ASSESSING THE SUITABILITY OF DIFFERENT BIOMASS FEEDSTOCKS FOR PROCESSING VIA GASIFICATION

*Matthew E. Boot-Handford,[a] Nick Florin,[b,c] Rafael Kandiyoti,[a] and Paul S. Fennell *[a]*

[a] Department of Chemical Engineering, Imperial College London, SW7 2AZ
E-mail: p.fennell@imperial.ac.uk; Tel: +44 (0)20 7594 6637

[b] Grantham Institute for Climate Change, Imperial College London, SW7 2AZ

[c] Institute for Sustainable Futures, University of Technology Sydney, NSW 2007

Introduction

Biomass utilisation has received renewed interest over recent years in response to growing concerns over volatile fossil fuel prices, energy security, and climate change.[1] Biomass is widely considered to be a renewable source of energy which is often available in large quantities and at a low cost as a by-product of agriculture and forestry. Its use is potentially CO_2 neutral as the amount of CO_2 released during combustion is equal to the amount removed from the atmosphere during photosynthesis (although emissions from fertiliser, transport, farming and pre-treatment usually result in its use being slightly CO_2 positive). Furthermore, biomass utilisation coupled with carbon capture and storage (BECCS) can result in negative CO_2 emissions *i.e.* a net removal of CO_2 from the atmosphere. The use of biomass for the production of heat and power also offers advantages over other renewable energy sources such as wind and solar in that it is capable of providing uniform and uninterrupted distribution.

Gasification is one of the most efficient and flexible methods for processing biomass, providing a means to convert 60 – 90% of the energy content of the biomass into a versatile gas with significantly improved distribution characteristics.[2] The gas that is produced can be used directly as a fuel in a gas turbine or fuel cell for heat and power generation, or as a feedstock for the production of liquid transportation fuels or chemicals. Gasification also enables the extraction of energy from a much wider range of materials that may not be considered fuels in the conventional sense, such as municipal solid waste (MSW) and sewage.[3]

Gasification is a complex process involving numerous parallel reactions resulting in a mixture of both useful and problematic products. Pyrolysis is the first step of the gasification process that involves the thermal decomposition of a solid fuel in the absence of oxygen to produce a complex mixture of gases, tars (oils), and char (containing ash). These species will go on to further react in gasification reactions with limited amounts of oxygen, steam and/or CO_2 to produce a gas with high concentrations of H_2 and CO.

Biomass pyrolysis yields significant amounts of vapour (typically 75 – 90 % of the initial weight compared with 20 – 40 wt.% for coal) a large proportion of which is tar.[4] Whilst most of the primary tar compounds produced during pyrolysis are cracked and reformed into useful, combustible gases in subsequent high temperature gasification and combustion reactions, small amounts of secondary and tertiary tars are also formed which exit the gasifier with the product gas. Tars are operationally defined as any organic material in the product stream that is condensable in the gasifier, downstream processing steps or conversion devices.[5] Its presence can lead to a whole host of downstream operational issues particularly in advanced technologies such as fuel cells that have very low tolerances < 80 ppb tar contamination. The high tar content of gas produced from biomass gasification represents a substantial obstacle to commercialisation and wide scale deployment of the technology as downstream conditioning to remove tars exacts substantial economic and efficiency penalties on the process.

Our research at Imperial College has had two main focuses: the first being the development of a simple protocol for assessing the suitability of different biomass feedstocks for use as a fuel for gasification. The second involved investigating the impact of operating conditions such as temperature and presence of low-cost materials with potential catalytic activity on the pyrolysis product distribution with the aim of minimising or even eliminating residual tar compounds exiting the process.

This work employed a lab-scale fixed-bed reactor that can be operated in either a single stage or two-stage configuration with independent heating of the two stages (Fig.1). For the first part of our work, the fixed bed reactor was operated in its single stage configuration to pyrolyse biomass feedstocks. The products obtained *i.e.* char and tars were then characterised using a range of analytical techniques to determine their chemical and physical properties. The idea here being that the information gained could aid in the design of an optimal process for the gasification of a particular biomass or waste feedstock, informing on the most appropriate operating conditions and gasifier type.

The second strand of our research made use of the reactor in its two-stage configuration. Here, the first stage was employed as a tar generating zone and the 2nd stage as a tar cracking zone. The 2nd stage was operated empty to assess the effect of elevated temperatures on the tar yield, and loaded with a bed of either sand, sand and calcined limestone, or sand and calcined dolomite to investigate whether any additional cracking could be achieved by these materials.

In this paper we present a summary of the key findings and conclusions of our work. A further paper is in preparation that will provide more detail and expand upon this first report.

Experimental

The development and operation of the 2-stage reactor employed in this work has been reported in detail in a number of previous publications[6] and will be described only briefly here. The version of the reactor employed in this work is the same as that described by Dabai *et al.*[6f]

Reactor Description. The first stage consists of a 12 mm ID (2mm wall thickness) stainless steel tube, 200 mm in length with a welded flange connection at its base to allow for connection to the 2nd stage or directly to the tar trap. A Swagelok Tee fitting is connected to the top of the first stage which acts as the inlet for the 1st stage gas supply and a thermocouple for 1st stage temperature control. Before each experimental run, 1 g of biomass (106 – 150 μm) was loaded into the 1st stage and supported in position with a strip of stainless steel wire mesh.
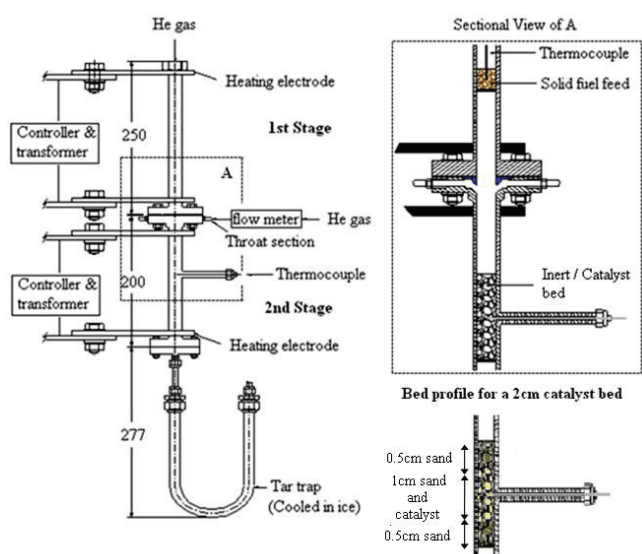
Figure 1. Diagram of the 2-stage, fixed-bed reactor, reproduced from Monteiro Nunes *et al.*[6d]

The 2nd stage is made up of a 12 mm ID (2mm wall thickness) Incoloy 800 HT tube, 150 mm in length with welded top and bottom flanges. The top flange has been specially designed to incorporate 3 equally spaced, lateral gas inlets such that the gas velocity can be varied independently of the 1st stage. A spigot welded to the outside of the 2nd stage allows for placement of a thermocouple inside the 2nd stage for controlling the temperature. For experiments investigating the effect of the different solids on the tar yield, 2cm beds comprising of a 1 cm section of either 20 wt.% limestone or 20 wt.% dolomite (355 – 425 μm) mixed with 80 wt.% sand (500 – 710 μm) positioned between two 0.5 cm sections of sand were loaded into the 2nd stage prior to assembly. The beds were held in position with a wire mesh plug.

The tar trap is a 12 mm ID, stainless steel U-tube. It is fitted with a stainless steel flange to enable connection of the trap to either the 1st or 2nd stage. The tar trap is submerged in a liquid nitrogen bath for the duration of the experiment to condense as many of the tars and other volatile products as possible for analysis. The exit of the trap is packed with wire mesh to enhance the internal surface area of the tar trap and ensure efficient trapping of the volatile products in the form of aerosol droplets.

The reactor is heated via four copper electrodes that are attached to the outside of the reactor body at the top and bottom of the two stages. The reactor body acts as a resistance heater. The electrode that attaches to the top of the 1st stage is rigid and acts as a support for the reactor. The other three electrodes are flexibly attached to the reactor with woven copper cables to allow for thermal expansion of the reactor body.

Materials. The biomass and waste samples used in this study were beechwood (BW), a risk husk originating from Brazil (BRH), a rice husk originating from Thailand (TRH) and a textile sludge waste collected in Brazil (TS). Their ultimate and proximate analyses can be found in table 1. The sand used in this investigation was supplied by David Balls Sand. The limestone originates from Purbeck, UK

and the dolomite was supplied by Steetley Dolomite, ltd. The XRF analysis of the sand, dolomite and limestone are present in tables 2.

Operating Conditions. A standard set of conditions were used when operating the first stage. A heating rate of 1 $°Cs^{-1}$ was used to heat the biomass sample from ambient to 500 °C where it was held for 900 s to ensure complete pyrolysis of the sample. A flow of helium with superficial velocity of 0.1 ms^{-1} at 500 °C was introduced at the top of the reactor to sweep the evolving volatiles from the sample bed downstream to the 2nd stage or tar trap.

The operating conditions of the 2nd stage were varied depending on the variable that was being tested. In all cases, the 2nd stage was heated to the experimental temperature (700 – 900 °C) prior to starting the first stage temperature program. When limestone or dolomite was used, the 2nd stage was heated to 900 °C for 300 s to ensure the dolomite and limestone was fully calcined before the 2nd stage was allowed to cool to the experimental temperature. During this period, the tar trap was not cooled so as not to trap any of the CO_2 or H_2O released in the calcination period which would interfere with the product analysis. An additional flow of He was added through gas inlets in the 2nd stage flange such that the total superficial flow through the 2nd was controlled at 0.25 ms^{-1}.

Product recovery. After each experiment, the reactor was dismantled and each of the reactor components were carefully washed with a 4:1 (v/v) solution of chloroform and methanol (150 ml) to extract the tars. The washings were then filtered into a flask using a pre-weighed Whatman no. 1 filter paper to collect any chars that were removed in the washing process. The bulk of the solvent was removed by evaporation on a rotary evaporator (BUCHI-Rotavapor 3000) operated at 80 °C at 40 rpm for 10 minutes. The tars were then transferred to an aluminium beaker and placed in a recirculating air oven at 35 °C for 2 hours (along with the chars that were removed from the 1st stage after the washing step) to ensure complete solvent removal from the samples. The tars and chars were then weighed to determine their respective gravimetric yields as a percentage of the initial weight of the biomass sample.

Gaseous product detection. CH_4 and CO which did not condense in the tar trap were detected using online ADC analysers connected after the tar trap. The amount of CO_2 produced was also measured using an online ADC detector; however due to the fact that CO_2 was condensed in the tar trap during the experiments, CO_2 had to be measured after the experiments when the tar trap was allowed to warm up to room temperature.

Product Characterisation. Char reactivity measurements with air and CO_2 were carried out using a TGA (TA Q5000). 2 mg of the char sample was loaded onto a platinum pan and heated up under a flow of N_2 (25 ml/min) to either 500 °C or 900 °C for reactivity measurements with air and CO_2 respectively. The temperature was held at the set-point temperature for 5 mins before the gas purge was switched to either air or CO_2. The weight loss of the chars was observed until constant weight was obtained. The normalised maximum reactivity (R_{max}) was obtained from the maximum rate of reaction (maximum rate of weight loss) using equation 1.

Table 1. Proximate and ultimate analyses of the biomass samples used in this study.

| Feed | Ultimate Analysis daf | | | | | | Proximate Analysis | | |
	C	H*	N	O^	S	Cl	Ash	Moisture	Volatiles
Beechwood	43.4	4.8	0.26	39.5	<0.04	0.01	0.5	11.6	75
Brazilian rice husk	43.1	5.6	0.4	50.9	0.00	0.02	13.4	6.9	45.2
Thai rice husk	47.0	5.	0.8	46.0	0.05	0.4	16.8	10.1	64.5
Textile sludge	57.5	9.0*	4.9	22.3	3.99	1.65	29.0	11.9	53.0

Values for the proximate analyses are calculated on the "as received" moisture.
daf dry, ash-free basis.
* denotes that the value has been corrected for moisture content *i.e.* it does not include the hydrogen in the moisture.
^ The oxygen content was determined by difference.
The analysis for beechwood was carried out by TES Bretby, UK.
The analysis for the Brazilian rice husk, Thai rice husk and textile sludge was carried out by H.Jorge, Private Communication, 2010.

Table 2. XRF Analysis of the Sand, Dolomite and Purbeck Limestone used in this study.

	Sand [wt.%]	Limestone [wt.%]	Dolomite [wt.%]
CaO	0.20	93.15	65.25
SiO$_2$	98.41	8.46	0.14
MgO	0.00	0.76	34.47
Fe$_2$O$_3$	0.10	0.55	0.04
Al$_2$O$_3$	1.09	0.47	0.08
P$_2$O$_5$	0.00	0.22	0.00
SO$_3$	0.00	0.15	0.00
K$_2$O	0.17	0.11	0.00
SrO	0.00	0.07	0.02
MnO	0.00	0.05	0.00
NiO	0.00	0.01	0.00
TiO$_2$	0.03	0.00	0.00

$$R_{max} = -\frac{1}{W_0}\left(\frac{dW}{dt}\right) \qquad (1)$$

Where W_0 is the initial weight of the char (daf basis), and (dW/dt) is the rate of weight loss, obtained from the first derivation of the weight loss curve.

The repeatability of the R_{max} determination is ± 9 % of the value quoted. Only single determinations have been reported as repeatabilities are usually high and well within ± 5 % of the measured reactivity value.

Pore surface area (BET) and pore volume distribution (BJH) measurements of the recovered chars and bed materials were determined using a Micromeritics Tristar 3000 N$_2$ sorption analyzer. Sample morphology was observed with a Hitachi S3400 SEM with 20 kV of accelerating voltage under high vacuum. The samples were coated with gold before SEM examination and images obtained by secondary electrons are presented here.

Results and Discussion
Single Stage Pyrolysis Experiments. Pyrolysis of beechwood produced more tars and less char than the other three fuel samples tested in this study (Fig. 2). The amount of volatiles released was fairly consistent for all three biomass varieties. Textile sludge produced the least amount of volatiles and most char.
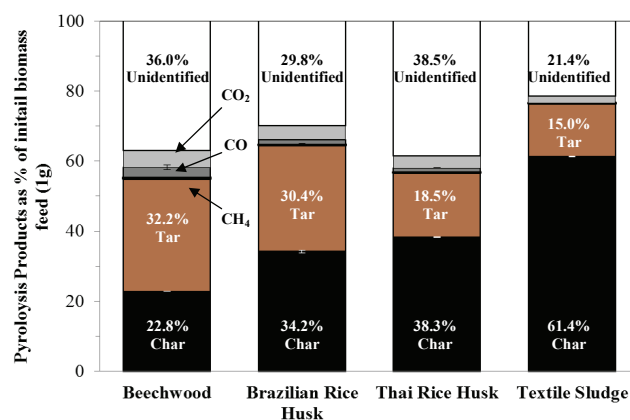

Figure 2. Distribution of the products generated during pyrolysis of four types of biomass feed in the single stage reactor.
Gas Yields: CO$_2$ = 3.9 % 4.0 % 3.5 %, 2.0 %; CO = 2.4%, 1.4%, 1.1 %, 0.1 %; CH$_4$ = 0.3 %, 0.2 %, 0.1 %, 0.1% for BW, BRH, TRH and TS respectively.

The amount of char generated during pyrolysis increased with increasing ash content as determined by proximate analysis (table. 1). This is consistent with previous works that have concluded a high ash content favours char forming reactions.[7]

It is noteworthy that although pyrolysis of the two rice husk samples produced similar amounts of char, the Thai rice husk produced approximately 40 % less tars than the Brazilian rice husk. This could be due to more pronounced cracking of the tar compounds by certain ash constituents as the tars evolve from the sample bed. Further work is currently underway to identify the different minerals present in the ash so as to gain a better understanding of the interactions that are taking place.

Another possible explanation for the trend in volatile release and char formation can be deduced from the SEM images of the chars recovered after pyrolysis (Fig. 3a-d). The beechwood char appears to have the most fibrous structure and largest pores which is known to aid volatile release by offering an easier path for the tars to the exterior of the particle[8] while textile sludge has the smallest pores
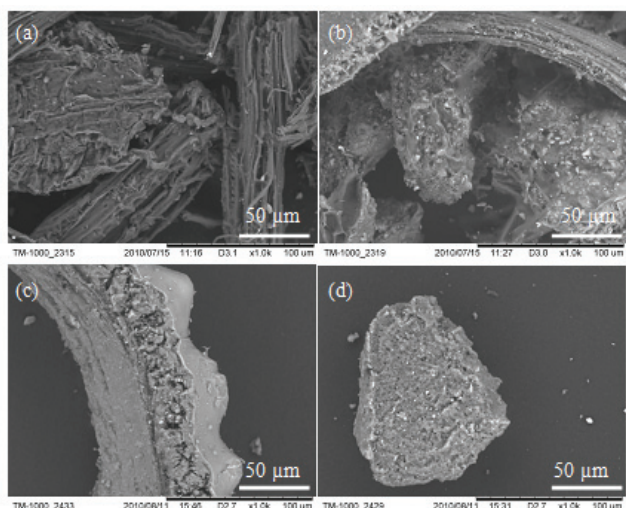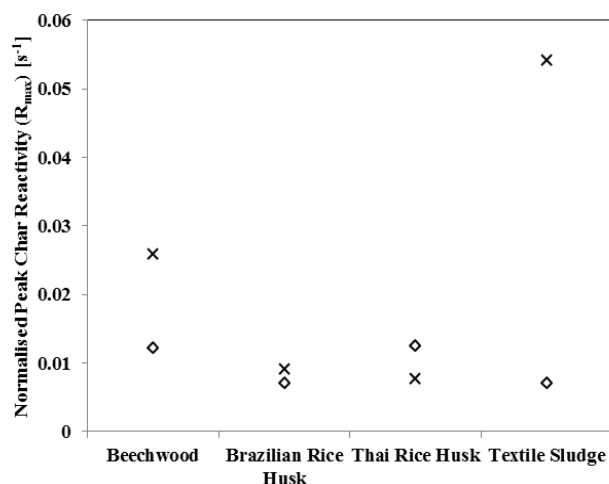
Figure 3. SEM images of the chars produced during the pyrolysis of the different feeds in the single stage reactor. (a) beechwood chars, (b) Brazilian rice husk chars, (c) Thai rice husk char, (d) textile sludge char.

(Fig. 3a,d). The two rice husk chars appear to have slightly smaller pores (Fig. 3b,c) which may contribute to the lower volatile yields compared with beechwood. There also seems to be a great deal more ash coating the surface of these chars (lighter coloured parts in the images), which in addition to catalysing char forming reactions may also cause blocking of pores, hindering the release of volatiles and enhancing char formation.

The TGA char reactivity experiments revealed some interesting behaviours (Fig. 4). The beechwood and Thai rice husk chars exhibited the highest peak reactivites in air at 500 °C with similar normalised reactivities of 0.012 and 0.013 s^{-1}. The peak normalised reactivites of the Brazilian rice husk and the textile sludge chars were lower at 0.007 s^{-1}. The trend in the reactivities of the chars with CO_2 at 900 °C were quite different with the textile sludge char exhibiting the highest normalised reactivity of 0.054 s^{-1}. The beechwood char displayed the second highest reactivity of 0.026 s^{-1} whilst the Brazilian and Thai rice husks were significantly less reactive with peak normalised reactivities of 0.009 and 0.008 s^{-1} respectively.

A possible explanation for the trends in the reactivities of the different chars may also be deduced from the SEM images of the chars (fig. 4). Beechwood exhibits a reasonably high reactivity with both air at 500 °C and CO_2 at 900 °C which is likely due to the large pores aiding mass transfer of the reactant and product gases through the char matrix. The trend in reactivity of the rice husks with air was consistent with their ash contents and could possibly be explained by a higher catalytic activity of the Thai rice husk ash constituents towards char combustion. It is also likely that this is the reason for the textile sludge exhibiting the highest reactivity with CO_2. A possible cause for the lower reactivities of the two rice husk chars in CO_2 could be that 900 °C is above the ash fusion temperature which led to the formation of a more severe ash coating on the surface of the char, blocking access to the pores and reducing the available reactive surface area.


Figure 4. Normalised peak reactivities of the four different chars produced during pyrolysis in the single stage reactor calculated from the maximum rate of weight loss in the TGA when reacted with air at 500 °C ◇; and CO_2 at 900 °C ×.

These initial results indicate that beechwood would be the most suitable gasifier feed of the four biomass varieties tested in this study. It produced the largest amount of volatiles containing the highest proportions of the combustible gases (CO and CH_4). It also produces the least amount of char, which demonstrated reasonable reactivity with both air and CO_2. The large amount of tars initially released in pyrolysis would be largely cracked and reformed in subsequent high temperature gasification and combustion reactions but may present some problems as biomass varieties that release larger amounts of tars during pyrolysis tend to produce gases with a higher tar content when gasified. It was for this reason that we chose to use beechwood in the second part of our study, investigating the effect of elevated temperatures and solids with potential catalytic activity on the tar yield.

Pyrolysis of the two rice husks released similar quantities of volatiles to the beechwood and less tars, however they both had high ash contents and produced chars with low reactivities. If our hypotheses are correct and it is the formation of an ash coating on the surface of the chars inhibiting the reactivity, then it would suggest a gasifier design based on a fluidised-bed reactor would be the optimal system for processing these feedstocks. The abrasive nature of a fluidised bed acts to etch away the surface of the char exposing new surfaces that can undergo reactions thus enhancing the observed reactivity. The low fusion temperature of the ash may cause issues relating to defluidisation of the bed material. Despite the apparent poor performance of these materials, exploitation of this potential energy source is made particularly attractive by the fact that these are a waste product produced in substantial quantities.

Textile sludge initially appeared to be the least feasible fuel for gasification. It released the least amount of volatiles and the largest amount of char and the char exhibited the poorest reactivity at 500 °C with air. However at 900 °C, the reactivity of the textile sludge char with CO_2 was significantly higher than any of the other biomass varieties tested in this study. This shows that higher temperatures are necessary for optimal gasification of this feedstock. The high ash
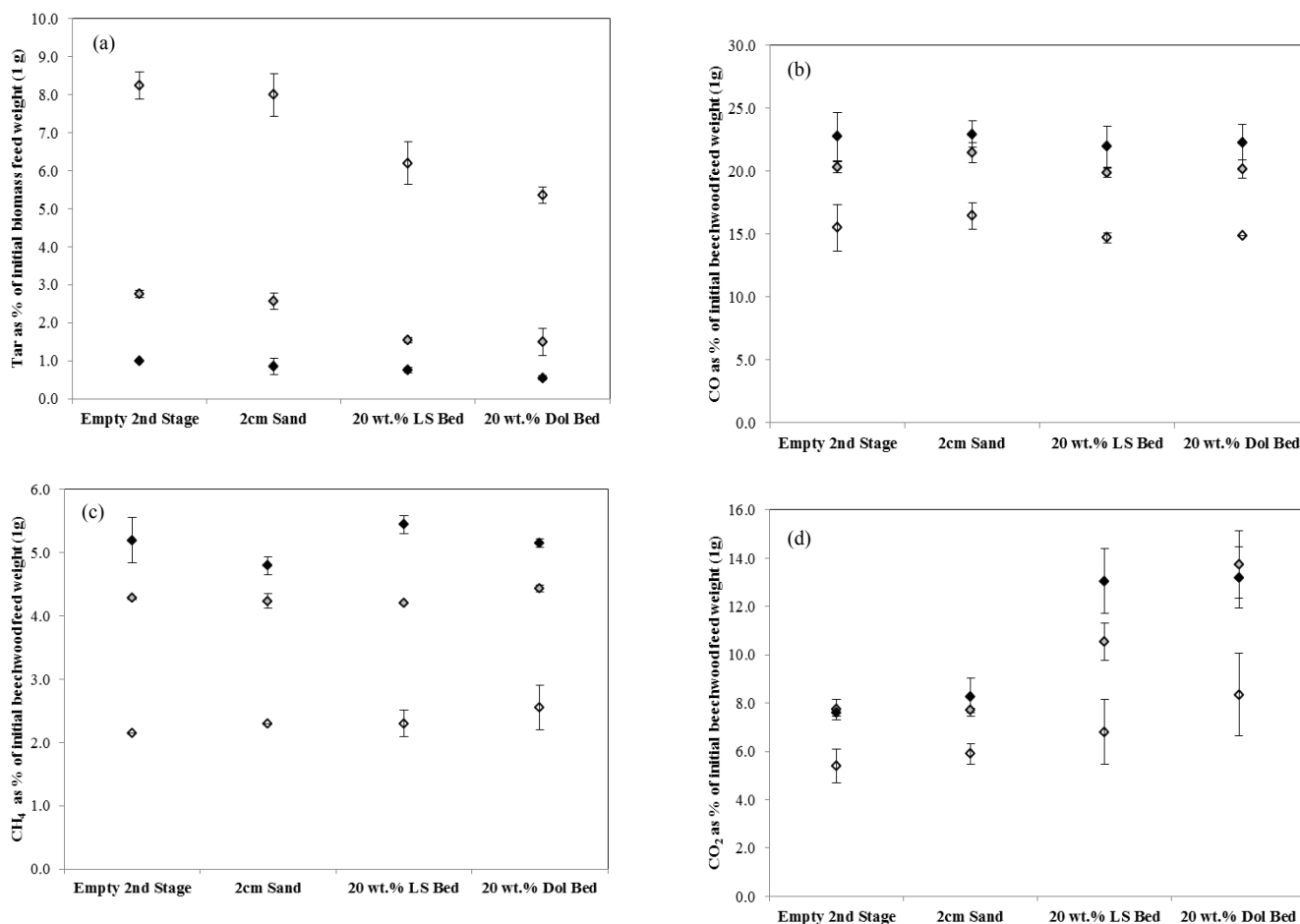
Figure 5. Yields of (a) Tar, (b) CO, (c) CH_4 and (d) CO_2 as a function of the different 2nd stage beds at 700 ˚C ◇ , 800˚C ◈ , 900˚C ◆ .

Table 3. BET surface areas and BJH average pore sizes for the limestone and dolomite particles retrieved from the 20 % LS and 20 % Dol beds.

2nd Stage Temperature [°C]	700	800	900
Limestone BET Surface Area [m^{2}g^{-1}]	11.59	8.82	4.78
Limestone BJH Average Pore Size [nm]	16.01	20.94	34.68
Dolomite BET Surface Area [m^{2}g^{-1}]	23.45	18.62	11.86
Dolomite BJH Average Pore Size [nm]	12.68	13.33	23.27

content also indicates that a fluidised bed reactor may be most suitable for processing this material particularly if using a larger particle size. Whilst still not the most attractive of feedstocks on account of its low gasifiable organic content, gasification may provide the most efficient method of extracting the energy from this

waste feedstock into a convenient fuel gas. This gas (along with the useful heat produced in the gasification process) could then be used to supplement on-site fuel, heat and power use whilst reducing the size of the waste stream and associated costs of disposal.

Two-stage experiments. The addition of the empty 2nd stage operated at elevated temperatures (700 – 900 °C) into the reactor setup resulted in a substantial reduction in the quantity of tars recovered after beechwood pyrolysis by 77 %, 93 % and 97 % at 700 °C, 800 °C and 900 °C respectively (fig. 5a). The reduced tar yields were accompanied by a significant rise in the amount of combustible gases (CO and CH_4) produced (fig 5b,c). At 900 °C, 22.2 % of the initial biomass mass was converted to CO and 5.2 % to CH_4.

Addition of the 20 wt.% Dolomite (20 % Dol) and 20 wt.% limestone (20 % LS) beds into the 2nd stage further acted to enhance tar destruction (fig. 5a). The effects were most pronounced at 700 °C and 800 ˚C, probably because at 900 °C, 97 % of the pyrolysis tars were cracked thermally. When the 2nd stage contained the 20 % LS bed, tar yields were 25 %, 43 % and 20 % lower than those observed with an empty 2nd stage at 700 °C, 800 °C and 900 °C respectively. The 20 % Dol bed appeared slightly more effective as a cracking catalyst causing tar reductions of 35 %, 47 % and 40 % at 700 °C, 800 °C and 900 °C respectively.

Although the addition of the different beds did not affect CO and CH_4 yields (fig. 5b,c), CO_2 production was enhanced by the addition of the 20 % LS and 20 % Dol beds (fig.5d). The presence of the 20 % LS bed increased CO_2 production by 26 %, 38 % and 73 %, whilst the 20 % Dol bed enhanced CO_2 production by 56 %, 78 % and 74 % at 700 ˚C, 800 ˚C and 900 ˚C respectively.

BET surface area measurements of the recovered limestone and dolomite (table 3) revealed that the calcined dolomite had a substantially larger surface area than the calcined limestone which may explain the increased reactivity towards tar cracking displayed by the 20 % Dol bed.

The addition of the sand bed had little effect on the product distribution compared with the empty 2nd stage experiments at all temperatures.

Conclusions
In the first section of our work, four different types of biomass or wastes were pyrolysed in a lab-scale fixed-bed reactor at 500 °C. The product distributions and the reactivity of the chars were determined. Each of the different biomass varieties behaved differently, which illustrates the importance of carrying out simple lab-scale experiments on potential biomass fuels to aid in the design of an optimal gasification process for a specific biomass feed.

The second focus of this paper was to assess the impact of elevated temperatures and the presence of low-cost, widely available materials with potential catalytic activity on the quantity of tar produced during high temperature pyrolysis of beechwood. Subjecting the pyrolysis vapours to elevated temperatures (700 – 900 °C) caused a significant decrease in the amount of tar recovered and an increase in the amount of combustible gases (CO and CH_4) produced. Further reductions in the tar yield were observed when the pyrolysis gases were exposed to sand beds containing calcined dolomite and limestone. Calcined dolomite appeared to be slightly more effective at reducing tars than limestone which was attributed to its larger surface area.

References
(1)   Demirbas, M. F.; Balat, M.; Balat, H., Potential contribution of biomass to the sustainable energy development. *Energy Conversion and Management* **2009,** *50* (7), 1746-1760.
(2)   Reed, T.; Reed, T. B.; Das, A.; Das, A., *Handbook of biomass downdraft gasifier engine systems*. Biomass Energy Foundation: 1988.
(3)   (a) Yassin, L.; Lettieri, P.; Simons, S.; Germana, A., Energy recovery from thermal processing of waste: a review. *Proceedings of the ICE-Engineering Sustainability* **2005,** *158* (2), 97-103; (b) Fytili, D.; Zabaniotou, A., Utilization of sewage sludge in EU application of old and new methods - A review. *Renewable & Sustainable Energy Reviews* **2008,** *12* (1), 116-140.
(4)   Reed, T. B.; Gaur, S.; Laboratory, N. R. E.; Biomass Energy Foundation, I., *A Survey of Biomass Gasification 2001: Gasifier Projects and Manufacturers Around the World*. National Renewable Energy Laboratory and Biomass Energy Foundation: 2001.
(5)   Milne, T. A.; Abatzoglou, N.; Evans, R. J., Biomass gasifier" tars": their nature, formation, and conversion. **1998**.
(6)   (a) Bolton, C.; Snape, C. E.; Obrien, R. J.; Kandiyoti, R., Influence of Carrier Gas-Flow and Heating Rates in Fixed-Bed Hydropyrolysis of Coal. *Fuel* **1987,** *66* (10), 1413-1417; (b) Pindoria, R. V.; Lim, J.-Y.; Hawkes, J. E.; Lazaro, M.-J.; Herod, A. A.; Kandiyoti, R., Structural characterization of biomass pyrolysis tars/oils from eucalyptus wood waste: effect of H2 pressure and sample configuration. *Fuel* **1997,** *76* (11), 1013-1023; (c) Collot, A. G.; Zhuo, Y.; Dugwell, D. R.; Kandiyoti, R., Co-pyrolysis and co-gasification of coal and biomass in bench-scale fixed-bed and fluidised bed reactors. *Fuel* **1999,** *78* (6), 667-679; (d) Monteiro Nunes, S.; Paterson, N.; Dugwell, D. R.; Kandiyoti, R., Tar Formation and Destruction in a Simulated Downdraft, Fixed-Bed Gasifier: Reactor Design and Initial Results. *Energy & Fuels* **2007,** *21* (5), 3028-3035; (e) Nunes, S. M.; Paterson, N.; Herod, A.; Dugwell, D.; Kandiyoti, R., Tar formation and destruction in a fixed bed reactor simulating downdraft gasification: optimization of conditions. *Energy & Fuels* **2008,** *22* (3), 1955-1964; (f) Dabai, F.; Paterson, N.; Millan, M.; Fennell, P.; Kandiyoti, R., Tar Formation and Destruction in a Fixed-Bed Reactor Simulating Downdraft Gasification: Equipment Development and Characterization of Tar-Cracking Products. *Energy & Fuels* **2010,** *24*, 4560-4570.
(7)   (a) Zanzi, R.; Sjöström, K.; Björnbom, E., Rapid pyrolysis of agricultural residues at high temperature. *Biomass and Bioenergy* **2002,** *23* (5), 357-366; (b) Venderbosch, R. H.; Prins, W., Fast pyrolysis technology development. *Biofuels, Bioproducts and Biorefining* **2010,** *4* (2), 178-208.
(8)   Kirubakaran, V.; Sivaramakrishnan, V.; Nalini, R.; Sekar, T.; Premalatha, M.; Subramanian, P., A review on gasification of biomass. *Renewable and Sustainable Energy Reviews* **2009,** *13* (1), 179-186.