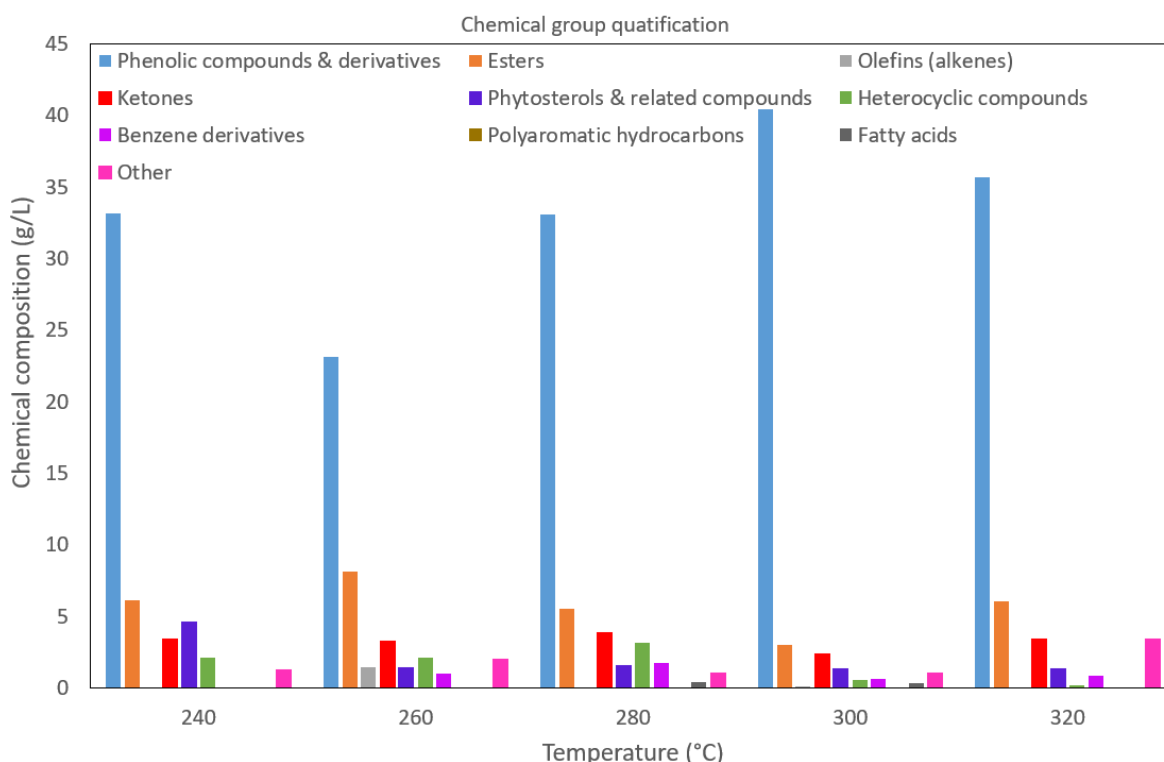


Fig. 59. Quantification of chemical groups that were present in bio-oils produced with a 20 min residence time

10 Fig. 59 supports the data obtained from the FTIR and elemental analyses. Firstly, notice
 11 how esters and ketones decreased as the temperature increased, while the phenolic
 12 compounds and derivatives increased. The turning point for the short residence time can
 13 now be seen clearly. The turning point was reached when the temperature increased
 14 beyond 300°C. The consequence will not only be an increased molecular weight, but the
 15 phenol content will decrease while oxygen-containing compounds (such as ketones and
 16 esters) and others, which include sulphonic groups, will increase. The depolymerisation of
 17 chemical compounds can also be seen in the decrease of heterocyclic compounds,
 18 phytosterols, and related compounds. The short residence time also produced bio-oils with
 19 almost no olefins or fatty acid contents. The presence of a large fraction of phenolics at

240°C suggests that the lignin in the sodium lignosulphonate had already experienced some degree of decomposition. Since lignin only decomposes at 280°C or higher, it is believed that most of this decomposition can be attributed to the pulping process. A very important group, polyaromatic hydrocarbons, was not present in any of these oils. This is an advantageous characteristic for bio-oil as a source for biodiesel production because it is believed that aromatics are mostly responsible for catalyst coking and deactivation.

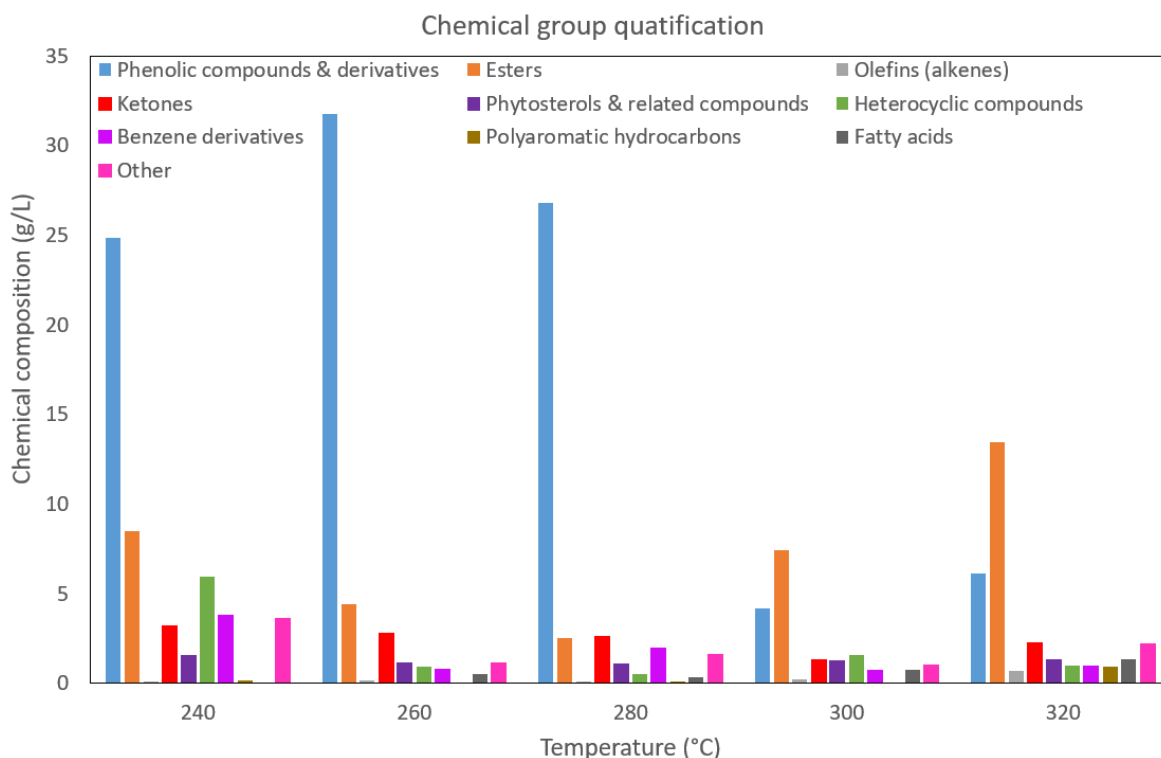


Fig. 60. Quantification of chemical groups that are present in bio-oils produced with an 80 min residence time

Fig. 99 in appendix B, quality analysis on bio-oils, shows the FTIR spectra of the bio-oils produced with a long residence time of 80 min and a catalyst loading of 5 mass%. The same peaks were identified in Fig. 99 as in Fig. 96 in appendix B, quality analysis on bio-oils, the only difference was that some of the peaks' shapes were different. The -OH stretch groups between 3600 cm⁻¹ and 3000 cm⁻¹ became sharper for the longer residence time. The small peaks at 2360 cm⁻¹ that could represent alkynes or nitrates became more prominent at the longer residence time. The peaks between 1000 cm⁻¹ and 800 cm⁻¹ that represent phenols and benzenes became less prominent as the temperature increased. The chemical groups were quantified in Fig. 60. The turning point for the 80 min residence time was between 260°C and 300°C when the phenolic and benzene-derived compounds started to decrease, and the esters increased. The increased temperature at long residence times also increased the fatty acid content, polyaromatic hydrocarbons, and others (sulphonic and

nitrous compounds). The increased temperature assisted in the decomposition of the heterocyclic compounds and the formation of some olefins at 320°C.

4.5.1.4.3 Interesting compounds found in bio-oils

Bio-oil contains a wide variety of compounds as seen in the GC-MS results. Besides all the esters, phenolics, and benzene compounds, some of the other compounds that were detected have high economical value in industries such as the pharmaceutical, while others are proof of the impurities of the original sodium lignosulphonate.

Compounds found in the bio-oils that have the potential for pharmaceutical uses:

- **Apocynin** is an organic compound that was found in some of the bio-oils. It is also known as acetovanillone and is related to vanillin. Apocynin has a variety of pharmacological properties.
- **Gamma-sitosterol** is a natural plant steroid; research has shown it has the potential to be used as a treatment for diabetes.
- **2-Naphthol** can be used as a metabolite for humans as well as an anti-nematode drug (a chemical to control parasitic worms and for pesticides).
- **Quinone** compounds were found; research suggests that quinones can help prevent and treat conditions like osteoporosis and cardiovascular diseases. Some cancer treatments and studies also involve quinones.
- **Xanthoxylin** was seen in some of the bio-oils that can be found in food as an additive and has antifungal and antispasmodic properties.
- **Vitamin E.**
- **Stigmastanol** can inhibit cholesterol absorption from the diet and inhibit the liver from biosynthesising cholesterol.
- **Podofilox** can be used in the treatment of human papilloma virus's external symptoms.
- **Ergosterol** is used to treat metabolic disorders.
- **Xylazine** is an animal tranquilliser and not meant to be used in humans. It is used as an anaesthetic, sedative, pain reliever and a muscle relaxer for non-human mammals and as an emetic drug for cats.
- **Homovanillyl alcohol** has been linked to lower risks for cardiovascular disease and death in elderly individuals.

- 1 • **Desaspidinol and aspidinol** were found in the bio-oils; they can be used as
2 antibacterial, antimicrobial, anthelmintic, and anti-protozoal treatments.
- 3 • **A lysergic acid derivative** was detected. Derivatives of this chemical include
4 lysergic acid diethylamide (LSD) which is a potent hallucinogenic and illegal
5 substance. Clinical research has been done to attempt to treat mental illnesses with
6 LSD, but so far, no success has been achieved.
- 7 • **Flopropione** is an antispasmodic agent that is mostly used to treat spasms in the
8 gastrointestinal, pancreatobiliary, and urinary systems (it also helps with the passing
9 of calculus in the urinary tract).
- 10 • **Demecolcine** is used in chemotherapy to prevent carcinogenic cell division.
- 11 • **Quinolones** were detected in bio-oils produced with long residence times.
12 Quinolones are a type of antibiotic that can be used on both humans and animals.
- 13 • **Malonodinitrile** can be used as an intermediate in synthesising vitamins and
14 medications.
- 15 • **Bufotalin** is a toxic steroid usually secreted by several toad species' parotoid
16 glands. However, it was also detected in bio-oils produced with low temperature and
17 long residence times. Bufotalin has antitumor properties and has been found to
18 encourage cancer cell apoptosis (death of cell).
- 19 • **Ethamivan** is a respiratory stimulant and was used to treat barbiturate poisoning or
20 overdose and chronic obstructive pulmonary disease, although it is not used as such
21 anymore.
- 22 • Different **azafluorenes** were also found in some of the bio-oils. Azafluorenes have
23 received research attention due to their antimalarial, antimicrobial and cytotoxic
24 properties. Azafluorene derivatives also have anti-depressant properties and have
25 been effective for treating neurodegenerative diseases. Some of the derivatives
26 have bronchodilating properties that are used for treating asthma. Antioxidant, anti-
27 inflammatory and antihistamine properties are also possessed by several
28 derivatives. Recently, some derivatives of azafluorenes have been suggested for
29 the treatment of COVID-19 (Venkateshan *et al.*, 2020).
- 30 • **Allocryptopine** is a quinoline, but has been patented as an ingredient in some
31 treatments for HIV-1 and HIV-2.

32 A synthetic version of α -tocopherol was detected by the GC-MS. It is a version of vitamin E
33 and is used in cosmetics as an antioxidant to stabilise ingredients that are sensitive to
34 oxygen. It can also be used in skin care products and dietary supplements. Other tocopherol
35 related compounds such as gamma-tocopherol were also discovered and play an important

1 role as an antioxidant in food preservation. The compound vanillin was also produced and
2 is mainly used as a flavouring agent in food and perfumes. 2, 4-Dimethylfuran is used in
3 food flavourings and can also be found in garlic.

4 There were also quite a few phosphine, catechol and cresol related compounds found in
5 the bio-oils that can be extracted for use in laboratories for the synthesis of various
6 chemicals.

7 A chemical called creosol was present in a few bio-oils. Creosol is an oily liquid that can be
8 extracted from guaiacum resin and wood tar and can be used in ore flotation, production of
9 resins, and as a disinfectant.

10 A catecholamine metabolite, homovanillic acid, was also detected. It is usually used as a
11 hydrogen-donating reagent (a Bronsted base) for oxidative enzyme detection and is also
12 associated with dopamine levels in the brain.

13 The quinolines that were present in some of the oils are mainly used as intermediates to
14 produce other chemicals such as dyes and polymers, but also as catalysts, corrosion
15 inhibitors and for anatomical specimen preservations.

16 1,3,5,7-Cyclooctatetraene is an interesting chemical to find in bio-oil. It can be used to
17 manufacture organic film for silicon surfaces and rubber.

18 Phthalic anhydride is used to manufacture artificial resins and as an intermediate in plastic
19 production.

20 Various types of naphthalene compounds were detected. Naphthalene is used as a
21 repellent and pesticide mostly for moths, but it can also repel squirrels and bats. Another
22 use is in the manufacturing of resins, dyes, lubricants, plastics, and fuels.

23 Anthracene which is usually a component of coal tar was found in some of the bio-oils – it
24 is mainly used to manufacture plastics, resins, dyes, and fibres.

25 Several silane compounds were also detected. These compounds are used in fibreglass,
26 paint, coatings, ink, sealants, composites, and adhesives for property improvements. Silane
27 is also used as a dispersing agent.

28 Different kinds of phenanthrene (a polyaromatic hydrocarbon) were also present. These
29 chemicals can be used to manufacture plastics, dyes, pesticides, medications, and
30 explosives.

1 Mesitylene was detected in bio-oils produced at long residence times (80 min) – it is toxic if
2 inhaled or ingested but is used to produce dyes, antioxidants and plastics. It is a chemical
3 found in petroleum and coal tar and it is flammable and explosive. It can also be used to
4 develop photosensitive sheet silicone.

5 Levoglucosenone (0.05 mass%) is a degradation product of cellulose proving that sodium
6 lignosulphonate contains a small amount of cellulose. It can be used to prepare catalysts,
7 organocatalysts and, chiral auxiliaries.

8 Dodecamethylpentasiloxane is used as a foam suppressant in petroleum oils, in the
9 manufacturing of grease and other lubricants, and in cosmetics.

10 Eicosane is used to make candles and paraffin waxes that have a capacity for solar energy
11 storage, and is used as a chromatographic analysis reference material.

12 Certain amides and sulphonic groups were also detected in some of the oils.

13 4.5.1.4.4 Confirmation of chemical groups in bio-oils

14 The NMR spectra can be seen in Fig. 102 shows the spectra of all the bio-oils produced
15 with the different variations, overlayed onto one graph. The results of the FTIR and GC-MS
16 were confirmed. The NMR spectra clearly show the presence of phenols and aromatics.
17 Monomeric aromatics are compounds such as phenols, naphthol derivatives, pyrroles,
18 benzenes, thiophenes and diphenyl disulphides, all of which were found in the GC-MS
19 results. Aliphatic compounds were also identified with NMR analysis, which included
20 alkanes and alkenes. These compounds were identified as olefins (alkenes), while alkanes
21 were grouped with other compounds under the label 'Others' for the chemical group
22 quantifications. Furthermore, from Fig. 100 to Fig. 104, it is possible to see that there were
23 a lot of oxygen-containing compounds, such as different kinds of guaiacyl and syringyl
24 derivatives.

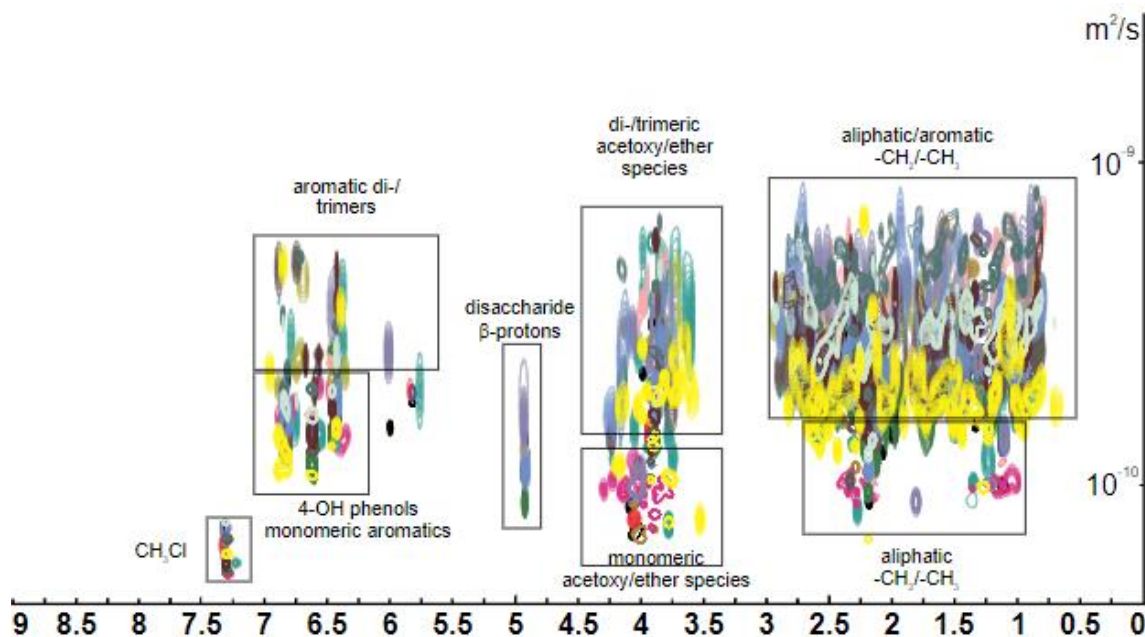


Fig. 61. Overlay of all the bio-oils' NMR DOSY spectrums

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2 4.5.1.4.5 Functional groups of biochars

3 In Appendix B, the FTIR spectra for the biochars produced at a short residence time can be
 4 seen in Fig. 128 and for long residence times in Fig. 131. For the biochars, the sample size
 5 could not be quantified and thus the FTIR spectra were only used to identify the different
 6 functional groups. For a short residence time -OH stretch groups were identified between
 7 3700 and 3000 cm^{-1} . Some small peaks were seen clearly at 240 and 320 $^{\circ}\text{C}$, representing
 8 hybridised $-\text{CH}_n$ bonds. A slight bend could be seen between 2320 and 2080 cm^{-1} , more
 9 clearly with the raw Lignex®, and lower temperatures' spectra. This bend could indicate
 10 nitrates or alkynes. At higher temperatures, there are aromatic combination rings present in
 11 the biochar. Benzene and phenols were also identified. The low temperatures also had
 12 some $\text{C}=\text{O}$ bonds while $\text{C}-\text{O}$ groups were identified in all the biochars. This confirms the
 13 high oxygen content detected by the elemental analyses.

14 With the longer residence time, the large -OH stretch at 3700–3000 cm^{-1} was still there along
 15 with the hybridised $-\text{CH}_n$ bonds, some nitrates or alkenes, aromatic combination rings and
 16 benzene rings. All the biochars contained $\text{C}-\text{O}$ groups although the FTIR did not detect $\text{C}=\text{O}$
 17 groups for the char with long residence times. The aromatic groups such as phenols had
 18 much more prominent peaks at low temperatures than at higher temperatures.

4.5.2 The effect of residence time on product quality

4.5.2.1 Elemental composition of products

4.5.2.1.1 Elemental composition of bio-oil

The total carbon recovery of all products produced at a low temperature of 260°C and different reaction temperatures were mostly above 75 mass%; however, the bio-oils all contained less than 14 mass% carbon content. When using a low temperature, a residence time increase will cause the elemental recovery to decrease. Even though the carbon and hydrogen content decreased with the increasing time, as seen in Fig. 62, the oxygen content also experienced a steady decrease. This means that even though the hydrogen and carbon content was low, the carbon content was still 1.4 to 2.06 times more than the oxygen content and the hydrogen content was 1.05 to 2.37 times larger than the oxygen content. In Fig. 65, an opposite trend is observed when using a higher temperature.

With a temperature of 300°C, an increase in residence time will improve the bio-oils' elemental recoveries. The carbon, hydrogen, and oxygen contents increased with time, but as the residence time increased the carbon-to-oxygen ratio decreased from 2.97 to 1.10 and the hydrogen-to-oxygen also decreased from 3.01 to 1.11. Although with a long residence time the carbon recovery remained relatively good as can be seen in Table 4-23, it would be advantageous to use a low temperature combined with a longer residence time or a high temperature combined with a short residence time if the goal is to have maximum carbon recovery with minimum oxygen content in the bio-oil. This will improve both the carbon-to-oxygen ratio and the hydrogen-to-oxygen ratio.

Table 4-23. Elemental ratios of bio-oils produced with various residence times

Residence time (min)	Low reaction temperature (260°C)		High reaction temperature (300°C)	
	O/C	H/C	O/C	H/C
20	0.49 ±0.01	1.15±0.00	0.34±0.01	1.01±0.00
40	0.67±0.01	0.70±0.00	0.43±0.01	0.90±0.00
60	0.49±0.01	1.01±0.00	0.51±0.01	1.10±0.00
80	0.70±0.01	1.21±0.00	0.91±0.01	1.00±0.00

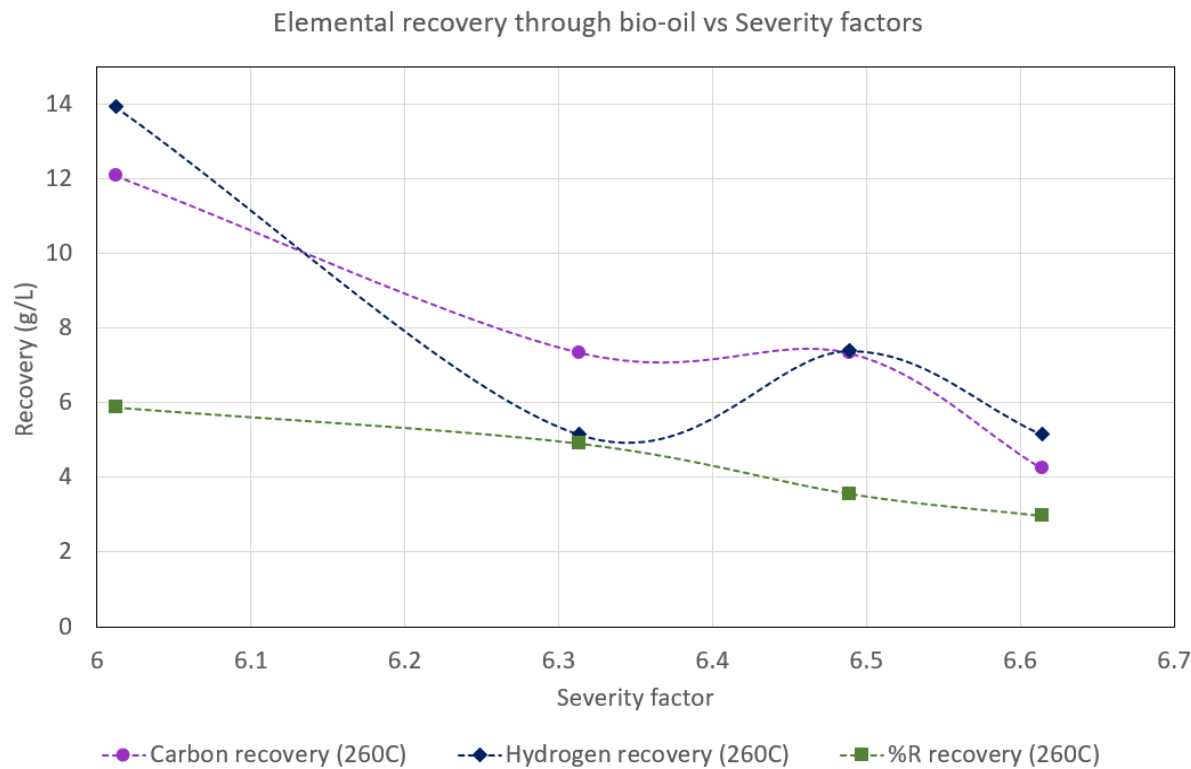


Fig. 62. Elemental composition of bio-oils formed at a low reaction temperature

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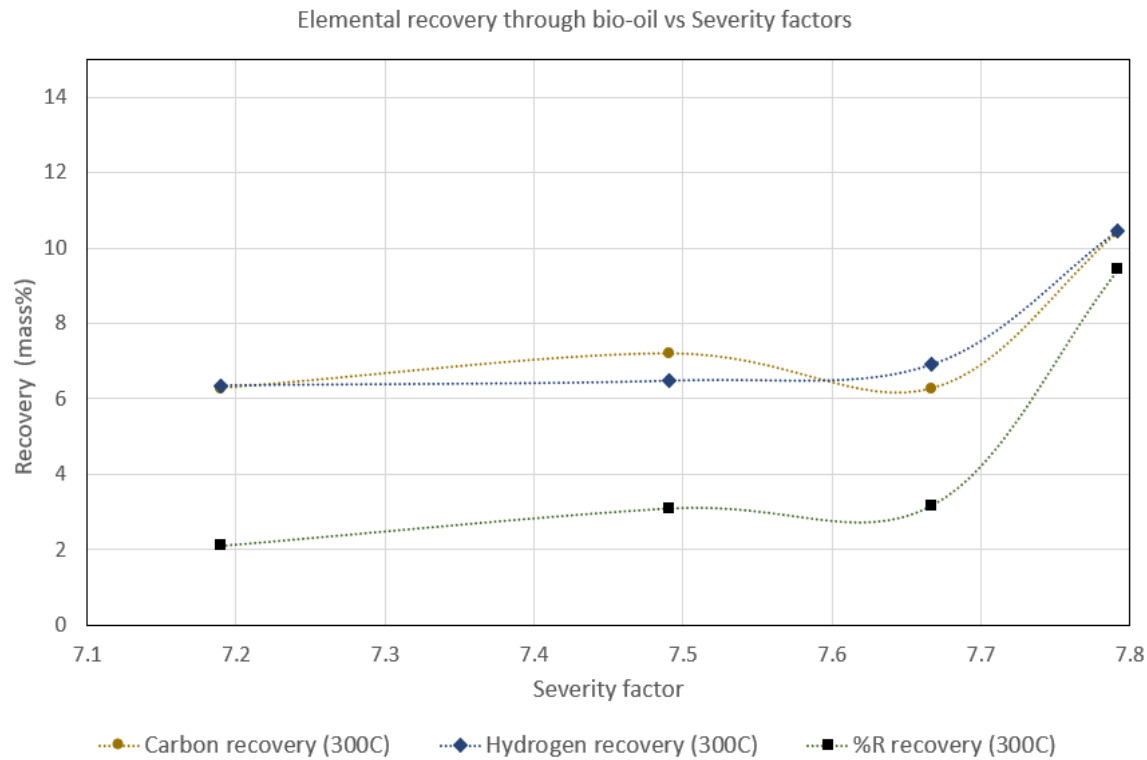


Fig. 63. Elemental composition of bio-oils formed at a high reaction temperature

1 4.5.2.1.2 Elemental composition of biochar

2 The elemental recoveries for all the biochars were quite high. At a low temperature (260°C),
 3 the carbon content remained above 50 mass% and the longer residence times (60 and 80
 4 min) helped to increase the carbon content to above 70 mass%. The longer residence time
 5 also increased the hydrogen content. The oxygen content was very high, which was a
 6 positive in this particular case as the goal was to remove as much oxygen as possible from
 7 the bio-oil. Thus, the higher the oxygen content in the biochar, the better the bio-oils'
 8 characteristics. The sudden decrease in oxygen content at 60 min did not affect the bio-oil's
 9 oxygen content; thus, with 60 min and a low temperature, it can be assumed that cracking
 10 reactions were dominating, and the oxygen was removed through the gas phase. Thereafter
 11 repolymerisation reactions took over as all the biochar's elemental recoveries increased
 12 while the elemental recoveries of the bio-oil decreased. The biochar's carbon-to-oxygen
 13 ratio increased from 0.76 to 0.86 and the hydrogen-to-oxygen ratio decreased from 0.58 to
 14 0.43. This means that an increase in residence time at a low temperature improved the
 15 elemental quality of the biochar.

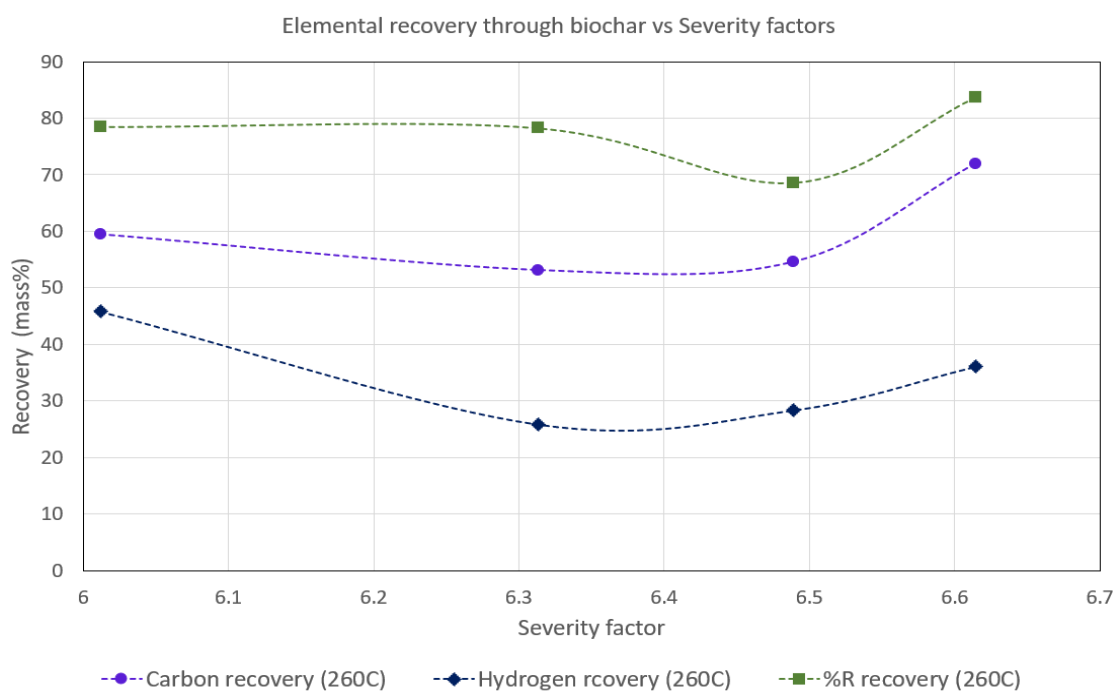


Fig. 64. Elemental composition of biochar produced with a low reaction temperature

16 For a high temperature such as 300°C, it appeared like there might have been
 17 repolymerisation and cracking reactions occurring simultaneously as the biochars' carbon
 18 content increased while the oxygen and hydrogen contents decreased. This could indicate
 19 the formation of more olefins, alkynes, and highly branched compounds in the solid phase.
 20 As the residence time was increased to 60 min there was a sudden increase in oxygen

content, indicating oxygenation of the biochar, probably due to condensation and repolymerisation reactions. When the time was increased further to 80 min, the depolymerisation reactions started to dominate again; unfortunately, this did not only allow carbon and hydrogen to increase in the bio-oil phase, but it also released some of the oxygen-containing compounds into the liquid phase. The higher temperature did allow for higher carbon-to-oxygen ratios, with the highest at 40 min (0.95) which decreased to 0.84 at 80 min. The hydrogen-to-oxygen ratio also did not improve with the increase in time (0.53 at 20 min to 0.41 at 80 min). However, it is still an advantageous condition, because it appears that if the biochars' elemental composition worsens, the bio-oils' elemental composition improves.

Table 4-24. Elemental ratios of biochars produced with various residence times

Residence time (min)	Low reaction temperature (260°C)		High reaction temperature (300°C)	
	O/C	H/C	O/C	H/C
20	1.3±0.002	0.77±0.01	1.21±0.00	0.64±0.01
40	1.47±0.00	0.49±0.01	1.05±0.00	0.51±0.01
60	1.25±0.00	0.52±0.01	1.23±0.00	0.48±0.01
80	1.16±0.00	0.50±0.01	1.19±0.00	0.49±0.01

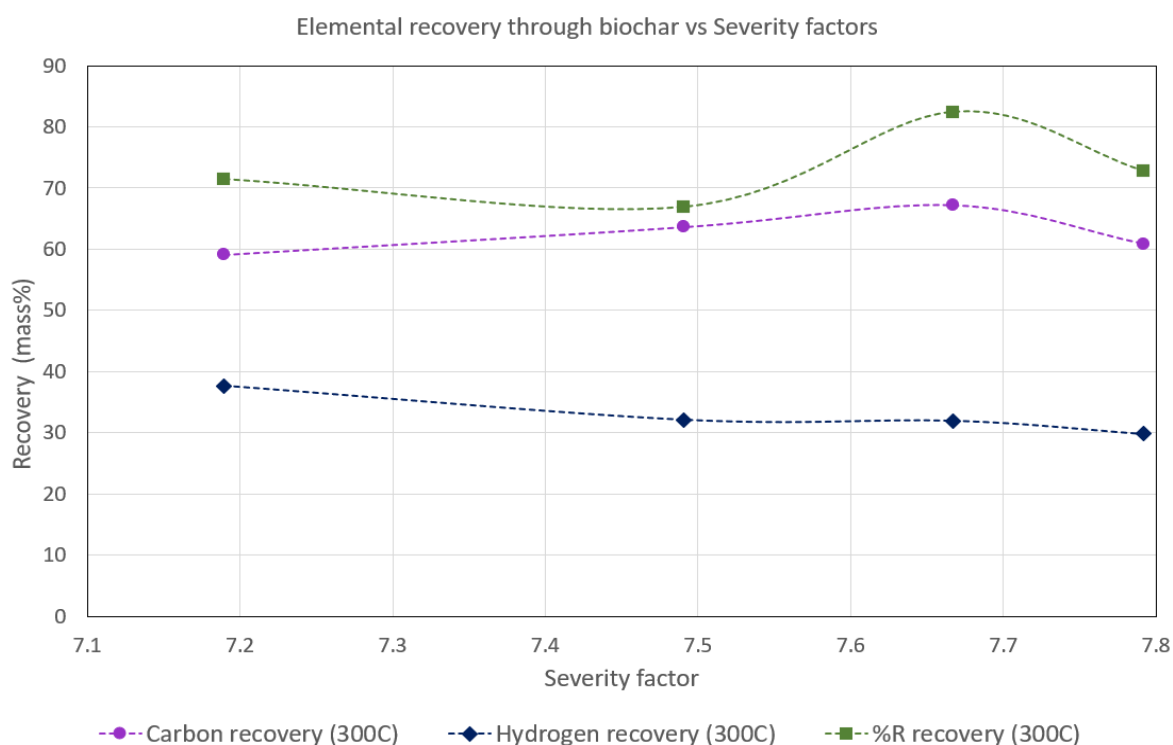


Fig. 66. Elemental composition of biochar produced with a high reaction temperature

4.5.2.2 Energy content of products

4.5.2.2.1 Energy content of bio-oil

From Table 4-25, the highest CV for the bio-oil produced at a low temperature, was achieved at the shortest residence time (20 min). Time did not have a large effect on the CVs of the bio-oil at a low temperature, because even though an increase in time caused the CVs to drop, the decrease was not very significant. The elemental composition for the bio-oils might have been because the carbon content of the bio-oil only decreased by 10 mass%, but the lack of a significant decrease might also be explained by the molecular weight of the bio-oil; it could be possible that most heavy and large compounds were present in these bio-oils which would allow for a high energy content.

For a high temperature such as 300°C, the CVs that could be obtained indicated particularly low energy contents. Especially, between 60 and 80 min, even though the elemental results showed an increase in carbon and hydrogen content when 60 min was increased to 80 min, the elemental results also showed a significant increase in oxygen content with the carbon-to-oxygen ratio becoming weaker. The very low CV may be explained when one considers that the effect of the oxygen content might have been overriding the effect of the carbon content.

Table 4-25. CVs of bio-oils produced with a low reaction temperature (260°C)

Residence times (min)	CV (MJ/kg)	DOC
Lignex®	11.64±1.48	-
20	24.66±1.48	2.12
40	-	-
60	21.12±1.48	1.81
80	23.18±1.48	1.99

Table 4-26. CVs of bio-oils produced with a high reaction temperature (300°C)

Residence times (min)	CV (MJ/kg)	DOC
Lignex®	11.64±1.48	-
20	-	-
40	-	-

60	19.18±1.48	1.65
80	10.626±1.48	0.91

4.5.2.2.2 Energy content of biochar

Even though biochars have higher carbon contents than bio-oils, the effect of the very high oxygen content can be seen in Table 4-27 and Table 4-28. The CVs support the results obtained from the elemental composition and even though the char had a high yield and high carbon content, the biochar was of low quality.

Table 4-27. CVs of biochars produced with a low reaction temperature (260°C)

Residence times (min)	CV (MJ/kg)	DOC
Lignex®	11.64 ±1.48	-
20	12.95±1.48	1.11
40	13.53±1.48	1.16
60	11.23±1.48	0.96
80	12.16±1.48	1.04

Table 4-28. Calorific values of biochars produced with a high reaction temperature (300°C)

Residence times (min)	Calorific value (MJ/kg)	DOC
Lignex®	11.64 ±1.48	-
20	12.53±1.48	1.08
40	13.09±1.48	1.12
60	11.67±1.48	1.00
80	12.23±1.48	1.05

4.5.2.3 Molecular weight distribution of bio-oils

For a low temperature, the molecular weights and PDI are presented in Table 4-29, while the molecular weight distribution is displayed in Fig. 67. Even though the molecular weight decreased, the increase in residence time was not effective in truly encouraging depolymerisation. A 20 min residence time was successful in significantly decreasing the molecular weight, but there was no change in the PDI of the bio-oil. This could indicate the

breaking of weaker bonds into equally sized molecules, but the PDI shows that there were no decomposition reactions; there was, however, a small degree of depolymerisation at 60 min as the PDI decreased slightly. The increase of the PDI and molecular weight that was seen at 80 min pointed towards repolymerisation reactions dominating after 60 min. Thus, the decreasing trend seen with the elemental recovery could be the small chains with weak bonds breaking off to form volatiles or radicals that would repolymerise. In Fig. 67, the different bio-oil graphs move more left on the axis as time is increased, indicating the production of smaller molecules, and when repolymerisation dominates like with 80 min the graph relocates more to the right side of the axis, indicating the formation of larger, heavier compounds.

With a higher temperature as seen in Fig. 68 and Table 4-30, the decomposition of the Lignex® occurred deeper than with the low temperature. This can be seen in the decrease of molecular weight and PDI. The depolymerisation was at a maximum with a 40 min residence time as can be seen by the very low PDI (1.9 ± 0.3). However, at some time between 40 and 60 the 'turning point' was reached, where reactions like condensation and repolymerisation started occurring faster. The molecular weight might have reached a minimum at 60 min, supported by the graph farthest left in Fig. 68, but the increase of the PDI indicates molecules condensing and becoming larger and heavier. Increasing the time, even more, would allow repolymerisation and condensation reactions to control the reaction progression. When considering the property of molecular weight, a higher temperature (280°C or higher) and an intermediate reaction time (40–60 min) would be more effective for decomposing a large molecule, though a lower temperature would require a longer time (280°C and 60 min).

Table 4-29. GPC analysis of bio-oils produced at a low temperature (260°C)

Residence time (min)	Mw (g/mol)	Mn (g/mol)	PDI
Lignex®	2468±1	945±1	2.6 ±0.3
20	683±1	260±1	2.6±0.3
40	656±1	233±1	2.8±0.3
60	432±1	192±1	2.2±0.3
80	953±1	250±1	3.8±0.3

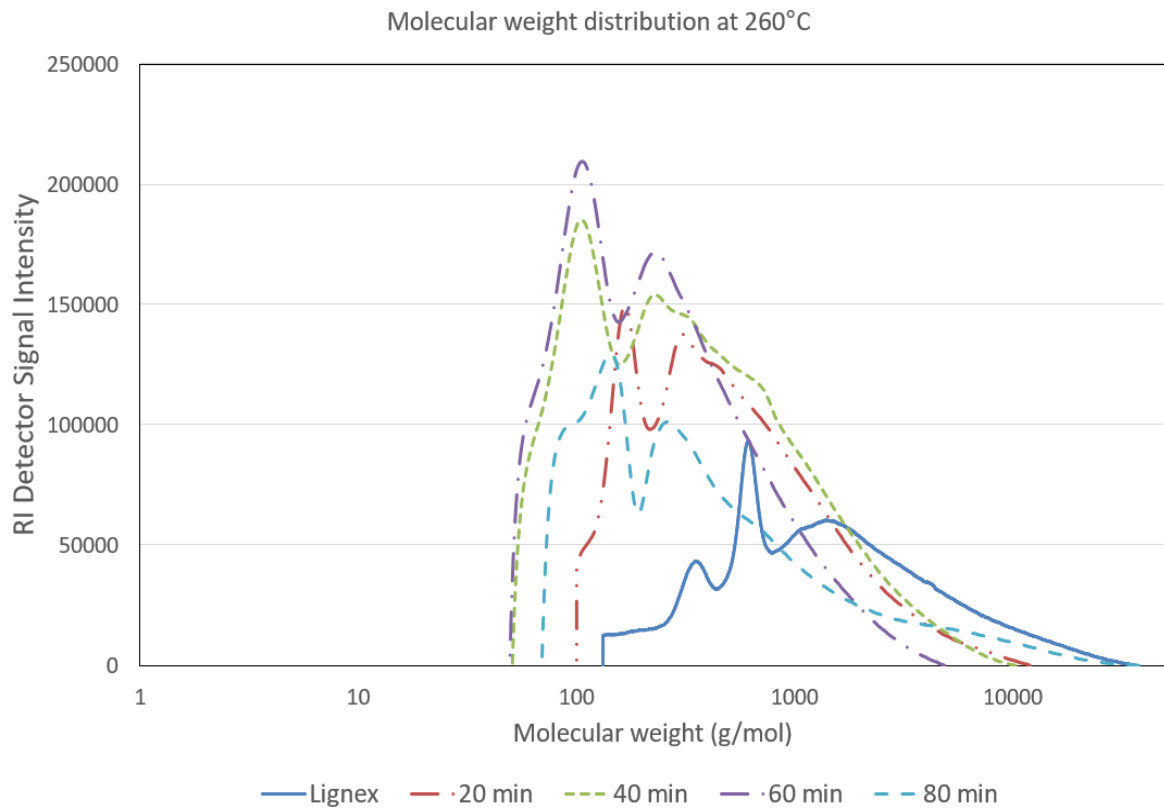


Fig. 67. Molecular weight distribution of bio-oils produced at a low temperature

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Table 4-30. GPC analysis of bio-oils produced at a high temperature (300°C)

Residence time (min)	Mw (g/mol)	Mn (g/mol)	PDI
Lignex®	2468±1	945±1	2.6±0.3
20	384±1	162±1	2.4±0.3
40	286±1	150±1	1.9±0.3
60	240±1	121±1	2.0±0.3
80	385±1	176±1	2.2±0.3

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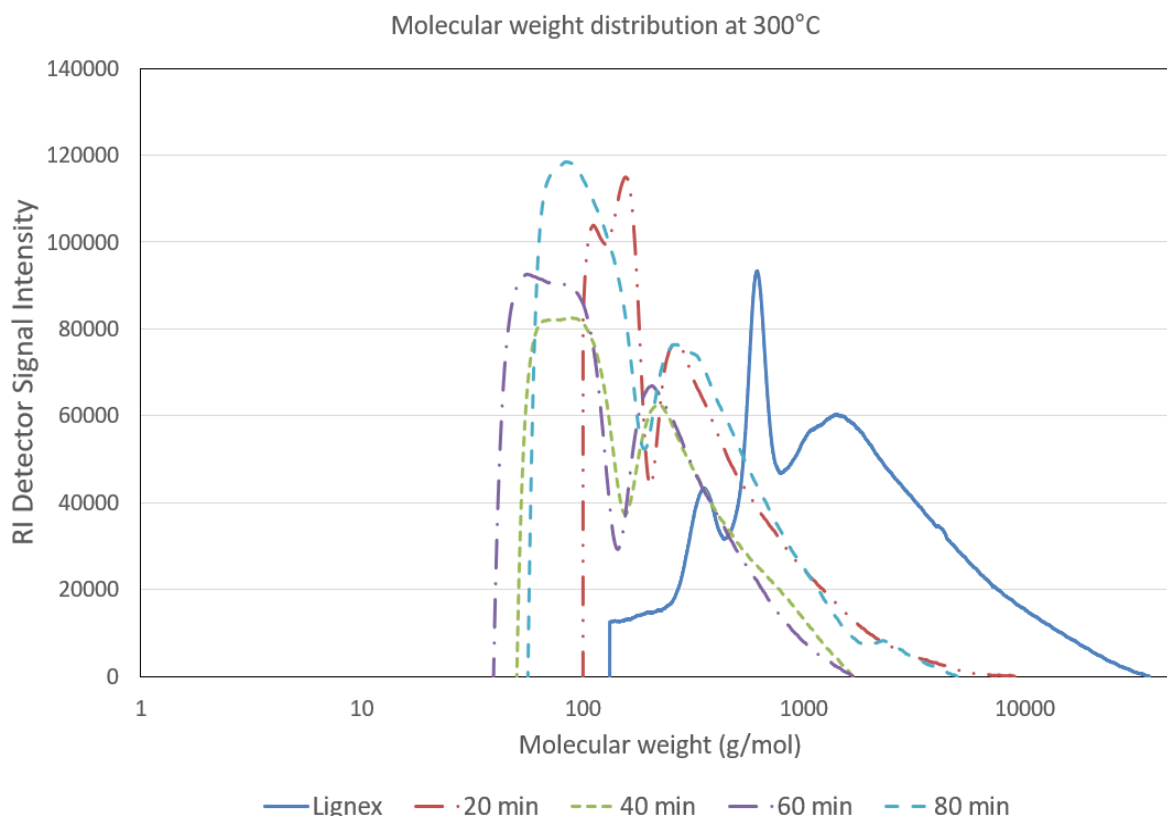


Fig. 68. Molecular weight distribution of bio-oils produced at a high temperature

2 4.5.2.4 Chemical composition of product

3 4.5.2.4.1 Boiling fractions of bio-oils

4 The same boiling ranges were used as identified in Table 4-20. With a low temperature, the
 5 increase in time decreased the heavy fraction and produced a large diesel fraction (almost
 6 75 mass% achieved). The heavy fraction did not decrease as dramatically as when there
 7 was a temperature change, indicating that even though previous results showed
 8 depolymerisation, there were also repolymerisation reactions occurring simultaneously. The
 9 distillation curves revealed that decomposition/depolymerisation was not the only reaction
 10 that occurred; between 20 and 40 min some cracking reactions also occurred and after 40
 11 min there were some repolymerisation and condensation occurring before the heavy
 12 fraction experienced further depolymerisation reactions. At a high temperature of 300°C,
 13 more repolymerisation reactions occurred with increasing residence time. This statement is
 14 substantiated by the decreasing kerosene (4.52 ± 1.71 mass% at 80 min) and diesel fraction
 15 (70.76 ± 0.08 mass% at 80 min), while the heavy fraction increased from 13.54 ± 0.37 to
 16 24.65 ± 0.37 mass%. An even higher temperature would allow for the heavy fraction to

increase even more at the expense of the lighter fractions. The boiling curve data proves that an increase in time allows more repolymerisation to occur, especially at high temperatures.

Table 4-31. Boiling fractions' distribution of bio-oil compounds at a low temperature

Boiling fractions (%)	20 min	40 min	60 min	80 min
Naphtha	0	0	0	0
Kerosene (±1.71)	5.52	16.16	6.92	7.56
Diesel boiling (±0.08)	58.08	62.91	66.13	74.36
Heavy fraction (±0.37)	36.00	20.82	26.55	17.96

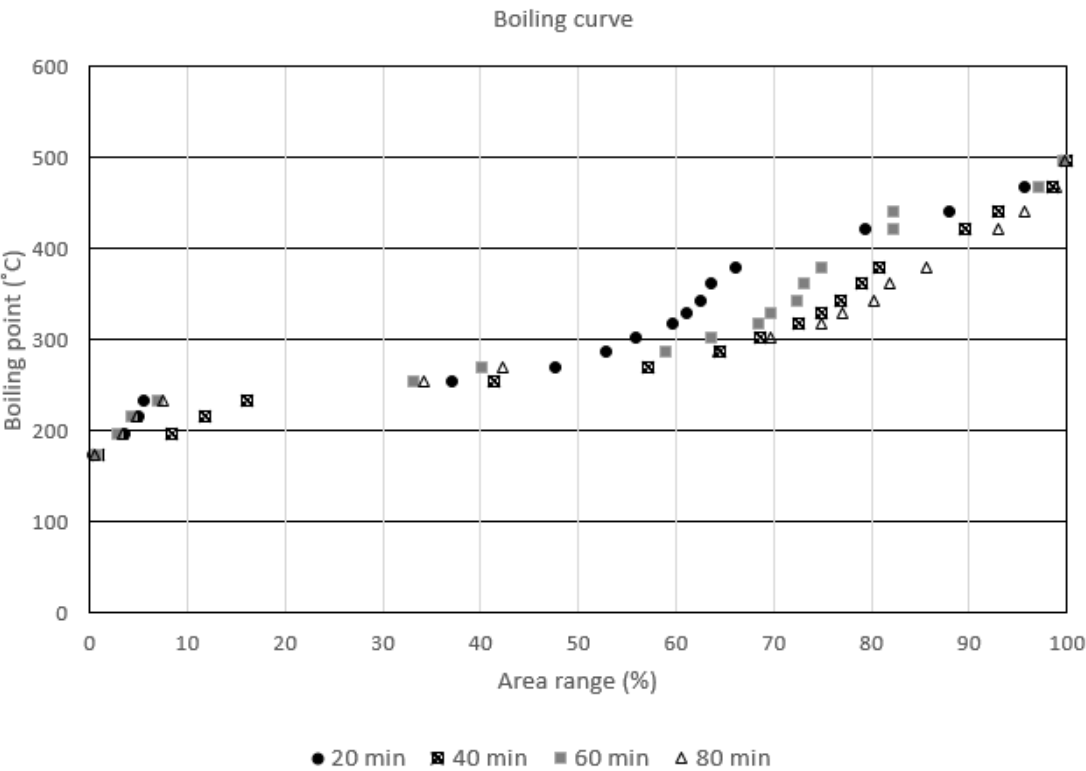


Fig. 69. Distillation curves of all bio-oils produced at a low temperature (260°C)

Table 4-32. Boiling fractions' distribution of bio-oil compounds at a high temperature

Boiling fractions (%)	20 min	40 min	60 min	80 min
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Naphtha	0	0	0	0
Kerosene (± 1.71)	14.64	8.91	8.20	4.52
Diesel boiling (± 0.08)	71.78	74.23	74.16	70.76
Heavy fraction (± 0.37)	13.54	16.84	17.55	24.76

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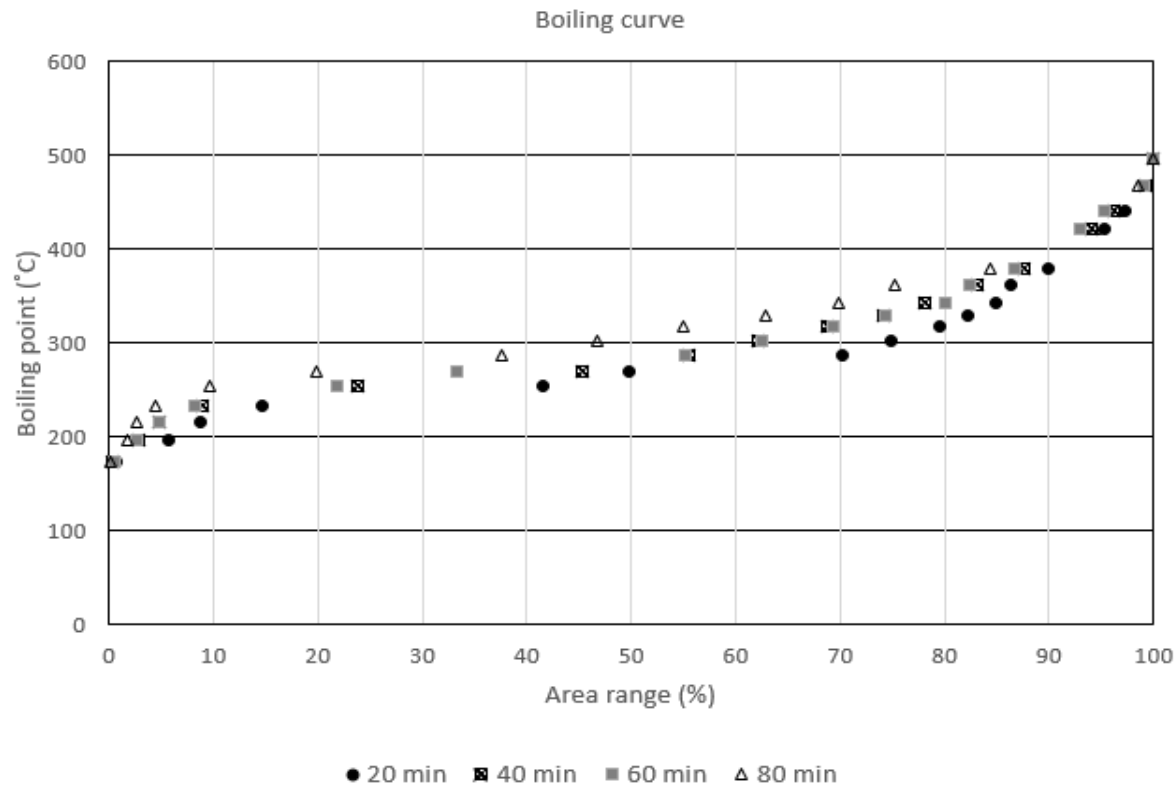


Fig. 70. Distillation curves of all bio-oils produced at a high temperature (300°C)

1 4.5.2.4.2 Functional and chemical groups of bio-oils

2 With a low temperature (260°C) it was possible to increase the number of phenolic
 3 compounds present in the bio-oil, by increasing the residence time; and, as seen with the
 4 boiling curves, before 40 min some depolymerisation took place as seen by the increase in
 5 kerosene and decrease in the heavy fraction group. Then between 40 and 60 min,
 6 repolymerisation took place when the kerosene group decreased and the heavy fraction
 7 increased before the heavy fraction was again dominated by depolymerisation. This could
 8 also be seen in the phenolic compound recovery shown in Fig. 71. The deoxygenation
 9 process could be observed by the decrease of esters and ketones. It did appear as if an
 10 increase in residence time, slightly improved the deoxygenation process. Heterocyclic,
 11 phytosterols, and related compounds were also decreased with time increase along with
 12 olefins and benzene derivatives. When the residence time was increased, other compounds
 13 such as nitrates, sulphates, and even fatty acids increased. The very low amounts of large
 14 compounds such as phytosterols and the high amounts of phenolic compounds indicated
 15 that the lignin in the feedstock was decomposed to a certain extent. Looking at Fig. 118 in
 16 Appendix B, all the bio-oils that were produced at 260°C were placed on one graph to
 17 compare the FTIR spectra of the different residence times, but only small changes were
 18 visible. Firstly, all bio-oils had a peak in the -OH stretch region (3700–3000 cm⁻¹); however,
 19 as the time reached 80 min the peak started to become slightly less prominent. In the 3000–
 20 2820 cm⁻¹ region sp³- hybridised -CH bonds were found; the shorter residence times had

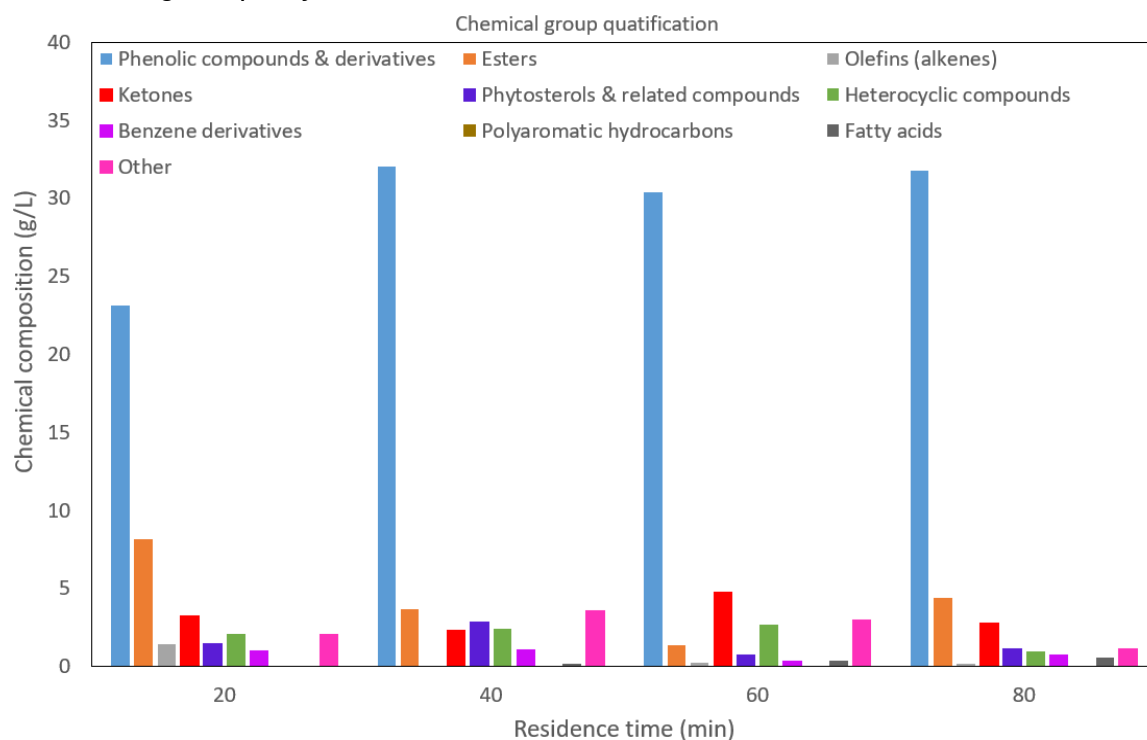


Fig. 71. Quantification of chemical groups present in bio-oils produced at a low temperature

two peaks, of which one was larger, but as time increased the smaller peak became equal in size to the larger peak. Around 2320 cm^{-1} there was a small peak that became more prominent as time increased. This peak probably represents the nitrates, since the GC-MS showed that more nitrogen-containing compounds formed at the longer residence times. Furthermore, at the C-O stretch bonds between 1360 and 1320 cm^{-1} , there is a small peak in the 20 min spectrum, but as the time increased this peak became less prominent and almost disappeared. The FTIR also detected aromatic compounds, phenols, and benzenes (peak became slightly less prominent with increased time), C=O bonds, and ketones, to name a few. Comparing the FTIR spectra of the bio-oils to the FTIR spectrum of the original feedstock, the changes caused by HTL were significant; however, some groups were prominent in the Lignex® even before HTL, like the C-O bonds.

With the high temperature, it was quite easy to see that a shorter residence time would be more advantageous. Not only would these conditions result in high phenolic content, but also in very low amounts of oxygen-containing compounds such as esters and ketones. The concentration of impurities, such as sulphonates, amides, and other nitrous oxides was very low. When the time was increased when using a high temperature, the number of compounds detected by the GC-MS decreased significantly. This was an indication of repolymerisation. It could be assumed that most of the compounds that were formed were too large for the GC-MS to detect. This assumption coincided with the increase of the heavy fraction as seen in Table 4-32. The repolymerisation reactions occurring were also proven

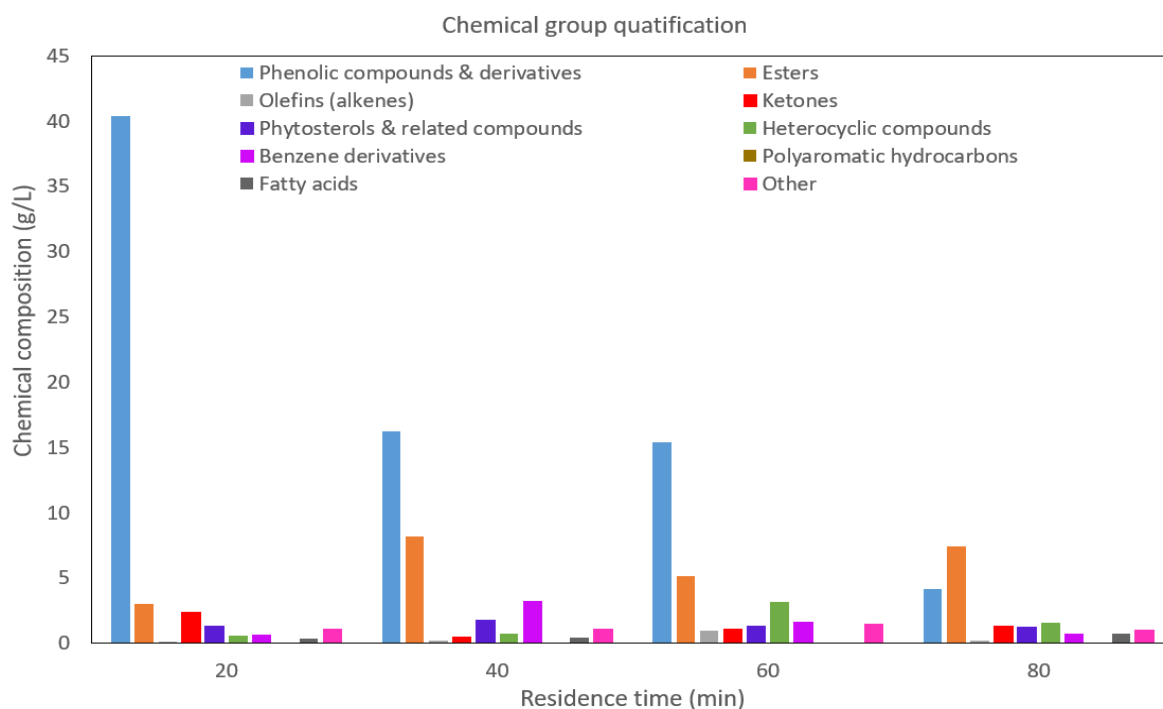


Fig. 72. Quantification of chemical groups present in bio-oils produced at a high temperature

by the increase in esters and heterocyclic compounds at long residence times. It was also noted that simple compounds such as olefins, aldehydes, and ketones decreased between 60 and 80 min, indicating accelerated repolymerisation for residence times longer than 60 min. The effect of residence time on the FTIR spectra of bio-oils produced at a high temperature can be seen in Appendix B in Fig. 120. At the higher temperature it did not seem as if the change in residence time had much of an effect, as only a few small changes could be seen on the spectra. As time increased, the large peak representing -OH stretch groups ($3700\text{--}3000\text{ cm}^{-1}$) became sharper. The nitrogen-containing groups identified at 2320 cm^{-1} became more prominent with time. The C-O bonds represented by the peak between 1280 and 1160 cm^{-1} also became a sharper peak as the time increased. Some small changes in the peaks between 1000 and 800 cm^{-1} representing aromatics, such as phenols and benzene, were seen.

4.5.2.4.3 Confirmation of chemical groups in the bio-oils

In Appendix B, the NMR spectra can be seen. Fig. 102 presents the spectra of all the bio-oils produced with the different variations, overlayed in one graph. The results of the FTIR and GC-MS are confirmed. The NMR spectra clearly show the presence of phenols and aromatics. Monomeric aromatics are compounds such as phenols, naphthol derivatives, pyrroles, benzenes, thiophenes, and diphenyl disulphides – all of which were found in the GC-MS results. Aliphatic compounds were also identified on the NMR. Aliphatic compounds include alkanes and alkenes. These compounds were identified as olefins (alkenes), while alkanes were grouped with other compounds under the label 'Other' for the chemical group quantifications. Furthermore, from Fig. 100 to Fig. 104, it is possible to see that there was a lot of oxygen-containing compounds, such as different kinds of guaiacyl and syringyl groups which support both the results of Fig. 120 and Fig. 118.

4.5.2.4.4 Functional groups of biochars

For low temperature, the FTIR spectra are depicted in Fig. 133 where groups with -OH stretch vibrations were identified between 3700 and 3000 cm^{-1} , and also a couple of groups with hybridised -CH_n groups, nitrates, or alkyne groups at $2320\text{--}2080\text{ cm}^{-1}$ and benzene rings. The inverted peaks between 2320 and 2400 cm^{-1} indicates some contamination that the FTIR detected. C=O and C-O groups along with phenols and other aromatics were also detected. For higher temperatures, such as 300°C , the FTIR spectra can be seen in Fig. 135. The FTIR detected -OH stretch groups, nitrates, a couple of aromatic compounds,

- 1 possible benzene rings and phenols, and some C-O groups. However, because this
- 2 analysis was done only to identify functional groups, the effect of time on the biochars
- 3 cannot be seen on the FTIR spectra.

4.5.3 The effect of catalyst loading on product quality

4.5.3.1 Elemental composition of products

4.5.3.1.1 Elemental composition of bio-oil

The increase in the recovery of carbon content through the liquid fraction caused by the increase in catalyst loading can be seen in Fig. 73. A higher catalyst loading also improved the hydrogen content and increased oxygen recovery. The carbon-to-oxygen ratio reached a maximum of 2.97 at 5 mass% catalyst loading with the 4 mass% achieving a ratio of 2.67. The hydrogen-to-oxygen ratio reached 3.01 at 5 mass% and 2.73 at 4 mass%. It appeared that the 3 mass% yielded the bio-oil with the worst elemental composition. The O/C ratio was the highest at 0.60; however, this value was still below 1.

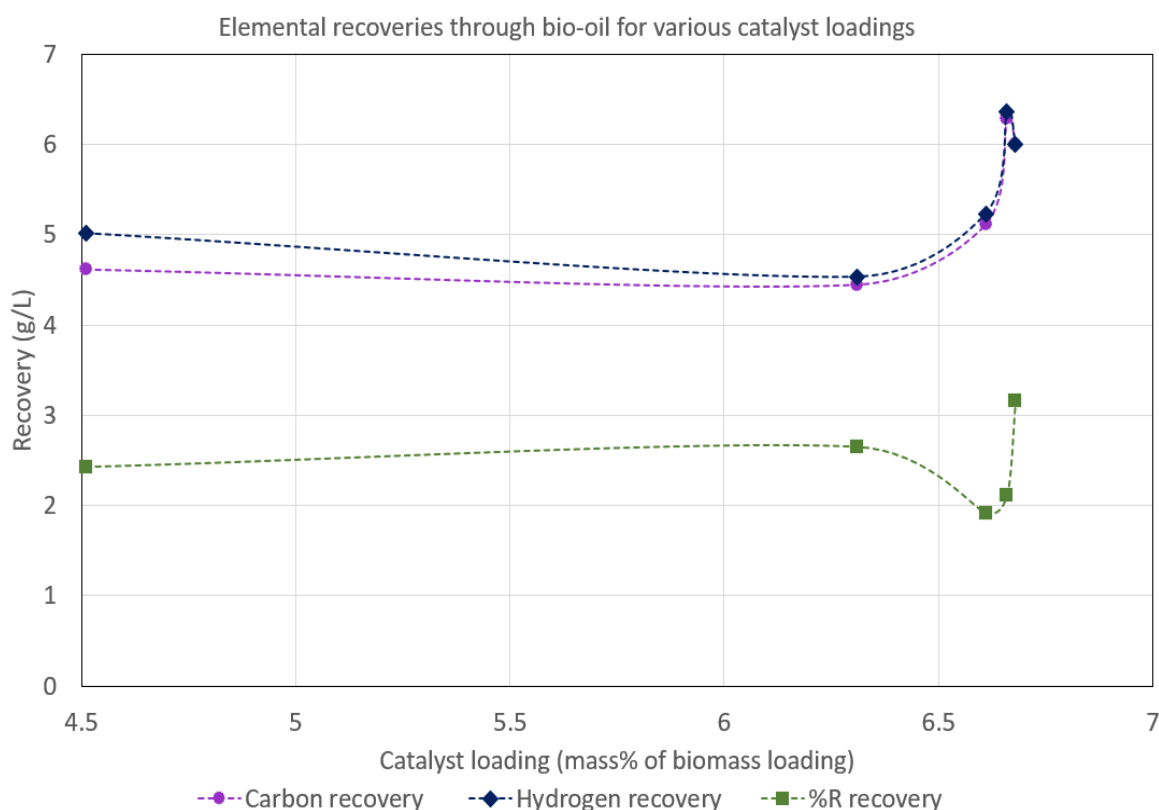


Fig. 73. Elemental composition of bio-oils formed with various catalyst loadings

As shown in Fig. 73 the lowest oxygen recovery was achieved with 4 mass% catalyst loading after which the oxygen content started to increase with what appeared to be a significantly steep trend. The maximum carbon and hydrogen recovery were at 5 mass%, but increasing the catalyst loading beyond 5 mass% would have resulted in a decrease of both carbon and hydrogen recovery. Based on this ratio, a catalyst loading of 4 and 5

mass% will be the optimum catalyst loadings to produce bio-oils with a high carbon and hydrogen content, while having the lowest oxygen content.

Table 4-33. Elemental ratios of bio-oils produced with various catalyst loadings

Catalyst loading (mass %)	O/C	H/C
2	0.53 ±0.01	1.09 ±0.00
3	0.60 ±0.01	1.02±0.00
4	0.38 ±0.01	1.02±0.00
5	0.34 ±0.01	1.01±0.00
6	0.53 ±0.01	1.00±0.00

4.5.3.1.2 Elemental composition of biochar

In the case of the biochar, the hydrogen recovery remained quite low as seen in Fig. 74; and even when the catalyst loading was increased, it was only after 4 mass% where the hydrogen content increased to 37.66 mass% before the content decreased to 31.44 mass% at a loading of 6 mass%. The opposite can be seen for the carbon recovery. The carbon recovery increased as the catalyst loading was increased to 4 mass% (64.46 mass% carbon content), but a further increase in the catalyst had a decreasing effect on the carbon content. The oxygen content of the biochar was higher than both the carbon and hydrogen content. However, with a low catalyst loading, the oxygen content appeared to be decreasing, but when the catalyst loading reached 4 mass% there was almost a 10 mass% increase in the oxygen recovered.

The carbon-to-oxygen ratio for the biochar was at its highest for the 2 and 3 mass% loadings (0.92 and 0.94 respectively). This relationship is also demonstrated in Table 4-34 where it is seen that the oxygen content was 1.09 and 1.06 times higher than the carbon content. With such a high oxygen content the chars' energy content will be very low. After 3 mass% loading the ratios between oxygen and carbon content became worse. The hydrogen-to-oxygen ratio was even worse by reaching only 0.53 at 3 and 5 mass% loading and the highest H/C ratio was 0.64 at 5 mass% loading.

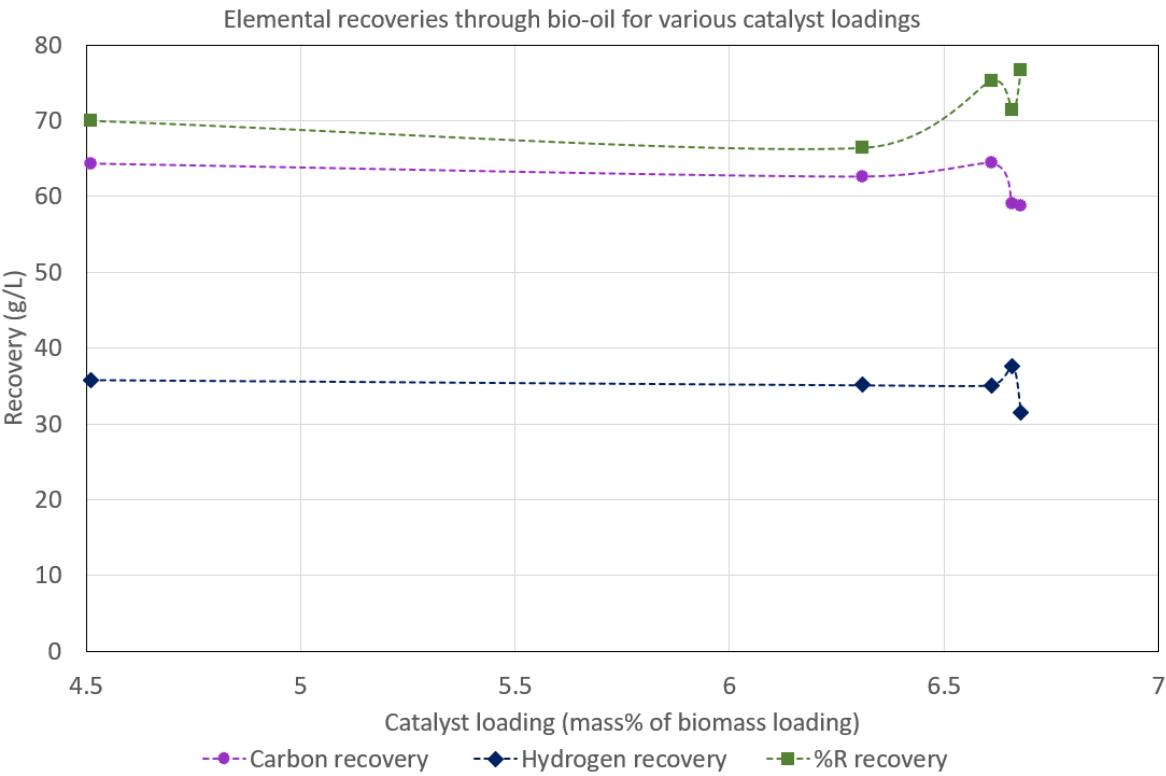


Fig. 74. Elemental composition of biochars formed with various catalyst loadings

Table 4-34. Elemental ratios of biochars produced with various catalyst loadings

Catalyst loading (mass %)	O/C	H/C
2	1.09 ±0.00	0.56±0.01
3	1.06±0.00	0.56±0.01
4	1.17±0.00	0.54±0.01
5	1.21±0.00	0.64±0.01
6	1.30±0.00	0.53±0.01

4.5.3.2 Energy content of products

4.5.3.2.1 Energy content of bio-oil

By increasing the catalyst loading the energy content of the bio-oils decreased significantly. This indicated depolymerisation reactions were breaking the larger molecules into smaller fragments, though it was suspected that the energy content of the 4 and 5 mass% loading

would have been higher than the 3 and 6 mass % due to the higher carbon content and lower oxygen content. Even though the CVs decreased with the addition of catalyst, the bio-oil's energy content was still an upgrade from the raw feedstock.

Table 4-35. CVs of bio-oils produced with various catalyst loadings

Catalyst loading	CV (MJ/kg)	DOC
Lignex®	11.64 ±1.48	-
2 mass%	21.43±1.48	1.84
3 mass%	16.48±1.48	1.42
4 mass%	-	-
5 mass%	-	-
6 mass%	15.69±1.48	1.35

4.5.3.2.2 Energy content of biochar

By increasing the catalyst loading, the energy content of the biochar lowered, so much so that a loading of 6 mass% yielded a biochar with an energy content of 11.11 ±1.48 MJ/kg which was lower than that of the original feedstock which was 11.64 ±1.48 MJ/kg. Thus, it could be assumed that the addition of an alkali catalyst would not have improved the higher heating values of the biochar.

Table 4-36. . CVs of biochars produced with various catalyst loadings

Catalyst loading	CV (MJ/kg)	DOC
Lignex®	11.64±1.48	-
2 mass%	12.36±1.48	1.06
3 mass%	12.48±1.48	1.07
4 mass%	11.59±1.48	1.00
5 mass%	12.53±1.48	1.08
6 mass%	11.11±1.48	0.95

4.5.3.3 Molecular weight distribution of bio-oils

In Table 4-37 it is clear from the first loading (2 mass%) that catalyst loading had a significant effect on the progression of the depolymerisation and the repolymerisation reactions. The addition of an alkali catalyst, in this case, sodium hydroxide, had a significant reducing effect on the molecular weight, the Mn, and the PDI. Rapid depolymerisation occurred at 2 and 3 mass%. The turning point for catalyst loading was between 3 and 4 mass%. The bio-oil started to experience some repolymerisation reactions before 4 mass%. This can be seen by the increase in molecular weight and the PDI. Even though the higher catalyst loadings allowed more repolymerisation to take place, the molecular weight and PDI were still very low compared to the original biomass's properties. Fig. 75 depicts the bio-oils' molecular weight distribution and even with the highest catalyst loading the graph depicts smaller molecules and has smaller peaks. It appears as though an alkali catalyst accelerated depolymerisation and when used in combination with lower temperatures and shorter times it could cause depolymerisation and even repolymerisation to occur earlier.

Table 4-37. GPC analysis of bio-oils produced with varying catalyst loading

Catalyst loading	Mw (g/mol)	Mn (g/mol)	PDI
Lignex®	2468 ± 1	945 ± 1	2.6 ± 0.3
2 mass%	384 ± 1	192 ± 1	2.0 ± 0.3
3 mass%	275 ± 1	173 ± 1	1.6 ± 0.3
4 mass%	347 ± 1	194 ± 1	1.8 ± 0.3
6 mass%	361 ± 1	217 ± 1	1.7 ± 0.3

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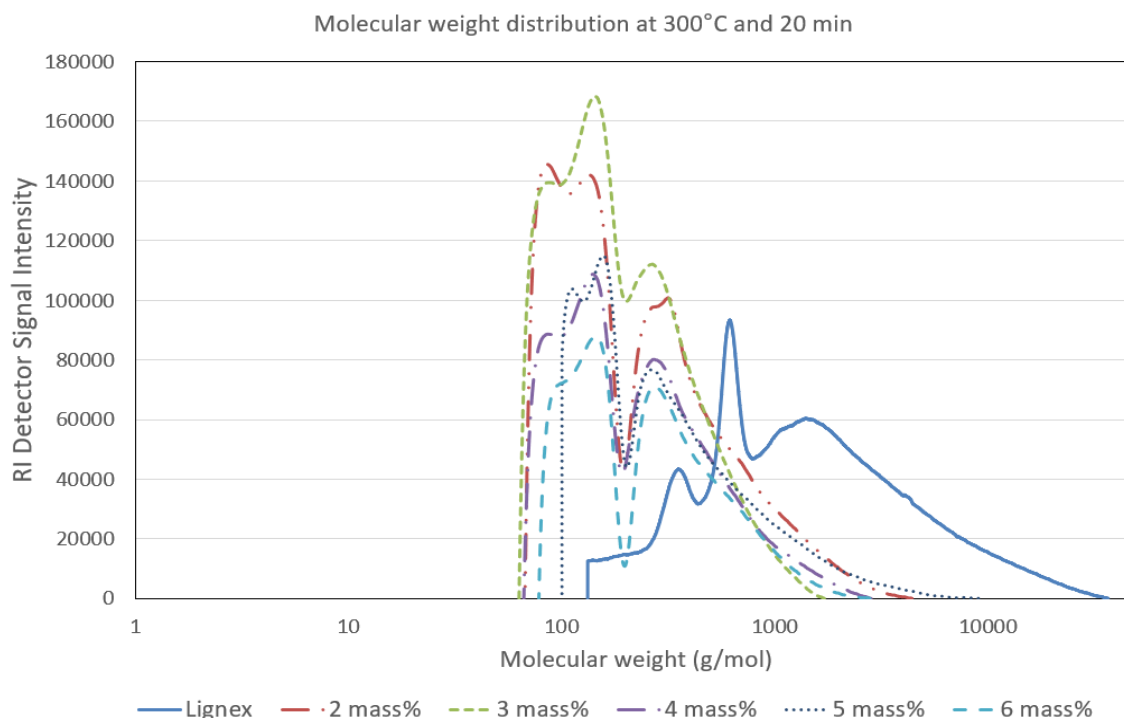


Fig. 75. Molecular weight distribution curve of bio-oil produced with varying catalyst loading

2 4.5.3.4 Chemical composition of products

3 4.5.3.4.1 Boiling fractions of bio-oils

4 In Fig. 76 the boiling curve data of bio-oil produced at 300°C, a residence time of 20 min,
 5 and different catalyst loadings are shown. The curve was used as an indicator as to the
 6 extent of the effect of catalyst loading on the properties of bio-oil produced from the sodium
 7 lignosulphonate, called Lignex®. As the catalyst loading was increased from 2 to 4 mass%,
 8 the mass fraction in the kerosene (lighter fraction) range also increased from 2.19 ± 1.71 to
 9 5.16 ± 1.71 mass% at 4 mass% loading. In Table 4-38 it is shown that a catalyst loading of
 10 5 mass% produced a bio-oil with a kerosene fraction of 14.64 ± 1.71 mass%. With the
 11 further addition of catalyst to the reaction, the kerosene fraction decreased dramatically
 12 (3.51 ± 1.71 mass%). The diesel fraction increased as more catalyst was added. With a 2
 13 mass% catalyst loading a diesel fraction of 62.63 ± 0.08 mass% was obtained. The addition
 14 of more catalysts increased the diesel fraction to more than 70 mass%. Increasing the
 15 catalyst loading by more than 4 mass% had a decreasing effect on the diesel fraction as it
 16 decreased to 73.61 ± 0.08 mass% with a 6 mass% catalyst loading. A higher catalyst
 17 loading decreased the number of compounds that were in the heavy fraction range. The
 18 maximum occurred with a 2 mass% of catalyst loading producing 35.08 ± 0.37 mass% of

1 the heavy fraction. The minimum was 13.54 ± 0.37 mass% when a catalyst loading of 5
2 mass% was used. However, a further increase in catalyst loading appeared to increase the
3 heavy fraction as a 6 mass% produced 22.82 ± 0.37 mass% of the heavy fraction. Thus,
4 with the increase in the heavy fraction, it is safe to assume that at 300°C and 20 min, the
5 turning point, where repolymerisation will dominate, is beyond 5 mass%.

6 Table 4-38. Boiling fractions' distribution of bio-oil compounds produced with various catalyst loadings

Boiling fractions (%)	2 mass %	3 mass%	4 mass %	5 mass%	6 mass%
Naphtha	0	0	0	0	0
Kerosene	2.19	4.88	5.16	14.64	3.51
(± 1.71)					
Diesel boiling	62.63	67.52	74.17	71.78	73.61
(± 0.08)					
Heavy fraction	35.08	27.44	20.56	13.54	22.82
(± 0.37)					

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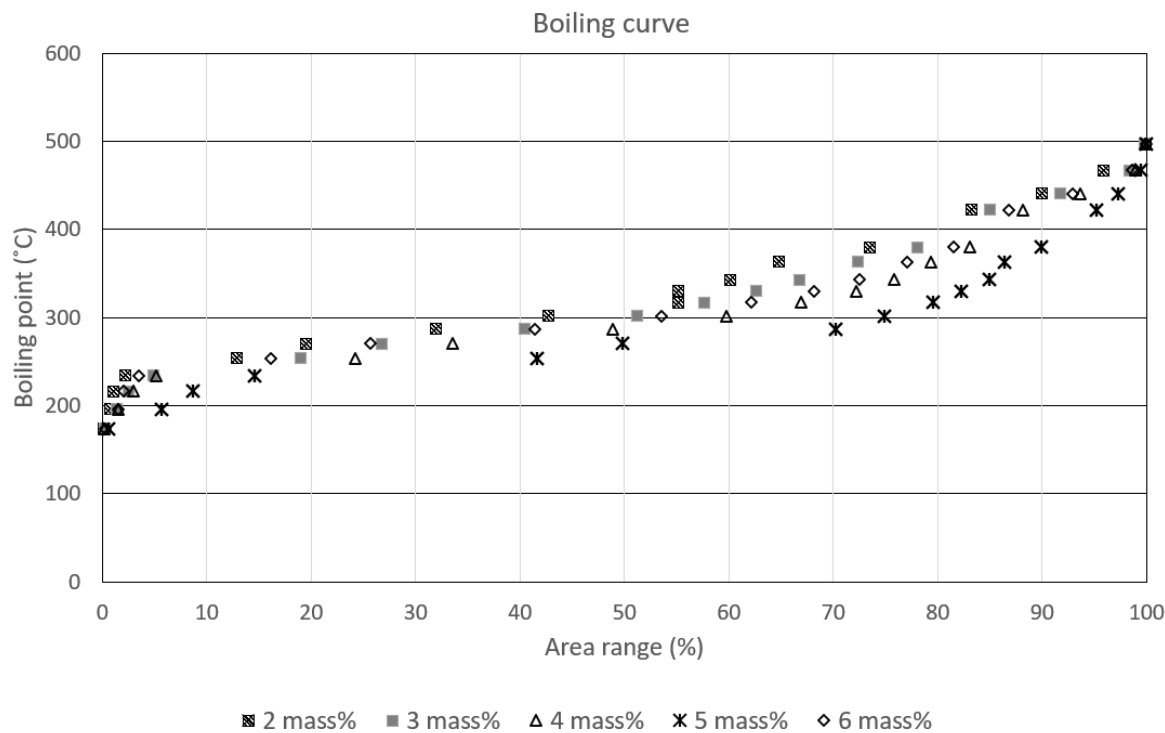


Fig. 76. Simulated boiling curve of bio-oil produced with varied catalyst loading

1 4.5.3.4.2 Functional and chemical groups of bio-oils

2 As with the results obtained from the boiling ranges, the effect of repolymerisation can also
 3 be seen in Fig. 77, proving that the turning point was after 4 but before 6 mass% catalyst
 4 loading. As the catalyst loading increased from 2 to 4 mass%, there was an increase in
 5 phenolic compounds, benzene derivatives, and polyaromatic compounds. Deoxygenation
 6 was also observed with the decrease in groups that contained oxygen atoms, such as esters
 7 and ketones. Even though a 5 mass% catalyst loading did not produce a bio-oil with the
 8 largest diesel fraction of the lowest molecular weight, it did, however, produce a bio-oil with
 9 a desired ratio of carbon-to-oxygen content; and as seen in Fig. 77, a 5 mass% catalyst
 10 loading combined with a reaction temperature of 300°C and a residence time of 20 min,
 11 produced a bio-oil that had a very high phenolic content and a very low amount of oxygen-
 12 containing chemical groups.

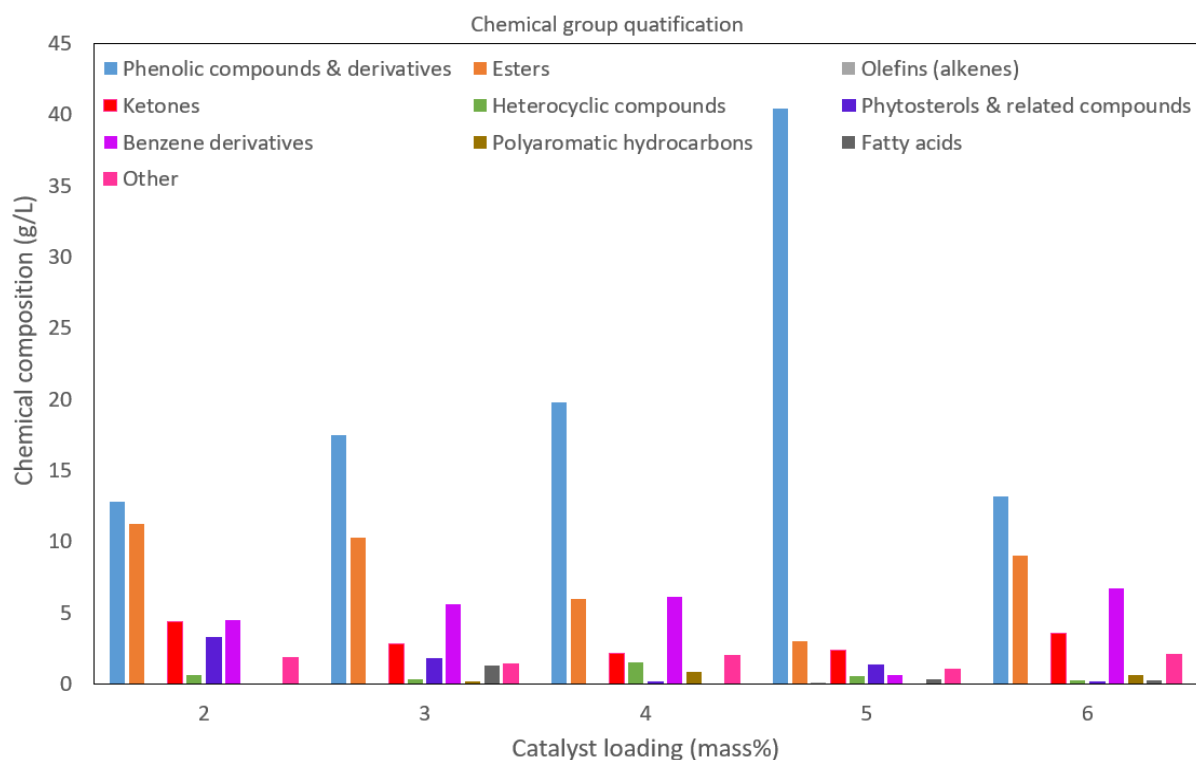


Fig. 77. Quantification of chemical groups in bio-oils produced with various catalyst loadings

13 It appears the alkali catalyst acts as an accelerator for depolymerisation reactions and also
 14 for the repolymerisation of the compounds. This is proven when considering the discussion
 15 of the effect of temperature where it was seen that with a short residence time such as 20
 16 min and a catalyst loading of 5 mass%, repolymerisation started to occur at higher
 17 temperatures than 300°C, specifically at 320°C. Now, the same effect can be achieved at
 18 300°C by adding more catalyst. Therefore, the addition of an alkali catalyst, such as sodium

hydroxide, will decrease the energy requirements for bio-oil production through HTL by lowering the required reaction temperature. By using a catalyst and the severity factor equation that incorporates pH, it is possible to reach a desired yield and property in a shorter time and lower temperature.

The FTIR spectra can be found in Appendix B in Fig. 122. As the catalyst loading was increased, the -OH stretch peak between 3700 cm^{-1} and 3000 cm^{-1} became slightly less prominent up until 5 mass% loading, but when the catalyst loading was increased even further (6 mass%), the peak started to become sharper. At roughly 2900 cm^{-1} for the 2 mass%, two peaks represented sp^3 -hybridised $-\text{CH}_n$ bonds, with the second peak being much larger. As the catalyst loading increased, the two peaks shifted to become the same size. This indicates the breaking of several carbon bonds to form different carbon chains. The 2 mass% spectrum shows a large peak at 2080 cm^{-1} . This peak usually indicates alkynes or nitrates and as there was a lot of depolymerisation taking place between 2 and 3 mass%, as proven by the molecular weights, it may be assumed that this peak represented alkynes which decomposed due to depolymerisation. It is also possible to see the flattening of all the peaks that represented oxygen-containing compounds as the catalyst loading increased. Furthermore, phenols, benzenes, and other aromatics were also detected with the FTIR.

4.5.3.4.3 Interesting compounds found in bio-oils

There were a few interesting compounds that were detected by the GC-MS specifically in the bio-oils that were produced at different amounts of catalyst loadings.

- Bonomycin hydrochloride is a very rare chemical and is used to reversibly bind to ribosomal subunits to inhibit the translation of proteins.
- Cyclobarbitol was seen in some of the bio-oils. It was used as a treatment for insomnia and is usually used with diazepam and other tranquillisers, but the use of cyclobarbitol has been discontinued in some countries.
- Amphetamines, such as tenamfetamine was detected. It is also known as MDA (3,4-methylenedioxyamphetamine); not to be confused with 3,4-methylenedioxy methamphetamine (MDMA – commonly known as ecstasy); however, MDA is a hallucinogen and has no accepted medical uses.

4.5.3.4.4 **Confirmation of functional and chemical groups in bio-oils**

In Appendix B, the NMR spectra can be seen. Fig. 102 confirms the results of the FTIR and GC-MS. The NMR spectra show the presence of monomeric aromatics such as phenols, naphthol derivatives, pyrroles, benzenes, thiophenes, and diphenyl disulphides, all of which were found in the GC-MS results. Aliphatic compounds were also identified with the NMR analysis. Aliphatic compounds include alkanes and alkenes. These compounds were identified as olefins (alkenes), while alkanes were grouped with other compounds under the label 'Other' for the chemical group quantifications.

4.5.3.4.5 **Functional groups of biochars**

The biochar FTIR analyses were not conducted for quantitative purposes, but rather for qualitative purposes to identify the functional groups that were present in the biochar. For the biochars produced with various catalyst loadings, the FTIR spectra can be seen in Fig. 137. The spectra show several peaks in the -OH stretch region for all the chars, as well as sp^3 -hybridised- CH_n bonds that were visible in the $3000-2850\text{ cm}^{-1}$ region. Most of the chars also had peaks in the nitrate and alkynes region. Aromatic combination rings, $C=C$ and $C=O$ bonds were also detected in their respective regions. There were also large peaks visible that represented C-O groups which agreed with the high oxygen content from the elemental analyses. Aromatic compounds such as benzenes and phenols were identified from 1000 to 800 cm^{-1} .

5 Conclusions and Recommendations

5.1 Conclusions

It was found that even before the biomass was converted or transformed, there was a large amount of phenols present. This suggested that the lignin in the raw feedstock had already experienced mild decomposition during the sulphite pulping process. From the fractionation characterisation it was proven that the Lignex® contained a wide variety of compounds, some with very low molecular weights while others were significantly heavier. The fractionation also proved to have a great potential for extracting a targeted type of compound or even molecular weight, but this finding requires more investigation before accuracy in selectivity can be achieved.

HTL of sodium lignosulphonate with ethanol as a solvent using an alkali catalyst will upgrade the properties of the feedstock into a bio-oil that has the potential to be used as a source for renewable fuel production. From the results, it is possible to deduce that for all combinations of the variables, depolymerisation and cracking reactions will take place and as the process gets closer to the 'turning point', some repolymerisation and condensation reactions will occur. The 'turning point' will be unique for the different combinations. When this point is reached repolymerisation and condensation reactions will dominate. All three reaction parameters had an effect on the bio-oil's yield and quality, and a combined effect, expressed as the severity factor, was also observed. The severity factor can be used as a guiding methodology to design process parameters in such a way that a specific yield or property can be achieved, even if there are process restrictions (maximum/minimum time or specific energy requirements).

5.1.1 Effect of reaction temperature and residence time on bio-oil

As both process temperature and residence time had a strong intertwined influence on the process results, it is difficult to consider their impacts individually. A temperature increase will lower the bio-oil yield and the molecular weight of the oil but improve the carbon-to-oxygen and hydrogen-to-oxygen ratio. When a high temperature is combined with a short residence time it will increase the bio-oil's diesel fraction, while decreasing heavy components. When a temperature increase is combined with a long residence time, repolymerisation will occur at much lower temperatures; thus, increasing the molecular weight and heavy fractions. Longer residence times will help processes at low temperatures

to achieve higher degrees of depolymerization (lower molecular weights and a larger diesel fraction) that high temperatures can provide but if the residence time is too long it could increase the production of heavy compounds and more oxygen-containing compounds. Ultimately, time had a lesser effect as the temperature increased, but overall, it appeared as if time mostly affected the progression of the different types of reactions (depolymerisation, repolymerisation, cracking, condensing, etc). Time could either delay or accelerate the occurrence of these reactions. Reaction time may also be able to control the speed at which these reactions occur.

5.1.2 Effect of catalyst loading on bio-oil

An increase in alkali catalyst loading will decrease cracking reactions and accelerate depolymerisation reactions to improve bio-oil yield. The catalyst will also improve deoxygenation, but a high catalyst loading could also accelerate the occurrence of repolymerisation.

5.2 Evaluation of objectives

The sodium lignosulphonate feedstock, called Lignex®, was thoroughly characterised as a whole and also specifically by dissolving the Lignex® in solvents to characterise various fractions thereof for a more in-depth look. Furthermore, all objectives were satisfied, and the effect on product yields of three different alkali catalysts was determined. The effect of three different solvents, ranging from polar and protic to non-polar and aprotic, was investigated on both product yield and quality. The effect of reaction temperature, residence time, and catalyst loading was also investigated on product yield and quality; and the combined effect on both yield and quality.

5.3 Recommendations

- Concerning the fractionation of Lignex®, more solvents should be investigated. Another option could be to investigate mixtures of various combinations of polar and non-polar solvents to see if it might be possible to improve the extraction selectivity. This would allow for more detailed characterization or even more selective extraction. As seen in Section 4.1.3 a large number of the compounds that were extracted could not be identified due to various reasons (molecules too large for technique to detect or compounds were unable to dissolve in the required analytical

medium). Thus using different solvent may help to decompose and identify these unknown compounds.

- The fractions that were extracted should be analysed using more techniques such as proximate analysis to determine the ash content, UV spectroscopy to quantify the lignin extracted with each solvent. The UV technique could thus determine which solvent extracts impurities and which extracts lignin, as theorized in the characterization chapter. More NMR techniques, such as ^{13}C , ^{19}F and ^{31}P could be utilized to provide more information on the molecular structure of the different fractions. Thus, using more analytical techniques may help to identify the unknown compounds mentioned above.
- It could be advantageous to not only observe the effect of alkali catalysts on product yields but also on the quality of the products. It might be possible to increase the calorific values and depolymerization with another catalyst.
- The biggest challenge experienced with this study was the low bio-oil yield. Conducting these experiments on a larger scale with a larger reactor to produce more bio-oil would allow the possibility for a larger variation of analyses and thus more information.
- Additional analytical tests could be done on the bio-oil samples to help identify the unknown/uncertain compounds. Analyses like the ICP could be helpful in determining the sulphur content. However, this would require conducting the experiments on a larger scale to produce larger quantities of the products. This would mean that proximate analyses to determine the ash contents would also be possible. Larger samples would also allow for repetition of analyses to verify the results.
- If it were possible to fractionate the bio-oil, as was done with the feedstock, it might be easier to identify the compounds and characterise the bio-oils.
- From the results obtained with fractionation and by using different solvents, it may be interesting to compare bio-oils produced from ethanol with bio-oils produced from acetone and methanol or even a mixture of these organic solvents. One might even attempt a mixture of polar and non-polar solvents, for example, a solution of 10 mass% THF and 90 mass% methanol. This combination might result in higher yields and better decomposition of the lignin.
- As the yield of bio-oil is so small it may be advantageous to consider pharmaceutical applications, because of the wide variety of compounds present in the bio-oil.

6 References

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7

7 Appendix A: Calculation methods and descriptions

7.1 Product yield calculation

$$Product\ yield = \frac{Product\ mass\ (g)}{Biomass\ loading\ (g)} \times 100$$

7.2 Proximate analysis

SANS 5925:2007 is the standard that was used for determining the moisture content of samples (SABS, 2007). The sample was heated in an oven at 105°C until a constant mass was reached. The loss of mass was used to calculate the moisture content.

$$Moisture\ content = \frac{m_2 - m_{3,1}}{m_2 - m_1} \times 100$$

SANS 50:2011 is the standard that was used to determine the volatile matter in the sample (SABS, 2011a).

$$Volatile\ matter = \frac{100 \times (m_2 - m_{3,2})}{m_2 - m_1} - moisture\ content$$

SANS 131:2011 was used to determine the ash content in the sample (SABS, 2011b).

$$Ash\ content = \frac{m_{3,3} - m_1}{m_2 - m_1} \times 100$$

7.3 Experimental error calculation

The experimental error was calculated by using the data of three experiments. The experiment for the HTL of Lignex® with 20 min at 280°C was repeated three times over three months.

$$error\ at\ 68\% = \frac{standard\ deviation}{average} \times 100$$

To convert the experimental error to a confidence level of 95% the following Excel formula was used:

$$conversion\ factor = TINV(0.05; 3)$$

The 0.05 is an indication that the confidence level was set at 95% (1-0.95) and the 3 represents the number of repeated experiments.

$$\text{error at 95\%} = \frac{\text{conversion factor} \times \text{standard deviation}}{\text{average}} \times 100$$

8 Appendix B: Additional data

8.1 From literature

Table 8-1. NMR peak assignments

Chemical shift	Assignments
• 7.5 ppm	Aromatic protons of H units
• 7 ppm	Aromatic protons of G units
• 6.5 ppm	Aromatic protons of S units
• 6.3-4.0 ppm	Aliphatic protons with linkages (β -O-4; β - β and β
• 4.0-3.5 ppm	Methoxyl group protons
• 3.10 ppm	Protons of anhydroxylose

Table 8-2. Functional groups and structures identified within lignosulphonates (Rodríguez-Lucena *et al.*, 2009)

Wavenumbers (cm ⁻¹)	Assignments and description	Functional groups and structures
3600-3300	Broad band; (accompanied by bands with varying intensity in fingerprint region [1900-800cm ⁻¹])	Hydroxyl groups in phenolic and carboxylic acids
1900-800	Fingerprint region	- Aromatic acetoxy groups (1770 cm⁻¹) - Unconjugated carbonyl-carboxyl stretching (1715-1630 cm⁻¹) - C=C skeletal vibrations (1600-1500 cm⁻¹) - C-H deformation combined with aromatic ring vibrations (1470-1460 cm⁻¹) - C=O stretch (1260 cm⁻¹) - C-C; C-O; C=O stretching (1230-1215 cm⁻¹) - C-H in plane deformation (1150-1140 cm⁻¹) - Complex vibrations associated with the C-C and C-O stretching and the C-OH bending in polysaccharides (1050 cm⁻¹) - Out-of-plane C-H deformations (840-810 cm⁻¹)
660-620	Band; S-O stretching vibrations	Sulphonic groups formed when sodium sulphite reacted with secondary OH of the lignin's aliphatic side chain

Table 8-3. Typical properties of standard bio-oil compared with fossil fuels (Sánchez-Borrego *et al.*, 2021)

Properties	Bio-oil	Gasoline	Diesel	Heavy fossil fuel oil
Density @ 15°C (kg/dm ³)	1.11-1.13	0.72-0.76	0.78-0.86	0.95
Moisture content (mass%)	20-30	-	0.05	0.32
Flashpoint (°C)	40-110	-43	50	110
Viscosity (cSt)	15-40 @ 10°C	0.5 @20°C	3 @ 40°C	130 @ 10°C
Higher heating value (MJ/kg)	14-19	45.7	47	42.9
Lower heating value (MJ/kg)	13-18	42.9	43	40.6
Elemental composition (mass%)	50-60 C	86 C	87.4 C	88.1 C
	7-8 H	12.8 H	12.1 H	10.85 H
	≤0.5 N	0 N	0.039 N	0.5 N
	35-40 O	1 S	1.39 S	0.35-0.64 O

8.2 Feedstock properties

Table 8-4. IC results of ashed Lignex® material

Component	Concentration (mg/L)	Component	Concentration (mg/L)
F	52.7	PO ₄	21.1
Cl	1 412.2	Na	49 109.7
NO ₂	102.1	NH ₄	208.8
Br	1.3	K	9 593.8
NO ₃	4 010.3	Mg	2 000.8
SO ₄	9 291.1	Ca	1 841.2

8.3 Product yields

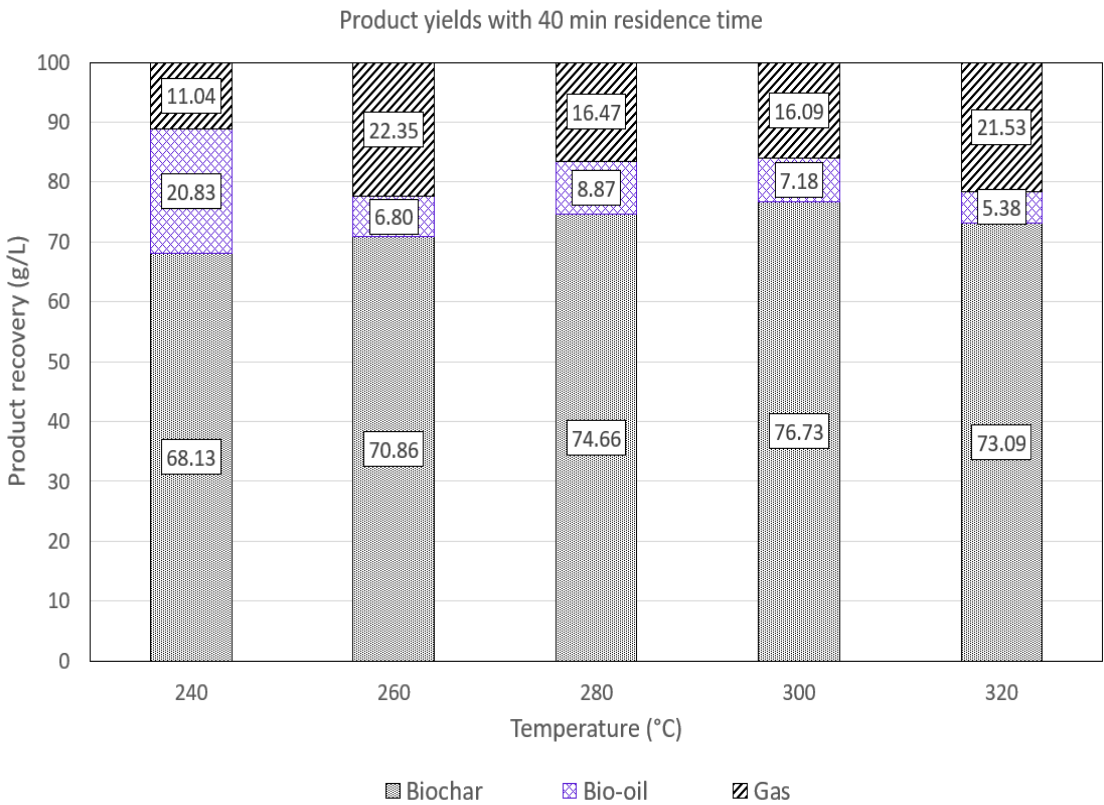


Fig. 78. Product yields with a residence time of 40 min (Dry ash-free)

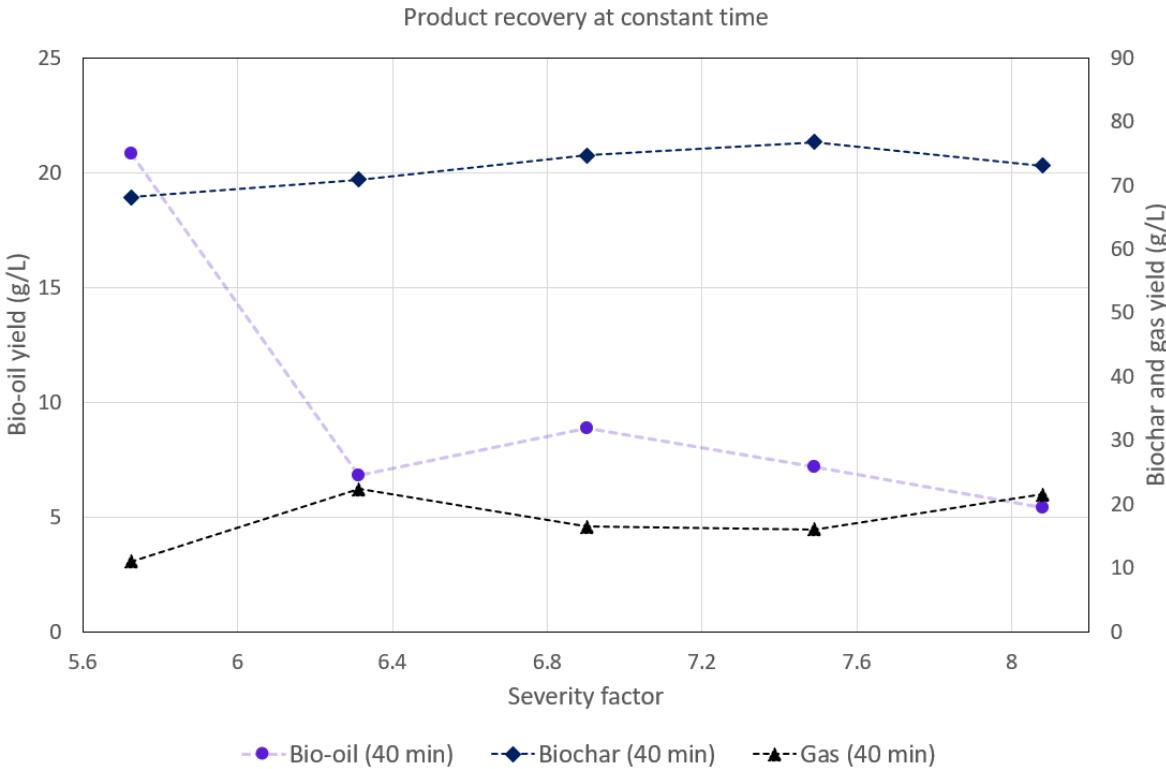


Fig. 79. Severity factor of products formed with 40 min

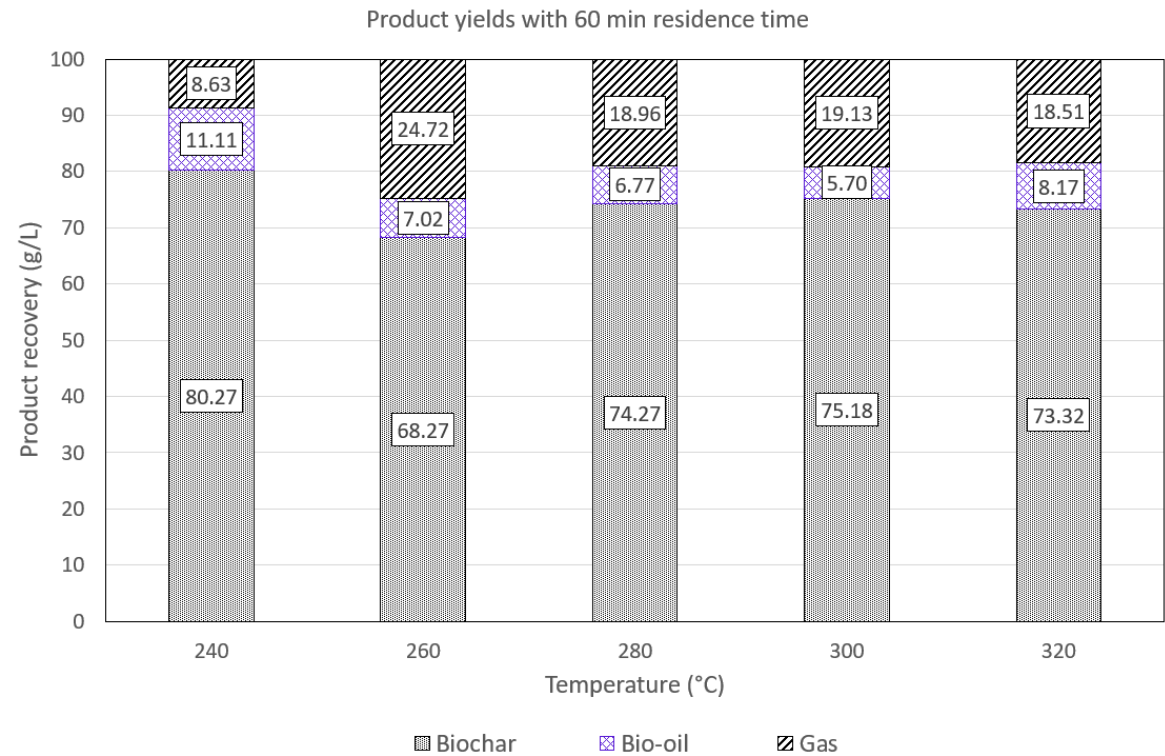


Fig. 80. Product yields with a residence time of 60 min (dry ash-free)

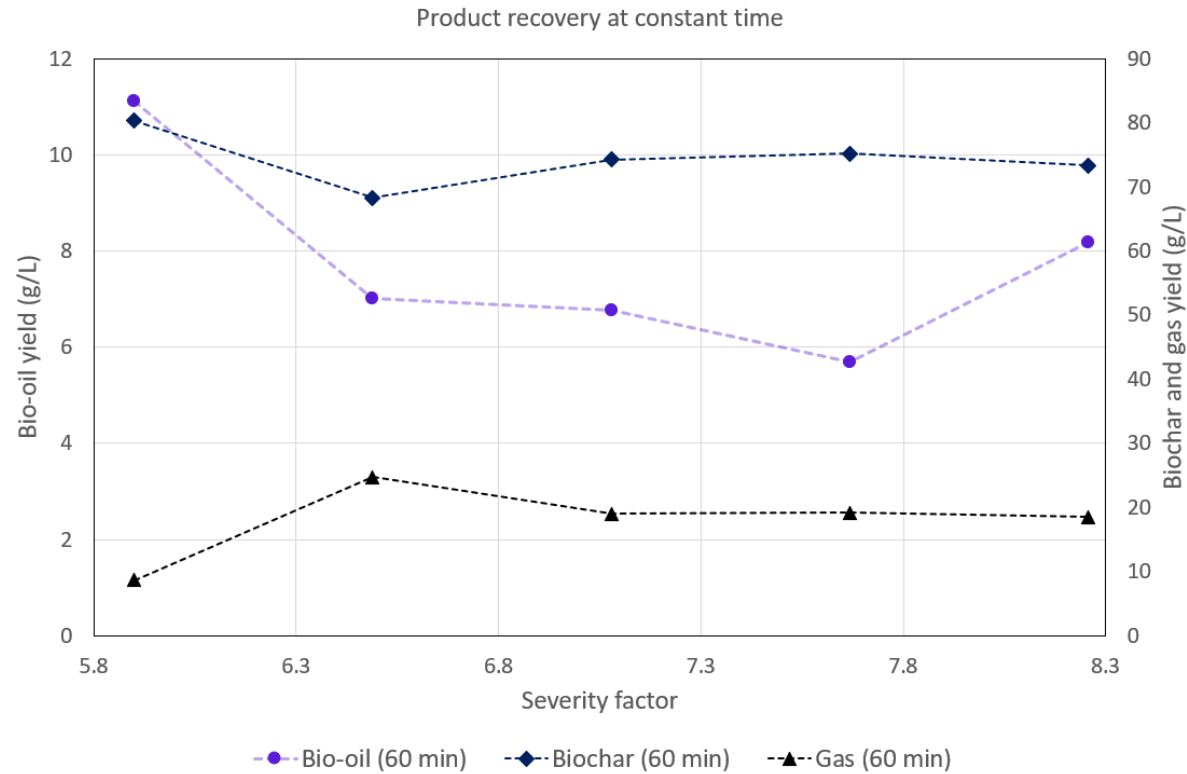


Fig. 81. Severity factor of products formed with 60 min

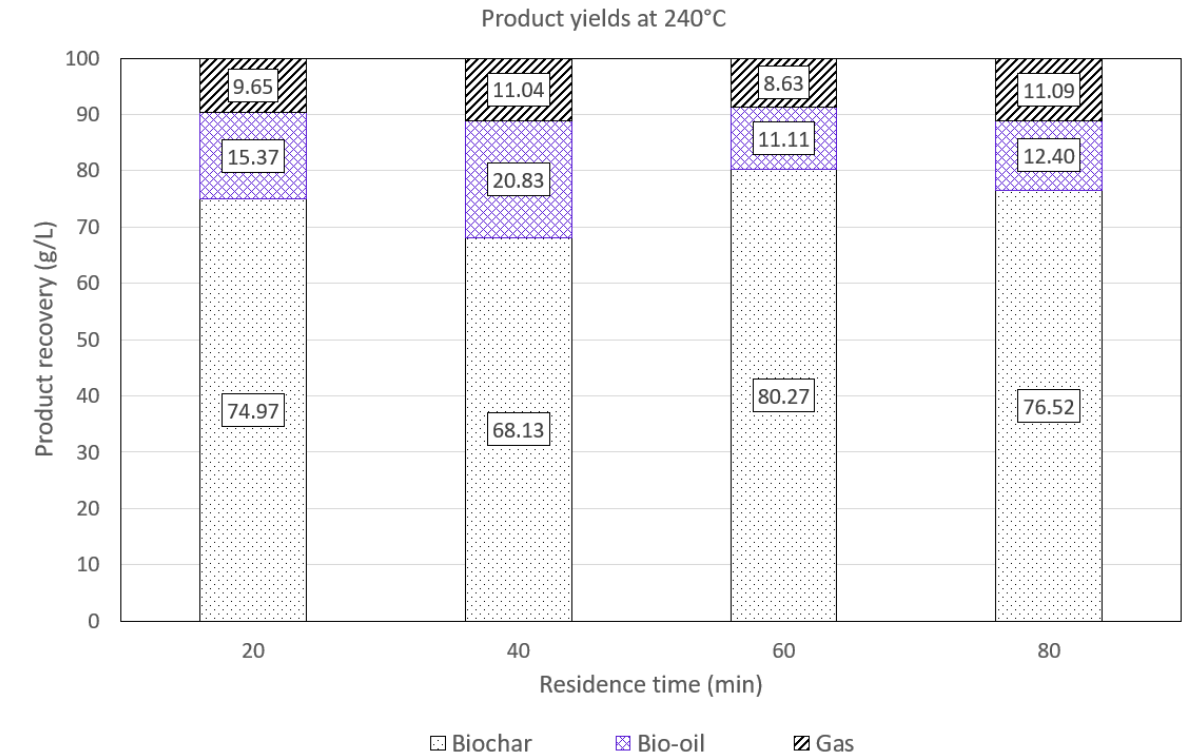


Fig. 82. Product yields with a reaction temperature of 240°C (dry ash-free)

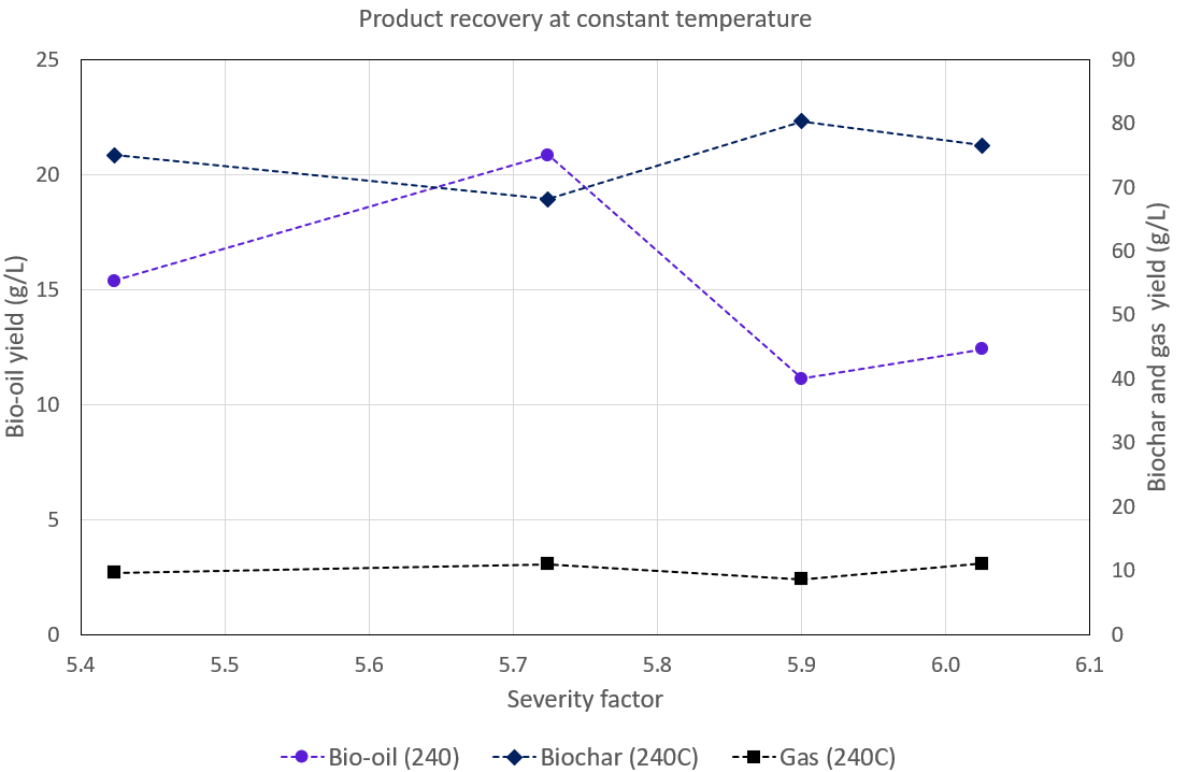


Fig. 83. Severity factor of products formed at 240°C

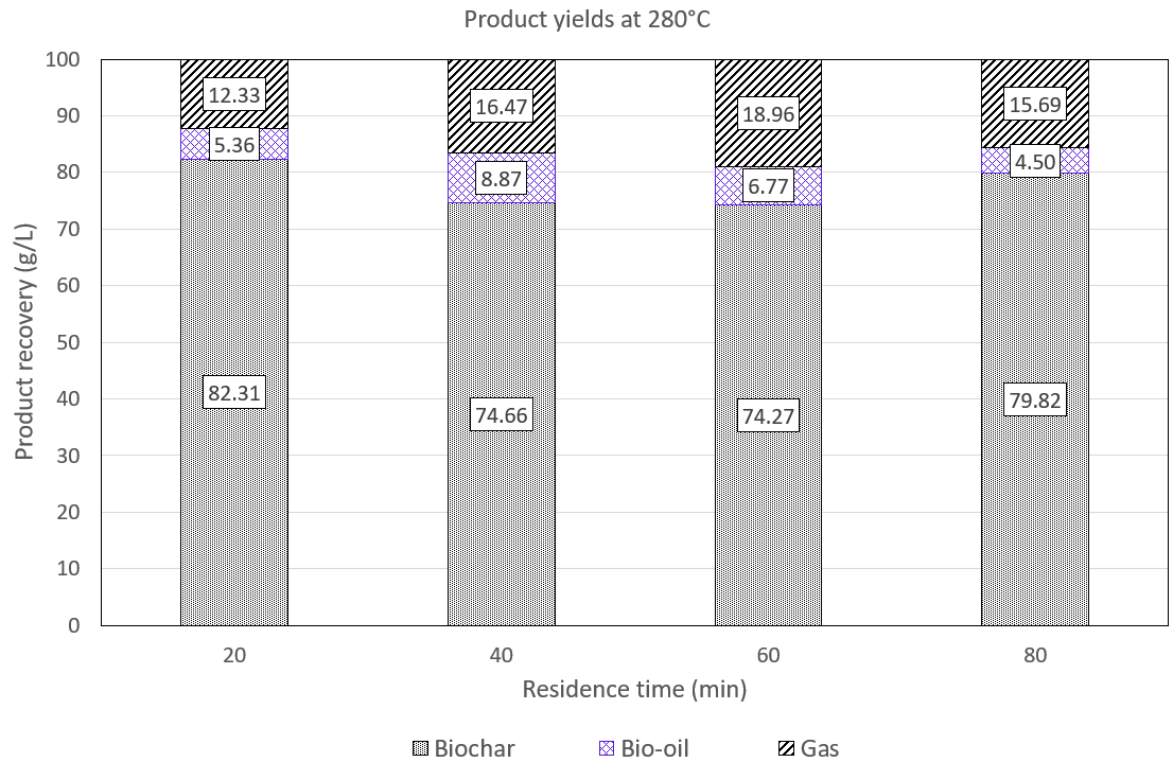


Fig. 84. Product yields with a reaction temperature of 280°C (dry ash-free)

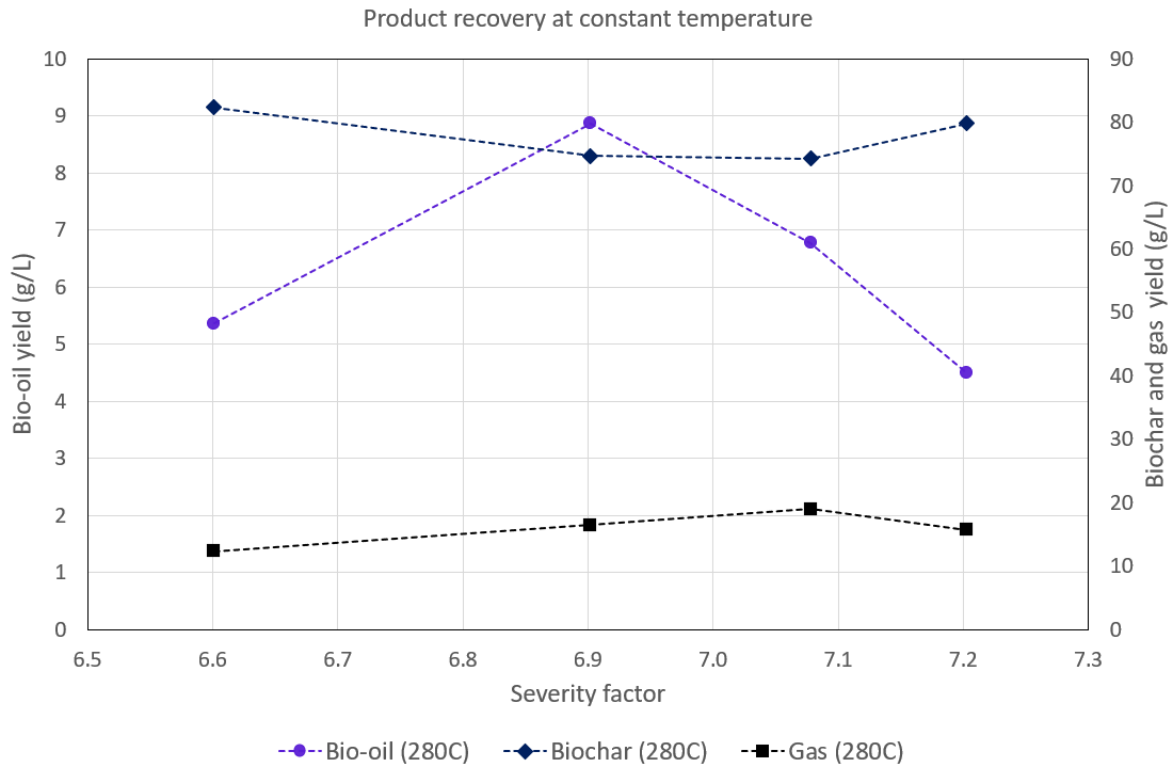


Fig. 85. Severity factor of products formed at 280°C

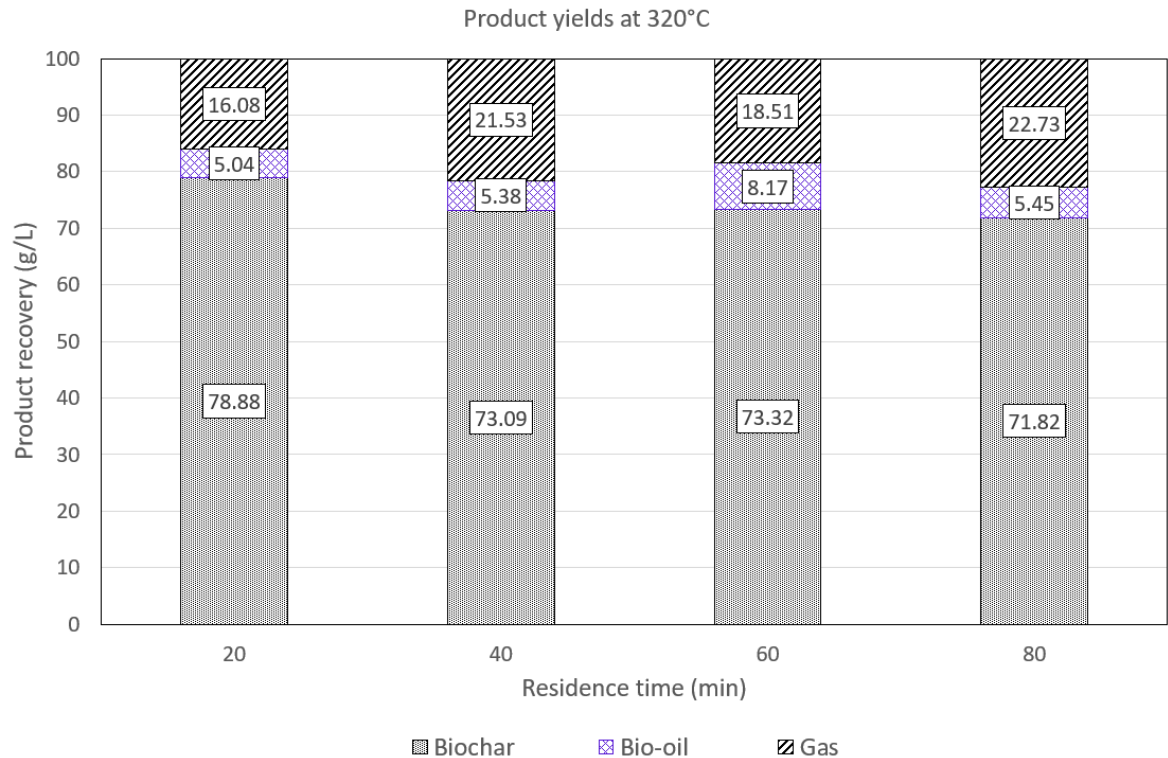


Fig. 86. Product yields with a reaction temperature of 320°C (dry ash-free)

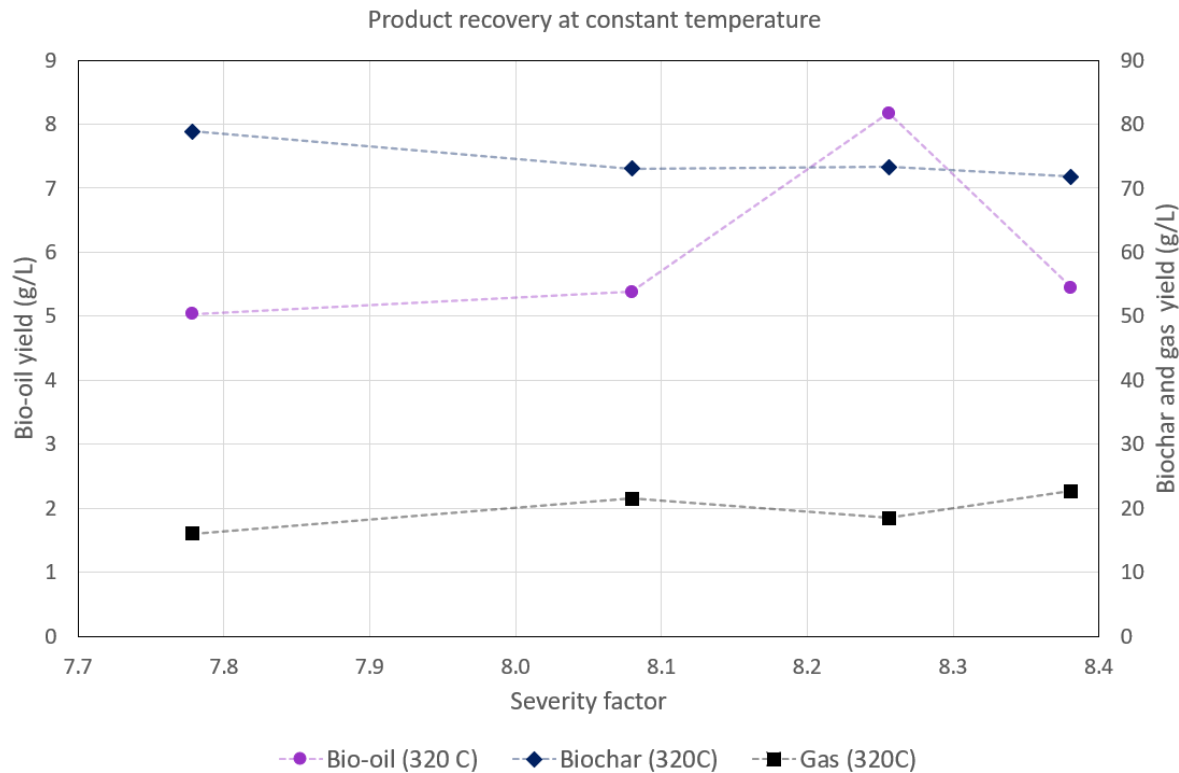


Fig. 87. Severity factor of products formed at 320°C

8.4 Quality analysis on bio-oils

Elemental data

Table 8-5. Elemental ratios of bio-oils produced with various reaction temperatures

Temperature (°C)	Short residence time (40 min)		Long residence time (60 min)	
	O/C	H/C	O/C	H/C
240	0.57 ± 0.01	1.03 ± 0.00	0.43 ± 0.01	0.60 ± 0.00
260	0.67 ± 0.01	0.70 ± 0.00	0.49 ± 0.01	1.01 ± 0.00
280	1.49 ± 0.01	0.99 ± 0.00	0.48 ± 0.01	1.13 ± 0.00
300	0.43 ± 0.01	0.90 ± 0.00	0.51 ± 0.01	1.10 ± 0.00
320	0.40 ± 0.01	0.99 ± 0.00	0.85 ± 0.01	1.26 ± 0.00

Table 8-6. Elemental composition of bio-oils produced with 20 min

Temperature (°C)	Carbon (mass%)	Hydrogen (mass%)	%R (mass%)
240	17.81 ± 0.53	21.01 ± 0.26	8.22 ± 0.71
260	12.08 ± 0.53	13.93 ± 0.26	5.88 ± 0.71
280	5.39 ± 0.53	6.07 ± 0.26	3.29 ± 0.71
300	6.28 ± 0.53	6.36 ± 0.26	2.11 ± 0.71
320	5.09 ± 0.53	5.19 ± 0.26	2.43 ± 0.71

Table 8-7. Elemental composition of bio-oils produced with 40 min

Temperature (°C)	Carbon (mass%)	Hydrogen (mass%)	%R (mass%)
240	18.75 ± 0.53	19.25 ± 0.26	10.71 ± 0.71
260	7.34 ± 0.53	5.15 ± 0.26	4.91 ± 0.71
280	4.25 ± 0.53	4.21 ± 0.26	6.33 ± 0.71
300	7.20 ± 0.53	6.48 ± 0.26	3.11 ± 0.71
320	5.64 ± 0.53	5.55 ± 0.26	2.26 ± 0.71

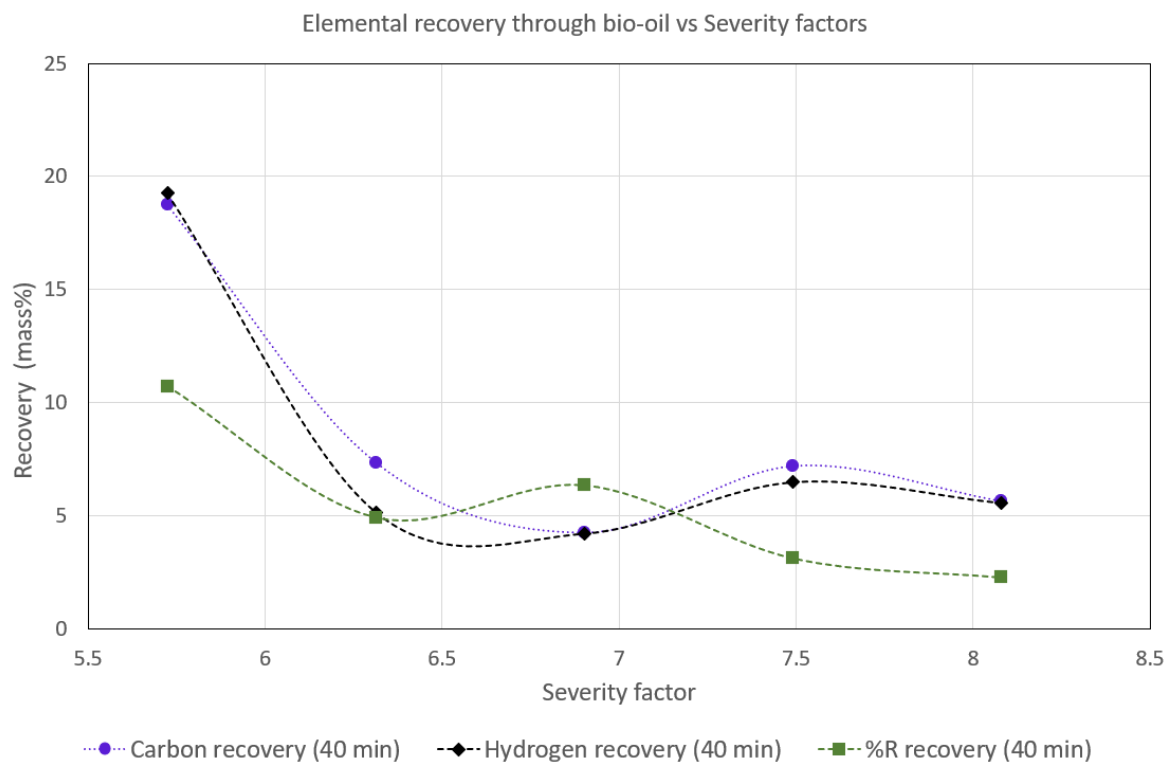


Fig. 88. Elemental composition of bio-oils formed with 40 min residence time

Table 8-8. Elemental composition of bio-oils produced with 60 min

Temperature (°C)	Carbon (mass%)	Hydrogen (mass%)	%R (mass%)
240	10.36 ± 0.53	6.23 ± 0.26	4.47 ± 0.71
260	7.33 ± 0.53	7.39 ± 0.26	3.56 ± 0.71
280	6.67 ± 0.53	7.56 ± 0.26	3.22 ± 0.71
300	6.28 ± 0.53	6.91 ± 0.26	3.18 ± 0.71
320	6.81 ± 0.53	8.57 ± 0.26	5.78 ± 0.71

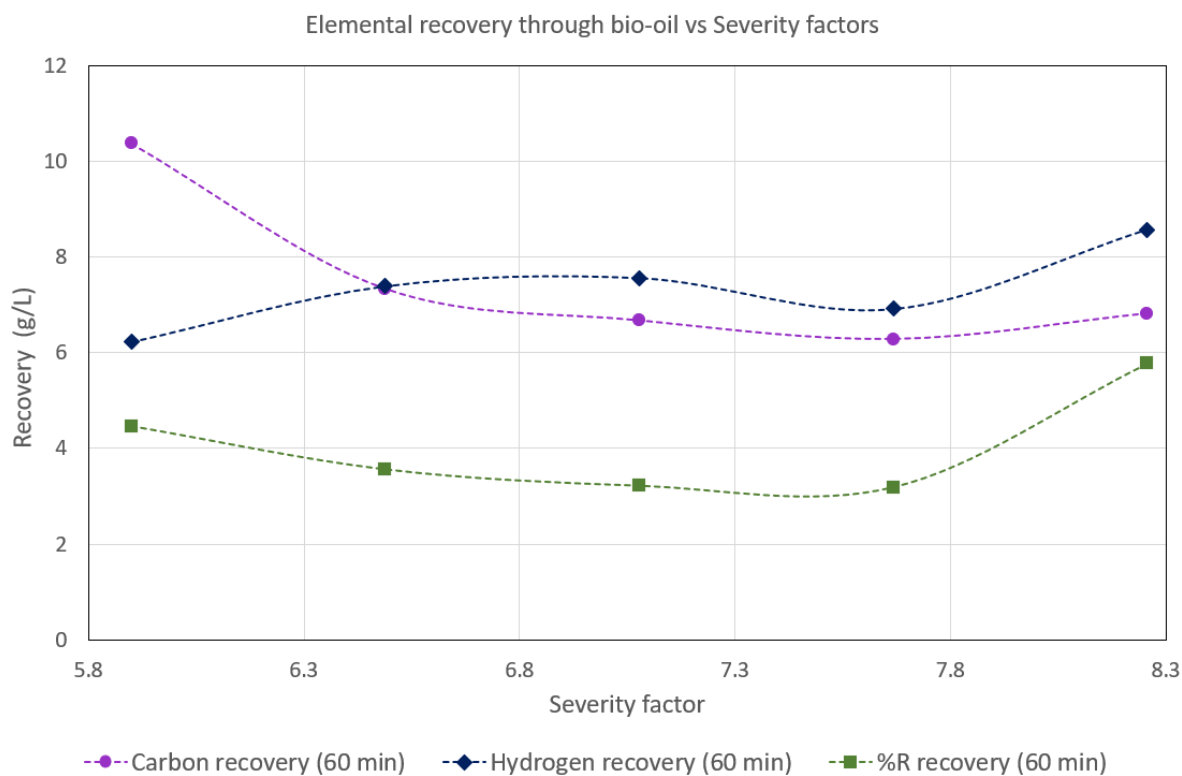


Fig. 89. Elemental composition of bio-oils formed with 60 min residence time

Table 8-9. Elemental composition of bio-oils produced with 80 min

Temperature (°C)	Carbon (mass%)	Hydrogen (mass%)	%R (mass%)
240	16.78 ± 0.53	17.11 ± 0.26	5.68 ± 0.71
260	4.24 ± 0.53	5.15 ± 0.26	2.97 ± 0.71
280	4.85 ± 0.53	5.54 ± 0.26	2.49 ± 0.71
300	10.42 ± 0.53	10.49 ± 0.26	9.44 ± 0.71
320	3.96 ± 0.53	4.74 ± 0.26	4.42 ± 0.71

Energy content

Table 8-10. CVs of bio-oils produced with a residence time of 40 min

Temperature	CV (MJ/kg)	DOC
Lignex®	11.64 ± 1.48	-
240°C	24.96 ± 1.48	2.14
260°C	-	
280°C	-	

300°C	-	
320°C	19.99 ± 1.48	1.72

Table 8-11. CVs of bio-oils produced with a residence time of 80 min

Temperature	CV (MJ/kg)	DOC
Lignex®	11.64 ± 1.48	-
240°C	25.85 ± 1.48	2.22
260°C	23.18 ± 1.48	1.99
280°C	22.12 ± 1.48	1.90
300°C	10.63 ± 1.48	0.91
320°C	23.55 ± 1.48	2.02

Molecular weight distribution data

Table 8-12. GPC analysis of bio-oils produced with a residence time of 40 min

Temperature	Mw (g/mol)	Mn (g/mol)	PDI
Lignex®	2468 ± 1	945 ± 1	2.6 ± 0.3
240°C	740 ± 1	289 ± 1	2.6 ± 0.3
260°C	656 ± 1	233 ± 1	2.8 ± 0.3
280°C	307 ± 1	157 ± 1	2.0 ± 0.3
300°C	286 ± 1	150 ± 1	1.9 ± 0.3
320°C	246 ± 1	125 ± 1	2.0 ± 0.3

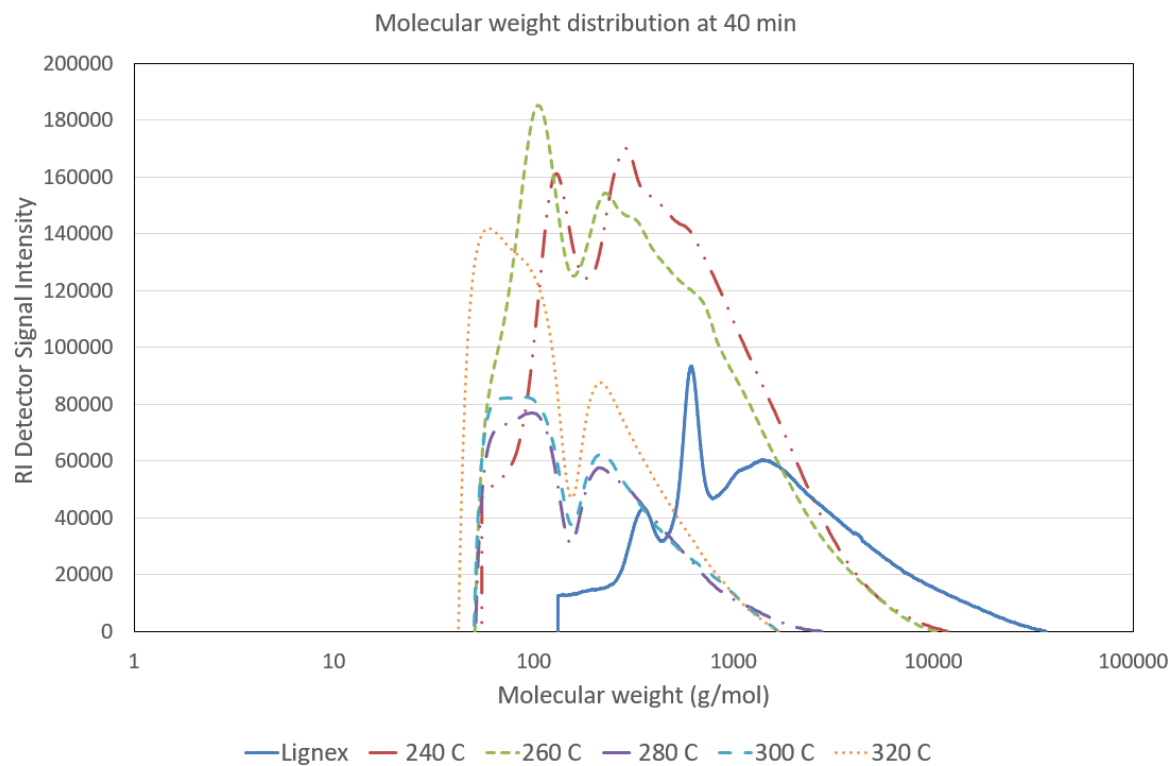


Fig. 90. Molecular weight distribution of bio-oils produced with 40 min residence time

Table 8-13. GPC analysis of bio-oils produced with a residence time of 60 min

Temperature	Mw (g/mol)	Mn (g/mol)	PDI
Lignex®	2468 ± 1	945 ± 1	2.6 ± 0.3
240°C	673 ± 1	263 ± 1	2.4 ± 0.3
260°C	432 ± 1	192 ± 1	2.2 ± 0.3
280°C	219 ± 1	131 ± 1	1.7 ± 0.3
300°C	240 ± 1	121 ± 1	2.0 ± 0.3
320°C	198 ± 1	108 ± 1	1.8 ± 0.3

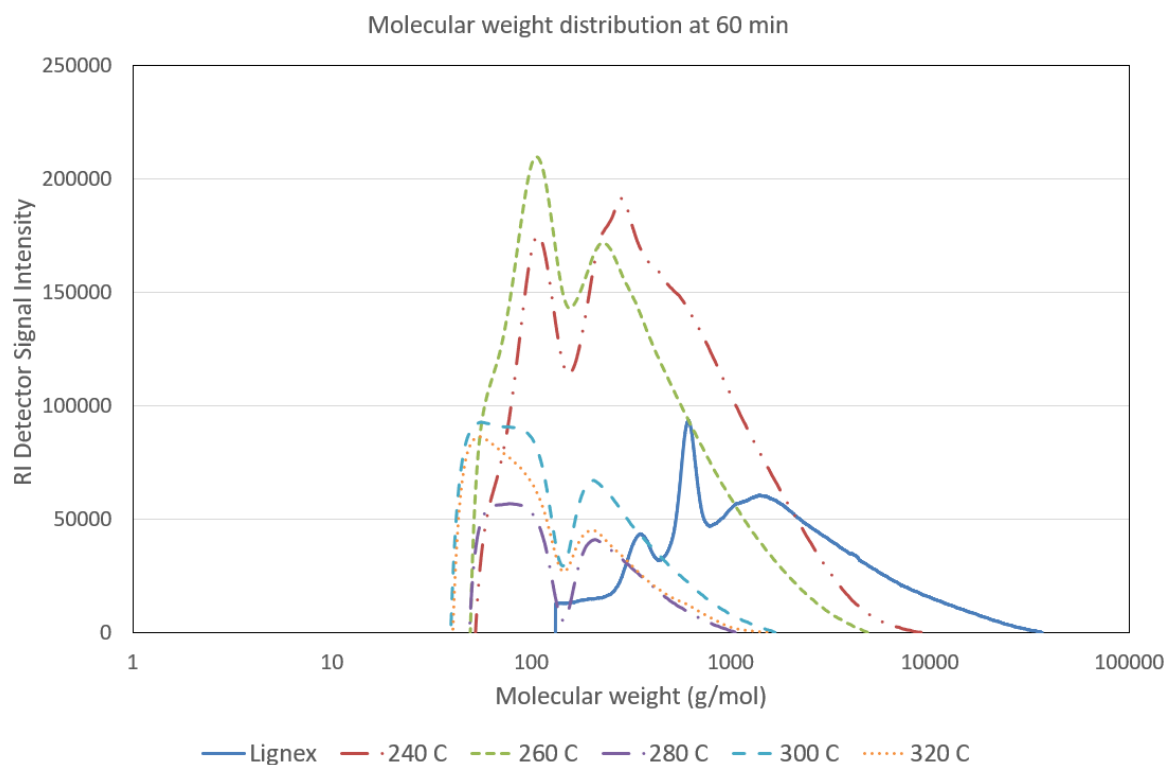


Fig. 91. Molecular weight distribution of bio-oils produced with 60 min residence time

Functional and chemical group data

Table 8-14. Boiling fractions' distribution of bio-oil compounds (40 min)

Compound fractions (%)	240°C	260°C	280°C	300°C	320°C
Naphtha	0	0	0	0	0
Kerosene (± 1.71)	12.51	16.16	23.64	8.91	10.48
Diesel Boiling (± 0.08)	56.36	62.91	67.64	74.23	75.59
Heavy fraction (± 0.37)	30.80	20.82	8.64	16.84	13.92

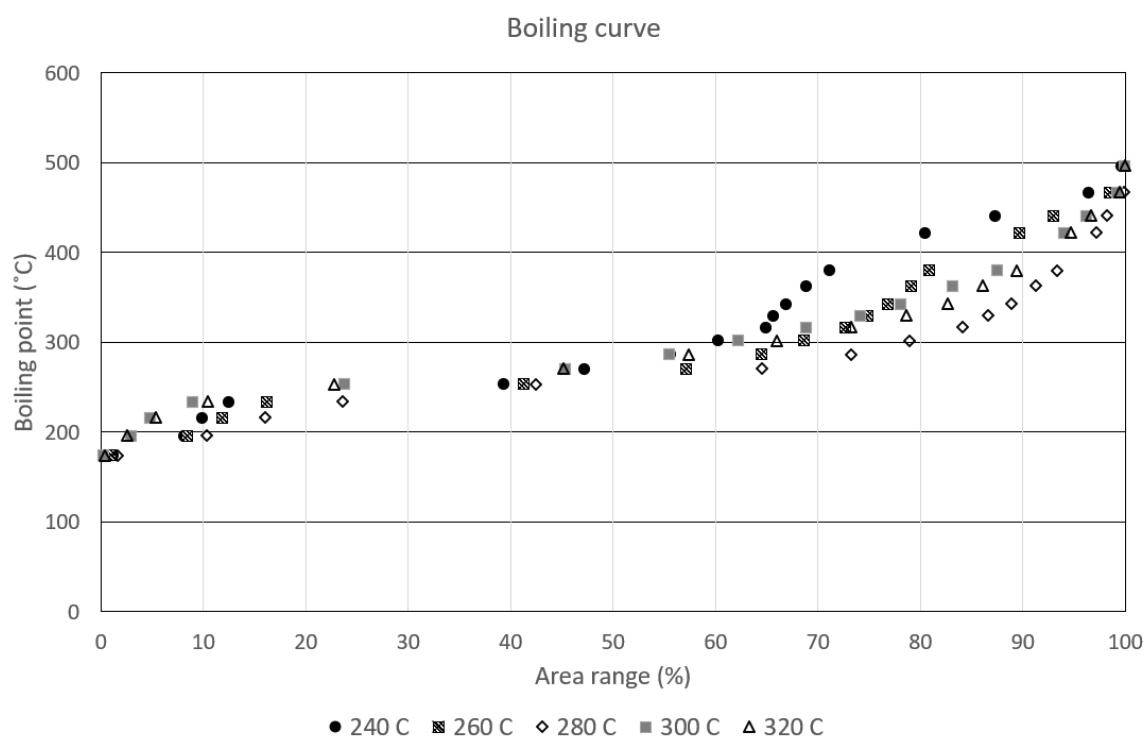


Fig. 92. Simulated distillation curve of bio-oils produced with a 40 min residence time

Table 8-15. Boiling fractions' distribution of bio-oil compounds (60 min)

Compound fractions (%)	240°C	260°C	280°C	300°C	320°C
Naphtha	0	0	0	0	0
Kerosene (± 1.71)	10.87	6.92	8.91	8.20	8.91
Diesel Boiling (± 0.08)	52.85	66.13	72.15	74.16	71.95
Heavy fraction (± 0.37)	33.13	26.55	18.68	17.55	19.09

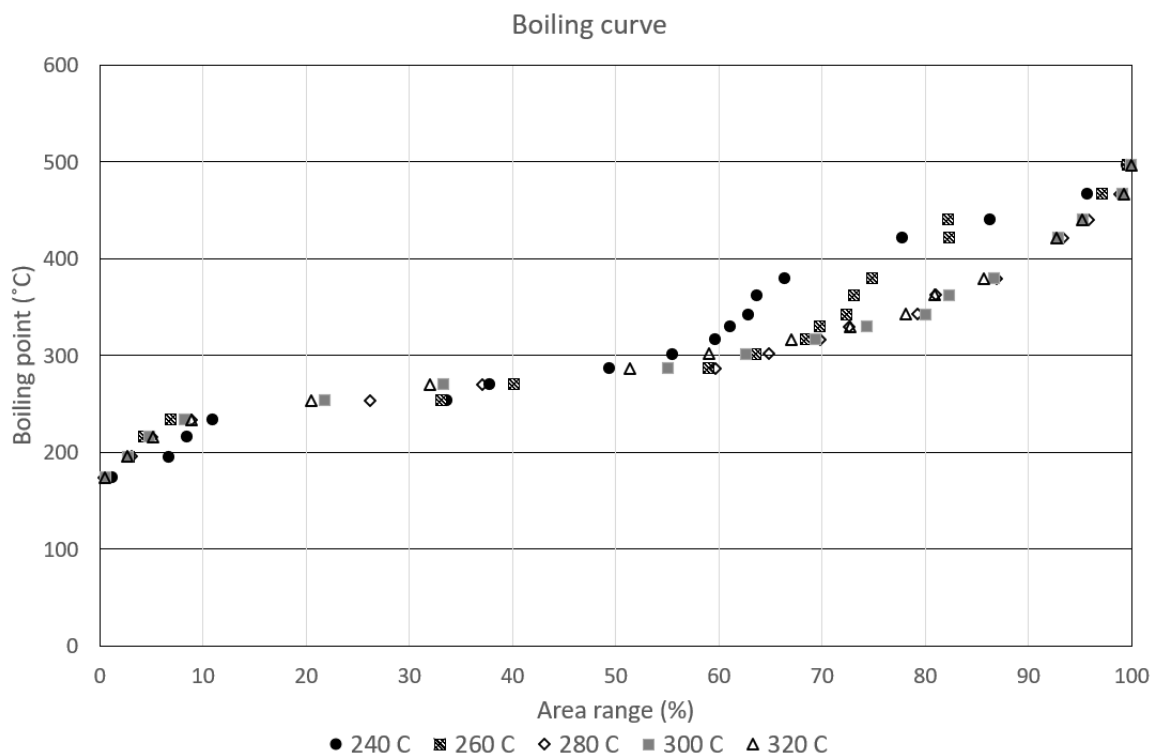


Fig. 94. Simulated distillation curve of bio-oils produced with a 60 min residence time

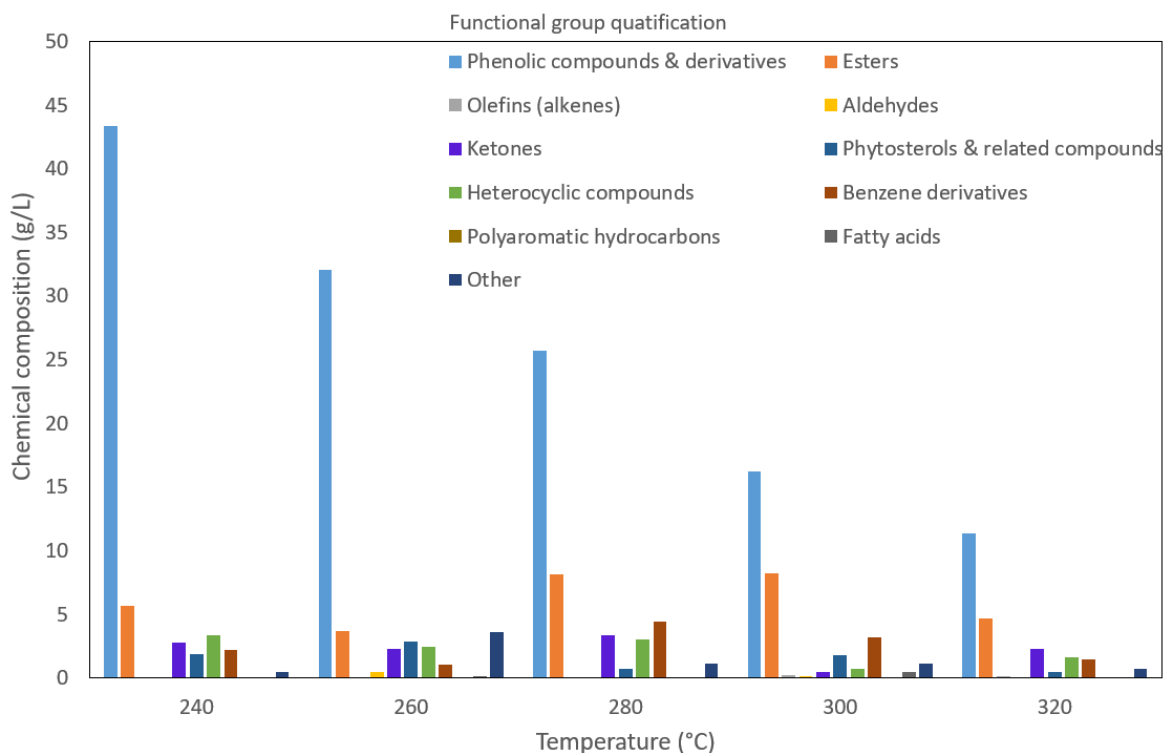


Fig. 93. Quantification of chemical groups that are present in bio-oils produced with a 40 min residence time

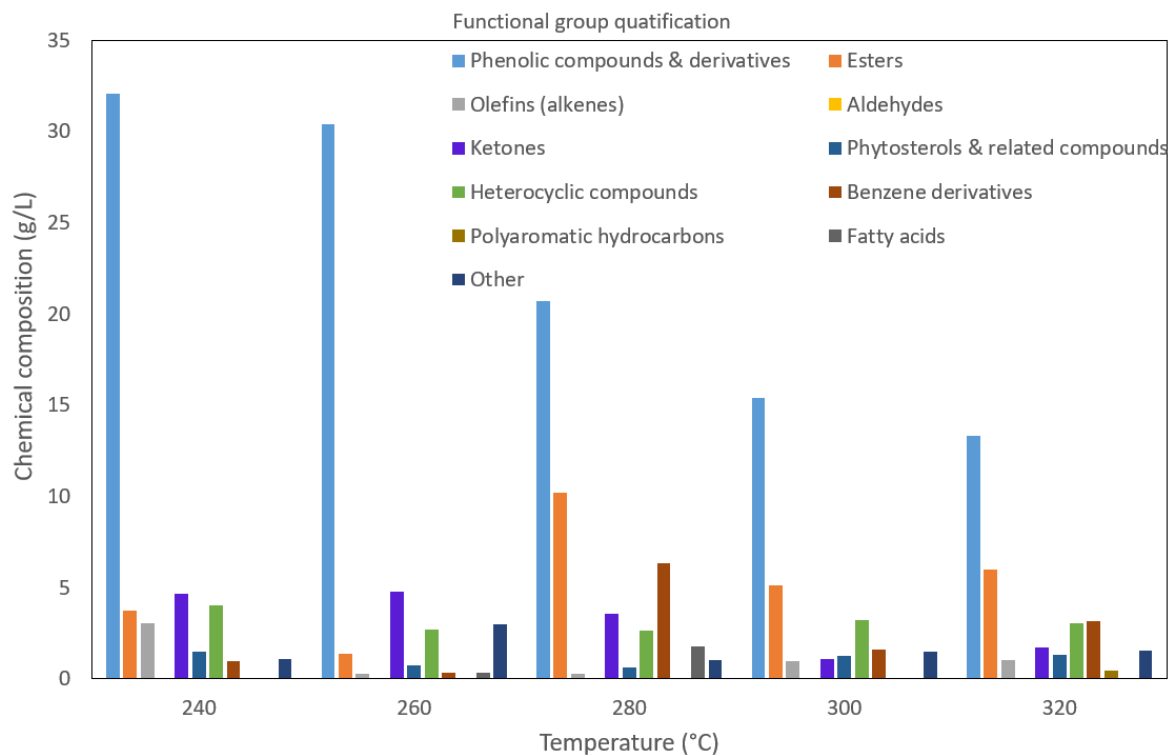


Fig. 95. Quantification of chemical groups that are present in bio-oils produced with a 60 min residence time

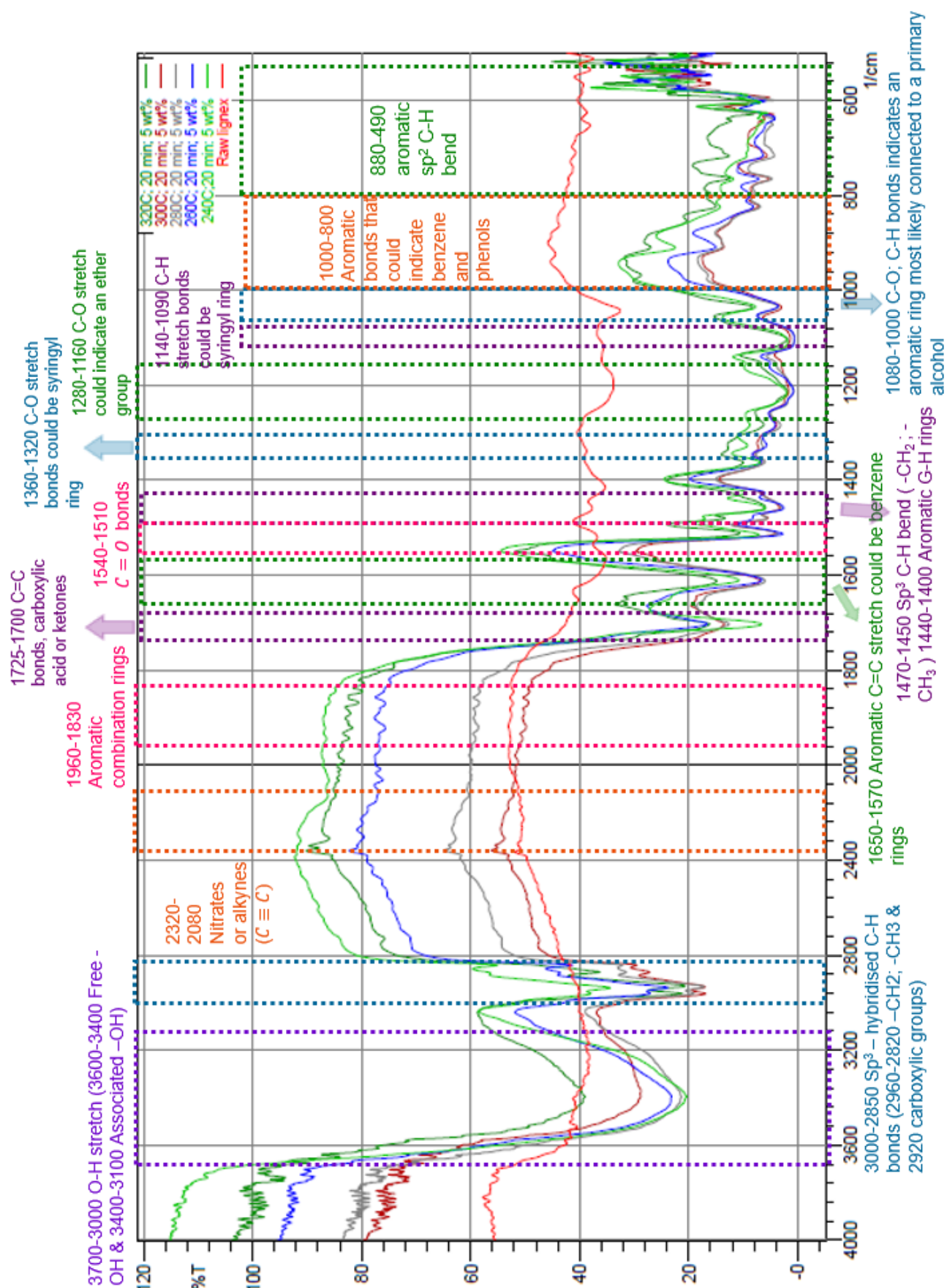


Fig. 96. FTIR spectra of bio-oils produced with a 20 min residence time

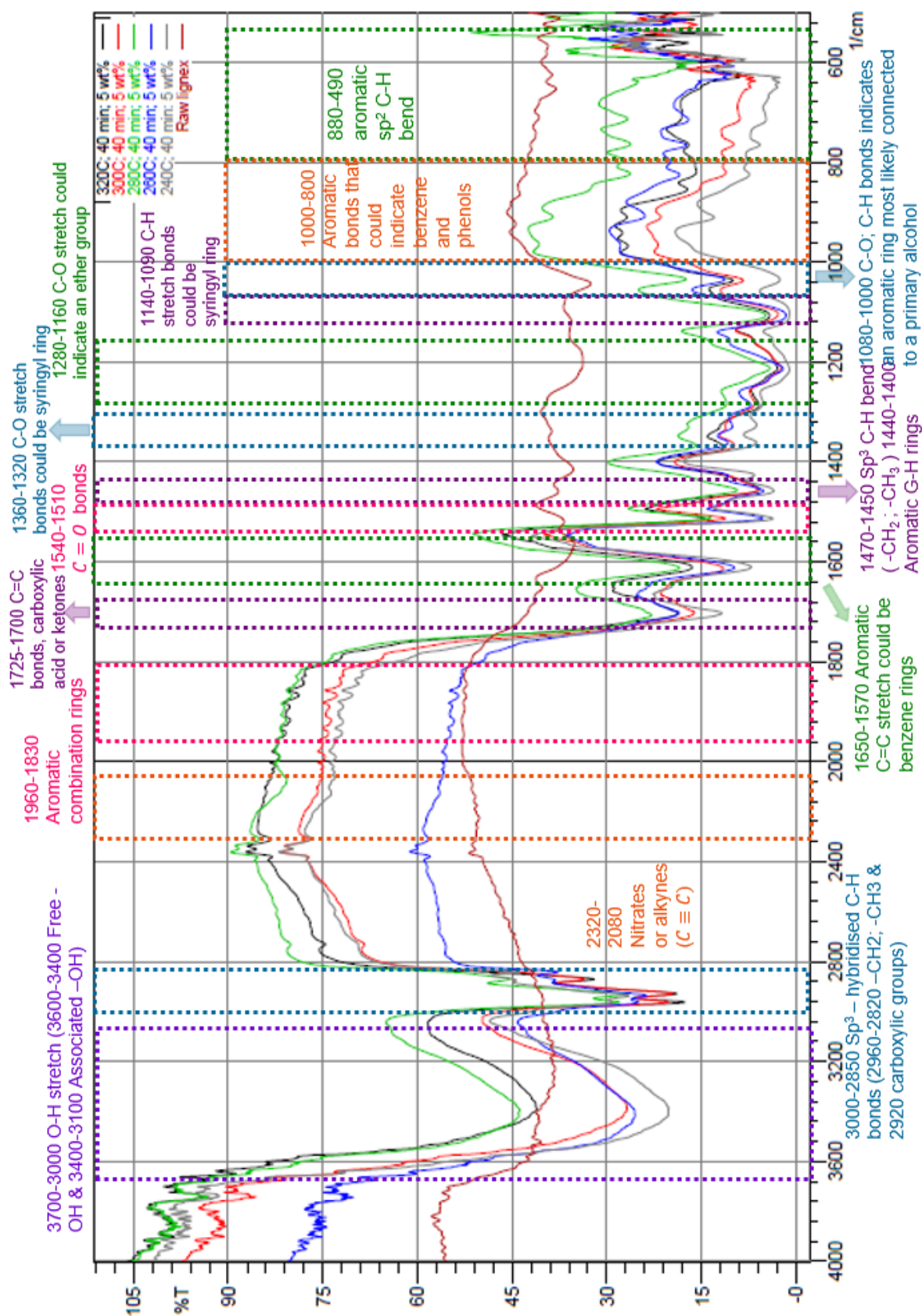


Fig. 97. FTIR spectra of bio-oils produced with a 40 min residence time

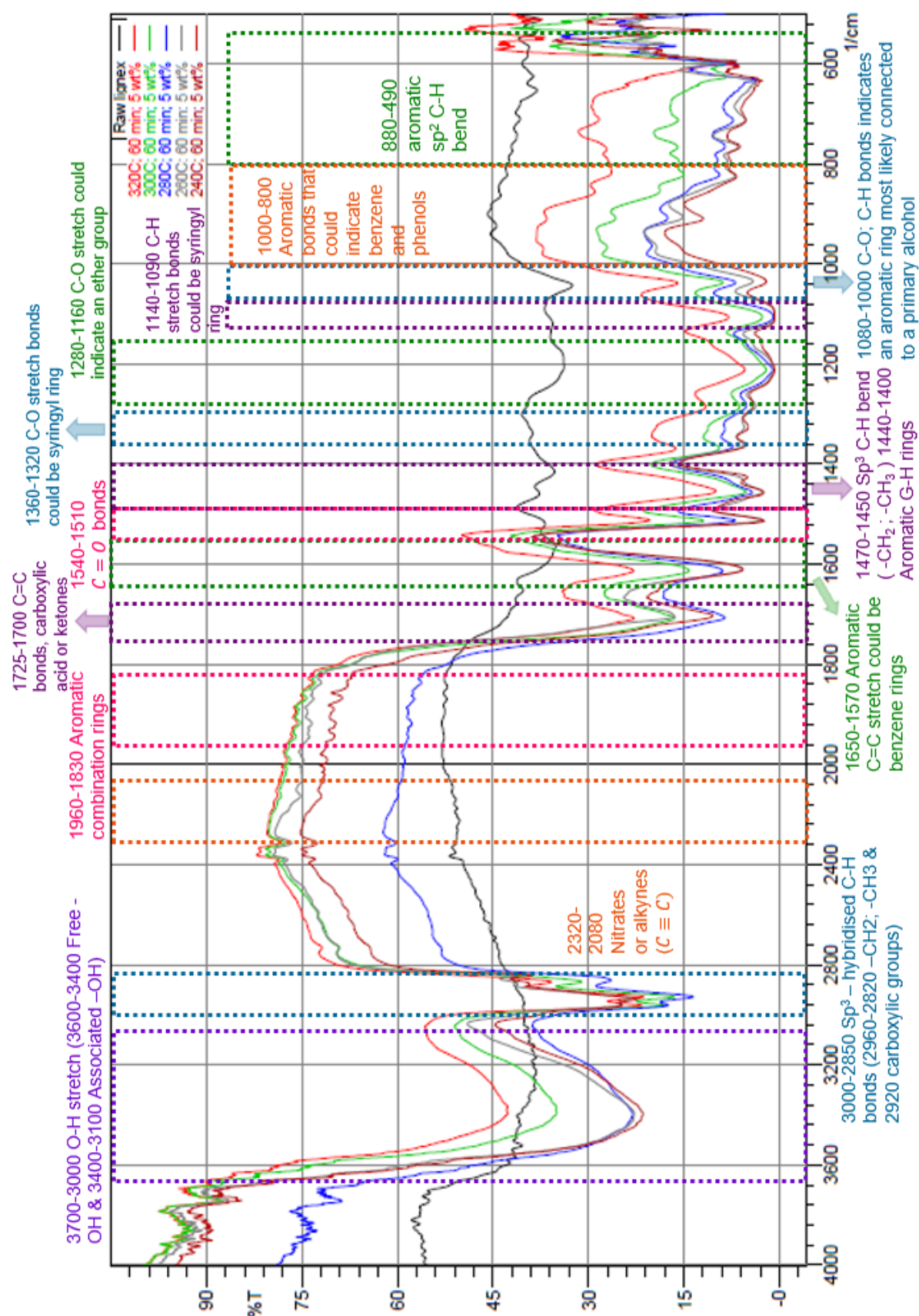


Fig. 98. FTIR spectra of bio-oils produced with a 60 min residence time

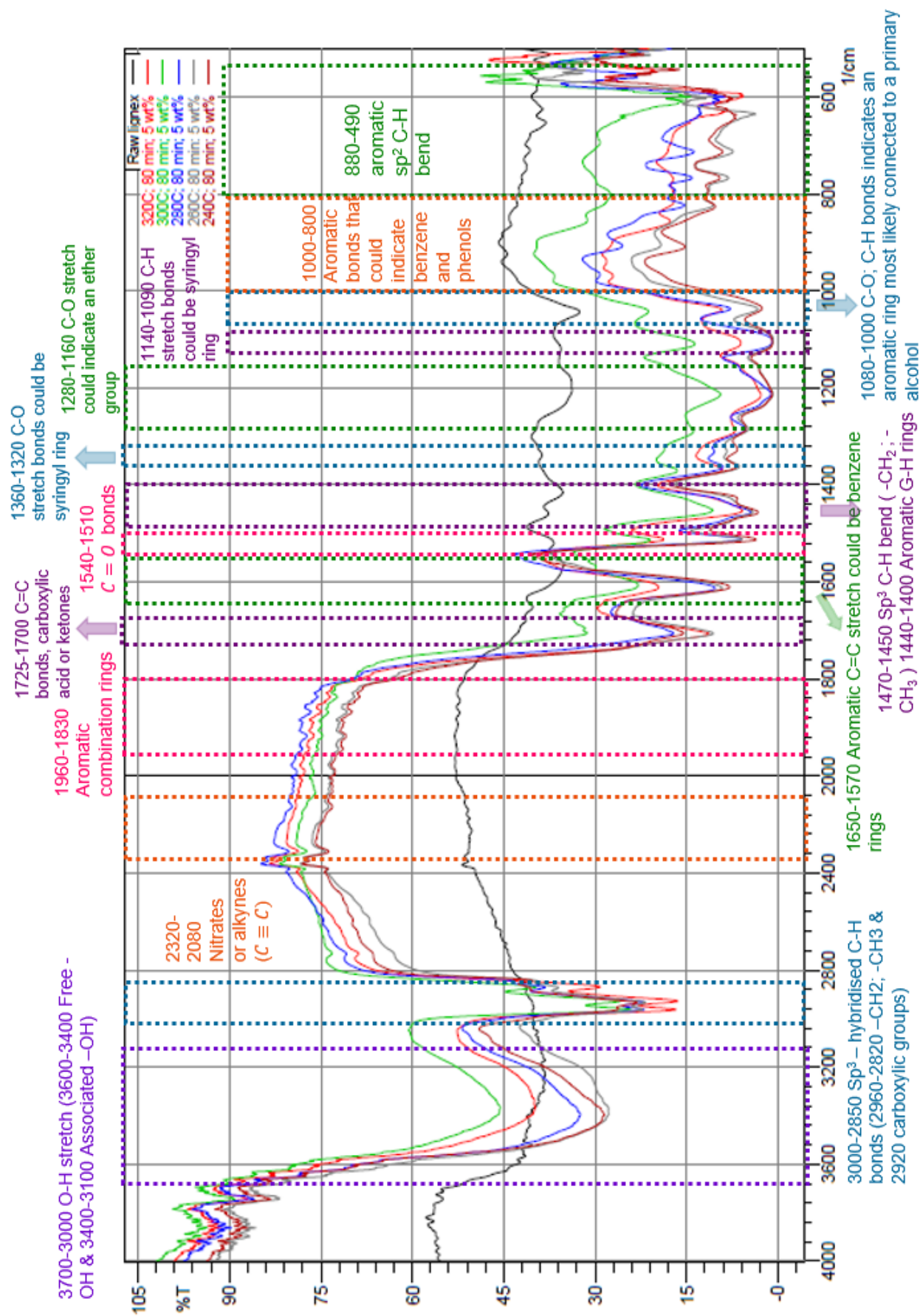


Fig. 99. FTIR spectra of bio-oils produced with an 80 min residence time

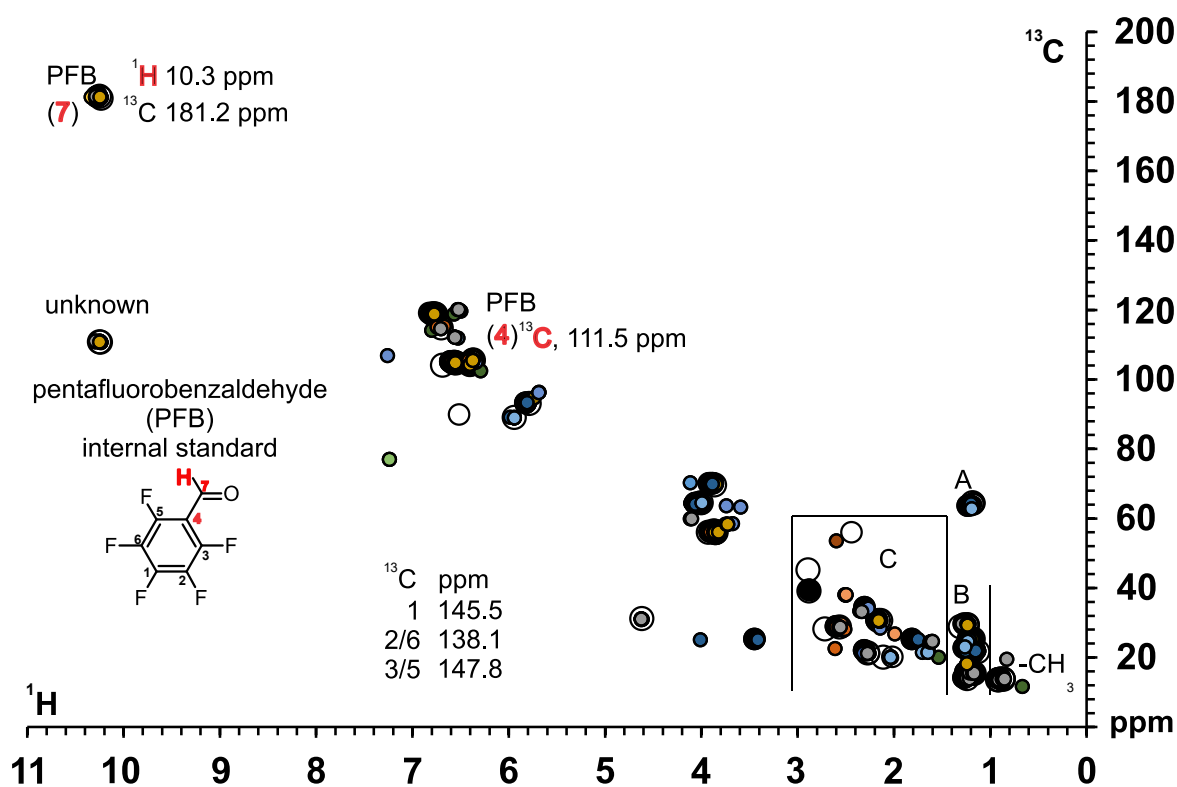


Fig. 100. HSQC NMR spectrums

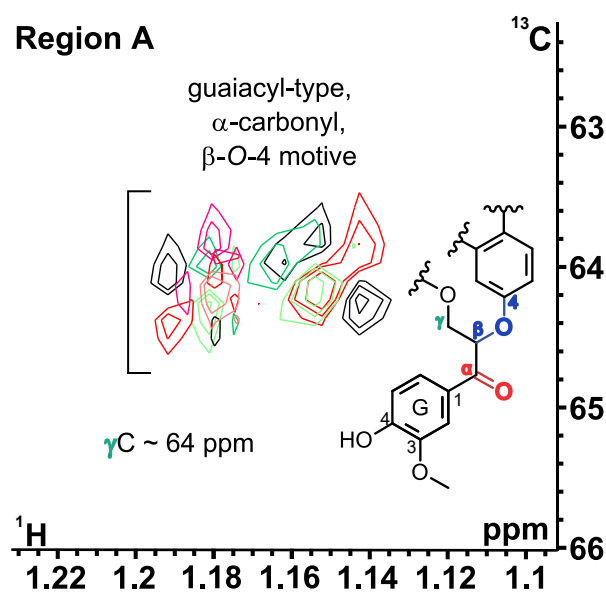


Fig. 101. Enlargement of region A

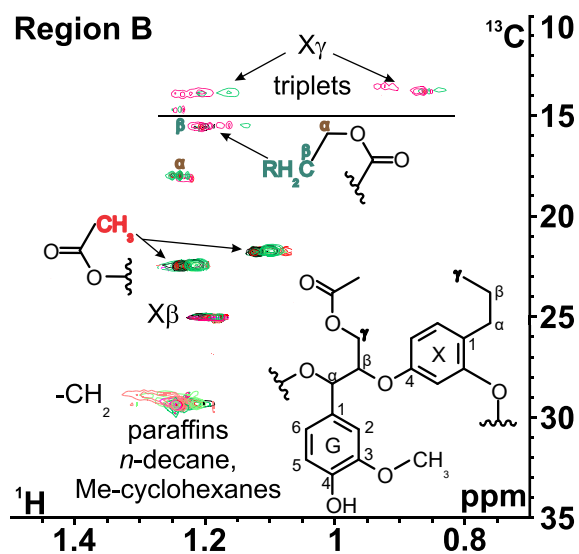


Fig. 103. Enlargement of region B

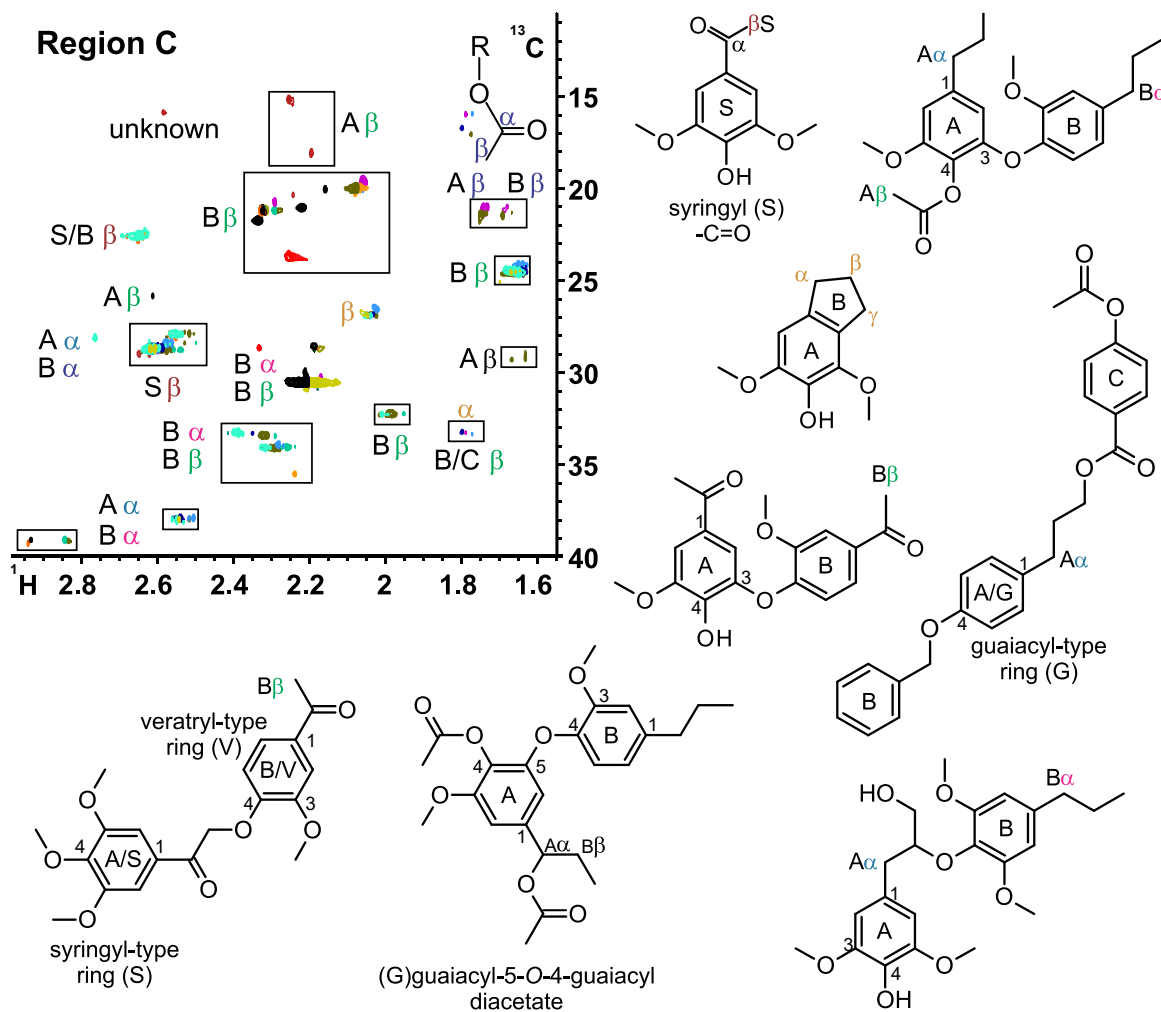


Fig. 104. Enlargement of region C

Elemental dataTable 8-16.
of bio-oils produced
residence timesElemental ratios
with various

High reaction temperature (320°C)				
Residence time (min)	O/C	H/C		
20	0.48 ± 0.01	1.02 ± 0.00		
40	0.40 ± 0.01	0.99 ± 0.00		
60	0.85 ± 0.01	1.26 ± 0.00		
80	1.12 ± 0.01	1.20 ± 0.00		
Low reaction temperature (240°C)			Medium reaction temperature (280°C)	
Residence time (min)	O/C	H/C	O/C	H/C
20	0.46 ± 0.01	1.18 ± 0.00	0.61 ± 0.01	1.13 ± 0.00
40	0.57 ± 0.01	1.03 ± 0.00	1.49 ± 0.01	0.99 ± 0.00
60	0.43 ± 0.01	0.60 ± 0.00	0.48 ± 0.01	1.13 ± 0.00
80	0.34 ± 0.01	1.02 ± 0.00	0.51 ± 0.01	1.14 ± 0.00

Table 8-17. Elemental ratios of bio-oils produced with various residence times (continued)

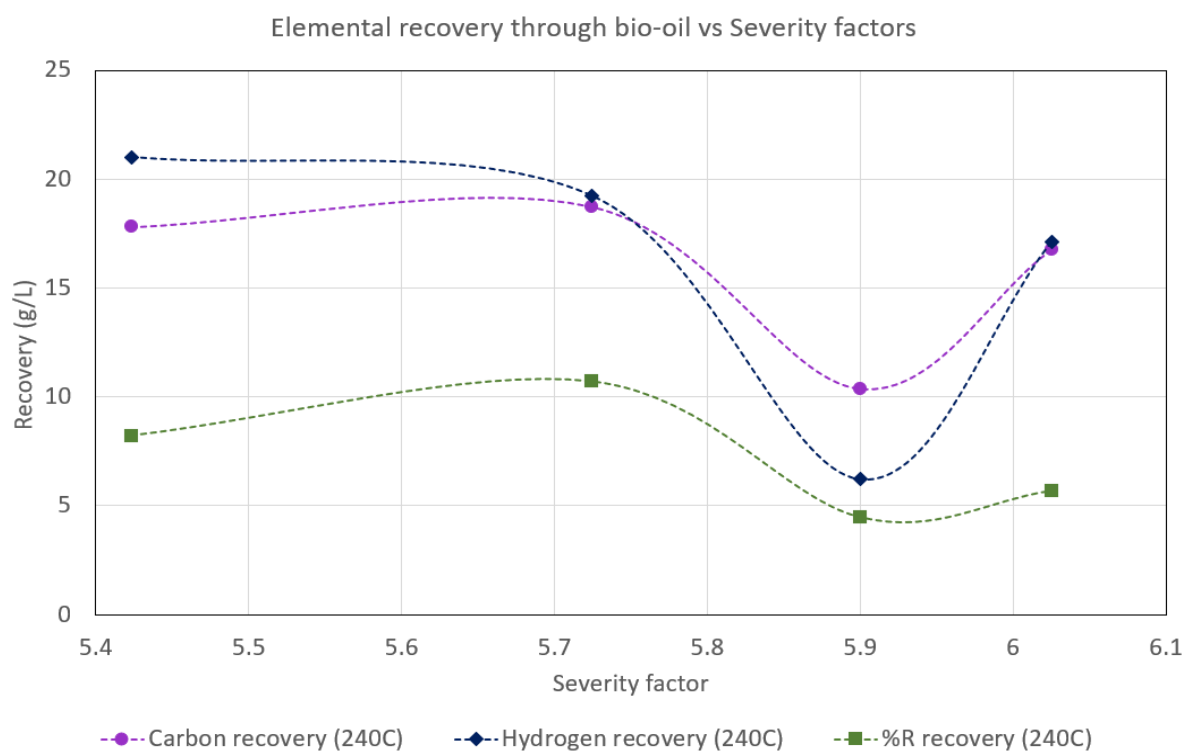


Fig. 105. Elemental composition of bio-oils formed at 240°C reaction temperature

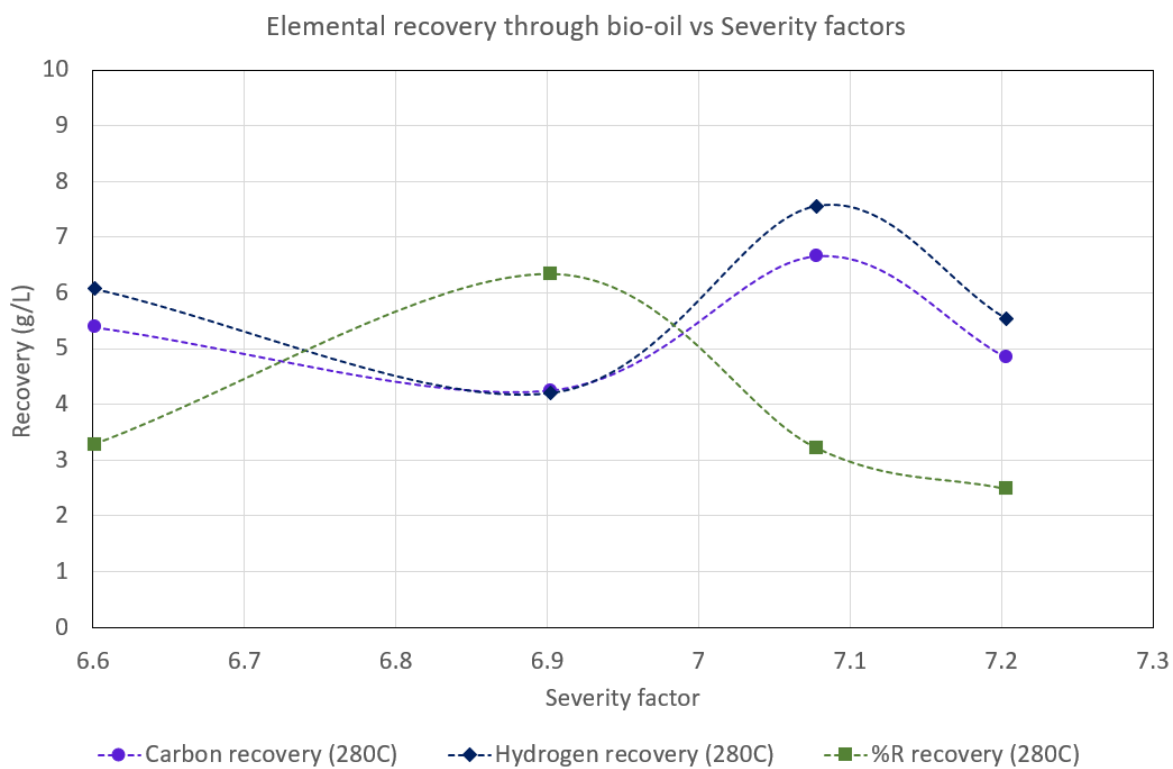


Fig. 106. Elemental composition of bio-oils formed at 280°C reaction temperature

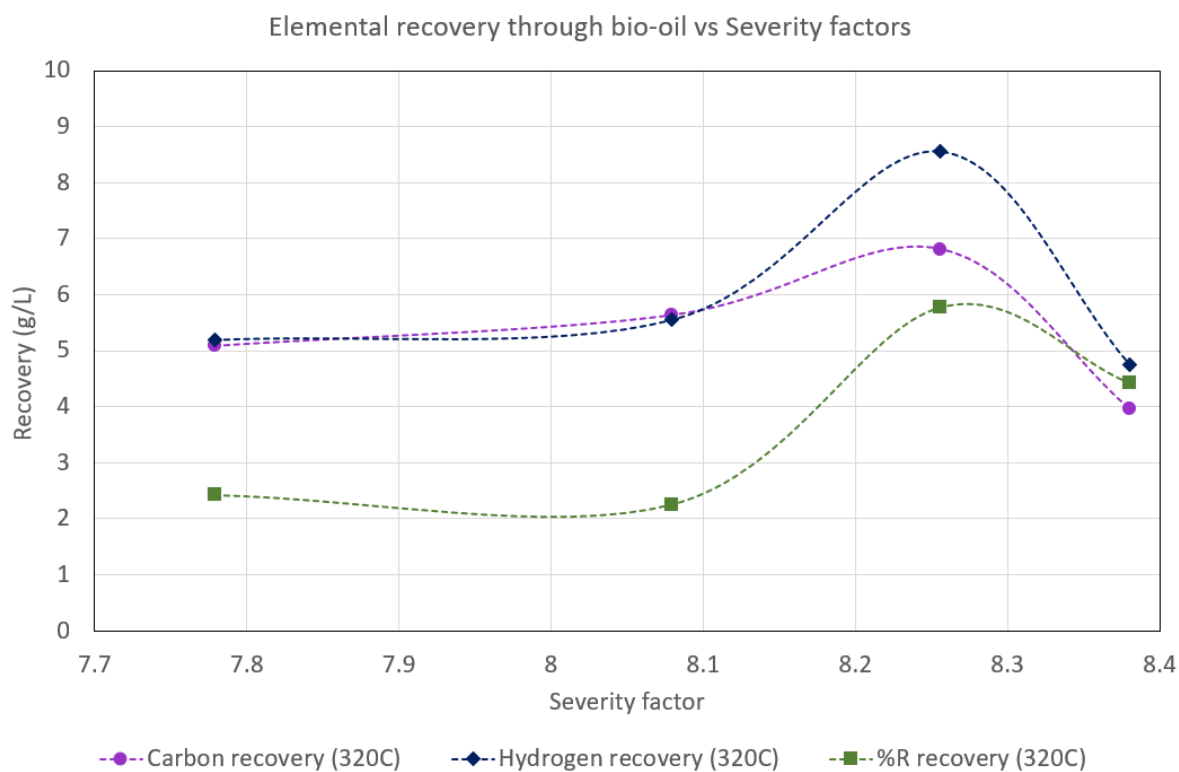


Fig. 107. Elemental composition of bio-oils formed at 320°C reaction temperature

Energy content data

Table 8-18. CVs of bio-oils produced with a low reaction temperature (240°C)

Residence times (min)	CV (MJ/kg)	DOC
Lignex®	11.64 ± 1.48	-
20	25.70 ± 1.48	2.21
40	24.96 ± 1.48	2.14
60	22.54 ± 1.48	1.94
80	25.85 ± 1.48	2.22

Table 8-19. CVs of bio-oils produced with a medium reaction temperature (280°C)

Residence times (min)	CV (MJ/kg)	DOC
Lignex®	11.64 ± 1.48	-
20	16.77 ± 1.48	1.44
40	-	-

60	19.35 ± 1.48	1.66
80	22.12 ± 1.48	1.90

Table 8-20. CVs of bio-oils produced with a high reaction temperature (320°C)

Residence times (min)	CV (MJ/kg)	DOC
Lignex®	11.64 ± 1.48	-
20	-	-
40	19.99 ± 1.48	1.72
60	17.93 ± 1.48	1.54
80	23.55 ± 1.48	2.02

Molecular weight distribution data

Table 8-21. GPC analysis of bio-oils produced at a low temperature (240°C)

Residence time (min)	Mw (g/mol)	Mn (g/mol)	PDI
Lignex®	2468 ± 1	945 ± 1	2.6 ± 0.3
20	767 ± 1	313 ± 1	2.5 ± 0.3
40	740 ± 1	289 ± 1	2.6 ± 0.3
60	673 ± 1	263 ± 1	2.4 ± 0.3
80	506 ± 1	210 ± 1	2.4 ± 0.3

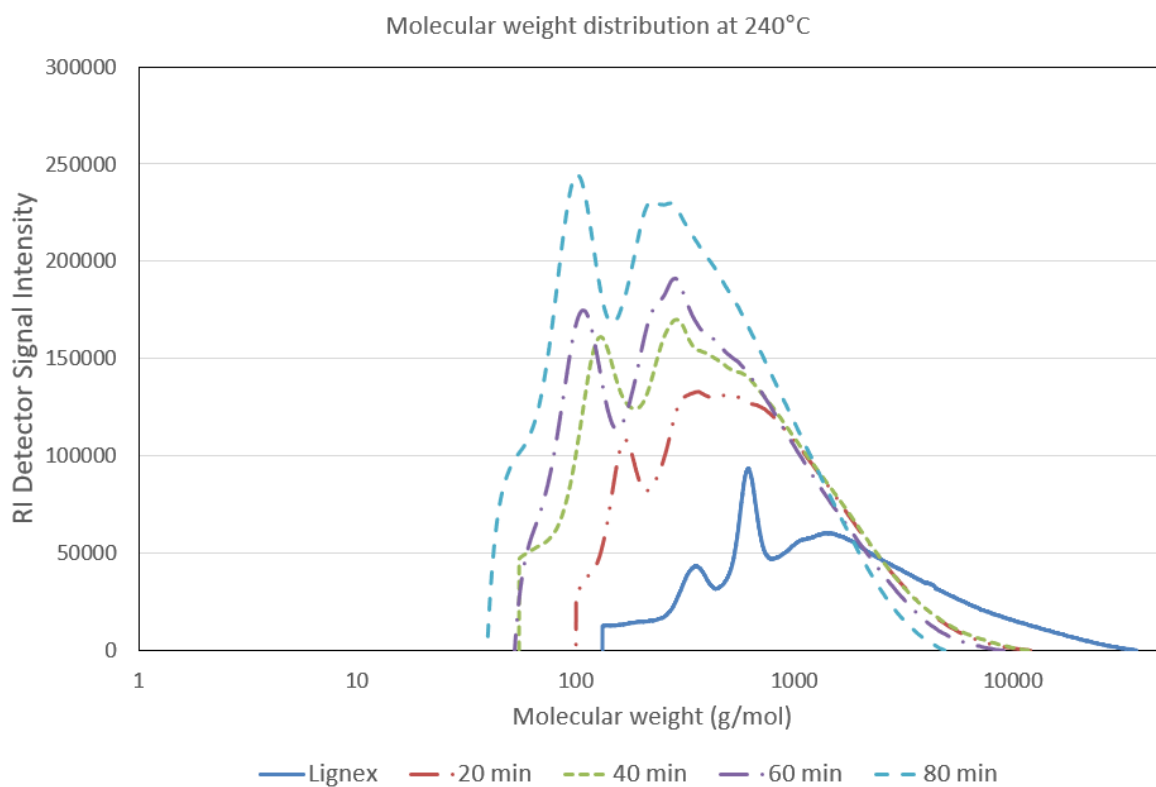


Fig. 108. Molecular weight distribution of bio-oils produced at 240°C

Table 8-22. GPC analysis of bio-oils produced at a medium temperature (280°C)

Residence time (min)	Mw (g/mol)	Mn (g/mol)	PDI
Lignex®	2468 ± 1	945 ± 1	2.6 ± 0.3
20	402 ± 1	167 ± 1	2.4 ± 0.3
40	307 ± 1	157 ± 1	2.0 ± 0.3
60	219 ± 1	131 ± 1	1.7 ± 0.3
80	351 ± 1	186 ± 1	1.9 ± 0.3

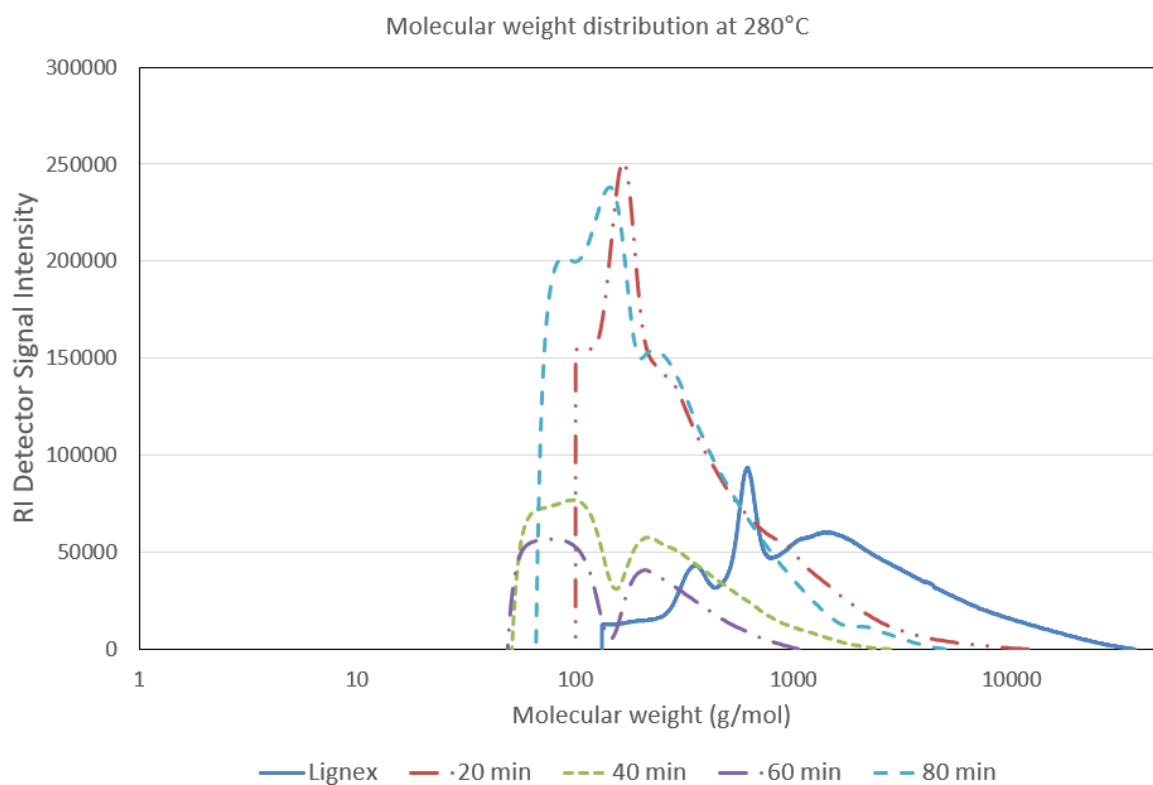


Fig. 109. Molecular weight distribution of bio-oils produced at 280°C

Table 8-23. GPC analysis of bio-oils produced at a high temperature (320°C)

Residence time (min)	Mw (g/mol)	Mn (g/mol)	PDI
Lignex®	2468 ± 1	945 ± 1	2.6 ± 0.3
20	395 ± 1	154 ± 1	2.6 ± 0.3
40	246 ± 1	125 ± 1	2.0 ± 0.3
60	198 ± 1	108 ± 1	1.8 ± 0.3
80	342 ± 1	172 ± 1	2.0 ± 0.3

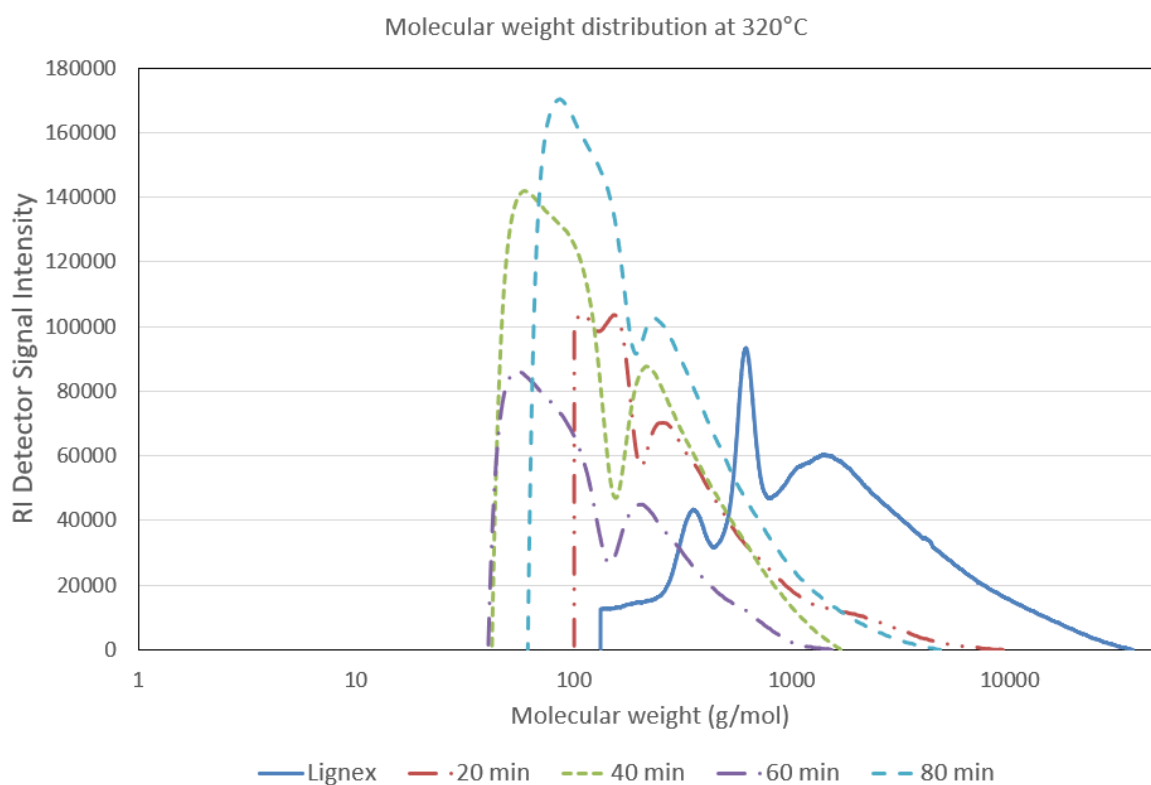


Fig. 110. Molecular weight distribution of bio-oils produced at 320°C

Functional and chemical group data

Table 8-24. Boiling fractions' distribution of bio-oil compounds (240°C)

Compound fractions (%)	20 min	40 min	60 min	80 min
Naphtha	0	0	0	0
Kerosene (± 1.71)	32.48	12.51	10.87	7.95
Diesel boiling (± 0.08)	28.45	56.36	52.85	46.44
Heavy fraction (± 0.37)	38.25	30.80	35.80	41.78

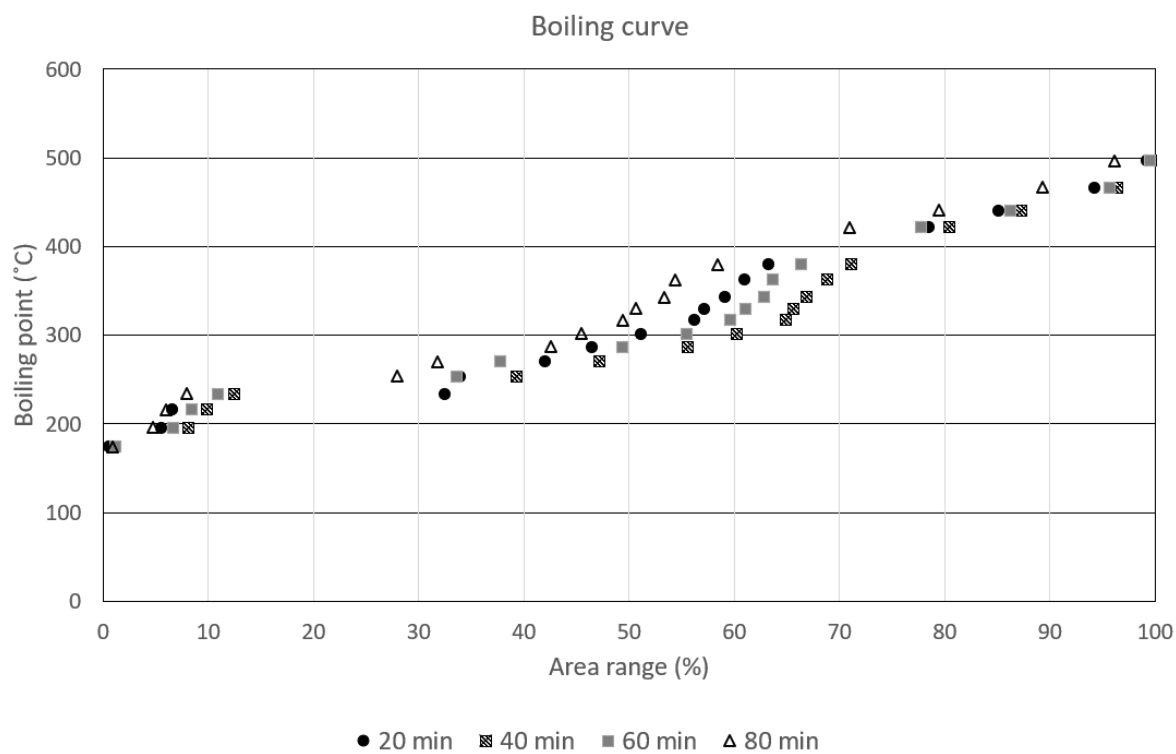


Fig. 111. Simulated distillation curve of bio-oils produced at 240°C

Table 8-25. Boiling fractions' distribution of bio-oil compounds (280°C)

Compound fractions (%)	20 min	40 min	60 min	80 min
Naphtha	0	0	0	0
Kerosene (± 1.71)	5.32	23.64	8.91	9.64
Diesel boiling (± 0.08)	75.92	67.64	72.15	76.12
Heavy fraction (± 0.37)	18.71	8.64	18.68	14.17

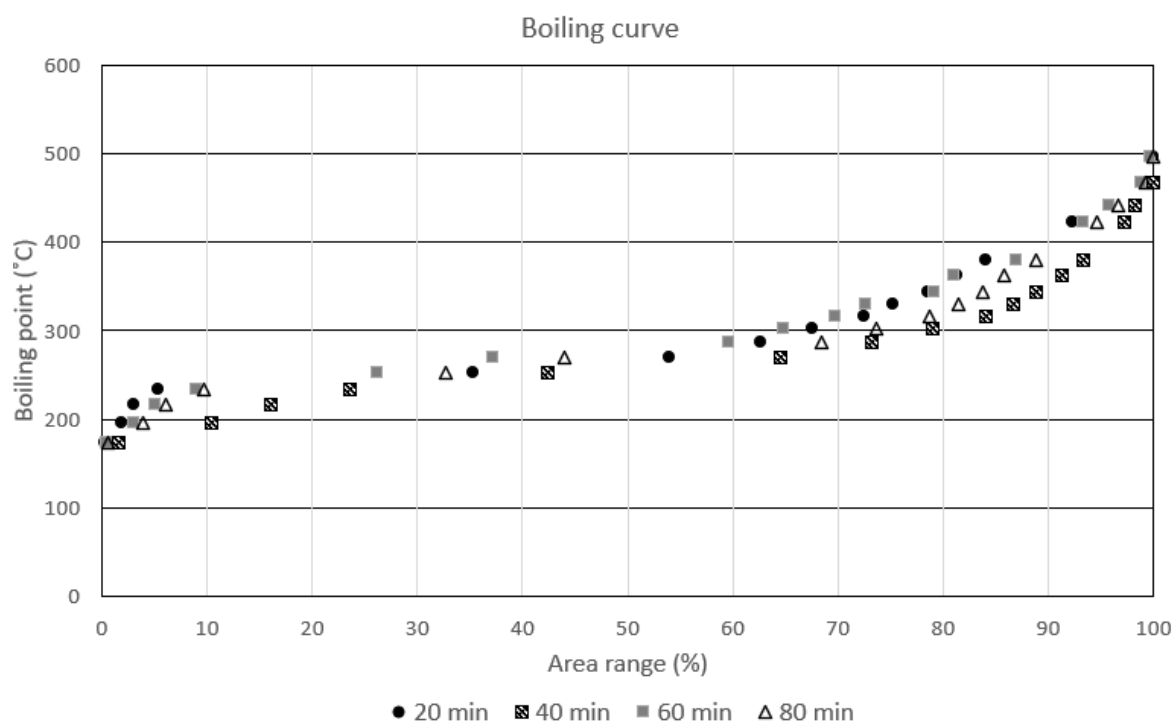


Fig. 112. Simulated distillation curve of bio-oils produced at 280°C

Table 8-26. Boiling fractions' distribution of bio-oil compounds (320°C)

Compound fractions (%)	20 min	40 min	60 min	80 min
Naphtha	0	0	0	0
Kerosene (± 1.71)	15.58	10.48	8.91	7.26
Diesel boiling (± 0.08)	77.73	75.59	71.95	65.27
Heavy fraction (± 0.37)	6.67	13.92	19.10	27.39

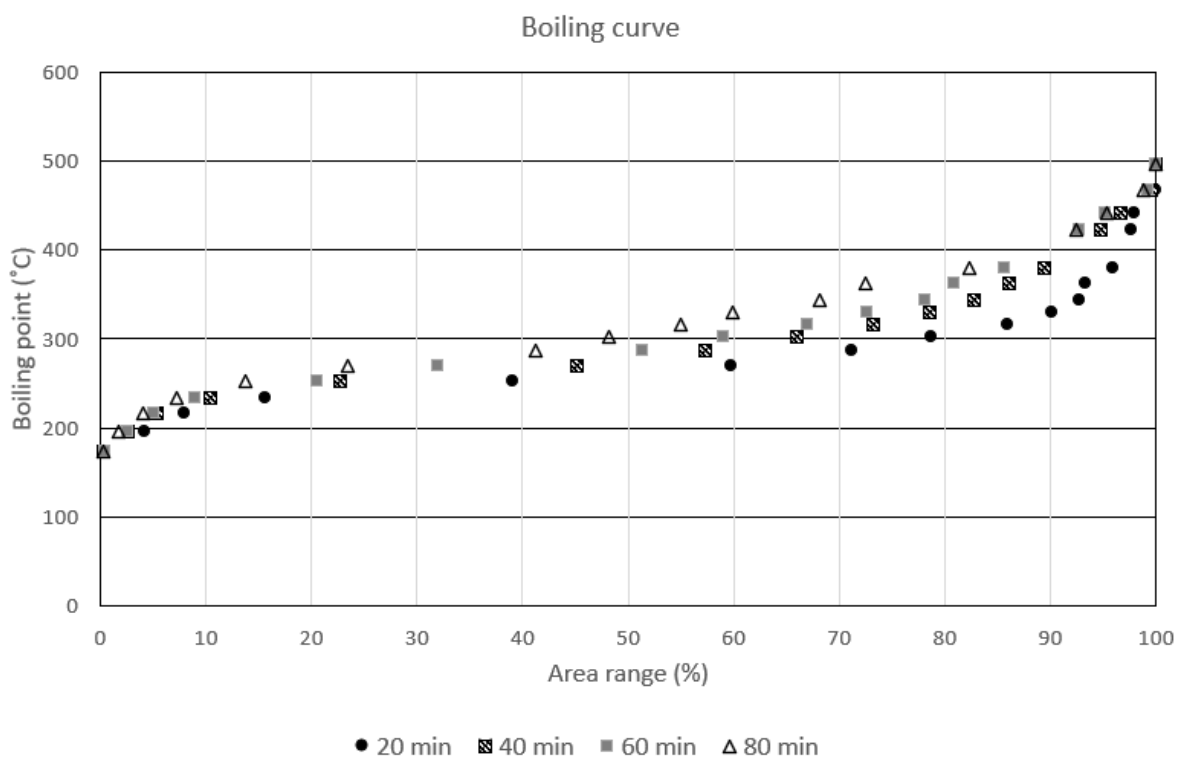


Fig. 113. Simulated distillation curve of bio-oils produced at 320°C

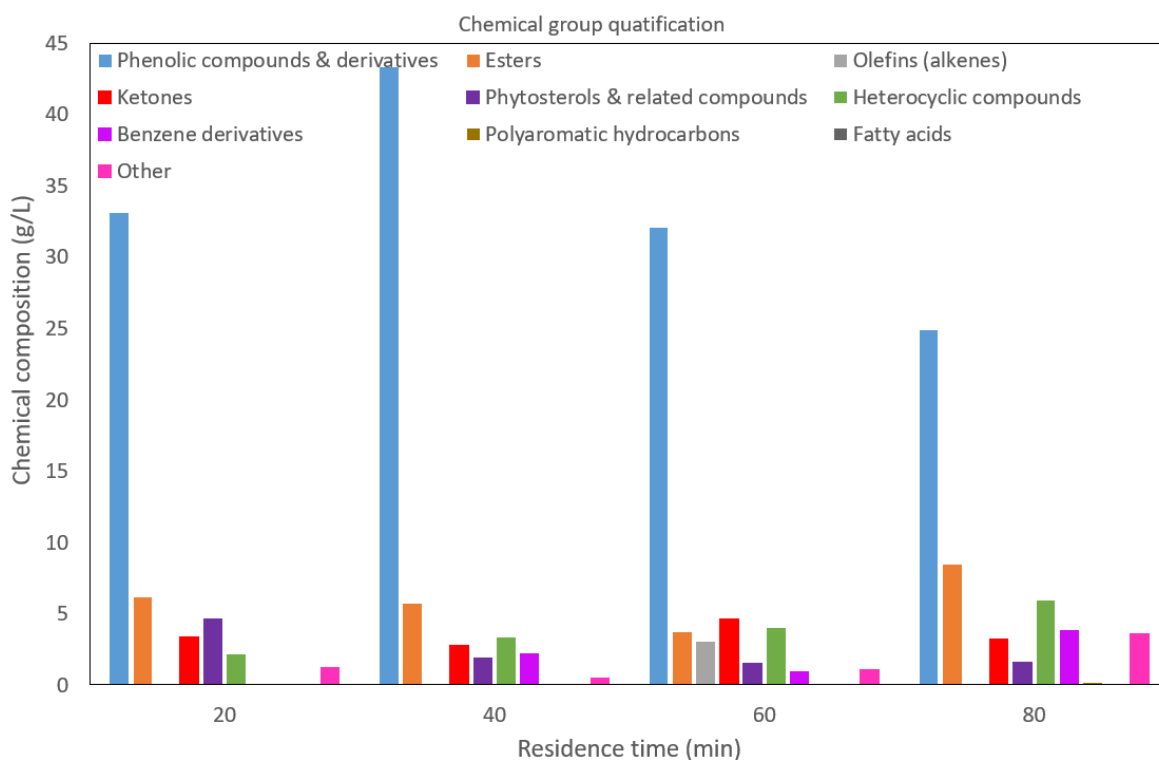


Fig. 114. Quantification of chemical groups that are present in bio-oils produced at 240°C

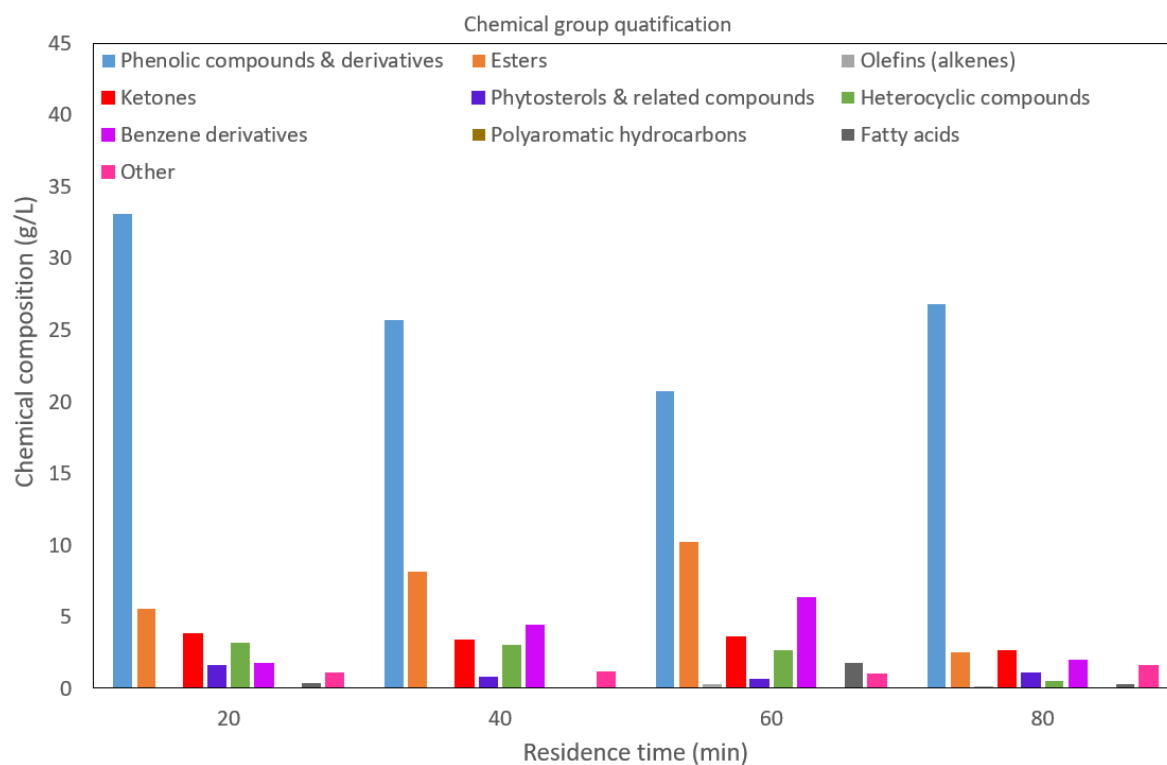


Fig. 115. Quantification of chemical groups that are present in bio-oils produced at 280°C

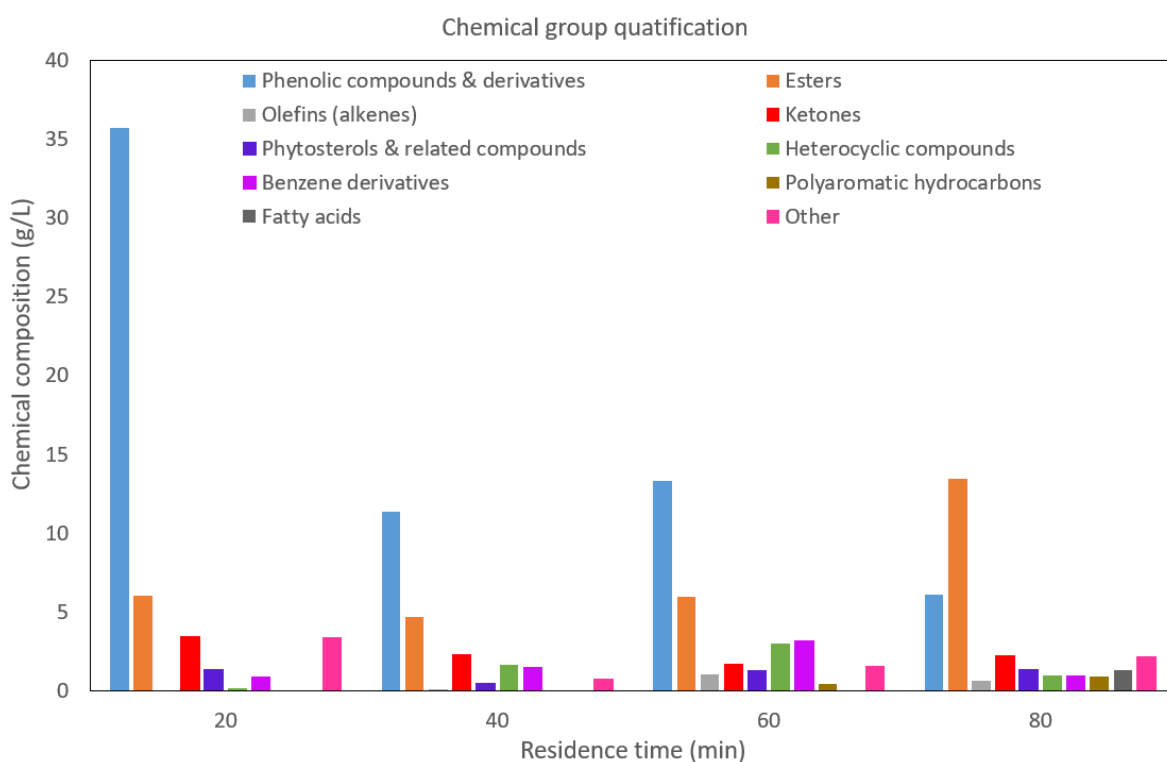


Fig. 116. Quantification of chemical groups that are present in bio-oils produced at 320°C

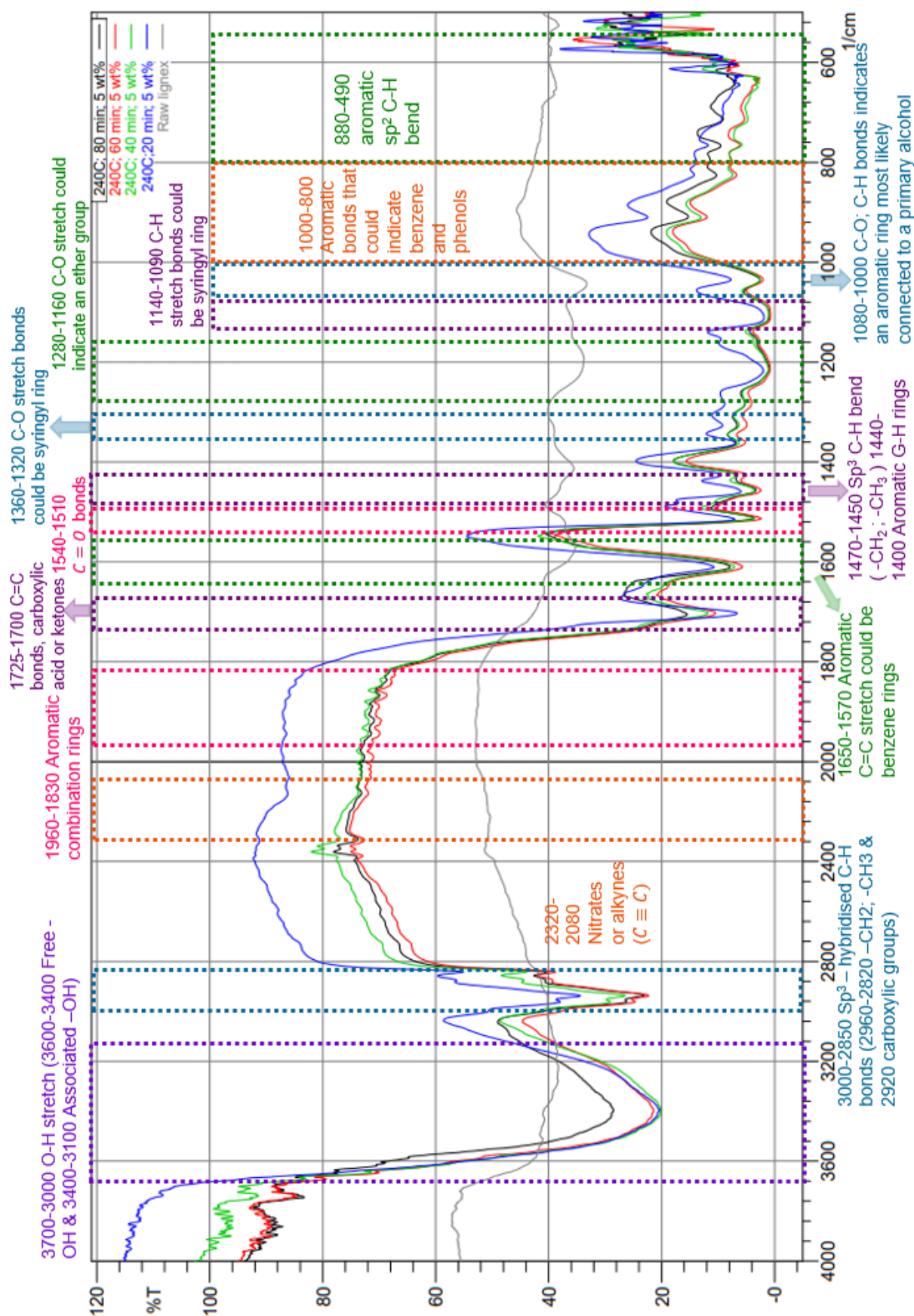


Fig. 117. FTIR spectrum of all bio-oils produced at 240°C

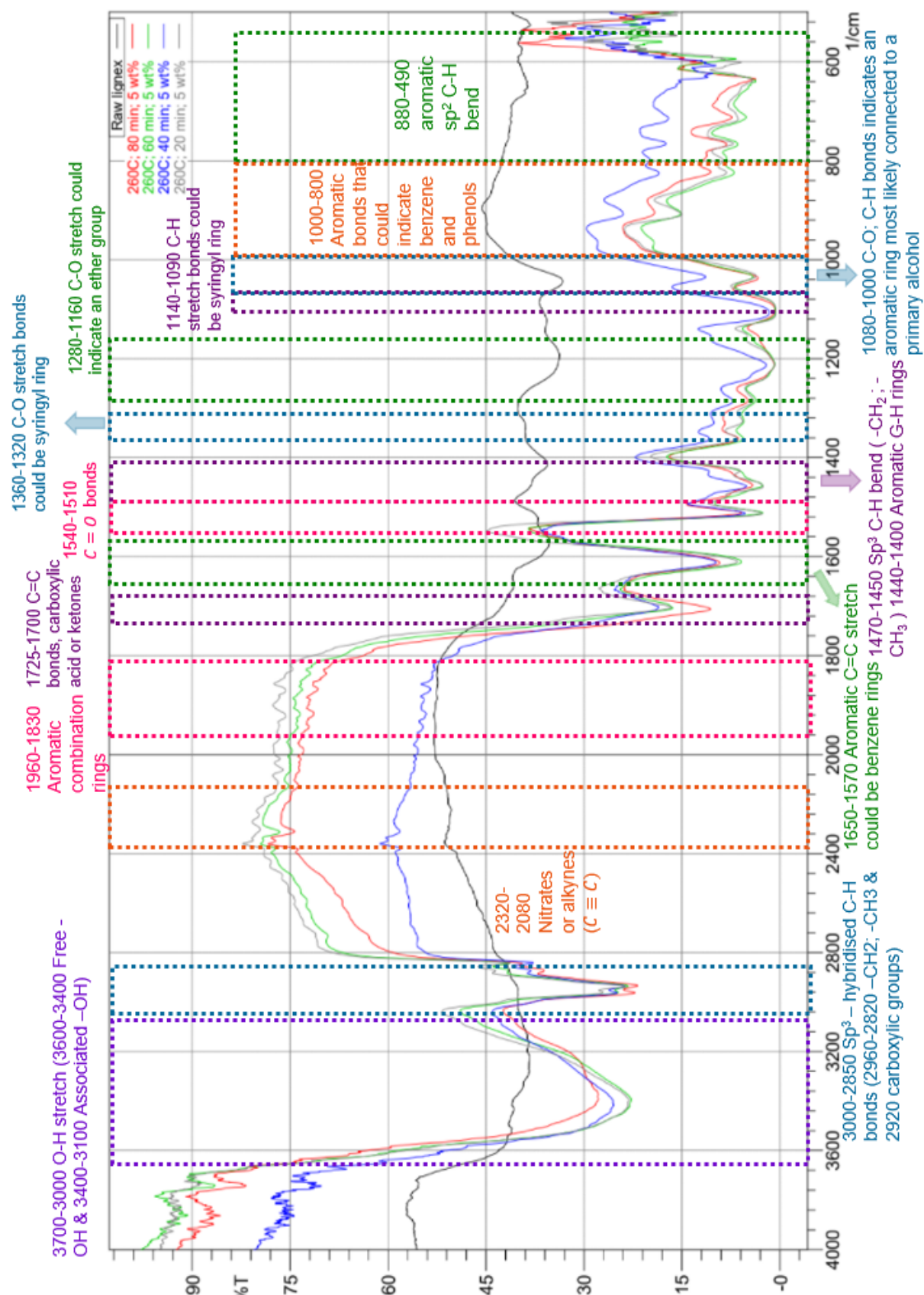


Fig. 118. FTIR spectrum of all bio-oils produced at 260°C

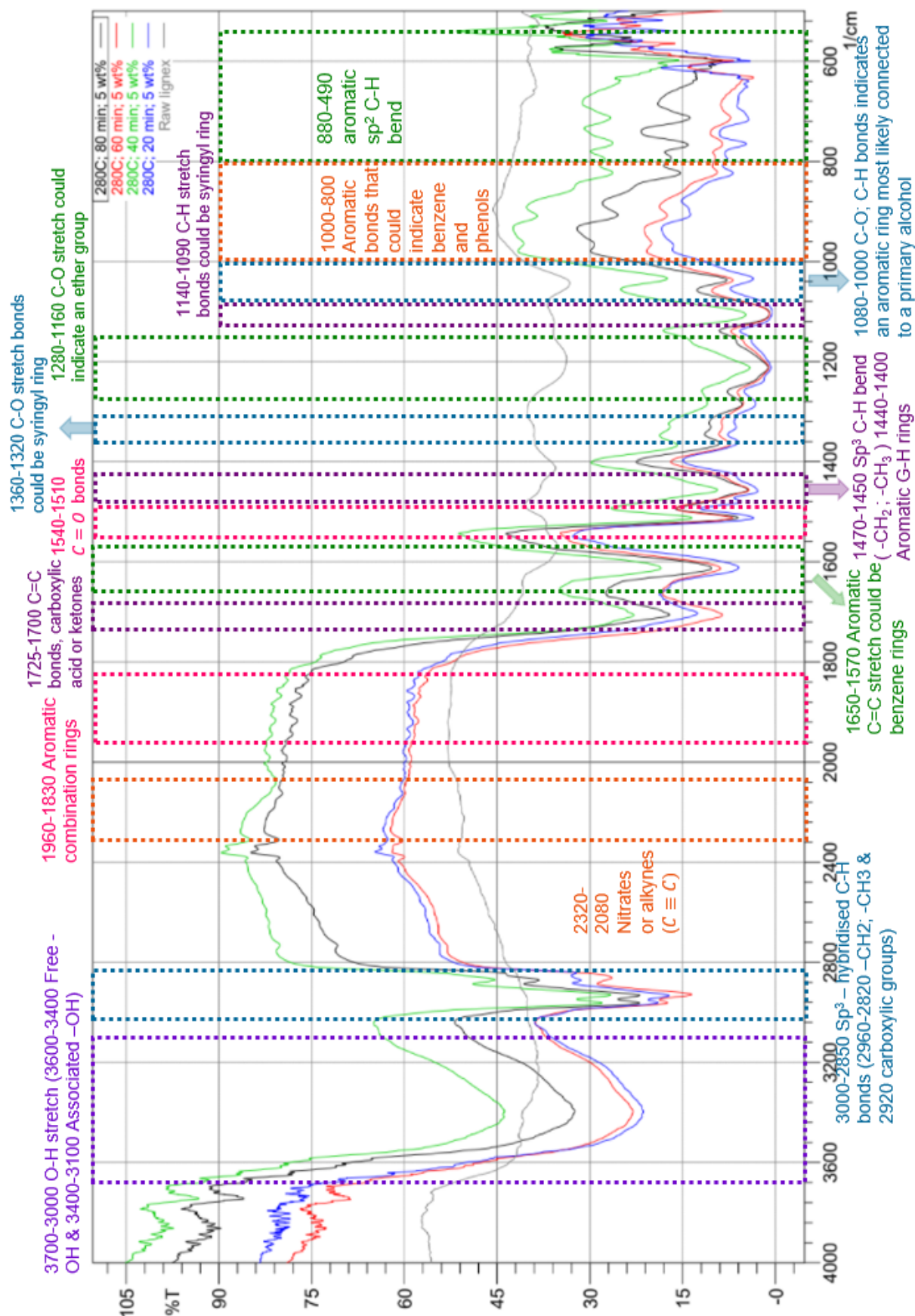


Fig. 119. FTIR spectrum of all bio-oils produced at 280°C

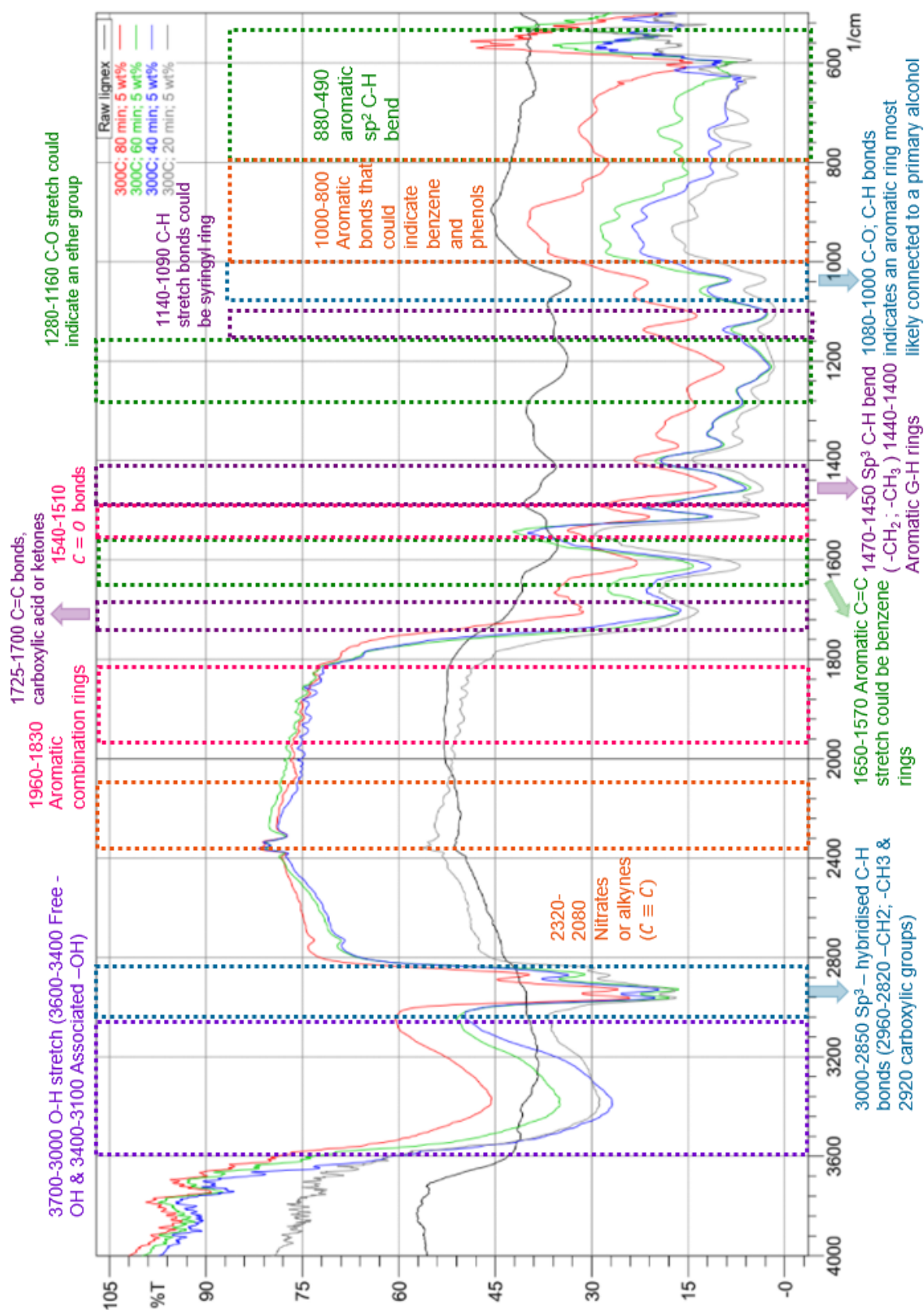


Fig. 120. FTIR spectrum of all bio-oils produced at 300°C

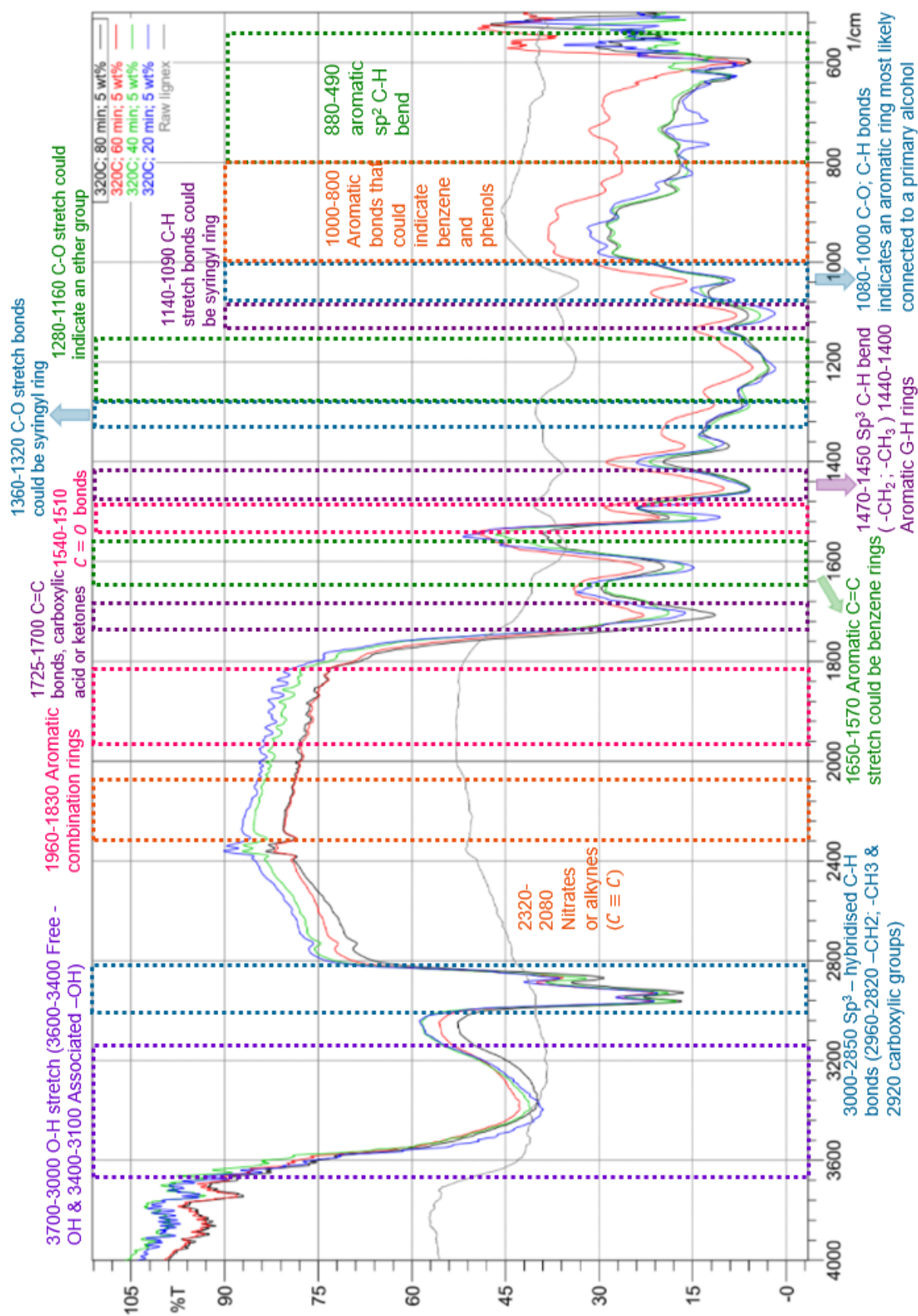


Fig. 121. FTIR spectrum of all bio-oils produced at 320°C

Elemental data for catalyst loading

Table 8-27 . Elemental composition of bio-oils produced at various catalyst loadings

Catalyst loading	Carbon (mass%)	Hydrogen (mass%)	%R (mass%)
2 mass%	4.61 ± 0.53	5.01 ± 0.26	2.42 ± 0.71
3 mass%	4.44 ± 0.53	4.53 ± 0.26	2.65 ± 0.71
4 mass%	5.11 ± 0.53	5.23 ± 0.26	1.92 ± 0.71
5 mass%	6.28 ± 0.53	6.36 ± 0.26	2.11 ± 0.71
6 mass%	6.00 ± 0.53	6.00 ± 0.26	3.15 ± 0.71

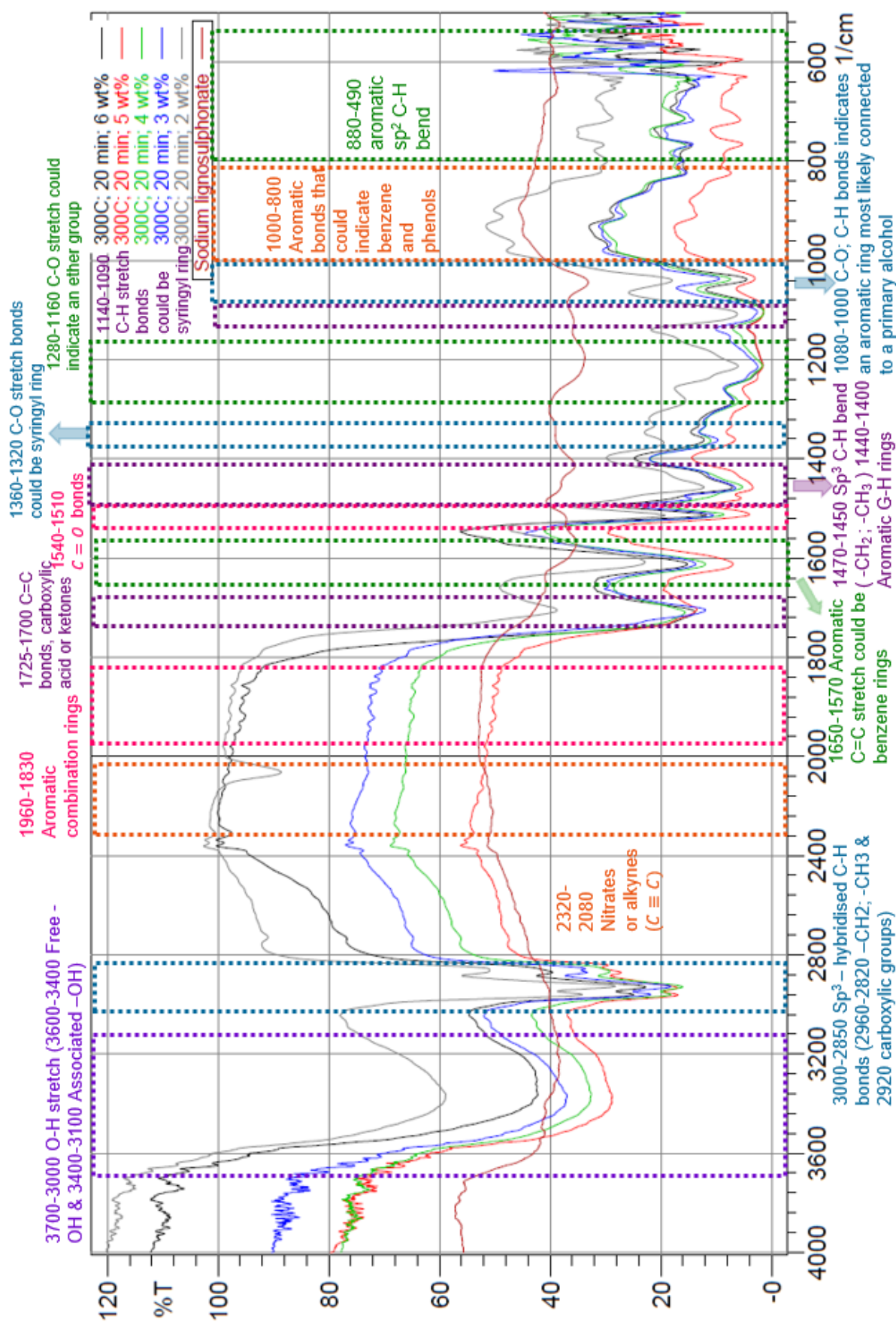


Fig. 122. FTIR spectrum of all bio-oils produced with various catalyst loadings

9 Appendix C: Additional data for biochar

9.1 Biochar quality

Biochar proximate analysis

Table 9-1. Proximate results of biochar produced with a 20 min reaction time

Temperature	% Moisture (± 0.50)	% Solids (± 0.03)	% Volatiles (± 0.07)	% Ash (± 1.14)	% Fixed carbon (± 0.20)
Lignex®	2.88	97.12	53.23	32.70	10.78
240°C	6.04	93.96	41.44	18.27	34.25
260°C	8.85	91.15	38.15	16.04	36.96
280°C	5.91	94.09	34.92	12.66	46.51
300°C	9.27	90.73	32.91	14.00	43.82
320°C	10.48	89.52	31.55	14.17	43.80

Table 9-2. Proximate results of biochar produced with a 40 min reaction time

Temperature	% Moisture (± 0.50)	% Solids (± 0.03)	% Volatiles (± 0.07)	% Ash (± 1.14)	% Fixed carbon (± 0.20)
Lignex®	2.88	97.12	53.23	32.70	10.78
240°C	6.00	94.00	40.22	19.58	34.20
260°C	4.16	95.84	37.10	16.14	42.61
280°C	7.32	92.68	34.49	16.42	41.77
300°C	7.53	92.47	31.19	16.38	44.90
320°C	8.60	91.40	30.62	14.23	46.55

Table 9-3. Proximate results of biochar produced with a 60 min reaction time

Temperature	% Moisture (± 0.50)	% Solids (± 0.03)	% Volatiles (± 0.07)	% Ash (± 1.14)	% Fixed carbon (± 0.20)
-------------	------------------------------	----------------------------	-------------------------------	-------------------------	-------------------------------------

Lignex®	2.88	97.12	53.23	32.70	10.78
240°C	5.75	94.25	39.06	17.81	37.38
260°C	6.30	93.70	33.87	15.93	43.90
280°C	6.49	93.51	32.82	14.29	46.40
300°C	7.16	92.84	32.48	15.59	44.76
320°C	5.77	94.23	30.23	15.23	48.77

Table 9-4. Proximate results of biochar produced with an 80 min reaction time

Temperature	% Moisture (± 0.50)	% Solids (± 0.03)	% Volatiles (± 0.07)	% Ash (± 1.14)	% Fixed carbon (± 0.20)
Lignex®	2.88	97.12	53.23	32.70	10.78
240°C	3.75	96.25	39.84	15.13	41.28
260°C	7.66	92.34	34.50	13.95	43.89
280°C	5.77	94.23	32.94	14.11	47.19
300°C	10.40	89.60	30.23	18.48	40.88
320°C	5.73	94.27	31.26	15.14	47.87

Table 9-5. Proximate results of biochar produced with varying catalyst loading

Temperature	% Moisture (± 0.50)	% Solids (± 0.03)	% Volatiles (± 0.07)	% Ash (± 1.14)	% Fixed carbon (± 0.20)
Lignex®	2.88	97.12	53.23	32.70	10.78
240°C	6.38	93.62	37.59	7.49	48.54
260°C	5.91	94.09	35.96	6.24	51.89
280°C	5.62	94.38	35.05	6.71	52.62
300°C	4.99	95.01	33.89	6.34	54.77
320°C	4.70	95.30	32.21	5.97	57.12

Elemental composition data

Table 9-6. Elemental composition of biochar produced at a residence time of 20 min

Temperature (°C)	Carbon (mass%)	Hydrogen (mass%)	%R (mass%)
240	66.79 ± 0.31	53.96 ± 0.34	83.57 ± 0.14
260	59.47 ± 0.31	45.81 ± 0.34	78.48 ± 0.14
280	59.53 ± 0.31	32.48 ± 0.34	79.45 ± 0.14
300	59.12 ± 0.31	37.66 ± 0.34	71.41 ± 0.14
320	58.46 ± 0.31	30.45 ± 0.34	80.23 ± 0.14

Table 9-7. Elemental composition of biochar produced at a residence time of 40 min

Temperature (°C)	Carbon (mass%)	Hydrogen (mass%)	%R (mass%)
240	41.79 ± 0.31	31.50 ± 0.34	71.46 ± 0.14
260	53.13 ± 0.31	25.80 ± 0.34	78.25 ± 0.14
280	41.75 ± 0.31	23.00 ± 0.34	71.61 ± 0.14
300	63.63 ± 0.31	32.15 ± 0.34	66.87 ± 0.14
320	60.35 ± 0.31	29.50 ± 0.34	64.43 ± 0.14

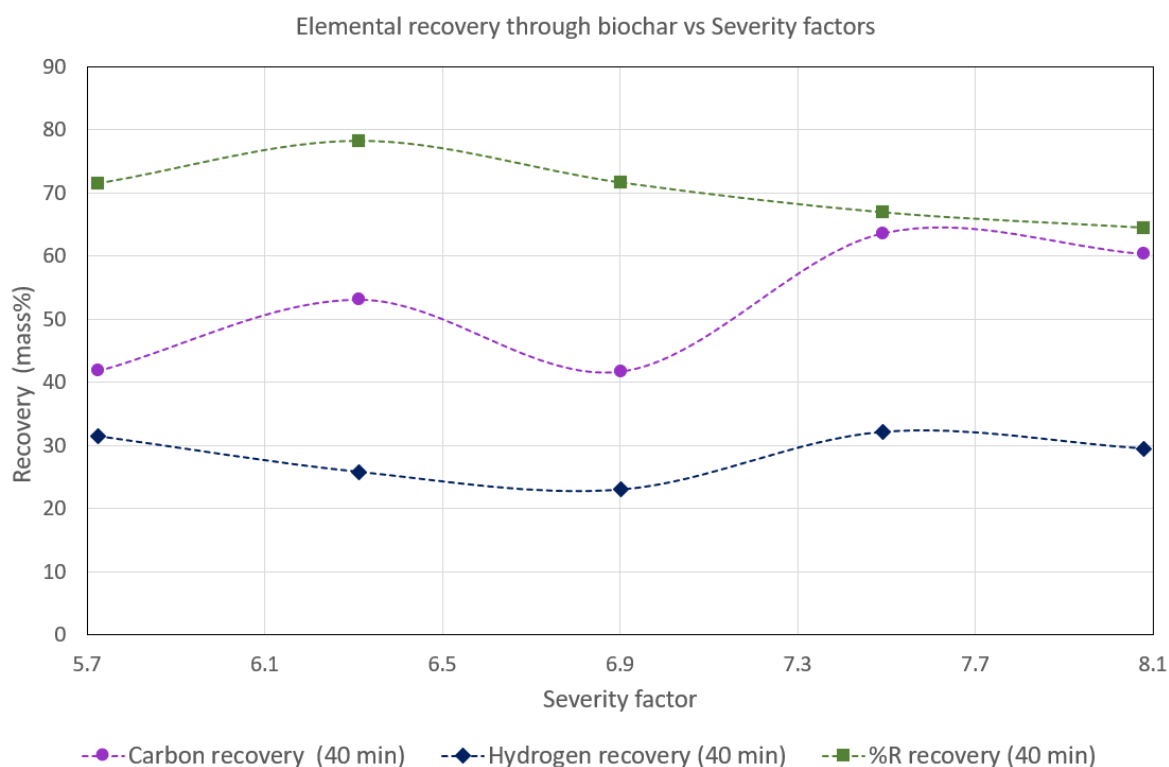


Fig. 123. Elemental recovery through biochars produced with 40 min residence times

Table 9-8. Elemental composition of biochar produced at a residence time of 60 min

Temperature (°C)	Carbon (mass%)	Hydrogen (mass%)	%R (mass%)
240	40.83 ± 0.31	26.49 ± 0.34	78.55 ± 0.14
260	54.59 ± 0.31	28.32 ± 0.34	68.50 ± 0.14
280	39.18 ± 0.31	16.28 ± 0.34	80.22 ± 0.14
300	67.20 ± 0.31	31.98 ± 0.34	82.42 ± 0.14
320	60.21 ± 0.31	26.23 ± 0.34	79.84 ± 0.14

Table 9-9. Elemental composition of biochar produced at a residence time of 80 min

Temperature (°C)	Carbon (mass%)	Hydrogen (mass%)	%R (mass%)
240	59.25 ± 0.31	37.64 ± 0.34	87.77 ± 0.14
260	72.01 ± 0.31	36.02 ± 0.34	83.69 ± 0.14
280	70.26 ± 0.31	30.95 ± 0.34	81.95 ± 0.14
300	60.91 ± 0.31	29.83 ± 0.34	72.72 ± 0.14
320	64.83 ± 0.31	30.54 ± 0.34	79.18 ± 0.14

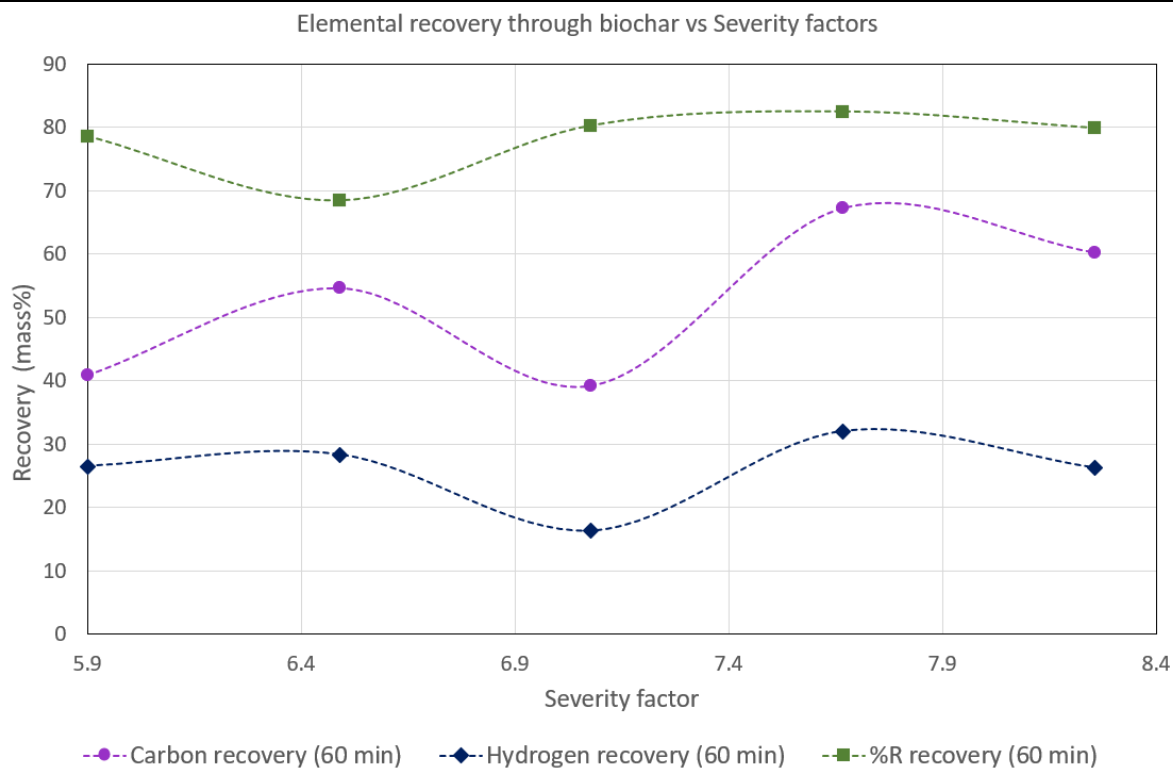


Fig. 124. Elemental recovery through biochars produced with 60 min residence times

Additional energy content

Table 9-10. Energy content of biochars produced with a residence time of 40 min

Temperature	CV (MJ/kg)	DOC
Lignex®	11.64 ± 1.48	-
240°C	12.32 ± 1.48	1.06
260°C	13.53 ± 1.48	1.16
280°C	12.80 ± 1.48	1.10
300°C	13.09 ± 1.48	1.12
320°C	12.39 ± 1.48	1.06

Table 9-11. Energy content of biochars produced with a residence time of 60 min

Temperature	CV (MJ/kg)	DOC
Lignex®	11.64 ± 1.48	-
240°C	10.16 ± 1.48	0.87
260°C	11.23 ± 1.48	0.96
280°C	10.49 ± 1.48	0.90
300°C	11.67 ± 1.48	1.00
320°C	13.11 ± 1.48	1.13

Elemental composition data

Table 9-12. Elemental composition of biochar produced at 240°C

Residence time (min))	Carbon (mass%)	Hydrogen (mass%)	%R (mass%)
20	66.79 ± 0.31	53.96 ± 0.34	83.57 ± 0.14
40	41.79 ± 0.31	31.50 ± 0.34	71.46 ± 0.14
60	40.83 ± 0.31	26.49 ± 0.34	78.55 ± 0.14
80	59.25 ± 0.31	37.64 ± 0.34	87.77 ± 0.14

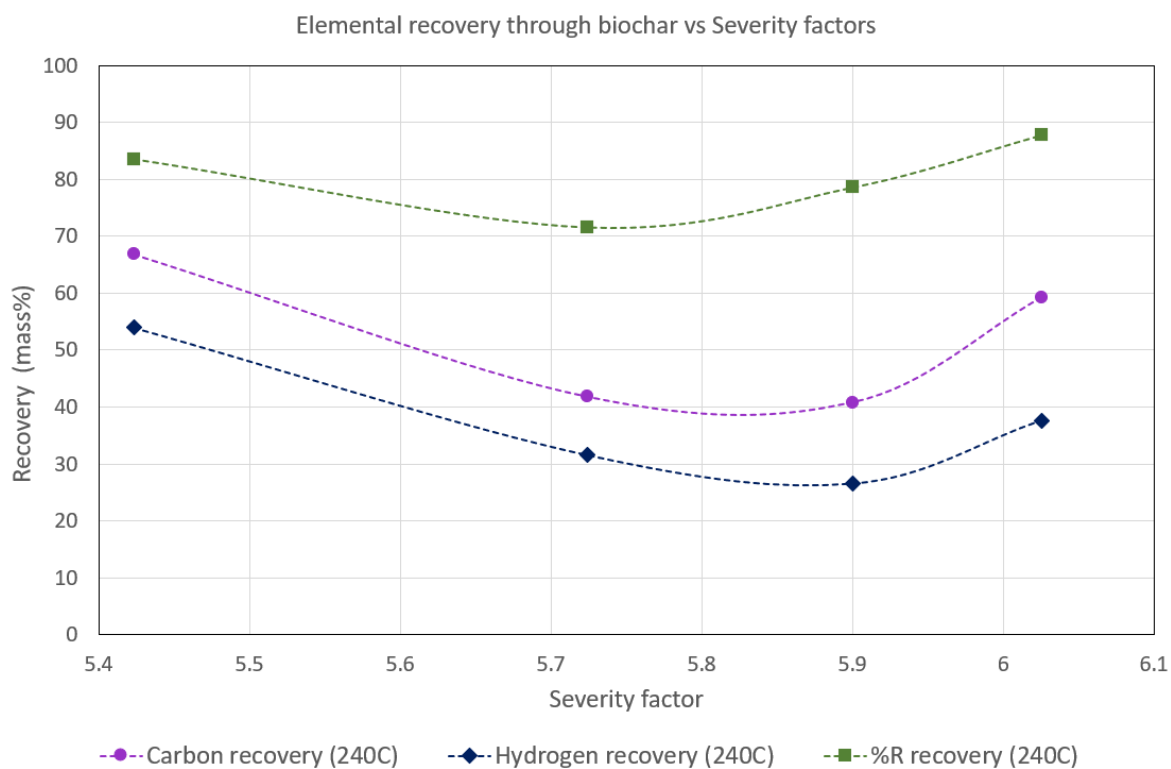


Fig. 125. Elemental recovery through biochars produced at 240°C

Table 9-13. Elemental composition of biochar produced at 280°C

Residence time (min))	Carbon (mass%)	Hydrogen (mass%)	%R (mass%)
20	59.53 ± 0.31	32.48 ± 0.34	79.45 ± 0.14
40	41.75 ± 0.31	23.00 ± 0.34	71.61 ± 0.14
60	39.18 ± 0.31	16.28 ± 0.34	80.22 ± 0.14
80	70.26 ± 0.31	30.95 ± 0.34	81.95 ± 0.14

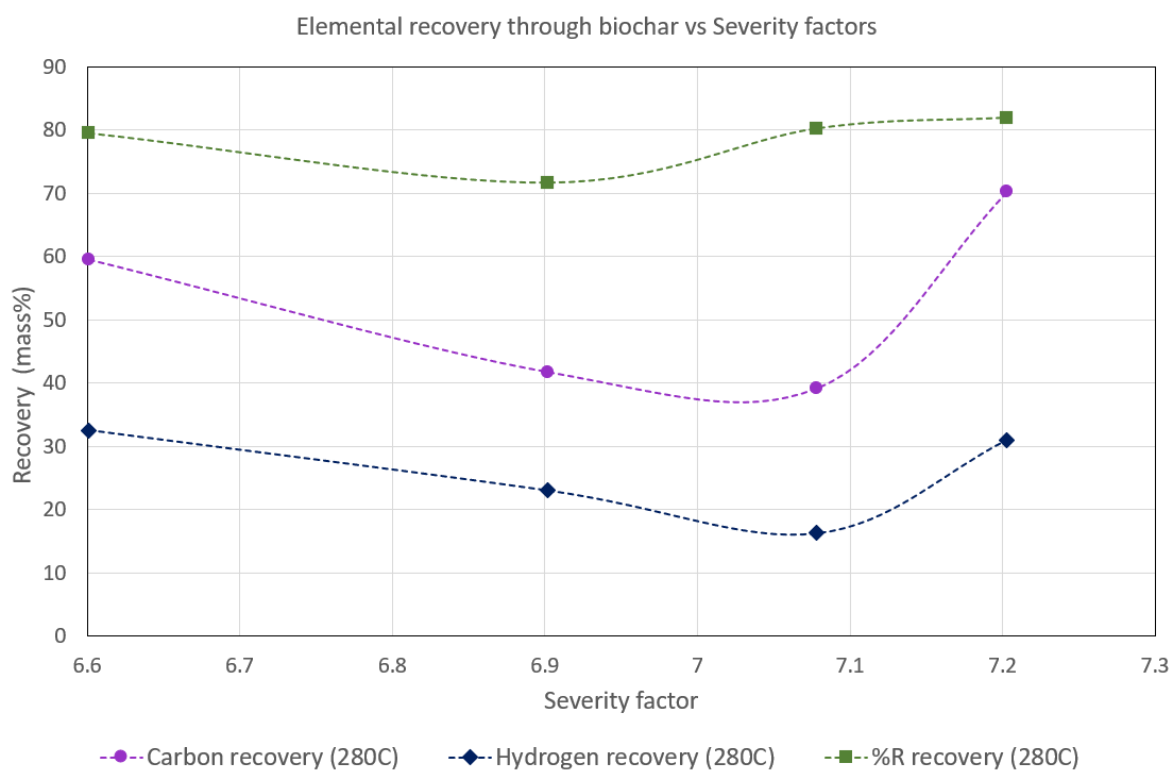
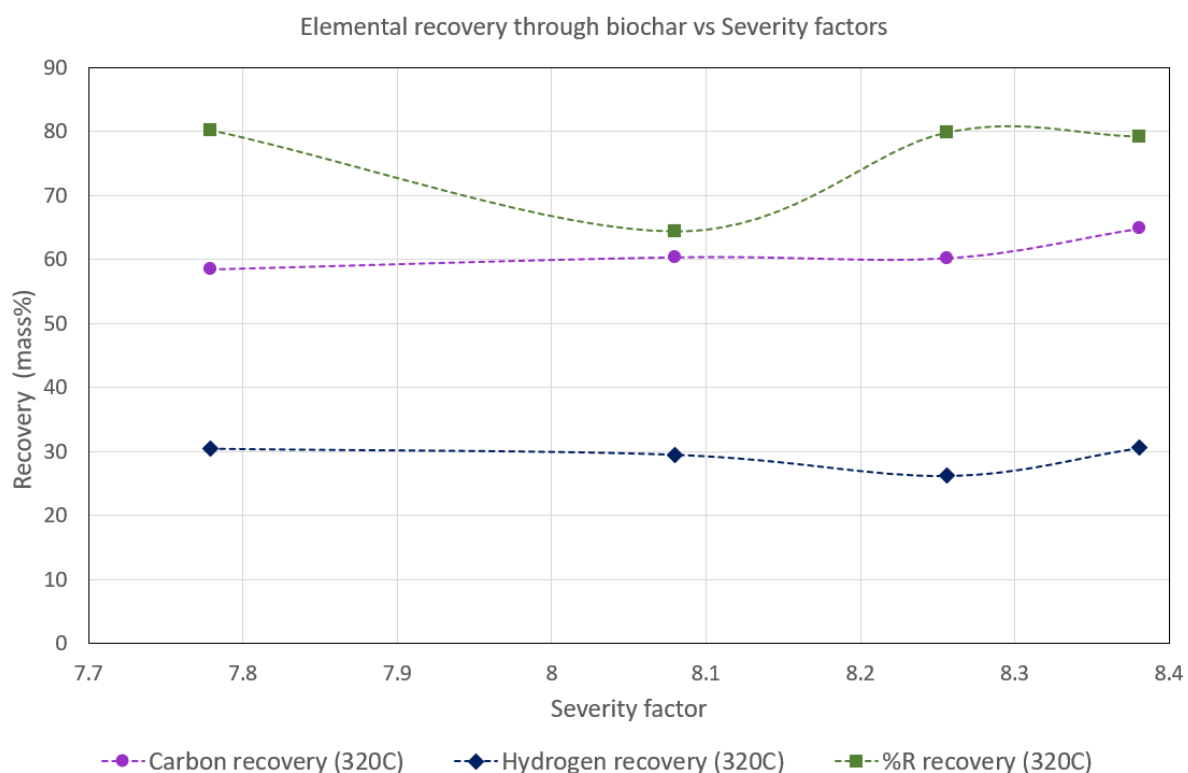


Fig. 126. Elemental recovery through biochars produced at 280°C

Table 9-14. Elemental composition of biochar produced at 320°C

Residence time (min))	Carbon (mass%)	Hydrogen (mass%)	%R (mass%)
20	58.46 ± 0.31	30.45 ± 0.34	80.23 ± 0.14
40	60.35 ± 0.31	29.50 ± 0.34	64.43 ± 0.14
60	60.21 ± 0.31	26.23 ± 0.34	79.84 ± 0.14
80	64.83 ± 0.31	30.54 ± 0.34	79.18 ± 0.14



Additional energy content

Table 9-15. Energy content of biochars produced at 240°C

Residence time (min)	CV (MJ/kg)	DOC
Lignex®	11.64 ± 1.48	-
20	13.05 ± 1.48	1.12
40	12.32 ± 1.48	1.06
60	10.16 ± 1.48	0.87
80	10.61 ± 1.48	0.91

Table 9-16. Energy content of biochars produced at 280°C

Residence time (min)	CV (MJ/kg)	DOC
Lignex®	11.64 ± 1.48	-
20	13.64 ± 1.48	1.17
40	12.80 ± 1.48	1.10
60	10.49 ± 1.48	0.90

80	11.45± 1.48	0.98
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Table 9-17. Energy content of biochars produced at 320°C

Residence time (min)	CV (MJ/kg)	DOC
Lignex®	11.64 ± 1.48	-
20	13.27 ± 1.48	1.14
40	12.39 ± 1.48	1.06
60	13.11 ± 1.48	1.13
80	12.62 ± 1.48	1.08

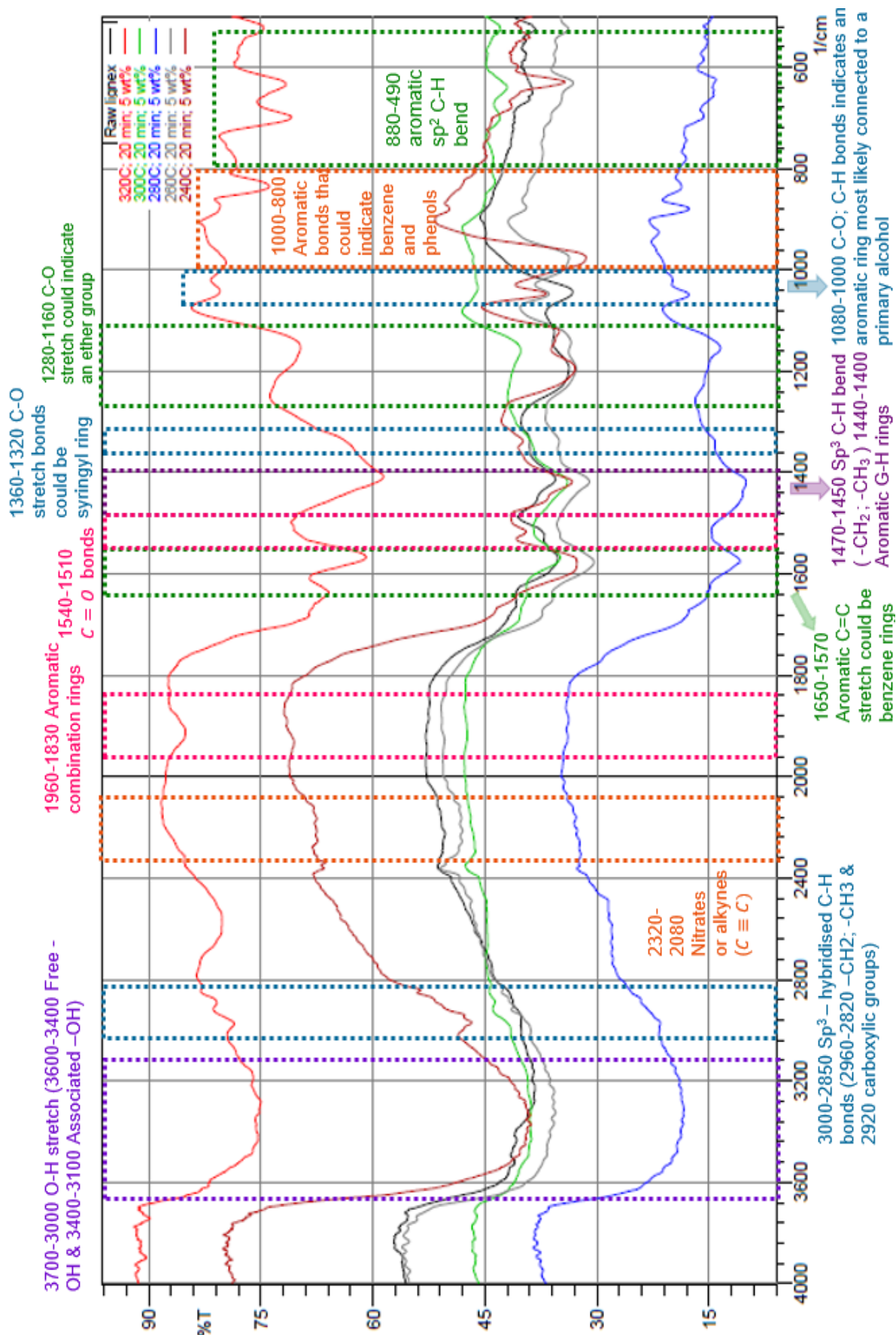


Fig. 128. FTIR spectra of biochars produced with a 20 min residence time

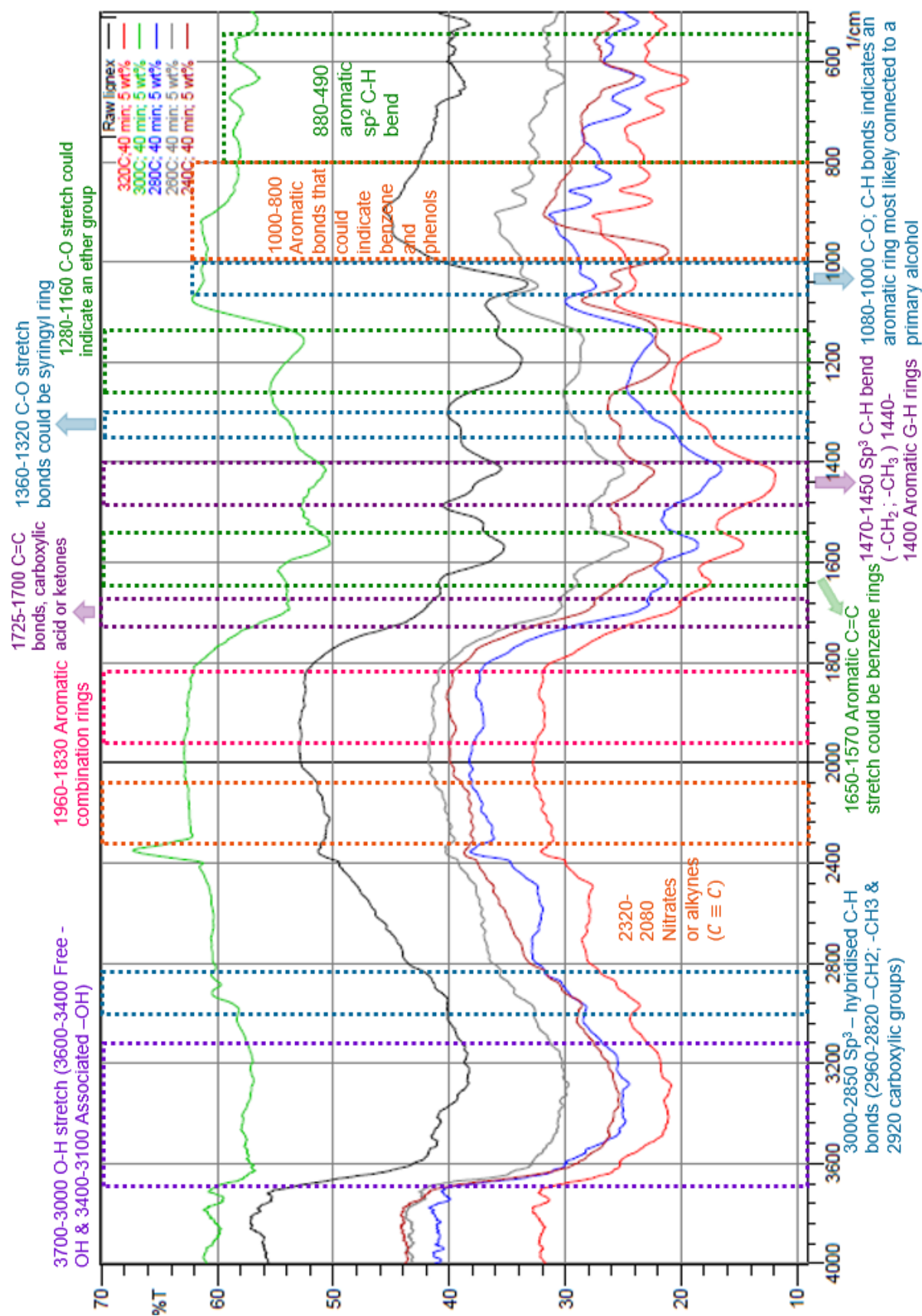


Fig. 129. FTIR spectra of biochars produced with a 40 min residence time

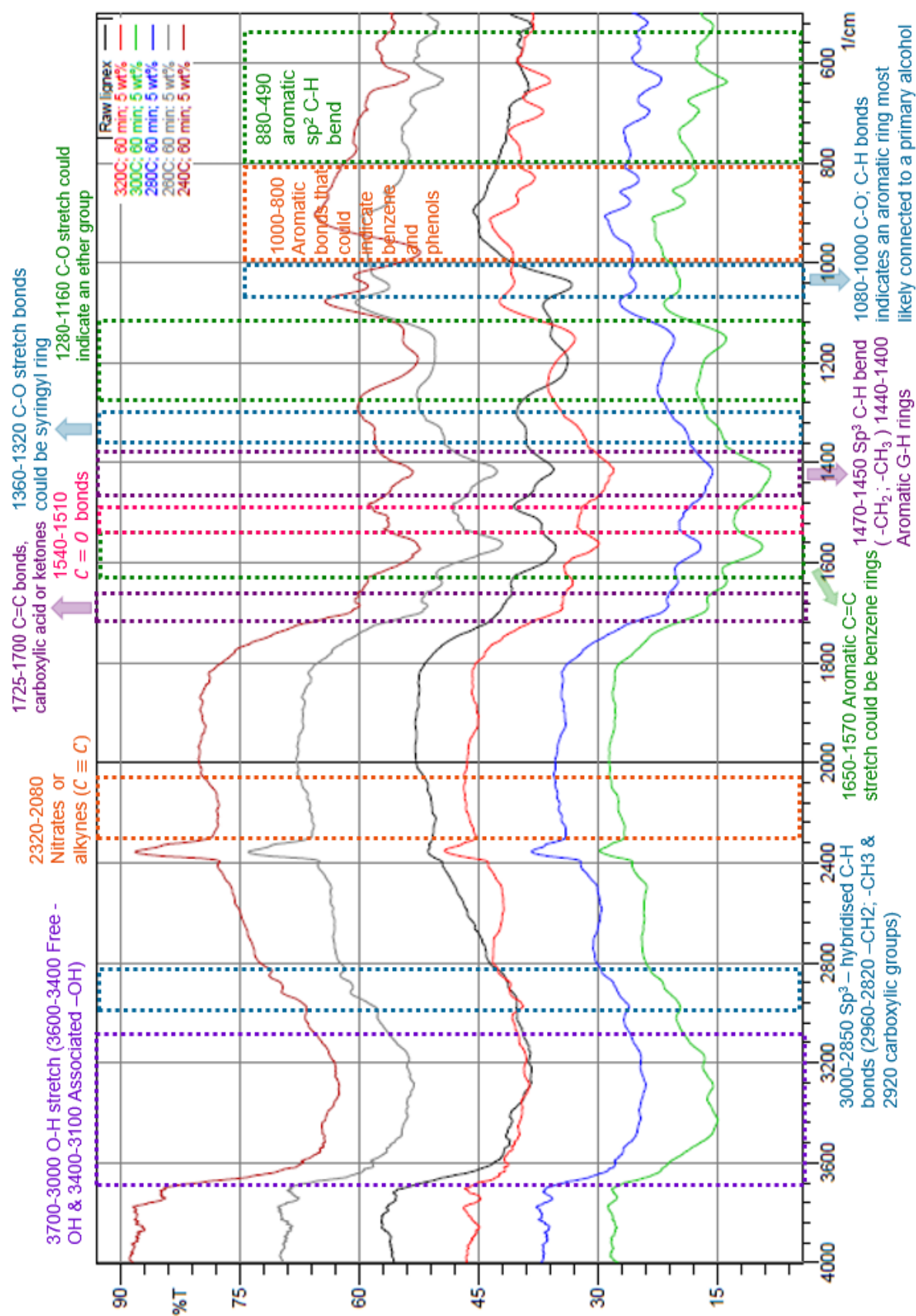


Fig. 130. FTIR spectra of biochars produced with a 60 min residence time

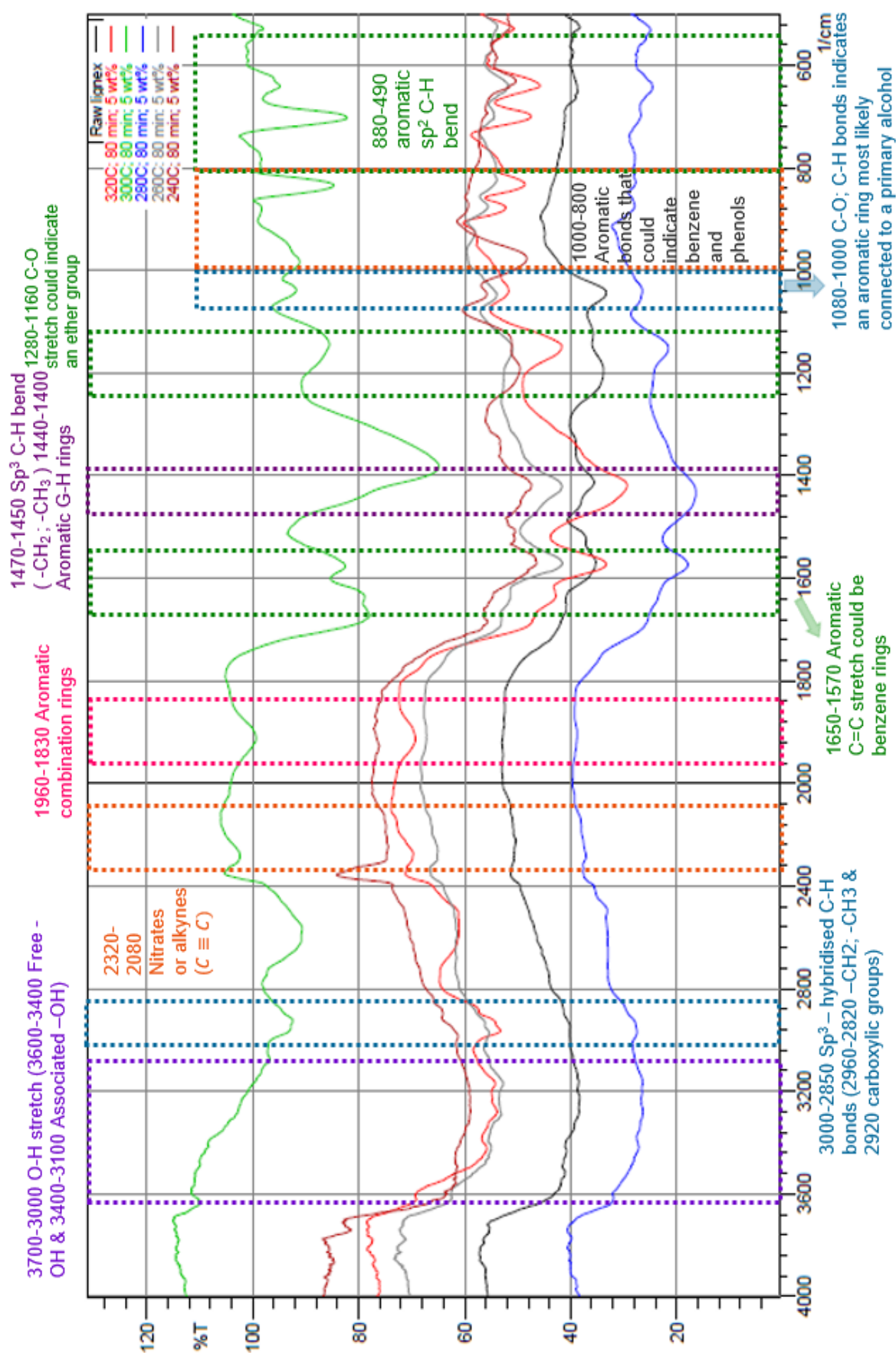


Fig. 131. FTIR spectra of biochars produced with an 80 min residence time

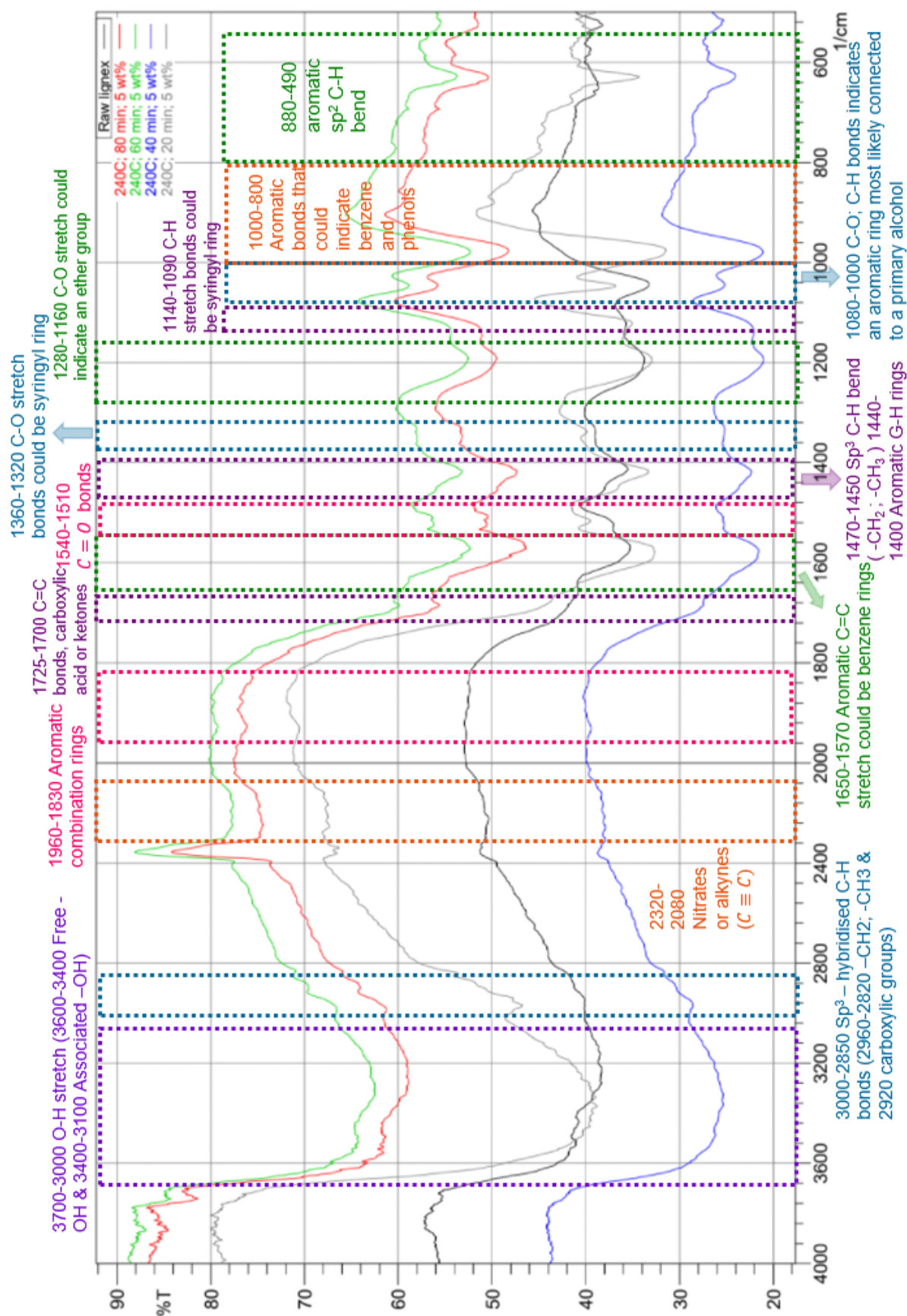


Fig. 132. FTIR spectrum of all biochars produced at 240°C

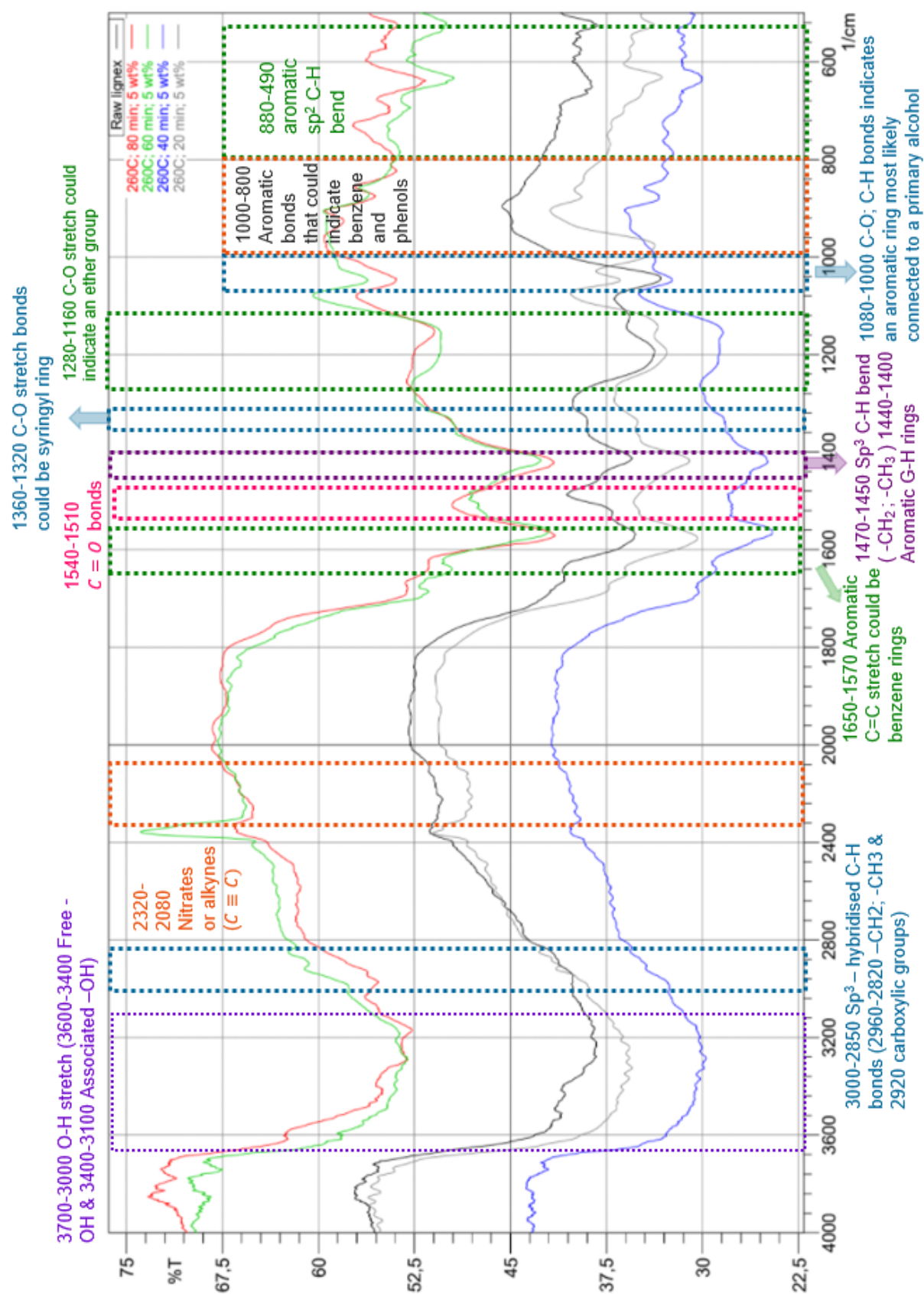


Fig. 133. FTIR spectrum of all biochars produced at 260°C

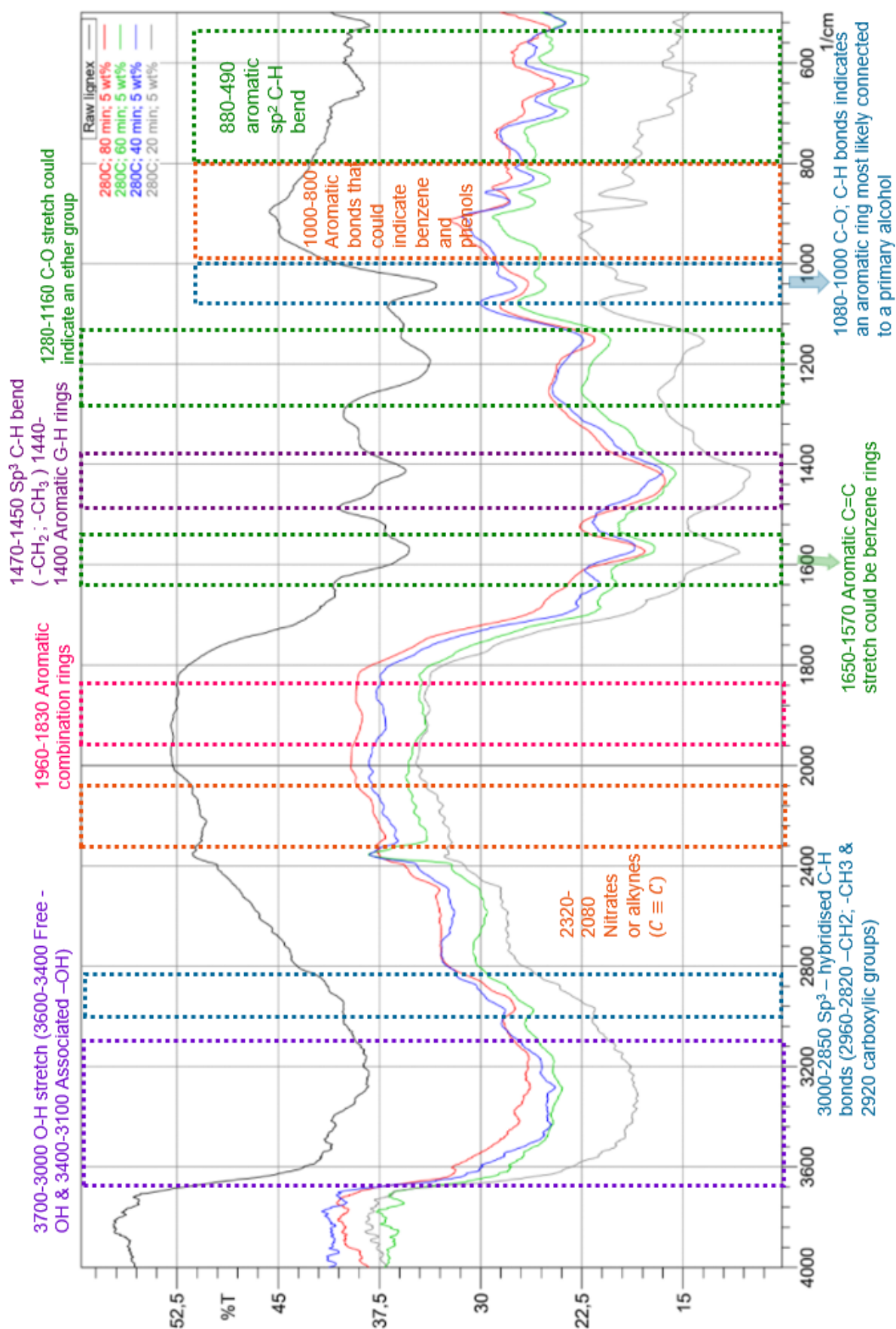


Fig. 134. FTIR spectrum of all biochars produced at 280°C

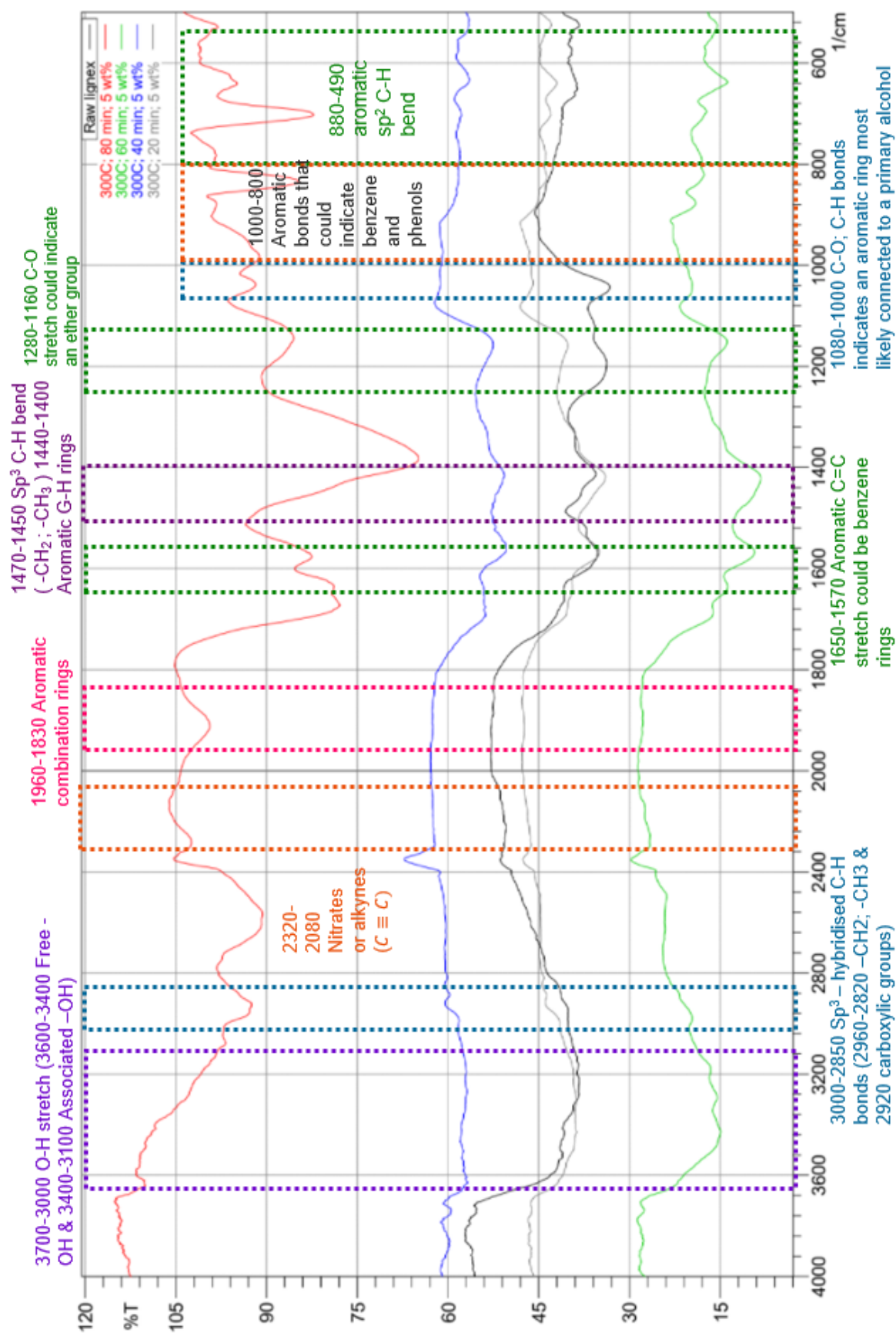


Fig. 135. FTIR spectrum of all biochars produced at 300°C

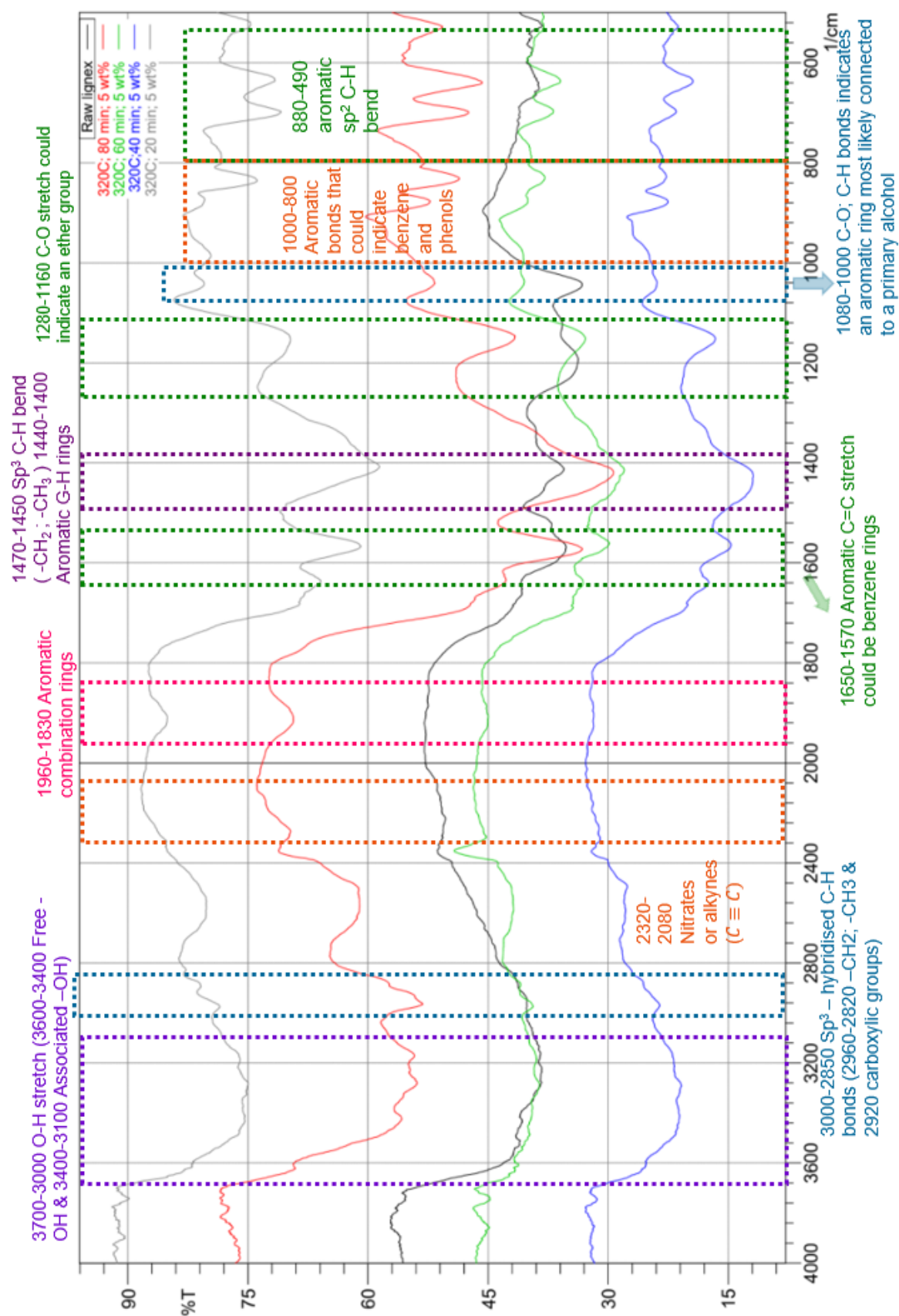


Fig. 136. FTIR spectrum of all biochars produced at 320°C

Elemental data for catalyst loading

Table 9-18. Elemental composition of biochars produced at various catalyst loadings

Catalyst loading	Carbon (mass%)	Hydrogen (mass%)	%R (mass%)
2 mass%	64.39 ± 0.31	35.81 ± 0.34	69.98 ± 0.14
3 mass%	62.69 ± 0.31	35.12 ± 0.34	66.40 ± 0.14
4 mass%	64.46 ± 0.31	35.11 ± 0.34	75.29 ± 0.14
5 mass%	59.12 ± 0.31	37.66 ± 0.34	71.41 ± 0.14
6 mass%	58.83 ± 0.31	31.44 ± 0.34	76.74 ± 0.14

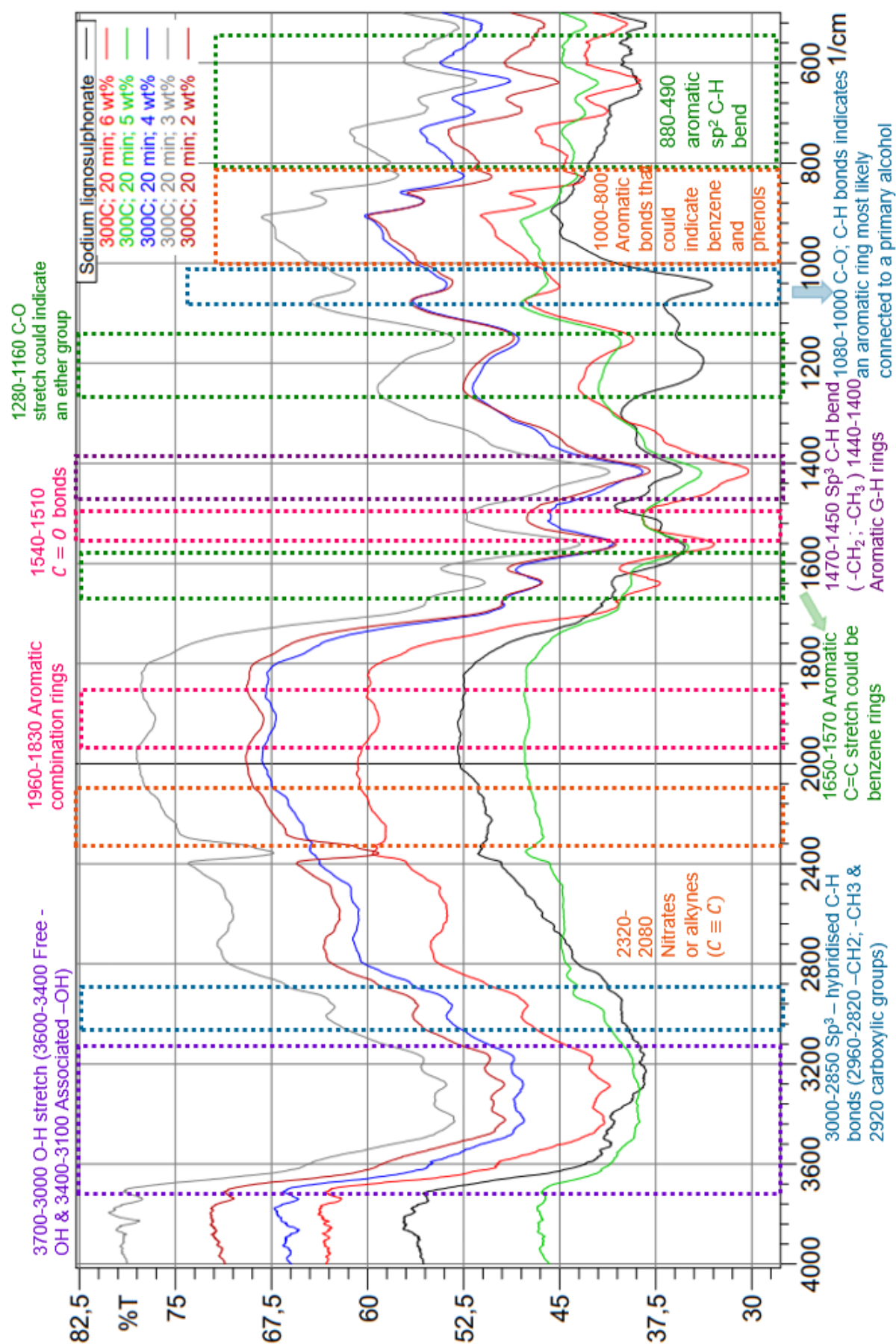


Fig. 137. FTIR spectrum of all biochars produced with various catalyst loadings