

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

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

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

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

^{*}h.deng@nottingham.ac.uk

Abstract

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

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

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

1 Introduction

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

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

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

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

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

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

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

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

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

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

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

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

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

2 Experimental

2.1 Feedstock and methods

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

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

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

2.2 Liquid solvent extraction (LSE) equipment and experimental procedures

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

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

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

2.3 Gas collection and analysis

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

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

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

2.4 Recovery of generated bitumen (toluene-solubles)

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

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

2.5 Pyridine extraction to obtain the pre-asphaltenes

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

2.6 Asphaltene isolation

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

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

3 Results

3.1 Proximate and ultimate analysis of biomass feedstocks

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

3.2 Overall conversions

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

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

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

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

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

During torrefaction, Scotch pine underwent a weight loss of 31 wt%. The experiments were conducted by using torrefied fresh pin wood sample with tetralin in the 25 ml reactor at 410 $^{\circ}\text{C}$ for 1 hour. The mass balance and the overall conversions (DAF %) are presented in Table 3. The overall conversion of the torrefied fresh Scotch pine sample has lower overall conversions than the initial fresh Scotch pine sample at 410 $^{\circ}\text{C}$. However, the conversions were slightly reduced when the mass loss was taken into account. In addition, torrefaction can reduce the moisture content in the 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

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

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

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

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

3.5 Hydrogen donation

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

4 Discussion

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

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

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

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

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

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

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

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

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

5 Conclusions

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

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

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

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

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

6. Non-hydrogen donor solvents like 1-methylnaphthalene, vegetable oil and decalin generally gave conversions of approximately 70 DAF %. Polymers, petroleum 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