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

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### 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.

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### 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 hydro-cracking. 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 behavior 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.

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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 t/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 CO<sub>2</sub> 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 (e.g., 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 Sulfur), 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.

**Table 1**  
The feedstocks and conditions for the 25 ml and 75 ml Parr reactors.

Biomass	Particle size	Solvent	Biomass to solvent ratio	Reactor volume (ml)
Miscanthus	<500 μm	Anhydrous	–	25
		Hydrous	1:1	25
		Tetralin	1:2.5	25
		1-MN		
		Polystyrene		
		Polyethylene		
		Decalin		
		Bitumen		
		Tetralin		
		Tetralin		
Lignin (low S)	<150 μm	Tetralin	1:2.5	25
Lignin	Mn ~ 10,000	Tetralin	1:2.5	25
Scotch pine (old)	Mn ~ 5,000	Tetralin	1:2.5	25
Torrefied Scotch pine	<500 μm	Anhydrous	–	25
Scotch pine (fresh)	<500 μm	Hydrous	1:1	25
		Tetralin	1:2.5	25
		1-MN		
		Pyrene		
		<i>m</i> -Cresol		
		Decalin		
		Vegetable oil		
		Glycerol		
		Kerosene		
Scotch pine (fresh)	<500 μm	Anhydrous	–	75
		Hydrous	1:1	75
		Tetralin	1:2.5	75
		Vegetable oil		
Scotch pine (old)	<500 μm	Naphthalene	1:2.5	75
		Kerosene		

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