Fast Pyrolysis of Eucalyptus *grandis*

Jan-Erns Joubert, Marion Carrier, Ralph Stahl, Johannes Hansie Knoetze*

Department of Process Engineering, University of Stellenbosch, Private Bag X1 Matieland, 7602, South Africa

*Corresponding author: Prof. Hansie Knoetze, Tel: 021 808 4488 Fax: 021 808 2059 Email: jhk@sun.ac.za

Centre for Renewable and Sustainable Energy Studies

Abstract

Eucalyptus g*randis* is a fast growing hardwood that is extensively used in the paper and pulp industry of South Africa (Godsmark, 2010). Pyrolysis has been shown to be an effective method for condensing bulky biomass such as wood into valuable and easily transportable products (Butt, 2006; Meier and Faix 1999), but very little data is available on the pyrolysis of eucalyptus species and specifically E.g*randis*, justifying the need to investigate this topic. Fast Pyrolysis was carried out on a 0.1 kg/h Bubbling Fluidised Bed Reactor (BFBR), a 1 kg/h BFBR and a 10 kg/h Lurgi® Twin-Screw Reactor. The influence of reactor temperature, initial moisture and biomass particle size were investigated. Reactor temperature was found to be the most significant parameter influencing the product yields and quality. An optimum liquid yield of 74 wt. % (daf) was achieved at 470 ℃ for the 1 kg/h BFBR (± 10 wt. % higher than the 0.1 and 10 kg/h reactors). Product properties compared for the different reactor configurations included the calorific values of the liquid and solid products, the water content of the liquid products and the acidity of the liquid products.

Keywords: biomass, bio-oil, eucalyptus, fast pyrolysis

1. Introduction

Fast Pyrolysis is the rapid thermal degradation of biomass, in the absence of oxygen, followed by immediate quenching of the product vapours to produce a high yield liquid product. Although many different reactor configurations are employed and presented in the literature, the main focus falls upon Bubbling Fluidised Bed Reactors (BFBR) for their superior heat and mass transfer capabilities.

Fast Pyrolysis data can be found in the literature for various Eucalyptus species (*globulus, regnans, loxophelba*) and forestry wastes (branches, stumps, bark, etc.), but almost no data is available for the Fast Pyrolysis of E.*grandis.* The Fast Pyrolysis data that are available for E.*grandis* are not easily comparable with other literature data due to limited information regarding the reactor configurations, the scale of the operations and the process parameters employed. In most instances it is also unclear whether optimum conditions were employed to generate the pyrolysis data.

The purpose of this investigation is to generate valuable Fast Pyrolysis data for E.*grandis* relating to product yields and product quality, and to compare the obtained FP data from 3 different reactor configurations used in this investigation.

2. Literature

2.1. Pyrolysis of E.*grandis*

Few pyrolysis studies have been done specifically on E.*grandis.* Pimenta *et al.* (1998) studied the slow pyrolysis, while Rencoret *et al.* (2007) used an analytical technique on a small scale such as pyrolysis coupled with mass spectroscopy (Py-GC/MS) to characterise volatiles. A recent paper by Kumar *et al.* (2010) investigated the optimisation of the Slow Pyrolysis of E.*grandis.*

A study by Oasmaa *et al.* (2010) focussed on Fast Pyrolysis of various types of feedstock, of which E.*grandis* was one. Debarked Brazilian E.*grandis* was pyrolysed in a 20 kg/h transported bed reactor with a reactor temperature between 480℃ and 520℃ and a vapour residence time between 0.5 and 2 seconds. Although results were generated for biomass characterisation, liquid product yield and liquid product analysis, no data was generated for the solid or gas phase products due to physical limitations of the reactor setup used. A liquid product yield of 70.8 wt. % (on dry feed basis) was reported in the study. The total yield of solid and gas products was calculated by difference seeing that the solid product was combusted to provide heat driving the endothermic pyrolysis reaction.

2.2. Process parameters influencing Fast Pyrolysis

2.2.1. Reactor configurations

The principles of Fast Pyrolysis and the reactor configurations accompanying it have received a lot of attention in literature and have been reviewed by various authors (Bridgwater, 2003; Bridgwater, 2011; Meier and Faix 1999; Mohan *et al.* 2006). The fluidised bed reactor is the most common type of FP reactor used both in industry and for research purpose, possibly due to the good heat transfer and mixing that can be achieved with these reactors and the relative ease of scaling-up. Other reactor configurations used include among others, transported bed, circulating fluidised bed, rotating cone, ablative, screw and microwave reactors (Bridgwater, 2011). Each reactor configuration provides its own advantages and disadvantages, but in essence they all have to adhere to the requirements set for Fast Pyrolysis:

- Moderate reactor temperatures (typically around 500 ℃);
- Vapour residence times below 2-3 seconds;
- High particle heating rates (> 102 K/min);
- Short solid residence times; and
- Rapid quenching of product vapours to yield bio-oil.

2.2.2. Reactor temperature

Temperature is one of the key variables affecting the pyrolysis reaction. Fast Pyrolysis is generally conducted in the temperature range 400-600℃ (Bridgwater, 2011; Mohan *et al.* 2006; Van de Velden *et al.* 2010), where the liquid phase makes out the main product, yielding typically between 60 wt.% and 70 wt.% on a dry basis. From kinetic data however it is known that the thermal degradation of hemicelluloses and celluloses may start at lower temperatures (Raveendran *et al.* 1996; Orfão *et al.* 1999), but a higher reactor temperature is needed to ensure a steep temperature gradient across the biomass particle and to ensure the required heating rate can be achieved. At high reactor temperatures (> 600 ℃) the thermal decomposition of the biomass continues to such an extent that the resulting products are mainly non-condensable gas and char (Azeez *et al.* 2010) and above 750 ℃ gasification starts dominating and gas becomes the main product (Bridgwater, 2011). Reactor temperature has also been shown to affect both the yield and the quality of the pyrolysis products in fast pyrolysis (Garcia-Perez *et al.* 2008; Demirbas, 2007).

2.2.3. Vapour residence time

Vapour residence time plays an important role on the extent of the thermal degradation of product vapours during pyrolysis. Residence times below two seconds limit secondary reactions of the vapour (Van de Velden *et al.* 2010) and this is a typical criterion for fast pyrolysis processes where the main product focus falls on the liquid component (Meier and Faix 1999). When char is the main focus of the study, long residence times are preferred (Bridgwater, 2003). It is believed that the char formed during pyrolysis could have catalytic effects on the vapour phase condensation reactions (Bridgwater, 2011) and should therefore be separated from the vapour phase immediately after formation.

2.2.4. Heating rate and particle size

The particle heating rate refers to the dynamic heat transfer within a biomass particle during pyrolysis and can be manipulated by changing the size of the biomass feed, the heat transfer medium used to heat the particle or by altering the reactor temperature. The heating rates for Fast Pyrolysis are normally a few orders of magnitude greater than that for Slow Pyrolysis and are usually estimated based on the reactor temperature, the particle size and the residence time of the particle within the reactor. As mentioned, in Fast Pyrolysis, the vapour residence time must be short to achieve a high liquid product yield and limit secondary cracking; therefore the particle heating rate must be as high as possible after entering the reactor.

Van de Velden *et al.* (2010) showed that the heating rate of the particle depends greatly on the Biot number and that theoretically, the biomass particle size used for pyrolysis should not exceed 200 µm. From a practical side, however, it is the consensus that biomass particle sizes should not exceed 2-6 mm depending on the scale of the operation (Meier and Faix 1999). Laboratory and bench scale studies however report using particle sizes ranging from 100 µm to 3000 µm (Bridgwater, 2011; Garcia-Perez *et al.* 2008; Guerrero *et al.* 2008a; Mourant *et al.* 2005; Oasmaa *et al.* 2010). Shen *et al.* (2009) investigated the effect of particle size on the yield and composition of the bio-oil produced with a bubbling fluidised bed reactor (BFBR) using E.*loxophelba*. It was found that an increase in the particle size decreased the yield of bio-oil between 300 µm and 1500 µm, but further increases in the particle size did not further decrease the yield significantly. It has also been shown that the particle size used affects the pyrolytic water formed under fast pyrolysis (Shen *et al.* 2009; Garcia-Perez *et al.* 2008).

Studies have also shown that char produced under high heating rates are more reactive to oxygen and has larger surface areas and more reactive sites (Guerrero *et al.* 2005; Guerrero *et al.* 2008a; Guerrero *et al.* 2008b), while the liquid yield is also improved under rapid heating rate (Meier and Faix 1999). Furthermore, the level of mixing that can be achieved in fast pyrolysis (FP) reactors are strong functions of the particle size used in FP reactors and that smaller particles improve both the heating rate of the particle and the mixing of the particles within a BFBR (dos Santos and Goldstein Jr. 2008; Meier and Faix 1999).

2.2.5. Lignocellulosic composition

The chemical composition of the biomass used proves to be another crucial aspect influencing pyrolysis products yield and quality (Garcìa-Pérez *et al.* 2007; Oasmaa and Czernik 1999; Sipilä *et al.* 1998). It has been suggested that relative fractional contributions of the respective lignocellulosic compounds making up a specific biomass, outweighs the influence of the intermolecular bonds existing between these compounds (Raveendran *et al.* 1996). It should however be remembered that the hemicelluloses and lignin, as lignocellulosic groups, are not uniform like cellulose, and their structures are not fully understood (Fengel and Wegener 2003). The building blocks of these super-molecular structures are known, which can indicate to some extent the products that might result from pyrolysis, but no accurate prediction can be made. The significance of the chemical composition of a biomass is further illustrated in literature when the kinetics of individual components, as well as that of the original biomass is considered (Raveendran *et al.* 1996). Knowing the lignocellulosic composition of the biomass used can therefore assist the understanding of how the whole biomass might behave kinetically.

3. Experimental

3.1. Materials and methods

All the biomass used in this investigation came from the Mondi paper mill in Richards Bay, South Africa. The typical lignocellulosic composition for the biomass is shown in **Table 1**.

Table 1. Biomass characterisation

	This study [a] wt. % (daf)	Oasmaa *et al.* (2010) wt. % (daf)
Moisture (wt. %)	7.9	7.6
Ash (wt. % dry)	0.5	0.4
Extractives	2.6	-
Lignin	15.2	± 27
Holocellulose	85.1	-
α-cellulose	57.5	± 51
Hemicelluloses	27.6	± 10
C (wt. %)	45.05	50.1
H (wt. %)	0.29	6.0
N (wt. %)	4.24	0.1
O (wt. % by difference)	49.93	44.0

[a] TAPPI test methods; Browning (1967)

3.2. Reactor configurations

Fast Pyrolysis was investigated using three separate reactor configurations in two legs, one leg at Stellenbosch University (SU) in South Africa, and the other at the Karlsruhe Institute of Technology (KIT) in Germany. A 1 kg/h Fast Pyrolysis plant was used for the experimental runs conducted at Stellenbosch University, while two plants, a 0.1 kg/h bench scale plant and a 10 kg/h Process Demonstration Unit (PDU), were used for the experimental runs conducted at KIT.

3.2.1. SU 1 kg/h bubbling fluidised bed reactor

A schematic representation of the 1 kg/h Fast Pyrolysis plant is shown in **Figure 1**. A 6.6 kW cylindrical furnace housed a 75 mm (ID) stainless steel BFBR, followed by two cyclones in series for solid and vapour separation. Sand (AFS 45 fused silica, from Consol minerals) was used as the heat carrier inside the reactor. Pyrolysis product vapours left the furnace via a heated pipe (maintained at 400 ℃ to prevent intermediate condensation) before entering the cooling tower. The condensation chain consisted of a spray cooling tower followed by two electrostatic precipitators (ESP) in series set to 14 kV and 12 kV respectively. An iso-paraffinic hydrocarbon liquid (Isopar from Engen Petroleum Limited) was used as direct contact quenching medium in the cooling tower. All non-condensable gasses were purged to atmosphere.

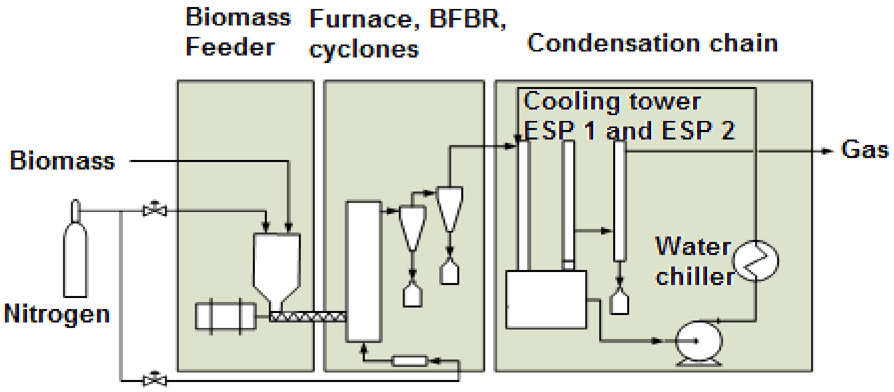

Figure 1. Stellenbosch University Fast Pyrolysis plant (1kg/h).

Reactor temperature and the biomass particle feed size were chosen as the manipulated variables for the experiment. A detailed description of the experimental setup has been given by Hugo, 2010). **Table 2** briefly summarises the process conditions for the South African FP experiments.

Table 2. Process conditions for the SA 1 kg/h FP plant

	Unit	Setting	Comments
Reactor Temperature	°C	440, 470, 500, 530	
Biomass particle size	µm	250 < x < 1000	2 mm Retsch mill
	µm	1000 < x < 2000	4 mm Retsch mill
Biomass feed rate	kg/h	± 0.85	
Nitrogen flow rate	m^3/h	2.4	
Average residence time	s	< 2	
Heat carrier		Nitrogen	High purity
Pipe heater	°C	400	
Isopar temperature	°C	13 °C ± 5	

3.2.2. KIT 0.1kg/h bubbling fluidised bed reactor

A 0.1 kg/h Fast Pyrolysis (FP) plant is used for initial pyrolysis testing before conducting experimental work on a larger scale, 10 kg/h Process Demonstration Unit (PDU). The main focus of this bench scale plant is to evaluate the mass balance and general behaviour of the biomass on a small scale, before moving to the PDU. This bench scale plant is shown schematically in **Figure 2**.

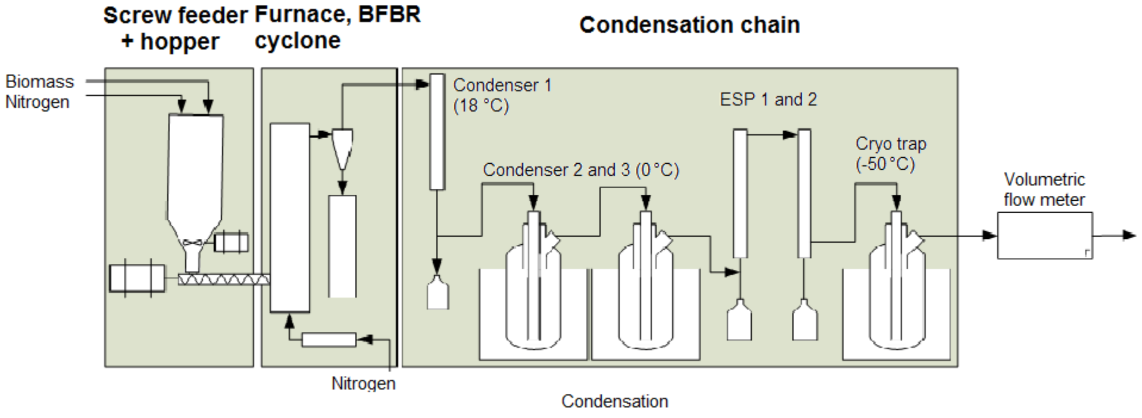

Figure 2: KIT bench scale Fast Pyrolysis plant (0.1 kg/h)

Inside the furnace a single cyclone separator followed the 40 mm (ID) bubbling fluidised bed reactor (BFBR). Silica sand was used as heat transfer medium in the reactor and nitrogen as the carrier gas which was supplied via a fixed line. The product vapour exiting the cyclone was first cooled down to room temperature by a single pass, counter-current, shell and tube heat exchanger at 18 °C, before passing through two well insulated condensers at 0 °C (using crushed ice and water). After the first three condensers, the vapour stream was passed through two electrostatic precipitators (ESPs) in series, at 8 kV and 4 kV respectively for ESP 1 and ESP 2, and then through a cryogenic trap (- 50 °C using dry ice and ethanol). Finally, the incondensable gas was passed through a Ritter Trommel-Gaszähler volumetric flow meter and purged to atmosphere.

Initial moisture content and biomass particle feed size were chosen as the variable process parameters for this reactor configuration. Both of these parameters could easily be manipulated due to the relatively small volumes of biomass needed per run and the high moisture content of the biomass as received (± 26 wt.%). The two biomass particle sizes chosen were those resulting from 1 mm and 2 mm sieve milling of the biomass using a Pulverisette granulator from Fritsch. Two initial moisture contents were chosen: as received and oven dry. The oven dry samples were prepared by drying the milled samples overnight at 105 °C and then letting the sample cool down to room temperature in a desiccator. All the experimental runs were conducted at 505 ± 2 °C and at a constant feed rate of 0.1 kg/h. Experimental runs were conducted in duplicate for repeatability.

3.2.3. KIT 10 kg/h Process demonstration unit (PDU)

A schematic representation of the 10 kg/h Lurgi® Twin-Screw Reactor, process demonstration unit (PDU), is shown in

Figure 3. The PDU was designed to use steel balls (1.5 - 2 mm) as the heat transfer medium. Milled biomass (5 mm) was introduced at the far left side of the Twin-Screw reactor while the hot steel balls (550 °C) were introduced at an offset as shown in **Figure 3**. A detailed description of the plant (with a hot cyclone installed after condenser K1 has been given previously by Henrich *et al.* (2007).

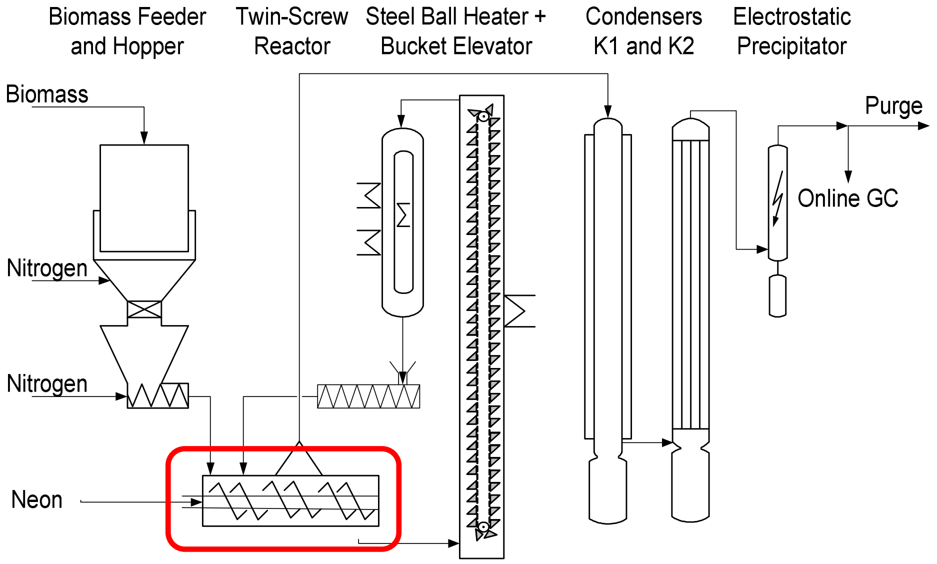

Figure 3: KIT 10 kg/h Process Demonstration Unit (PDU)

The steel balls and biomass were mixed by the rapidly revolving twin screws (60-240 RPM) and pyrolysis was initiated. All the over-size char particles and steel balls fell down from the reactor and were re-cycled via the heated bucket elevator system at 600 °C. Product vapours and char formed were entrained with a nitrogen stream to the first condenser K1, a single pass shell and tube heat exchanger equipped with an automated scraping mechanism to remove char and tar build-up on the inner walls of the condenser. The product resulting from the collection vessel of K1 was a mixture of liquid and solid phases, due to the absence of the hot cyclone at the time of the investigation.

The uncondensed vapour and gas exiting K1 (50 - 70 °C) was passed through a second shell and tube heat exchanger, K2, with an inlet coolant temperature of 10°C. K2 made use of direct contact quenching on the tube side as well as shell side cooling to condense most of the vapour entering the condenser. For the first run of a particular biomass being investigated, approximately 5.5 litre of clean water is used as the circulating quenching medium for K2. The watery product resulting from the first run was then analysed and reused in the following experimental run and so forth, accumulating organic matter with each run. After K2, the remaining vapours and gas stream were passed through an electrostatic precipitator at 20 kV before being analysed by an online GC-MS and finally purged to atmosphere. An overview of the operating conditions used is given in **Table 3**.

Table 3. PDU operating conditions

	Unit	Run 1	Run 2	Run 3	Run 4	Run 5
Moisture content	m%	10.6	21.7	23.4	22.4	9.5
K1 Inlet temp.	℃	20	20	40	40	60
Reactor temp.	℃	500	500	500	500	500
K2 Inlet temp.	℃	10	10	10	10	10
Avg. biomass feed	kg/h	8.1	8.8	9.5	8.8	8.0
Steel balls feed rate	kg/h	1200	1200	1200	1200	1200

3.3. Product characterisation

3.3.1. SU 1 kg/h product analysis

Water content was determined using a Metrohm KF Titrino (ASTM E871). The calorific value (HHV) of the liquid product was determined using an IKA C200 bomb calorimeter. The HHV of the char was measured using a DDS CP500 automatic calorific processor from Digital Data Systems, with a CP501-A solid state cooler and a DDS CP502 filling station. A 509900 Utech Instruments pH probe was used to measure the pH of the liquid product. The BET surface area of the char was determined using a Micrometrics ASAP 2010 system. Liquid product viscosity was determined using a rheometer (Physica MCR 501, Anton Paar).

3.3.2. KIT 0.1 kg/h and KIT 10 kg/h product analysis

A Metrohm pH lab 827 probe was used to measure the pH of the liquid product. The water content was determined using a Metrohm 774 KF Titrino. The calorific value (HHV) was determined using an IKA, model C 5000 control bomb calorimeter. A TruSpec CHN Vario EL III Leco Elementar elemental analyser was used for ultimate analysis. The calorific values reported for liquid products of the $\text{KIT}_{10\ \text{kg/h}}$ FP plant were calculated using the Channiwala correlation as shown in **Equation 1** where the subscript ‘x’ refers to the weight fraction/elemental composition of the organic product and the ash content (Channiwala and Parikh 2002). Methanol extraction was used to separate the liquid and solid fractions found in the product mixture of condenser K1.

Equation 1. $\text{HHV (MJ/kg)} = 0.3491x_C + 1.1783x_H + 0.1005x_S - 0.1034x_O - 0.0151x_N - 0.0211x_{ash}$

3.4. Comparison of the results

The results achieved for the $\text{SU}_{1\text{kg/h}}$ FP plant were subjected to analysis of variance (ANOVA) using Statistica software (version 10) and a mixed factorial design with 2 factors. Particle size and the reactor temperature were varied at 2 and 3 levels respectively.

The reactor configurations used at KIT were operated at constant temperature while other parameters (particle size and initial moisture content) were varied. Therefore, only point values (at similar operating conditions) could be compared to evaluate the influence of the reactor configurations on the product yields and quality. The point values considered were those achieved at a reactor temperature of ± 500 ℃ and an initial water content of ± 10 wt. %. An additional datum point was generated at 500℃ for the $\text{SU}_{1\text{kg/h}}$ FP plant and at an initial moisture content of ± 10 wt. % for the $\text{KIT}_{0.1\text{kg/h}}$ FP plant for comparative purposes. All the product yields reported were calculated and reported on a dry and ash-free basis of the initial biomass fed.

The KIT$_{0.1kg/h}$ FP plant yielded very small quantities of liquid product fractionated over 6 components making up the condensation chain. The product characterisation that could be done was consequently limited by these small volumes and could not be performed for each experimental run.

4. Results and discussion

4.1. Product yields

The influences of the relative process parameters chosen for the SU$_{1kg/h}$ FP plant are shown in **Figure 4**. The optimum operating conditions found for the SU$_{1kg/h}$ FP plant for producing a high liquid yield was at a reactor temperature of 470 ℃ using the smaller particle size distribution (average particle size of ±570 µm). Following the trend of the fitted surface plot it was found that the fitted model predicted well the additional datum point at 500 ℃ (data not shown). At 500 ℃, the liquid, solid and gas yields were found to be 68.6 wt. % daf, 11.4 wt. % daf and 20.0 wt. % daf respectively.

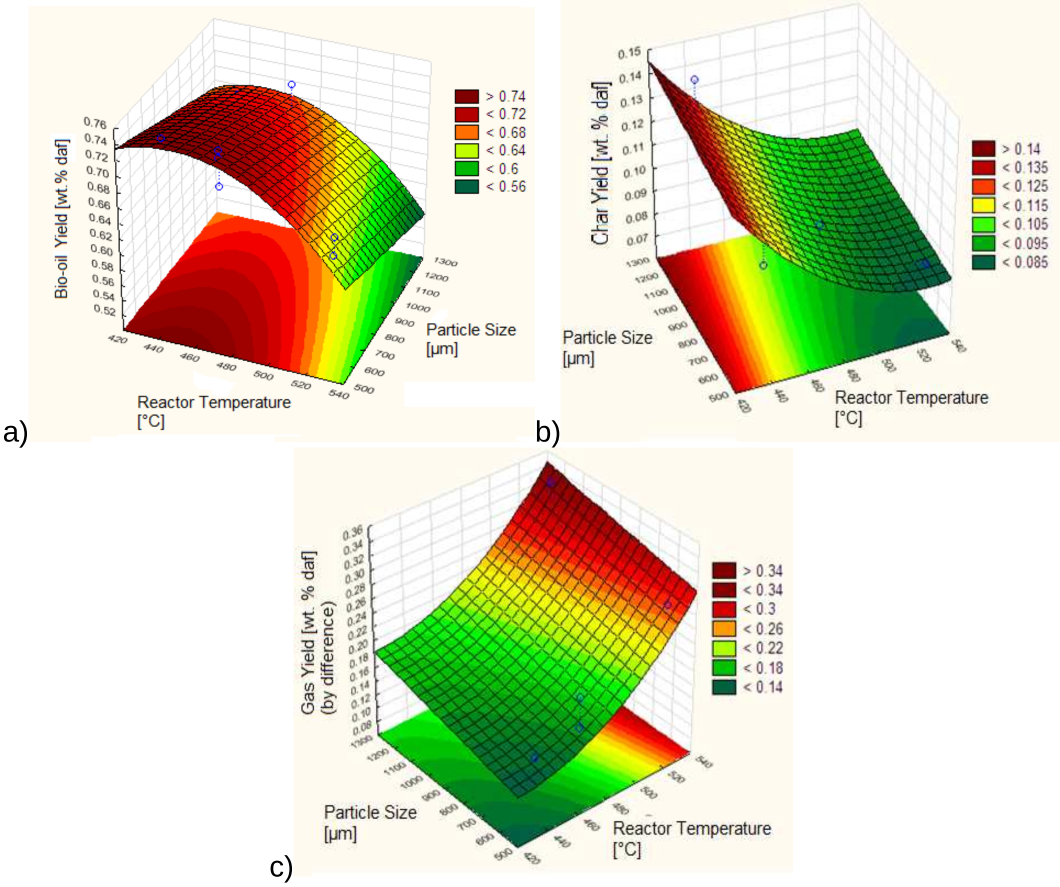

Figure 4. SU$_{1kg/h}$ product yields: a) bio-oil yield; b) char yield; c) gas yield (by difference)

The ANOVA revealed that both the particle size and the reactor temperature had significant effects on the overall liquid yield at a confidence level of 95 %. From the fitted surface plot it is evident that the overall liquid yield is favoured toward the lower temperatures and smaller biomass particle size range chosen for this investigation. This observation is consistent with literature findings for the Fast Pyrolysis of eucalyptus species (Garcia-Perez *et al.* 2008; Kumar *et al.* 2010; Shen *et al.* 2009). The optimum conditions found in this investigation to achieve the highest liquid yield was at a reactor temperature of 440 - 460 ℃ and a particle size range greater than 250 µm but smaller than 1000 µm.

The yields achieved for the bio-oil in this study are comparable with the results achieved by Oasmaa *et al.* (2010) (70.8 wt. % dry basis) on a 20 kg/h FP plant using debarked E.*grandis*, but higher than those reported by Garcia-Perez *et al.* (2008) (61 - 66 wt. %) using oven-dry mallee eucalyptus on a 2 kg/h setup. These deviations can be ascribed to the lower lignin content (15.2 % compared to ± 25 % in the literature) of the biomass used in this investigation and the initial moisture content of the biomass used in these studies (Demirbaş, 2005). No strong statistical conclusions could be drawn at the 95 % confidence interval for the influence of the process conditions on char product, but at a 90 % confidence interval it is clear that the reactor temperature had a significant influence on the overall char yield.

The product yields achieved with the KIT$_{0.1kg/h}$ FP plant are shown in **Figure 5** for the different particle sizes investigated. When considering the variations denoted by the error bars, it appears that the initial moisture content of the biomass did not affect the product yields significantly for this reactor configuration, and similarly it can be argued that the particle size also had a minor effect on the overall yields. The larger particle size showed a decrease in liquid yield at high initial moisture content, which was unexpected when considering the findings of Demirbaş, (2005) regarding the effects of the initial moisture.

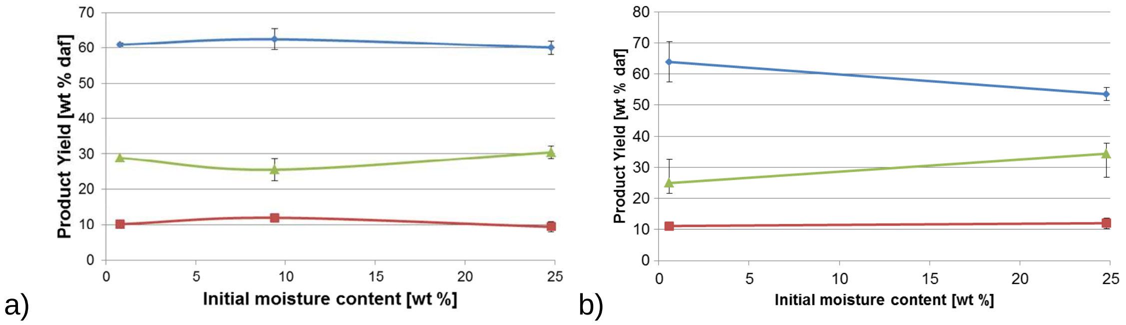

Figure 5. KIT$_{0.1\ kg/h}$ product yields: a) 1 mm (milled) particle size; b) 2 mm (milled) particle size with (◆) Total condensates; (■) Char; (▲) Gas (by difference).

This deviation might be explained by the inefficiency of the solid separation observed while conducting the experimental work. It was found that significant quantities of char particles were entrained from the reactor and hot cyclone, sticking to the inner walls of the first condenser. In some cases the fouling was found to be so severe that the entire inner diameter of the first condenser was blocked. Char is believed to have an unwanted catalytic effect on the on the overall pyrolysis reaction whereby it facilitates vapour condensation and other side reactions, and consequently increasing the final char yield at the expense of the liquid yield (Bridgwater, 2011).

The product yields achieved for the 10 kg/h FP plant are shown in **Figure 6**. Of specific interest is the result from run1 as it was conducted at an initial moisture content of ± 10 wt. %. The results from run 5, at similar conditions, have been omitted as the closure of the mass balance was found to be unsatisfactory. Good repeatability was however observed for the results from run 2 and 3, conducted at the same operating conditions. As expected the liquid yield increased when feeding biomass with higher moisture content (Demirbaş, 2005). Raising the inlet temperature of K1 (run 4), while keeping the initial moisture content constant with that of runs 2 and 3, did not result in significant changes to the overall yields. The liquid yield was found to be lower than that of the SU$_{1kg/h}$ FP plant at similar operating conditions while the overall gas and char yields were higher. This observation is consistent literature suggesting unwanted catalytic cracking of product vapours by the char product which consequently increases the gas and char yields at the expense of the liquid product (Bridgwater, 2011).

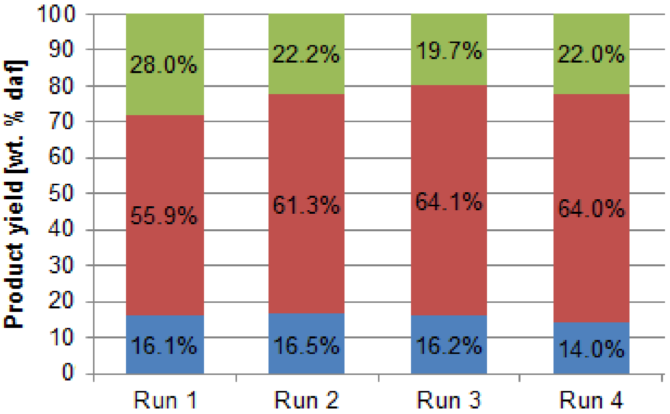

Figure 6. KIT$_{10\ kg/h}$ product yields: Char (🟦 bottom); Total condensates (🟥 middle); Gas by difference (🟩 top).

4.2. Product quality

Table 4 summarises the product quality for the SU$_{1kg/h}$ FP reactor. Where more than one run was conducted at a specific set of process conditions, the average values are reported. The ANOVA showed that the biomass particle size used had a significant effect on the pyrolytic water content produced and that larger particle sizes will result in higher water content. This trend is consistent with the work of Shen *et al.* (2009) on E.*loxophelba.* Garcia-Perez *et al.* (2008) also reported this trend showing that when pyrolysing similar biomass at similar temperatures, the water content of the produced bio-oil can be manipulated by varying the particle size.

Table 4. SU$_{1kg/h}$ products quality

Temp. [℃]	**Average particle size** [µm]	**HHV (l)** [MJ/kg]	**HHV (s)** [MJ/kg]	**Water content** [wt. %]	**pH** [-]	**Viscosity** [mPa.s]	**BET surface area** [m ^{2}/g]
440	570	16.38	32.74	25.68	2.37	36.6	-
470	570	16.78	30.56	24.90	2.46	35.3	356.6
500	570	17.21	32.86	22.08	2.41	43.1	337.9
530	570	17.38	29.14	22.76	2.41	42.6	344.2
440	1200	16.14	31.98	27.08	2.33	29.6	294.9
470	1200	16.03	32.38	27.31	2.50	26.4	-
530	1200	16.24	27.82	29.24	2.74	28.3	128.2

From the results of the ANOVA it was clear that the reactor temperature had a significant effect on the HHV of the char product at a 95 % confidence interval, while no strong conclusions could be drawn for the effects of the particle size at the same confidence interval. The HHV found for the char is higher than that of petroleum cokes (Van de Velden *et al.* 2010) which makes it an attractive fuel source especially toward the lower reactor temperatures investigated. It is well known that the rate of decomposition of cellulose and hemicelluloses are favoured at lower temperatures compared to that of lignin, and that the lignin fraction of biomass contributes significantly to the final char yield (Orfão *et al.* 1999). It could therefore be assumed that at lower reactor temperatures more of the lignin remains intact compared to the higher reactor temperatures. This supports the high calorific values found for the char at lower reactor temperatures.

Although no strong conclusions could be drawn at a 95 % confidence interval for the influence of the process parameters on the HHV of the liquid product, a clear trend could be observed. When considering the pyrolytic water production shown in **Table 4**, it would seem that the process conditions do have an indirect effect on the HHV of the liquid through the pyrolytic water produced. The calorific value of the liquid product was found to increase toward the process conditions favouring low pyrolytic water production i.e. small particle size and high reactor temperature.

According to the ANOVA, it could not be demonstrated at a significance level of 95 % that the particle size or reactor temperature had significant influences on the pH of the bio-oil. Oasmaa *et al.* (2010) found the pH of Fast Pyrolysis oil produced at 500 ℃ to be 2.2, while Azeez *et al.* (2010) found the pH of various African woody biomass species to be within the range of 2.5 and 2.9. A recent study by Kumar *et al.* (2010) on the Slow Pyrolysis of E.*grandis* reported pH values varying between 1.8 and 2.9.

The range of viscosities reported in **Table 4** (19.6 - 43.1 mPa.s) was higher than the point values reported in literature (16.9 mPa.s by Kumar *et al.* (2010) and 28.3 mPa.s by Oasmaa *et al.* (2010)) for E.*grandis*, possibly due to the time elapsed between analysis of the samples and the production thereof. The samples were sent for analysis in two batches, for organisational purposes in the analytical lab, and was not analysed immediately after production which could have resulted in re-polymerisation of the bio-oil components consistent with bio-oil ‘aging’ (Mohan *et al.* 2006).

The BET (Brunauer, Emmett and Teller) surface area was found to be greater for the 570 µm particles than for the 1200 µm particles, ranging between 337 and 356 m^2/g. This finding is in agreement with the literature suggesting that increasing the particle heating rate consequently increases the porosity of the resulting char particles (Guerrero *et al.* 2008a).

Figure 7 shows the overall pyrolytic water yield for each experimental run conducted on the KIT$_{10\ \mathrm{kg/h}}$ FP plant. The average pyrolytic water yield found for the KIT$_{10\ \mathrm{kg/h}}$ FP plant were much lower in comparison to that found for the SU$_{1\mathrm{kg/h}}$ FP plant, stressing the significance of the configuration and equipment used in the condensation chain of a FP plant.

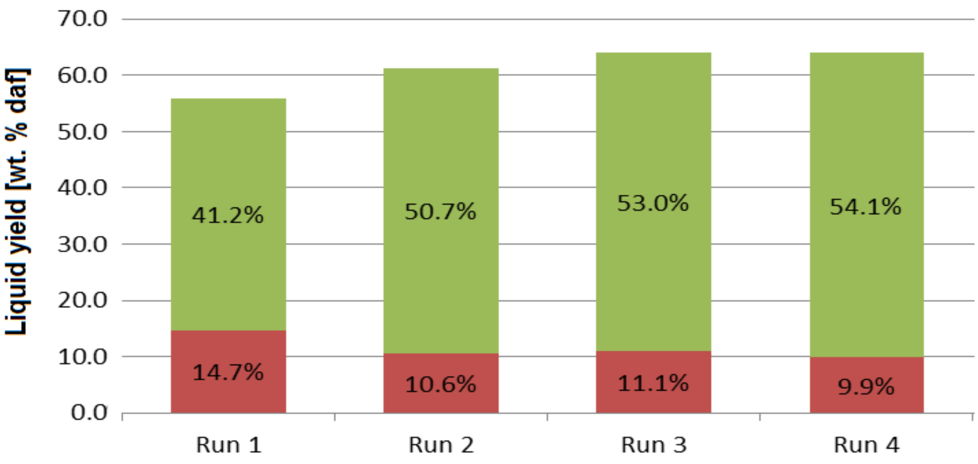

Figure 7. Overall pyrolytic water yield for the KIT$_{10\ \mathrm{kg/h}}$ FP plant: Pyrolytic water (🟥 bottom); and Organic condensates (🟩 top)

The elemental composition of the liquid and solid products from the $KIT_{10\ kg/h}$ FP plant is given in **Table 5** while the gas composition is given in

Table 6. From these results the calorific values were calculated using the Channiwala correlation as shown in **Figure 8**. The calorific values shown in **Figure 8** are expressed on a dry basis, due to the methanol extraction required to separate the respective phases before conducting elemental analysis for each product phase. The calorific values of the K1 condensates are reported by difference of the K1 extracted char and the original K1 product containing both char and condensates.

Table 5. Elemental compositions (wt. %) of $KIT_{10kg/h}$ FP plant products.

	C	H	O	N	S
K1 Extracted char	83.1	3.6	13.2	0.1	0
K1 Oil and char mixture	64.7	5.3	29.7	0.2	0
K1 Organic condensate	55.3	6.3	38.2	0.2	0
K2 condensate	44.4	9.1	46.5	0	0

Table 6. Gas composition (wt. % daf) for $KIT_{10kg/h}$ FP plant.

Compound	**Run 1**	**Run 2**	**Run 3**	**Run 4**
H_2	0.3	0.2	0.2	0.2
CO	34.9	37.5	37.7	37.5
CO_2	53.5	56.8	56.8	56.6
CH_4	3.8	4.3	4.2	4.2
C_2H_4	0.4	0.0	0.2	0.4
C_2H_6	0.5	0.8	0.7	0.6
C_3H_8	0.8	0.2	0.2	0.2
C_4's	2.2	0.2	0.0	0.2
C_5+	3.7	0.0	0.0	0.0

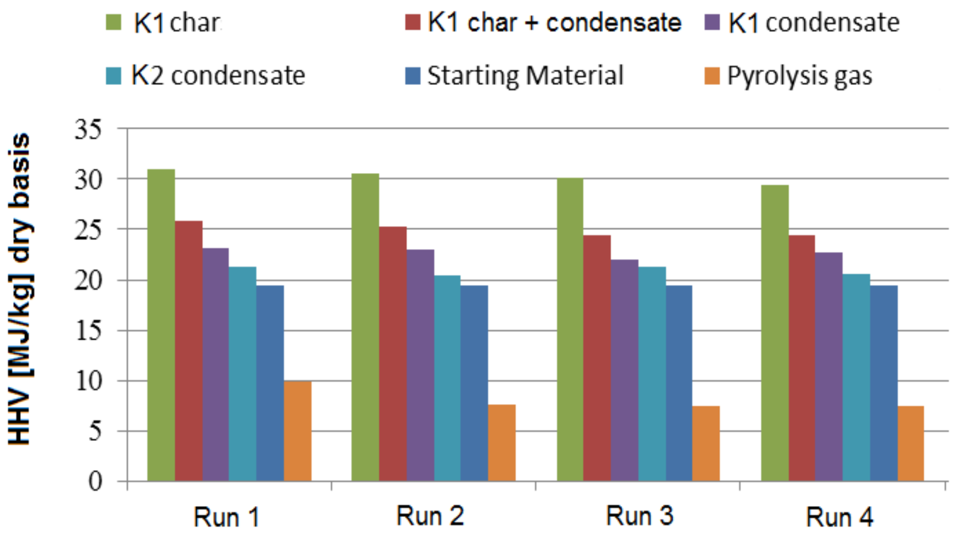

Figure 8. Calculated calorific values for the $KIT_{10\ kg/h}$ FP plant on dry basis

The calorific values found for the extracted char resulting from the K1 condensate and char mixture were comparable to those found for the char produced by the $US_{1\ kg/h}$ FP plant (**Table 4**). When considering the results for the liquid products however, a direct comparison could not be made based on the method used to achieve these results and basis on which the results are reported. Due to the complex nature of the products resulting from K1 and K2, direct determination of the respective calorific values (using a bomb calorimeter) of the liquid phase products were impossible. It was however observed that the average theoretical calorific value of the condensates resulting from K1 and K2 (22.2 MJ/kg) was higher than that of the bio-oil produced by the $US_{1\ kg/h}$ FP plant (17.2 MJ/kg). This observation was expected as the calorific values expressed for the $US_{1\ kg/h}$ FP plant included the pyrolytic water content of the bio-oil, while the theoretical calculated values for the $KIT_{10\ kg/h}$ FP plant did not.

5. Conclusions and recommendations

Valuable data was generated for the Fast Pyrolysis of E.*grandis* and compared for three different reactor configurations. The results from the $SU_{1kg/h}$ FP plant compared well with literature data generated for other eucalyptus species. It was shown that the particle size and reactor temperature had significant effects on both the product yield and quality and that an optimum liquid yield of 74 wt. % (daf) could be achieved at 470 °C for the $SU_{1kg/h}$ FP plant using an average biomass particle size of 570 µm.

Table 7 summarises the product yields and quality which could be compared directly among the three reactor configurations investigated. When considering the product yields achieved at similar conditions it was clear that the $SU_{1kg/h}$ FP plant resulted in the highest liquid yield

Table 7. Comparison of product yields for 3 FP reactors at 500 °C and 10 wt. % initial moisture

	Unit	**$SU_{1kg/h}$**	**$KIT_{0.1\ kg/h}$**	**$KIT_{10\ kg/h}$**
Liquid yield	wt. % daf	68.6	62.5	55.9
Char yield	wt. % daf	11.4	12.0	16.1
Gas yield [a]	wt. % daf	20.0	25.5	28.0
Liquid product water content	wt. %	22.1	-	14.7
HHV (char)	MJ/kg	32.9	-	31.0

[a] by difference

Differences in the reactor configurations, especially with regard to the condensation chain proved to be of vital importance in the results achieved. Significant differences were observed for the overall liquid yields achieved as well as the water content of the overall liquid product. The char and gas yields for the KIT reactor configurations were found to be higher than those for the $SU_{1kg/h}$ FP plant, possibly due to extended contact of the product vapours and char caused by inefficient solid separation for the $KIT_{0.1\ kg/h}$ FP plant and the absence solid separation for the $KIT_{10\ kg/h}$ FP plant. Unlike the $SU_{1kg/h}$ FP plant, the two reactor configurations at KIT produced mixed phase product streams (solid, organic and aqueous phases) requiring chemical extraction for qualitative and quantitative analyses. As a result of these complex mixtures the characterisation of the individual product phases and the direct comparison thereof with the other reactor configurations and literature were limited.

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