

1 **Impact of solvent type and condition on biomass liquefaction to produce heavy**
2 **oils in high yield with low oxygen contents**

3 *Hui Deng^{a*}, Will Meredith^a, Clement N. Uguna^{a,b} and Colin E. Snape^a*

4 *^aDepartment of Chemical and Environmental Engineering, Faculty of*
5 *Engineering, University of Nottingham, University Park, NG7 2RD, UK*

6 *^bCentre for Environmental Geochemistry, British Geological Survey, Keyworth,*
7 *Nottingham, NG12 5GG, UK*

8 *[*h.deng@nottingham.ac.uk](mailto:h.deng@nottingham.ac.uk)*

9

10 **Abstract**

11 Bio-oils produced by processes such as slow or fast pyrolysis typically contain high
12 water and oxygen contents, which make them incompatible with conventional fuels. It
13 is therefore necessary to upgrade the bio-oils to reduce their oxygen and water
14 contents. The bio-oil upgrading process can consume up to 84 wt. % of the initial
15 bio-oil it is therefore important to develop other alternative approaches to generate
16 high quality bio-oil. Thermolytic liquid solvent extraction (LSE) has been considered
17 as a potential viable process due to the high liquid yield, better product quality and
18 water free nature of the final products.

19 In this study, a novel LSE process of biomass liquefaction has been studied under
20 various conditions of solvent type, temperature, and biomass species. Compared to
21 currently available commercial pyrolysis approaches, this process using tetralin as a
22 solvent is shown to be capable of generating high quality bio-oil with low oxygen
23 contents (ca. 5.9 %) at extremely high overall conversions of up to 87 and 92 (%) dry
24 and ash free basis (DAF) from Scotch pine and miscanthus respectively. Overall, the
25 study has demonstrated the advantages of LSE for bio-oil generation from biomass, in
26 terms of producing high conversions to liquid products that are compatible with
27 existing petroleum heavy feedstocks.

28 **Keywords:** Biomass, Thermolytic liquid solvent extraction, Pyrolysis, Hydrogen
29 donor solvent, Bio-oil, Low oxygen contents

30 1 Introduction

31 Biomass pyrolysis to produce liquid fuel is one of the best solutions to answer major
32 challenges such as climate change and the current economically damaging high oil
33 price. The “bio-oil” produced from biomass pyrolysis is considered to be an
34 environmentally friendly fuel since it does not generate extra greenhouse gases [1-3].

35 However, due to the characteristics of conventional bio-oils such as those produced
36 from fast pyrolysis, it is necessary to upgrade them before they can be used as an
37 energy source. For example biomass to liquids (BTL) is a commercialized process
38 which can produce high grade transportation fuels from whole pyrolysis oil. However,
39 BTL process can only produce 2 wt. % of liquefied petroleum gas (LPG), 7 wt. %
40 naphtha and 18 wt. % diesel from pyrolysis oil [4], and during this process more
41 energy is consumed from the gasification and Fischer-Tropsch units. Therefore, it is
42 important to develop other alternative approaches such as thermolytic liquid solvent
43 extraction (LSE) to generate high quality bio-oil.

44 LSE is a two-stage process that was initially been developed for coal [5]. Compared to
45 normal pyrolysis, the use of hydrogen donor solvents has the advantage of giving
46 higher overall conversions to produce liquids and gases and producing bitumen like
47 heavy bio-oils that are amenable to upgrading to distillate fuels via hydrocracking.
48 Curran et al. [6] found that the percentage of extraction was proportional to the
49 amount of hydrogen donated and relatively independent of solvent composition.
50 Neavel [7] reported that in tetralin at 400 °C, coal was converted to benzene-soluble
51 products with vitrinite becoming almost completely soluble in pyridine. Hydrogen
52 transfer from tetralin increased exponentially with increased conversion of the coal to
53 benzene-soluble material. Abdel-Baset et al. [8] investigated tetralin extraction for
54 sixty-eight coal samples and found linear equations to predict the liquefaction
55 behaviour and help the feedstocks selection.

56 A benefit of LSE is that it can avoid introducing any significant quantity of hydrogen
57 donor solvent as the make-up solvent [9]. The solvent after hydrogenation generally
58 contains high concentrations of hydroaromatic compounds which can act as

59 hydrogen-donors to aid coal dissolution. However, as it is a two-stage process, it is
60 necessary for both stages to operate in tandem which has limited the number of
61 demonstration plants built (e.g. LSE Point of Ayr, UK) [9,10], and subsequent its
62 commercialisation.

63 LSE is an extremely flexible process, having been applied to a wide range of coals [5],
64 and it can be operated on a relatively small-scale. The Point of Ayr pilot plant has
65 already demonstrated a production rate of 2.5 tons/day, and a 65 tons/day
66 demonstration plant was also been designed [9], hence it does not suffer from
67 economies of scale. This gives a possibility of using the same process to liquefy
68 biomass materials (e.g. sewage sludge, wood waste, energy crops) and plastics close
69 to the point of their generation. Furthermore, a variety of waste solvents can be
70 considered for use in the process including engine oils, fats, greases and waste
71 glycerol from bio-diesel production.

72 The flexible range of abundant potential feedstocks will enable biomass liquefaction
73 plants to generate intermediate heavy oil products suitable for blending into existing
74 downstream process, as well as earning CO₂ credits from co-processing bio-waste.
75 Thus, solvent components will be imported to the site of plants and the primary liquid
76 products exported either for further processing (eg. upgrading at existing oil refineries)
77 or sold as heavy fuel oil substitutes.

78 The efficiency of LSE is controlled by a number of variables including the type of
79 biomass, particle size and the type of solvent employed. Most biomass waste contains
80 cellulose, hemicellulose, lignin and starch, which show different degrees of reactivity
81 under liquefaction. In general, under hydrothermal conditions, hemicellulose and
82 starch react faster than cellulose and all of them are more reactive than lignin, hence
83 higher cellulose, hemicellulose and starch content in biomass indicates more bitumen
84 yield [11-15].

85 A suitable particle size can avoid the limitation of heat and mass transfer during
86 liquefaction, increase contact surface area and more importantly, reduce energy
87 consumption by reducing the need of further grinding [16-18]. However during LSE,

88 the liquid solvent acts not only as a heat transfer medium but also as an extractant.
89 Thus, particle size has a negligible effect, and is a secondary parameter in the process
90 [16].

91 A number of different solvent types were investigated in the early studies of biomass
92 liquefaction [19-26]. In addition, the effect of hydrogen pressure and the kind of
93 catalysts employed were found to be two key factors controlling the increase of heavy
94 oil yields by using non-hydrogen donor solvents [27-29]. For donor solvents, the
95 hydrogen was transferred mainly from the solvent itself rather than from the initial
96 pressurised hydrogen gas, and the catalyst had less effect on enhancing oil yields with
97 the hydrogen donor solvents [29].

98 Compared with non-hydrogen donor solvents, hydrogen donor solvents showed
99 significant improvement not only in conversion and product distribution to liquid but
100 also on the quality of bio-oil due to the improvement of hydrogenation and
101 hydrocracking reactions with inhibition of polycondensation. These abilities were also
102 much higher than with gaseous hydrogen as the hydrogen donor. This is due to the
103 low strength bonding in tetralin C-H compared to hydrogen gas H-H bond. In terms of
104 its composition, the bio-oil produced contained more fully saturated hydrocarbons but
105 less esters and alkenes when using hydrogen donor compare to non-hydrogen donor
106 solvents [30-32].

107 This study has for the first time demonstrated that the LSE process using hydrogen
108 donor solvents at high temperatures and high pressures which has traditionally been
109 limited to for coal liquefaction, can also be used for biomass liquefaction to maximize
110 the production of low oxygen bio-oils that can be blended with existing petroleum
111 heavy feedstocks.

112 **2 Experimental**

113 **2.1 Feedstock and methods**

114 The LSE experiments were carried out using six feedstocks: miscanthus, lignin (low
115 Sulphur), lignin, fresh Scotch pine, old Scotch pine and torrefied fresh Scotch pine. In

116 these feedstocks, miscanthus represents grass-like biomass which gives a high dry
117 weight annual yield per hectare [33]. Scotch pine represents woody biomass with
118 good regional accessibility and security of provision. Lignin is considered as a waste
119 material from the paper industry.

120 These feedstocks were pyrolysed under the following conditions: anhydrous, hydrous,
121 with hydrogen donor solvents and with non-hydrogen donor solvents. Full details of
122 the different solvents used are listed in Table 1 for the 25 ml and the 75 ml reactor.
123 Feedstocks were ground to a particle size of less than 500 μm as received, in order to
124 eliminate the limitations of heat and mass transfer. The low S lignin and lignin were
125 purchased from Sigma-Aldrich. Lignin (low S) contains approximately 4 % of sulfur
126 with an average molar weight of $M_n \sim 10,000$, while the lignin sample has an average
127 molar weight of $M_n \sim 5,000$. The Scotch pine (old) sample had been cut and stored
128 over one year, while Scotch pine (fresh) sample is a freshly cut sample. The sample of
129 torrefied Scotch pine was prepared in a horizontal furnace with a heating rate of
130 $10\text{ }^\circ\text{C}/\text{min}$ and an average temperature of $250\text{ }^\circ\text{C}$ for 1 hour with nitrogen present as
131 the carrier gas. The duration of each experiment was 1 hour. In addition, the detail of
132 the process flow is shown as a block diagram in Figure 1.

133 **2.2 Liquid solvent extraction (LSE) equipment and experimental procedures**

134 The reactors for liquefaction were Parr 4740 series stainless steel (25 ml and 75 ml
135 cylindrical) pressure vessels, connected to a pressure gauge with a maximum safety
136 pressure up to 586 bar at $350\text{ }^\circ\text{C}$. The reactor was heated by means of a fluidized sand
137 bath which was controlled by an external temperature controller. Temperature was
138 monitored by an additional K-type thermocouple, which was connected to computer
139 and recorded every 10 seconds. Compressed air entered into the sand bath from the
140 bottom through a gas distributor and evenly bubbled inside container to mix the sand,
141 and so evenly distribute the heat though the sand bath. The schematic diagram of the
142 liquefaction equipment is shown in Figure 2.

143 The standard conditions employed was a temperature at $410\text{ }^\circ\text{C}$, a residence time of
144 one hour and a feedstock to solvent mass ratio of 1:2.5. (For the 25 ml reactor 5 g of

145 biomass together with 12.5 g of solvent, and for the 75 ml reactor 10 g of biomass
146 together with 25 g of solvent). After sealing the reactor and attaching the pressure
147 gauge, it was purged 20 times with nitrogen gas to remove the air, and then 2 bar of
148 nitrogen gas was introduced to provide an inert atmosphere. The sand bath was
149 pre-heated to the required temperature and left for 10 minutes to equilibrate. The
150 pressure vessel was then lowered into the sand bath and the experiment was left to run
151 with a constant air flow through the sand bath. As soon as the experiment was
152 finished, the reactor was removed from the sand bath immediately, compressed air
153 was used for approximately 30 minutes to cool the reactor to room temperature in
154 order to prevent secondary reactions before product recovery.

155 **2.3 Gas collection and analysis**

156 Two different gas chromatographs were used in this report due to a change of
157 instrumentation during the study. They were a Carlo Erba HRGC 5300 GC and
158 PerkinElmer Clarus 580 GC. The Carlo GC had only a FID channel to analyse the
159 hydrocarbon gases, while the Clarus GC had a TCD channel available with a FID
160 channel to analyse both hydrocarbon and non-hydrocarbon gases. Therefore in this
161 report, all gas analysis containing non-hydrocarbon gases were analysed by the Clarus
162 GC.

163 For the Carlo GC, separation was achieved with a CP poraplot-Q capillary column
164 (27.5 m × 0.32 mm i.d., 10 µm), with helium as the carrier gas, FID detector and an
165 oven programme of 70 °C (hold 4 min) to 90 °C (hold 3 min) at 40 °C/min, increase
166 to 140 °C (hold 3 min) at 40 °C/min, increase to 180 °C (hold 49 min) at 40 °C/min.

167 For the Clarus GC, separation was achieved with a Rt® Alumina Bond/KCl capillary
168 column (30 m × 0.32 mm i.d., 5 µm) with helium as the carrier gas for hydrocarbon
169 gases analysis and a Haysep N6 packed column (60-80, 7'×1/8" sulfinert)
170 non-hydrocarbon gas analysis with argon as carrier gas. FID and TCD detectors were
171 used and the oven programme of 60 °C (hold 13 min) to 160 °C (hold 2 min) at
172 10 °C/min for both columns.

173 **2.4 Recovery of generated bitumen (toluene-solubles)**

174 The liquid and solid contents of the reactor were washed with approximately 150 ml
175 of toluene and recovered into a round bottom flask. A Dean-Stark apparatus was used
176 to separate and measure the water content of the products. The flask was heated by a
177 heating mantle at 110 °C for 7 hours. After reflux, the set-up was allowed to cool, and
178 the volume of water generated from reaction was recorded. The residue was separated
179 from the generated bitumen (toluene-solubles) by filtration using a pre-weight 0.5 µm
180 glass fibre filter paper. The residue and filter paper were dried in desiccator using
181 activated charcoal, with the final dried weight used to determine the total overall
182 conversion.

183 The toluene solubles fraction (solvents, bitumen) were transferred to a round bottom
184 flask and distilled at 110 °C under atmospheric pressure. Once all the toluene was
185 distilled, a vacuum pump was applied for vacuum distilling high boiling point
186 solvents such as tetralin and naphthalene. The solvents were collected and transferred
187 to freezer for storage and further analysis. After distillation of all solvents, the
188 bitumen was collected and weighed to calculate the bitumen yield.

189 **2.5 Pyridine extraction to obtain the pre-asphaltenes**

190 0.5 g of the toluene insoluble residue was refluxed with 30 ml pyridine for 7 hours at
191 120 °C in a 100 ml round bottom flask. The pyridine insoluble fraction was separated
192 from the pre-asphaltenes (pyridine soluble fraction) by filtration using a pre-weighed
193 0.5 µm glass fibre filter paper. The pyridine insoluble fraction and filter paper were
194 dried in desiccator using activated charcoal and the final dried weight was used to
195 determine the pre-asphaltene yield by difference.

196 **2.6 Asphaltene isolation**

197 Approximately 100 mg of the dry bitumen was scooped by spatula, and dissolved in 1
198 ml of dichloromethane (DCM). An ice bath was prepared with a 250 ml beaker filled
199 with 90 ml n-heptane and a magnetic stirrer. The dissolved bitumen was slowly
200 dropped into the n-heptane, and after 5 minutes mixing, the solution was transferred

201 into four glass vials for centrifugation at 2500 rpm for 5 minutes. The supernatant was
202 then decanted into a round bottom flask, and the solid precipitate was re-dissolved in
203 1 ml DCM and the process was repeated until a colourless supernatant after centrifuge.
204 The final precipitate was collected, dried and weighed, with the n-heptane insoluble
205 material defined as the asphaltene fraction, and the difference between initial weight
206 and precipitate weight was defined as the n-heptane soluble, maltene fraction [34].

207 **3 Results**

208 **3.1 Proximate and ultimate analysis of biomass feedstocks**

209 Triplicate runs of proximate and ultimate analysis were conducted by using thermal
210 gravimetric analysis (TGA) and elemental analyser (EA) for each biomass sample.
211 The average data for each proximate and ultimate analysis results are listed in Table 2.

212 **3.2 Overall conversions**

213 A number of solvents namely, tetralin, 1-methylnaphthalene (1-MN), polystyrene
214 (PS), polyethylene (PE), decalin and petroleum bitumen, were investigated for
215 miscanthus liquefaction, while other solvents namely tetralin, 1-methylnaphthalene,
216 pyrene, m-cresol, decalin, vegetable oil, glycerol, kerosene and naphthalene were also
217 been investigated for both fresh and old Scotch pine liquefaction. Figure 3, Figure 4
218 and Figure 5 show the overall conversions to toluene soluble products for miscanthus
219 and Scotch pine with different solvents at 410 °C for 1 hour.

220 For miscanthus liquefaction, the baseline conversions under anhydrous and hydrous
221 conditions were 58 DAF % and 60 DAF % respectively. The highest conversion was
222 obtained with tetralin (92 DAF %), while intermediate conversions were obtained
223 with the other non-hydrogen donor solvents. 1-methylnaphthalene and decalin were
224 both giving conversions close to 70 DAF %. Petroleum bitumen gave an overall
225 conversion at approximately 50 DAF %, which was lower than the baseline anhydrous
226 conditions. Polystyrene gave a negative effect resulting in reduced conversions (*ca.* 40
227 DAF %), with the overall conversion for polystyrene was lower than polyethene (*ca.*
228 60 DAF %).

229 Furthermore, two experiments were conducted using different particle sizes (<500 μm
230 and <150 μm) of miscanthus with tetralin as the extraction solvent in the 25 ml
231 reactor at 410 °C for 1 hour. The results reveal that there was no significant
232 improvement in the conversion when using a smaller particle size (92.0 DAF % vs.
233 92.8 DAF % for <500 μm and <150 μm samples respectively).

234 For Scotch pine liquefaction, the lowest overall conversion observed was 55 DAF %
235 from both the 25 ml and 75 ml reactors, anhydrous experiments, while the highest
236 overall conversion observed was 87 DAF % from the 25 ml reactor with tetralin
237 present as a hydrogen donor solvent. Overall conversions of 64 and 84 DAF % were
238 observed by using old Scotch pine at with water (hydrous) and tetralin used as
239 solvents respectively. The conversions were lower than for the miscanthus
240 experiments (58, 60 and 92 DAF % for anhydrous, hydrous and tetralin conditions
241 respectively) due to the higher lignin content in Scotch pine compared to miscanthus
242 [17,35]. The results also suggest that there is no significant difference in the overall
243 conversions between the experiments conducted with the 25 ml and 75 ml reactors
244 when using same biomass to solvent ratio, or between old Scotch pine and fresh
245 Scotch pine samples.

246 Compared to the conversions for Scotch pine with tetralin, the non-hydrogen donor
247 solvents proved less effective but still gave generally higher conversions than under
248 anhydrous and hydrous conditions (*ca.* 55–64 DAF %). The overall conversions for
249 1-methylnaphthalene, vegetable oil and decalin (*ca.* 70 DAF %) were higher than for
250 pyrene, m-cresol, kerosene and glycerol.

251 During torrefaction, Scotch pine underwent a weight loss of 31 wt%. The experiments
252 were conducted by using torrefied fresh pin wood sample with tetralin in the 25 ml
253 reactor at 410 °C for 1 hour. The mass balance and the overall conversions (DAF %)
254 are presented in Table 3. The overall conversion of the torrefied fresh Scotch pine
255 sample has lower overall conversions than the initial fresh Scotch pine sample at
256 410 °C. However, the conversions were slightly reduced when the mass loss was
257 taken into account. In addition, torrefaction can reduce the moisture content in the
258 biomass hence increase the energy density and reduce the transport costs for the

259 feedstocks.

260 **3.3 Comparison of tetralin and non-hydrogen donor solvents**

261 Table 4 shows the extremely high conversions to toluene soluble products (*ca.* 92
262 DAF %, 84 DAF % and 87 DAF % for the miscanthus, old Scotch pine and fresh
263 Scotch pine respectively) obtained using tetralin. Lower conversions were shown in
264 Table 3 by using two different lignin samples.

265 In addition, Table 5 shows the comparison of the total conversions and product yields
266 on a dry ash free basis from liquefaction of Scotch pine at 410 °C for 1 hour using
267 hydrogen donor solvent, tetralin and the other 4 non-hydrogen donor solvents. The
268 non-hydrogen donor solvents were found to be less effective than the hydrogen donor
269 solvents, but still gave a higher conversion to toluene soluble products than both the
270 hydrous and anhydrous experiments (*ca.* 55-64 DAF %). Furthermore, the overall
271 conversions for 1-methylnaphthalene and decalin were significantly higher than for
272 pyrene and m-cresol.

273 **3.4 Carbon conversions**

274 To understand conversion trends on different feedstocks and solvents, it is more
275 convenient to use conversions on a carbon basis for biomass (see following tables).
276 The biomass and residues were analysed by EA (shown in Table 6 and Table 7), while
277 hydrocarbon gases were analysed by GC. From the elemental compositions of each
278 sample, the carbon mass balances for miscanthus with extractant solvents are listed in
279 Table 8.

280 The carbon mass balance also been calculated for Scotch pine anhydrous and hydrous
281 experiments with the results listed in Table 9. The non-hydrocarbon gas were
282 analysed by the Clarus GC for better closure of the mass balances. It was showed that
283 the bitumen carbon content under hydrous conditions was significantly higher than
284 under anhydrous conditions, which was indicated that the presence of water was a
285 benefit during the extraction process. The closure of the carbon balances was also
286 better than for those experiments conducted using tetralin, which indicated that

287 heavier toluene fractions were formed under anhydrous and especially hydrous
288 conditions. They contained less lower boiling point light ends were generated and
289 subsequently lost during the distillation of excess tetralin and naphthalene.

290 Some assumptions were made to complete the mass balance as non-hydrocarbon gas
291 data was not available for those experiments analysed by the Carlo Erba GC. The
292 assumptions are listed under each table, for example, the CO and CO₂ yields were
293 assumed to be at the same level of fresh Scotch pine anhydrous experiments (0.6 and
294 11.8 % respectively, on a carbon basis) as shown in Table 9. In addition the bitumen
295 carbon contents were calculated by difference as some experiments were conducted
296 by using high boiling point solvents and those solvents are difficult to distil off from
297 the bitumen.

298 From the carbon mass balance, it is clearly showed that out of the non-hydrogen
299 donor solvents, tetralin gave the highest overall conversion and bitumen yield on
300 carbon basis for miscanthus (*ca.* 71 DAF %). In addition, polystyrene and bitumen
301 gave negative values on bitumen carbon content as they both donated large portion of
302 their carbon into the system.

303 The residues and bitumen products were analysed by the EA and listed in Table 10.
304 More detail of the carbon mass balances are obtained by using lignin samples and
305 Scotch pine samples with tetralin in Table 11. Taking the carbon conversion data for
306 the residue, hydrocarbon and non-hydrocarbon gases and the light end lost during
307 distillation of bitumen samples into account, the mass balance showed that the liquid
308 products represent over *ca.* 62 % of the initial carbon for Scotch pine samples (for
309 example from old Scotch pine sample 42.9 % from bitumen as measured plus 20.1 %
310 light ends lost during distillation) which are slightly lower than miscanthus. The
311 conversions were lower for the lignin samples but the closure of the carbon balances
312 were much better (total carbon recovered percentage over 100 %) than Scotch pine
313 samples. This is possibly due to the liquid products generated from lignin samples
314 being considerably heavier than those from Scotch pine samples.

315 **3.5 Hydrogen donation**

316 Table 12 shows the composition of the recovered solvents from a blank run (tetralin
317 without biomass) at an extreme condition at 460 °C, and fresh Scotch pine LSE at
318 410 °C in the 75 ml reactor for 1 hour. The percentages of hydrogen donated (to form
319 naphthalene) and hydrogen lost during rearrangement (to form an isomer,
320 1-methylindan) were included in Table 12. From the blank run it was found that more
321 than *ca.* 90 % of initial tetralin remained after the 1 hour experiment, which indicated
322 that the tetralin was relatively stable at 460 °C. For LSE of the Scotch pine at 410 °C ,
323 it was found that approximately 1.3 % hydrogen donated from tetralin to the biomass,
324 which was consistent with the values of *ca.* 1.0 - 2 % for bituminous coals [36]. Due
325 to the high remaining tetralin concentration *ca.* 84 %, the solvent may recycled
326 multiple times under the operation conditions of 410 °C duration for 1 hour.

327 **4 Discussion**

328 Based on this study, it is found that the cellulosic biomass samples are highly reactive
329 and so give high conversions during LSE. By using tetralin as a hydrogen donor
330 solvent, extremely high conversions to toluene soluble products (*ca.* 92 DAF %, 84.2
331 DAF % and 87 DAF % for the miscanthus, old Scotch pine and fresh Scotch pine
332 respectively) were obtained. Non-cellulosic biomass such as lignin gave lower
333 conversions to pyridine and toluene soluble products. Compare the different type of
334 solvents been employed to LSE, the conversions from biomass to pyridine and toluene
335 soluble products are extremely high under hydrogen donor conditions, especially on a
336 carbon basis. Non-hydrogen donor solvents are less effective than hydrogen donor
337 solvents but still give a higher conversions (*ca.* 70 DAF %) compared to the toluene
338 soluble products than both hydrous and anhydrous experiments (*ca.* 55-64 DAF %).
339 The experiments conducted under hydrous conditions suggested that the presence of
340 water in the LSE system can promote an increase in the yield of liquid products.
341 However, compared to those hydrothermal liquefaction process [15,16,26,28,37,38],
342 the LSE process under hydrous conditions is generally conducted at higher
343 temperatures, higher pressures but over a longer residence time. Consequently, the
344 overall conversion and bio-oil yield was suppressed, which is consistent with the
345 finding from Akhtar and Amin [16]. Furthermore, a negative effect was observed in

346 the experiments conducted on polymers and bitumen indicating that waste polymer
347 streams and bitumen are not going to be effective solvents for liquefying biomass.
348 Polystyrene gave a lower overall conversion compare to polyethylene, this may be
349 because the polystyrene was more reactive with biomass, therefore more free radical
350 hydrogen was donated from biomass to polystyrene than to polyethene. In addition,
351 the low conversions obtained by polymers were consistent with the findings from
352 Paradela et al. [39] that the higher percentage of biomass employed in the system, the
353 lower overall conversion it has. Therefore, it was suggested that waste polymer
354 streams are not going to be effective solvents for liquefying biomass since the
355 biomass donated excess free radicals to crack the polymer. In addition, two
356 experiments conducted by different particle size at $<500\ \mu\text{m}$ and $<150\ \mu\text{m}$ shown that
357 there was no significant improvement in the conversion by using a smaller particle
358 size. Therefore, further grinding of the biomass sample to a smaller particle size is not
359 required and less grinding energy can be used. Furthermore, torrefaction can reduce
360 the moisture content in the biomass hence increase the energy density and reduce the
361 transport costs for the feedstocks.

362 When comparing the different solvent types, it was found that tetralin, as a hydrogen
363 donor solvent can donate free radical hydrogen and cleave the chemical bonding from
364 biomass and stabilize the fragments during LSE process. Therefore, extremely high
365 conversions were obtained from the lignocellulosic biomass experiments with tetralin.
366 It was found that the conversions to toluene soluble products were considerably lower
367 for the two lignin samples due to the lower volatile matter contents (Table 3), which
368 were consistent with the findings of Zhong and Wei [11] and Bhaskar et al. [12] that
369 high lignin contents reduce the overall conversions. The lower yield of toluene soluble
370 products is due to the free phenoxy radicals formed during the process having a
371 random tendency to form solid residue by condensation or repolymerisation [11].
372 However, the toluene soluble liquid products contained significant quantities of low
373 molecular weight light ends. The light ends were lost during toluene reflux and
374 removed by distillation of the toluene, tetralin and naphthalene. Furthermore, it was
375 found that the non-hydrogen donor solvents have less effective compare to tetralin
376 which is consistent with previous studies [31,32].

377 From the carbon conversion data, it is clear that out of the non-hydrogen donor
378 solvents, tetralin gave the highest overall conversion and bitumen yield on carbon
379 basis (*ca.* 71 DAF % for miscanthus and 62 DAF % for Scotch pine) which clearly
380 was a high product yield. The lowest oxygen content was recorded when using old
381 Scotch pine samples with tetralin at 5.9 % in the bitumen, which indicated that the
382 bitumen may not undergo further upgrading process but can be introduced to
383 conventional petroleum steam directly. Polystyrene and bitumen both donated large
384 portion of their carbon into the system, consequently gave a negative values on the
385 carbon balance. The better closure of the carbon balance conducted by the two lignin
386 samples indicated that large molecular hydrocarbons were formed hence reduced the
387 mass lost during distillation of tetralin from the liquid products.

388 During the LSE process with the use of tetralin as a hydrogen donor solvent, two
389 chemical reactions occurred: i) 1 mole of tetralin donated 4 moles of free radical
390 hydrogen to the biomass and formed 1 mole of naphthalene; ii) the isomerisation
391 reaction as 1 mole of tetralin formed 1 mole of 1-methylindan, which were shown in
392 Figure 6.

393 In the first reaction, the generated free radical hydrogen contribute to cleave and
394 attach biomass molecular to form hydrocarbon fractions and also remove oxygen by
395 forming water, which count as the hydrogen donated. In the second reaction,
396 hydrogen does not contribute to biomass liquefaction, which count as the hydrogen
397 lost during rearrangement (to form isomer).

398 Vacuum distillation of the liquid products was conducted after the LSE process in
399 order to recover the excess tetralin and naphthalene. The tetralin to naphthalene and
400 tetralin to 1-methylindan ratios from the recovered solvents were determined by GC.
401 It is important to know the ratio of each component in the recovered solvent, and to
402 calculate the amount of hydrogen donation to form bitumen and water. The results can
403 help to predict the quality of the bitumen. More importantly, the recovered solvent
404 from the laboratory-based batch experiment simulated the composition of solvent in a
405 scaled-up pilot plant recycle stream. Therefore, artificial recycled solvent can be
406 blended with exactly the same composition as the recovered solvent in order to study

407 the production efficiency and the portion of make-up stream needed in the scaled-up
408 pilot plant.

409 Regarding hydrogen donation potential, tetralin was relatively stable during pyrolysis
410 at 460 °C for 1 hour. When the biomass was introduced into the system at 410 °C
411 duration for 1 hour, it was found that approximately 1.3 % of the available hydrogen
412 was donated from the tetralin to the Scotch pine. This indicated that the high
413 remaining tetralin concentration *ca.* 84 %, the solvent may recycled multiple times
414 without makeup stream.

415

416 **5 Conclusions**

417 1. Extremely high conversions of miscanthus and Scotch pine were obtained (87-92
418 DAF %) by using tetralin, with liquid products accounting for at least 60 % of the
419 initial carbon. Lower conversions were achieved for lignin.

420 2. Hydrous experiments showed that the moisture present in the miscanthus and
421 Scotch pine feedstock can promote conversion, therefore drying of the feedstock
422 before LSE is not necessary.

423 3. The overall conversion for miscanthus with tetralin reached its maximum with a
424 particle size of <500 µm. Therefore, no further grinding is required.

425 4. Torrefaction reduced both the moisture and light volatile matter content of the
426 initial biomass, and hence generated less hydrocarbon gases. Accounting for mass loss
427 during torrefaction overall conversions to soluble products are the same as the initial
428 sample, although torrefaction was found to increase oxygen content of the products.

429 5. Due to its higher lignin content conversions for Scotch pine were lower than
430 miscanthus, with lignin samples giving lower conversions than cellulosic biomass.

431 6. Non-hydrogen donor solvents like 1-methylnaphthalene, vegetable oil and decalin
432 generally gave conversions of approximately 70 DAF %. Polymers, petroleum
433 bitumen, Pyrene and m-cresol were found not to be effective solvents for biomass

434 liquefaction.

435 7. Overall, this study has demonstrated the advantages of thermolytic solvent
436 extraction for biomass, in terms of producing high conversions to liquid products that
437 should be compatible with existing petroleum heavy feedstocks, without the need for
438 using high pressure hydrogen in the primary conversion stage.

439 **6 Acknowledgements**

440 The authors would like to acknowledge BP plc for the financial support on this
441 project.

442

443 **References**

- 444 [1] A.V. Bridgwater, *Chemical Engineering Journal*, 91, (2003) 87.
- 445 [2] A.V. Bridgwater, D. Meier and D. Radlein, *Organic Geochemistry*, 30, (1999)
446 1479.
- 447 [3] A. Demirbas, *Progress in Energy and Combustion Science*, 33, (2007) 1.
- 448 [4] Nexant Ltd. Report 40661: The Exploitation of Pyrolysis oil in the Refinery
449 Main Report. Prepared for: The Carbon Trust (2008).
- 450 [5] G. Kimber, *University of Kentucky, Center of Applied Energy research*, Vol. 2,
451 No. 2, (1991).
- 452 [6] G.P. Curran, R.T. Struck and E. Gorin, *Industrial & Engineering Chemistry*
453 *Process Design and Development*, 6, (1967) 166.
- 454 [7] R.C. Neavel, *Fuel*, 55, (1976) 237.
- 455 [8] M.B. Abdel-Baset, R.F. Yarzab and P.H. Given, *Fuel*, 57, (1978) 89.
- 456 [9] R. Kamall, Dti Technology Status Report 010 Coal Liquefaction, Department
457 of Trade and Industry, 1999.
- 458 [10] A. Thompson, in *newsletter of the coal research forum* 2003.
- 459 [11] C. Zhong and X. Wei, *Energy*, 29, (2004) 1731.
- 460 [12] T. Bhaskar, A. Sera, A. Muto and Y. Sakata, *Fuel*, 87, (2008) 2236.
- 461 [13] Y. Yu, X. Lou and H.W. Wu, *Energy & Fuels*, 22, (2008) 46.

- 462 [14] F. Behrendt, Y. Neubauer, M. Oevermann, B. Wilmes and N. Zobel, *Chemical*
463 *Engineering & Technology*, 31, (2008) 667.
- 464 [15] S.S. Toor, L. Rosendahl and A. Rudolf, *Energy*, 36, (2011) 2328.
- 465 [16] J. Akhtar and N.A.S. Amin, *Renewable and Sustainable Energy Reviews*, 15,
466 (2011) 1615.
- 467 [17] S. Mani, L.G. Tabil and S. Sokhansanj, *Biomass and Bioenergy*, 27, (2004)
468 339.
- 469 [18] P. Adapa, L. Tabil and G. Schoenau, *Biomass and Bioenergy*, 35, (2011) 549.
- 470 [19] C. Vanasse, E. Chornet and R.P. Overend, *The Canadian Journal of Chemical*
471 *Engineering*, 66, (1988) 112.
- 472 [20] T.Y. Yan, in T.N. Veroglu (Ed.), *Hydrocarbon technology environment,*
473 *alternate energy sources IV*, Ann Arbor Science, 1980, p. p. 79.
- 474 [21] C. Crofcheck, M.D. Montross, A. Berkovich and R. Andrews, *Biomass and*
475 *Bioenergy*, 28, (2005) 572.
- 476 [22] Z. Fang, T. Sato, R.L. Smith Jr, H. Inomata, K. Arai and J.A. Kozinski,
477 *Bioresource Technology*, 99, (2008) 3424.
- 478 [23] Y. Yang, A. Gilbert and C. Xu, *Applied Catalysis A: General*, 360, (2009)
479 242.
- 480 [24] H. Li, X. Yuan, G. Zeng, J. Tong, Y. Yan, H. Cao, L. Wang, M. Cheng, J.
481 Zhang and D. Yang, *Fuel Processing Technology*, 90, (2009) 657.
- 482 [25] Z. Liu and F.-S. Zhang, *Energy Conversion and Management*, 49, (2008)
483 3498.
- 484 [26] M. Sugano, H. Takagi, K. Hirano and K. Mashimo, *Journal of Materials*
485 *Science*, 43, (2008) 2476.
- 486 [27] C. Xu and T. Etcheverry, *Fuel*, 87, (2008) 335.
- 487 [28] S. Yin, R. Dolan, M. Harris and Z. Tan, *Bioresource Technology*, 101, (2010)
488 3657.
- 489 [29] U. Schuchardt and O.A. Marangoni Borges, *Catalysis Today*, 5, (1989) 523.
- 490 [30] A.I. Afifi, E. Chornet, R.W. Thring and R.P. Overend, *Fuel*, 75, (1996) 509.
- 491 [31] G. Wang, W. Li, B. Li and H. Chen, *Fuel*, 86, (2007) 1587.
- 492 [32] G. Wang, W. Li, B. Li, H. Chen and J. Bai, *Chemical Engineering and*

- 493 *Processing: Process Intensification*, 46, (2007) 187.
- 494 [33] L. Price, M. Bullard, H. Lyons, S. Anthony and P. Nixon, *Biomass and*
495 *Bioenergy*, 26, (2004) 3.
- 496 [34] C.A. Russell, C.E. Snape, W. Meredith, G.D. Love, E. Clarke and B. Moffatt,
497 *Organic Geochemistry*, 35, (2004) 1441.
- 498 [35] L. Mastny, *Biofuels for transport: global potential and implications for*
499 *sustainable energy and agriculture* Earthscan, 2007, p.
- 500 [36] G.M. Kimber, Energy for the Future Coal Liquefaction for the European
501 Environment, Report No. Coal R 078, *Department of Trade and Industry*,
502 1997.
- 503 [37] B. Zhang, M. von Keitz and K. Valentas, *Journal of Analytical and Applied*
504 *Pyrolysis*, 84, (2009) 18.
- 505 [38] M.K. Akalin, K. Tekin and S. Karagöz, *Bioresource Technology*, 110, (2012)
506 682.
- 507 [39] F. Paradela, F. Pinto, A.M. Ramos, I. Gulyurtlu and I. Cabrita, *Journal of*
508 *Analytical and Applied Pyrolysis*, 85, (2009) 392.
- 509