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ARTICLE *in* ENERGY & FUELS · MARCH 2014

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Tar Formation and Destruction in a Fixed Bed Reactor Simulating Downdraft Gasification: Effect of Reaction Conditions on Tar Cracking Products

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ABSTRACT: A lab scale, two stage fixed bed reactor has been used to study the cracking of tars formed during the pyrolysis of biomass, under conditions that are intended to simulate those in the downdraft gasifier. Experiments were done at near atmospheric pressure, with tars being produced at 500 °C under pyrolysis conditions in the first stage and then cracked in the second stage under a range of conditions. These conditions simulated those in the gasification zone of a downdraft gasifier. Both condensable and gaseous products were collected, quantified, and characterized. Cracking in an empty second stage reduced the tar from an inlet value of 33% (of input biomass) to 0.7% under the optimum conditions (temperature 1000 °C, velocity 0.4 ms⁻¹). The presence of char in the second stage decreased the tar to 0.2%. The extent of cracking was not influenced by the source of the second stage char or particle size, within the ranges studied. The addition of a low percentage of O₂ to the inlet of the second stage had variable effects depending on the conditions in that stage, particularly the presence of char which scavenged the O₂. A selection of biomasses was also studied, and in general, less than half of the volatile matter in the parent biomass was emitted as primary tar. Cracking of this tars in the presence of char decreased the tar by over 98% for all feedstocks. The effects observed in this work can be explained in terms of changes in the extents of cracking, reforming, gasification, and water–gas shift as a function of temperature, time, and presence of char.

1. INTRODUCTION

The gasification of biomass produces a fuel gas that is suitable for many applications, such as hydrogen, methanol, and other petrochemical syntheses, and for power generation in internal combustion engines, turbines, and fuel cells.^{1–3} However, gasification involves numerous complex parallel reactions with many byproducts and impurities, which can cause operating problems downstream of the gasification stage.^{4,5} One such byproduct is tar, which is defined as material that can be condensed under specific conditions.⁶ Tar is harmful to equipment (e.g., converted diesel engines and gas turbines) and is a hindrance to clean fuel production from biomass gasification. Moreover, tar has a high content of chemical energy and cracking provides a way of ensuring that as much as possible of this can be converted to useful product. This will enhance the efficiency, and therefore the economics, of the process. Of the three common biomass gasifier types (downdraft, updraft, and fluidized bed), the downdraft gasifier produces fuel gas with the least tar ($\sim 1 \text{ g/Nm}^3$).^{3,6} The low tar levels currently achievable from downdraft gasifiers makes their produced fuel gas more suitable for engine operations, which require ‘clean’ fuel.⁷ The present study focuses on further improving the efficiency and operation of this type of gasifier by investigating ways of achieving further reductions in tar emissions. Gasification reactions and products, including tars, depend on the gasifier conditions, such as temperature, pressure, gas velocity, feed size and type, and presence of catalyst.^{3,8–13}

In the present study, a comprehensive suite of tests has been conducted using a two-stage fixed bed reactor, which was developed to simulate relevant operating conditions in downdraft gasifiers. The first stage serves to pyrolyze biomass

under standard conditions to generate tar, while the second stage is the tar destruction/reduction zone. This reactor has been used to investigate the impact of conditions in the flaming pyrolysis and char reduction zones of the downdraft gasifier on the suite of products that are formed. A full description of the reactor and its operation, together with a study on the effect of temperature and presence of char in the second stage on the tar and light gas products formed, has been provided elsewhere.^{14–17} In this work, the effects of residence time (bed height and velocity), char particle size and type, biomass source, and addition of reactive gas (O₂) have been investigated.

The standard conditions used in biomass pyrolysis in the first stage have been shown to result in the complete release of volatiles from the sample. In this reactor, the biomass is static and the temperature is ramped, whereas in downdraft gasifiers, the biomass gravitates down and is heated as it approaches the high temperature throat. The release of the pyrolysis gases occurs in the region of the throat, and some of the pyrolysis products (gases and tars) can be combusted to form CO₂ and steam, which are then available for gasification reactions in the char reduction zone to produce CO and H₂. In the laboratory scale reactor, the products of pyrolysis are swept through to the second stage via a specially designed flange where additional gas, either inert or containing a limited amount of O₂, is added. The addition of high concentrations of O₂ is not relevant to the flaming pyrolysis and gasification sections of downdraft gasifiers. The energy to heat the second stage and for endothermic reactions was provided by using the reactor wall

Received: November 20, 2013

Revised: January 31, 2014

Published: February 14, 2014

Table 1. Proximate and Ultimate Analyses of the Biomasses Used in This Study^a

feed	ultimate analysis (wt %)						proximate analysis (wt %)		
	C	H	N	O	S	Cl	ash	moisture	volatiles
silver birch	52.0	7.0	0.1	40.8	<0.1	N/A	1.9–0.3	N/A	N/A
pine sawdust	46.5	5.1*	0.22	40.7	0.01	0.01	0.2	7.3	79
beechwood	43.4	4.8*	0.26	39.5	<0.04	0.01	0.5	11.6	75
palm fiber	43.2	5.2*	0.8	36.3	0.03	0.22	2.8	11.4	69
olive bagasse	45.6	5.1*	1.36	38.9	0.06	0.07	5.2	3.7	67
sewage sludge	33.3	3.3*	4.83	15.9	1.15	N/A	25.9	15.7	50

^aAnalyses (except silver birch) are calculated on the “as received” moisture basis. * Corrected for moisture content; i.e., it does not include the hydrogen in the moisture. Analyses carried out by TES Bretby, U.K. O determined by difference.

as a resistance heater. In a downdraft gasifier, char is formed from the feed as it gravitates downward toward the char reduction zone. Combustion in the throat heats it to a high temperature as it passes into the char reduction zone. In this zone, the aim is for it to be gasified completely and for tars remaining from the pyrolysis step to be consumed. The present study has been carried out with the aim of identifying conditions for further reducing tar emissions and improving tar conversion into gases in downdraft gasifiers, thereby improving the efficiency and reliability of commercial scale equipment.

The study of tar destruction during gasification in a downdraft gasifier is an area of very active research. Our first paper describing the study with the two stage reactor at Imperial College London was published in 2010.¹⁵ Since then, several papers (by other workers) that make a valuable contribution to the understanding of the field have been published. The cracking of primary tar (from rice straw) in a two stage reactor has helped to clarify the stages in the decomposition. The tar is initially converted to polyaromatic hydrocarbons (PAHs), one ring aromatics, and noncondensable gases. Char was found to be effective at decomposing PAHs, while steam was the most efficient reforming agent.¹⁸ The reforming of tars from woody biomass over charcoal in the presence of steam and air has been studied.¹⁹ Almost total decomposition was found, and this was attributed to the deposition and coking of tar on the charcoal surface and the accompanying reaction of steam, which maintained the activity of the surface. A tubular reactor has been used to study the reaction scheme in the decomposition of tars formed from wood chips.²⁰ The use of K as a catalyst, loaded onto char formed from a woody biomass, has been used to enhance the steam reforming and char gasification reactions.²¹ The use of chars (to crack tars) directly following pyrolysis (without cooling) has been compared with cooled and then reused chars. The directly used char was more effective, and this is thought to be due to its higher BET surface area and greater concentration of micropores. The ordering of the structure of the char increased with temperature, and this also contributed to a decrease in the reactivity of the reused char.²² A novel burner has been used to crack/destroy the tars formed from the pyrolysis of wood pellets. A high % reduction of tar was found.²³ This selection of references shows the wide range of studies that are being pursued to assist in the commercialization of this technology.

2. EXPERIMENTAL SECTION

2.1. Two-Stage Reactor. The development of the reactor was described previously.^{15,17} As mentioned above, it is comprised of two stages connected via an intermediate flange

joint. The first stage is tubular with an internal diameter of 12 mm (2 mm wall thickness) a length of 250 mm, and it is made from AISI 316 grade stainless steel. The second stage is also tubular, with an internal diameter of 12 mm (2 mm wall thickness) and a length of 200 mm, and it is made of Incoloy 800 HT. The second stage has been specially designed to enable gasification agent (or inert gas) to be injected via the flange at the junction of the two stages, to simulate the throat of a downdraft gasifier. This also allows the control of gas superficial velocities in the second stage independently of the first stage velocity. The second stage may be used empty or packed with a fixed amount of char to simulate tar cracking conditions in the char reduction zone of a downdraft gasifier. The bottom of the second stage is connected to a tar trap. The trap is a U-tube with an internal diameter of 12 mm, and it is made from stainless steel. This trap is placed in a liquid nitrogen bath, so that the volatiles released can be condensed and trapped. The design of the trap allows samples of the volatiles to be taken with a syringe via a septum. The assembled reactor is heated to the desired conditions by electrical resistance. Temperatures in the first and second stage can be controlled independently from each other.

2.2. Operating Conditions. A fixed mass (1 g) of biomass was placed in the first stage before each test. The biomass was then pyrolyzed by heating the first stage up to 500 °C, at a rate of 1 °C s⁻¹. A low flow of inert gas (He), at superficial velocity of 0.1 m s⁻¹, was used to sweep the released volatiles into the second stage. These are the ‘standard’ conditions used for all tests to generate a repeatable quantity of tar and char. The char was retained in this first stage and could not interact with products in the second stage of the reactor. The evolved tar was swept into the second stage to undergo cracking reactions. Once the first stage reached 500 °C, it was held at this temperature for 15 min, before the test was ended and the reactor allowed to cool to ambient temperature. These first stage operating conditions were used in previous work and have been shown to be suitable for maximizing production of tar (and volatiles) by pyrolysis. The operating conditions of the second stage were varied to investigate their impact on the quantity of tar collected at the outlet of the reactor. Before the program to heat the first stage was initiated, the second stage was heated to a fixed temperature in the range 700–1000 °C. Inert gas was injected at the flange union between the two stages, and the gas superficial velocity in the second stage was fixed in the range 0.4–2.4 m s⁻¹. All measuring equipment was calibrated to ensure accuracy. The spread of the data has been estimated by calculating the standard deviation from the results of multiple tests.

2.3. Materials. The analyses of the biomass samples used in this study are shown in Table 1.

Table 2. Identified Products from Pyrolysis in the First Stage^a

	weight of measured component as % of initial biomass (1g), dry basis							total (wt %)
	tar	char	lights	CO	CH ₄	CO ₂	H ₂ O	
single stage only	33.4	24.5	1.4	2.4	0.5	7.2	20.8	90.3
SD (%)	±1.5	±0.8	±0.2	±0.2	±0.0	±0.4	±1.2	±0.6

^aSingle stage reactor: feed, beechwood (size 106–150 μm), superficial velocity = 0.1 m s^{-1} , inlet pressure = 2.2 bar, temperature = 500 $^{\circ}\text{C}$, heating rate = 1 $^{\circ}\text{C s}^{-1}$. Lights: C_2H_4 , C_2H_6 , C_3H_6 , C_3H_8 , C_4H_8 , C_4H_{10} , C_5H_{10} and C_5H_{12} . SD: standard deviation.

The biomasses were ground and sieved to 106–150 μm and then dried in a recirculating air oven at 35 $^{\circ}\text{C}$ for 16 h prior to storage and use. The low drying temperature was used to avoid structural changes in the biomass and to only remove surface moisture. It is the method used in our studies with biomass and was used in the work covered by the previous paper. The char was sieved to the required size range. All samples were stored in small glass bottles, which were purged with He, before being tightly sealed to avoid readsorption of moisture. Although the size of feedstock used is limited by the size of the laboratory reactor, it is expected that the trends in tar values with changing conditions should be valid and should provide a useful insight into factors governing the release and cracking of tars in larger scale systems.

2.4. Gas Analysis. Most of the gases formed during pyrolysis condensed inside the liquid N_2 tar trap (-196°C). The trap collected condensable light hydrocarbons (C_2 – C_5 alkanes and alkenes), CO_2 , and H_2O . Once the trap reached ambient temperature, gas samples were taken with a syringe via a septum on the tar trap and analyzed by gas chromatography (GC). While warming to ambient temperature, the pressure in the trap was monitored as a safety measure and to enable the volume of gas produced from the frozen material to be measured based on the final pressure. The approximate water content was determined by washing the tar trap with dry methanol (<0.01% water content) and determining the water content in the solution by GC. The assayed water content of the ‘dry’ methanol (available from the supplier) was used to calibrate the GC. The value was also used to adjust the measured sample value for the water introduced with the solvent.

Light Hydrocarbons (C_2 – C_5 Alkanes and Alkenes), CO_2 , and H_2O . Gas chromatography was used to analyze the components condensed in the tar trap. These components were identified by their retention times and quantified using certified gas mixtures. The gas chromatograph (GC) had a flame ionization detector (FID) for hydrocarbons and a thermal conductivity detector (TCD) for CO_2 and H_2O . Columns used were a packed Alumina F-1 60/80 column for analysis of hydrocarbons and a packed Hayesep N60/80 mesh column for CO_2 determinations.

CH_4 , CO , and H_2 . Two online infrared analysers were used to measure the amounts of the CO and CH_4 that did not condense in the tar trap. The analysers were installed downstream of the trap. In addition, for several tests, a Hitec K1550 analyzer, based on TCD measurement, was also installed downstream of the tar trap, to enable measurement of the H_2 concentration in the gas stream.

2.5. Tar and Char Analyses. **Tar.** After each run and cooling period, the system was carefully taken apart and the first stage, second stage, and tar trap were washed to determine the tar collected during the run. A 4:1 (v/v) mixture of chloroform and methanol was used as the washing agent. The solution was then filtered using a preweighed Whatman

number 1 filter paper and collected in a flask. A BUCHI Rotavapor R-3000 was used to evaporate most of the solvent. The rotary evaporator was operated at 90 $^{\circ}\text{C}$ (water bath temperature) and 40 rpm for 15 min. The remaining solution was washed, with a minimal amount of the solvent, into a small, aluminum beaker (weight of 5 g) and then dried in a recirculating air oven, operated at 35 $^{\circ}\text{C}$ for 2 h, to evaporate the residual solvent and allow tar to be isolated. After this time, the tar was a very thick, sticky semisolid. It is considered that compounds with a boiling point up to 250 $^{\circ}\text{C}$ will have been lost during this procedure. The tar was then weighed (weight range 0.003–0.4 g), and its yield was determined as a percentage of the initial weight of biomass, on a dry basis.

The approximate water content of the liquid product in the tar trap (‘tar solution’) was determined in several tests by washing the tar trap with methanol (water content given on bottle) and injecting a (0.1 μL) sample of the solution into the GC. The initial water content of the methanol was used to calibrate the GC for the approximate determination of water in the tar solution. The water in the washing solvent was subtracted from the measured value to determine the water content of the collected material. During a tar determination, water and other light material was lost as a result of evaporation in the rotavap and oven.

Size exclusion chromatography (SEC) analysis of the tars was carried out using an in-house method that has been used in many studies in our laboratory.^{24–28} The column used was a 300 mm long, 7.5 mm i.d., polystyrene/polydivinylbenzene-packed, Mixed D column (Polymer Laboratories, U.K.), operated at 80 $^{\circ}\text{C}$ and a flow rate of 0.5 mL min^{-1} with 1-methyl-2-pyrrolidinone (NMP) as the mobile phase. Signal detection was carried out using a Knauer diode array Smartline 2600 detector, with UV absorbance at 270, 300, 350, and 370 nm. NMP is opaque at 254 nm but partially transparent at the aforementioned wavelengths.

Char. After the reactor was washed with solvent, the char and preweighed wire mesh plug in each stage were pushed out into a preweighed beaker. The residual solvent was then evaporated, and the mass of char measured.

3. RESULTS

The work described here follows on from a previous study,¹⁵ in which data obtained with the second stage in the temperature range 700–1000 $^{\circ}\text{C}$, both in the absence and presence of a char bed, were discussed. In this paper, the effects of changing conditions in the second stage are considered further. The effects of velocity in the second stage (with and without a char bed), char bed height (i.e., gas residence time in the char bed), char particle size and type, and addition of reactive gas to the ‘throat’ between the first and second stages are described. Most of the work was done using the standard set of conditions in the first stage described in the Experimental Section, with beechwood as the biomass, although the effect of using different feedstock in the first stage was also investigated.

Table 2 shows the distribution of products at the outlet of the first stage. These products (with the exception of char) are swept into the second stage for further reaction at different second stage conditions. The amount of tar entering the second stage was equivalent to 33% (dry basis) of the biomass pyrolyzed in the first stage. The consistency in the value of residual char left in the first stage shows the reliability of the pyrolysis stage. Approximately 90% of the original biomass was accounted for in the data. The missing material is thought to be H_2 and light oils/tars lost during the tar recovery procedure, particularly in the solvent evaporation step.

3.1. Effect of Velocity on Tar Cracking Products Using an Empty Second Stage. Tar.

It is clear from Figure 1 that a

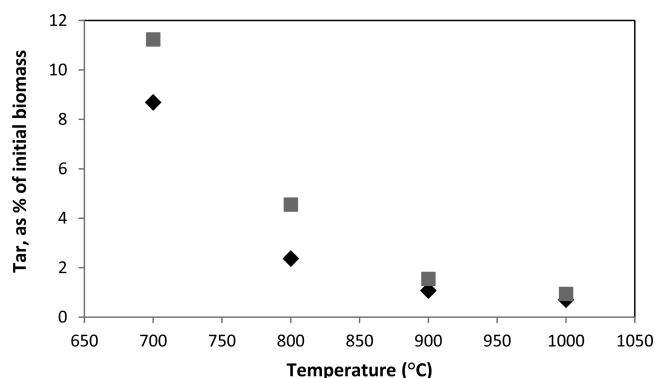


Figure 1. Tar (% dry basis) recovered as a function of second stage temperature. Tar is shown as a percentage of the initial biomass weight, dry basis. 1st stage: feed = beechwood, superficial velocity = 0.1 m s^{-1} , inlet pressure = 2.2 bar, temperature = 500°C . 2nd stage: empty, inlet pressure = 2.1 bar, temperature = variable. Results for superficial velocities: $v = 0.4 \text{ m s}^{-1}$ ◆, $v = 1.6 \text{ m s}^{-1}$ ■.

high proportion of the tar was destroyed during its passage through the second stage. As expected, the higher the temperature in the second stage, the larger the amount of tar destroyed.

An increase in superficial velocity in the second stage from 0.4 to 1.6 m s^{-1} and the subsequent shorter gas/vapor residence time, which diminished from 0.52 to 0.13 s , resulted in a decrease in the extent of tar cracking. This led to an actual increase in the amount of tar recovered. At 1000°C , an intermediate superficial velocity (0.8 m s^{-1}) was also tested. It was observed that the initial increase from 0.4 to 0.8 m s^{-1} resulted in a decrease in tar cracking, while the subsequent increase to 1.6 m s^{-1} did not have a significant effect. Work by other researchers has shown that tar yield decreased with residence time in the range $0.3\text{--}4 \text{ s}$ ¹¹ and tar yield is not influenced much in the range $3.2\text{--}4.8 \text{ s}$,¹² indicating that most cracking has already taken place by then. The present study extended the range investigated to shorter residence time and higher temperature, as downdraft gasifiers are known to operate in a wide range of velocity and temperature.

CH_4 . The CH_4 concentration was higher at the outlet of the second stage than at the outlet of the first stage, showing that CH_4 was formed by cracking reactions in the second stage. It is also possible that CH_4 generation was in competition with reforming, which removed CH_4 by reactions with CO_2 and steam. The overall effect observed is therefore dependent on the impact of the operating conditions on these opposing reactions.

As shown in Figure 2, at temperatures of 700 and 800°C , the CH_4 released was slightly higher at the lower superficial velocity

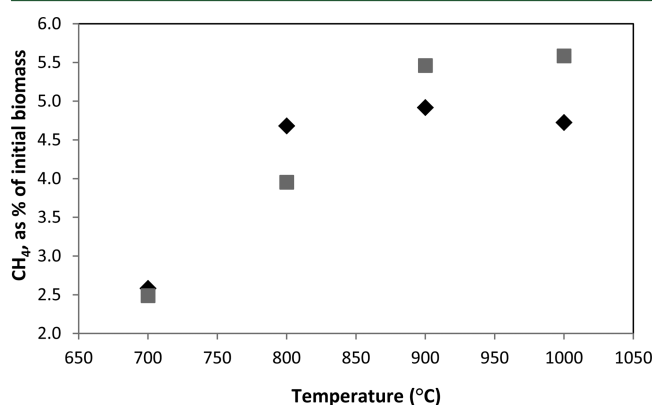
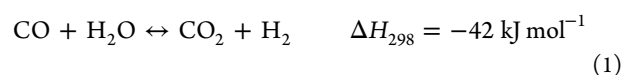


Figure 2. CH_4 (% dry basis) released as a function of second stage reactor temperature. CH_4 is shown as a percentage of the initial biomass weight, dry basis. 1st stage: feed = beechwood, superficial velocity = 0.1 m s^{-1} , inlet pressure = 2.2 bar, temperature = 500°C . 2nd stage: empty, inlet pressure = 2.1 bar, temperature = variable. Results for superficial velocities: $v = 0.4 \text{ m s}^{-1}$ ◆, $v = 1.6 \text{ m s}^{-1}$ ■.

of 0.4 m s^{-1} (longer residence time), showing that the impact of cracking dominated the reactions in the second stage. Conversely, at 900 and 1000°C , the CH_4 released was slightly lower at the lower superficial velocity, which is consistent with reforming reactions having a predominant influence at these temperatures.

CO. The CO concentration at the exit of the second stage was high compared with that exiting the first stage. The formation of CO in the second stage depends on the relative extents of cracking, reforming, gasification, and water–gas shift reactions. The former three reactions will increase the CO concentration, while the influence of the fourth will depend on the direction in which the water–gas shift reaction (1) has to proceed to achieve equilibrium.

water–gas shift reaction



For a given velocity, the CO concentration increased with temperature, as the extent of tar destruction (by cracking and gasification) and CH_4 reforming increased. Increases in superficial velocity (i.e., decrease in residence time) resulted in increases in the amount of CO released, especially at the higher temperatures (900 and 1000°C), when the rates of the gasification and reforming reactions became more significant. The velocity effect (increased concentrations at lower residence times) could be a result of the effect of the water–gas shift reaction. As the steam content was significant and the CO content was high, the shift reaction would favor the formation of CO_2 and H_2 . As velocity was raised, reaction time decreased, and therefore, the exit CO content was higher. The steam content is consistent with this interpretation. In the absence of an effect of the shift reaction, the CO content would be expected to decrease with the increase in velocity.

Light Hydrocarbons ($C_2\text{--}C_4$ Alkanes and Alkenes). The amounts of hydrocarbons released were higher at the lower superficial velocity (longer residence time) for temperatures of 700 , 800 , and 900°C , which is in line with literature findings.²⁹ This is consistent with their formation by tar cracking at the

longer residence time. At 1000 °C, the light hydrocarbon content decreased with lower velocities (increased residence times), showing the impact of reforming reactions on their concentrations at high temperature.

CO₂. At 700 °C and both velocities (0.4 and 1.6 m s⁻¹), the CO₂ at the outlet of the second stage (Figure 3) was similar to

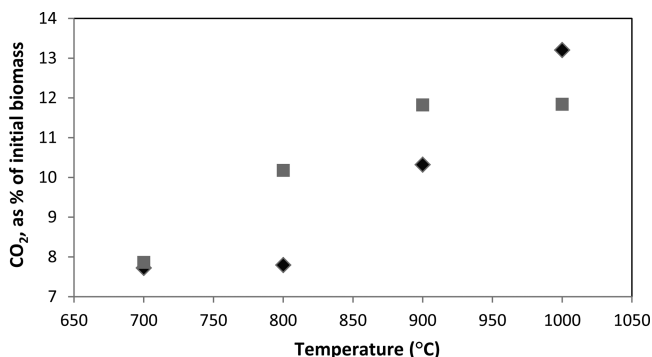


Figure 3. CO₂ (% dry basis) released as a function of second stage reactor temperature. CO₂ is shown as a percentage of the initial biomass weight, dry basis. 1st stage: feed = beechwood, superficial velocity = 0.1 m s⁻¹, inlet pressure = 2.2 bar, temperature = 500 °C. 2nd stage: empty, inlet pressure = 2.1 bar, temperature = variable. Results for superficial velocities: $v = 0.4 \text{ m s}^{-1}$ ♦, $v = 1.6 \text{ m s}^{-1}$ ■.

that at the outlet of the first stage. This must suggest that CO₂ formation and destruction reactions are balanced at this temperature. As temperature was increased from 800 to 1000 °C, CO₂ release increased. The velocity also had a significant effect on the CO₂ released. At a velocity of 0.4 m s⁻¹ CO₂ was relatively constant between 700 and 800 °C and increased as the temperature increased from 800 to 1000 °C, while at a velocity of 1.6 m s⁻¹ CO₂ increased as temperature was raised from 700 to 900 °C and stayed constant between 900 and 1000 °C.

Moisture Analysis. The determination of moisture had a larger experimental error, but the data suggest decreased levels in the fuel gas at 1000 °C compared with lower temperatures. This is consistent with its consumption by gasification and reforming to form CO and H₂ and matches the higher CO concentration measured in the fuel gas.

3.2. Effect of Velocity on Tar Cracking Products Using a Packed Char Bed in the 2nd Stage. The effect of superficial velocity with the second stage fully packed with char (char bed height of 180 mm) was investigated and the results for a second stage temperature of 1000 °C are shown in Table

3. This table also shows (*in italics*) data obtained under the same conditions without char in the second stage (from Table 4). The presence of char provides a hot surface area to enhance tar cracking reactions and C for gasification and reforming reactions with steam/CO₂ released by pyrolysis of the parent biomass in the first stage. The maximum superficial velocities for commercial downdraft gasifiers are within the range 0.13 to 2.50 m s⁻¹.³ For this study gas superficial velocities of 0.4 m s⁻¹ and 1.6 m s⁻¹ in the second stage were studied.

At a given velocity and at 1000 °C, the presence of char in the second stage decreased the tar, light hydrocarbons, CH₄, CO₂, and H₂O in the exit gas, while the CO concentration increased. The tar decreased through enhanced cracking and further char formation on the hot char surface. The decreases in CH₄ and lights are consistent with improved reforming of the hydrocarbons, and the CO₂ and steam decreases are consistent with reforming reactions and gasification of C from the char bed. Overall, less material was accounted for, as a fraction of the original biomass, when char was present in the second stage than when it was empty. Part of the difference, but not all, was due to increased H₂ concentrations, caused by the gasification reaction with steam, as discussed below. This was not measured for the majority of the work as the use of He as carrier gas would interfere with H₂ determination. There was 4.8% H and 11.6% moisture in the beechwood feed placed in the first stage, as shown in Table 1. If all the H in the feed had been converted into fuel gas as H₂, it would only be equal to 6.1% of the biomass feed (i.e., it cannot account for the whole decrease in the recovery). It is therefore possible that the missing material is C (in the form of soot), lost from the system without being determined and condensable hydrocarbons recovered from the reactor with the tars but lost during the solvent drying procedure.

As the gas superficial velocity in the char-packed second stage was increased from 0.4 m s⁻¹ to 1.6 m s⁻¹, the amount of tar recovered decreased slightly. However, the values at both velocities were low and showed that the tar content has almost been eliminated with a residence time of less than 0.5 s in the reactor. The amount of CH₄ increased slightly, suggesting less was reformed at the lower residence time. CO increased markedly with the increase in velocity, showing that there was a net consumption of CO under these conditions, likely due to the impact of the water gas shift reaction. The change in superficial velocity did not have any significant effect on the released amounts of CO₂ and H₂O; they were both zero, because of their removal by gasification with C in the reactive char bed. The light hydrocarbons were fully consumed by

Table 3. Identified Components as a Function of Superficial Velocity in the Char Packed Second Stage^a

superficial velocity (m s ⁻¹)	tar	1st stage char	as % of initial biomass feed (1 g), dry basis						2nd stage char wt loss (g)	2nd stage char wt loss (%)
			lights	CO	CH ₄	CO ₂	H ₂ O	total identified		
0.4	0.3 ± <0.05	22.7 ± 0.4	0.0 ± <0.05	33.9 ± 1.4	2.3 ± 0.2	0.1 ± <0.05	0.0 ± <0.05	59.3 ± 1.6	0.19	4.7 ± 0.2
	0.7	22.8	0.8	20.6	4.7	13.2	15	78		
1.6	0.2 ± <0.05	23.2 ± 0.2	0.0 ± <0.05	49.2 ± 0.4	3.1 ± <0.05	0.1 ± <0.05	0.0 ± <0.05	75.9 ± 0.2	0.20	5.1 ± 0.1
	0.9	23.3	1.6	28.5	5.6	11.8	16.7	88		

^a1st stage: feed= beechwood, superficial velocity = 0.1 m s⁻¹, inlet pressure = 2.2 bar, temperature = 500 °C. 2nd stage: superficial velocity = variable, inlet pressure = 2.1 bar, temperature = 1000 °C, packed bed = 4 g of spruce char, char size = 212 – 500 μm. Values are shown ± SD. Values in *italics* represent values obtained with an empty second stage.

Table 4. Identified Components as Function of Temperature and Gas Velocity with an Empty Second Stage^a

temp. (°C)	velocity (m s ⁻¹)	as % of initial biomass feed, dry basis							total identified
		tar	char	lights	CO	CH ₄	CO ₂	H ₂ O	
700	0.4	8.7 ± 0.9	22.4 ± 0.8	2.9 ± 0.4	14.4 ± 0.5	2.6 ± 0.2	7.7 ± 0.2	23.3 ± 3.1	82.0 ± 2.4
700	1.6	11.2 ± 1.1	22.8 ± 0.5	2.1 ± 0.1	17.2 ± 0.8	2.5 ± 0.1	7.9 ± 0.4	25.8 ± 3.1	89.5 ± 3.0
800	0.4	2.4 ± 0.2	22.3 ± 0.5	3.4 ± 0.3	18.8 ± 0.3	4.7 ± 0.3	7.8 ± 0.2	22.5 ± 2.0	81.9 ± 2.5
800	1.6	4.6 ± 0.1	22.6 ± 0.5	2.6 ± 0.0	20.4 ± 0.5	4.0 ± 0.3	10.2 ± 0.1	27.5 ± 2.5	91.9 ± 2.6
900	0.4	1.1 ± 0.1	22.9 ± 0.2	2.6 ± 0.3	19.6 ± 0.6	4.9 ± 0.2	10.3 ± 0.1	25.0 ± 2.0	86.5 ± 2.4
900	1.6	1.5 ± 0.1	22.4 ± 0.4	2.1 ± <0.05	23.8 ± 0.8	5.5 ± 0.3	11.8 ± 0.2	21.3 ± 1.3	88.4 ± 0.3
1000	0.4	0.7 ± <0.05	22.8 ± 0.5	0.8 ± 0.1	20.6 ± 0.6	4.7 ± 0.1	13.2 ± 0.3	15.0 ± 2.0	77.9 ± 1.9
1000	0.8	1.0 ± 0.1	22.4 ± <0.05	1.2 ± <0.05	21.2 ± 0.1	5.6 ± 0.1	13.4 ± <0.05	18.8 ± 1.3	83.4 ± 1.0
1000	1.6	0.9 ± 0.1	23.3 ± 0.6	1.6 ± 0.2	28.5 ± 0.5	5.6 ± 0.1	11.8 ± 0.1	16.7 ± 3.1	88.4 ± 2.9

^aFeed = beechwood. 1st stage: superficial velocity = 0.1 m s⁻¹, pressure = 2.2 bar, temperature = 500 °C. 2nd stage: Empty, superficial velocity = variable, pressure = 2.1 bar, temperature = variable. Values given ±SD (%).

Table 5. Product Distribution with Different Amounts of Char in the 2nd Stage^a

amount of char	as % of initial biomass feed (of 1 g), dry basis							total identified	2nd stage char wt loss (g)	2nd stage char wt loss (%)
	tar	1st stage char	lights	CO	CH ₄	CO ₂	H ₂ O			
4 g (full)	0.2 ± <0.05	23.2 ± 0.2	0.0 ± <0.05	49.2 ± 0.4	3.1 ± <0.05	0.1 ± <0.05	0.0 ± <0.05	75.9 ± 0.2	0.20	5.1 ± 0.1
2 g (half full)	0.2 ± <0.05	23.5 ± 0.4	0.1 ± <0.05	49.5 ± 0.8	2.7 ± 0.4	0.3 ± 0.1	0.0 ± <0.05	76 ± 1.0	0.16	7.8 ± <0.05
0.3 g	0.9 ± 0.1	23.0 ± 0.7	0.8 ± 0.1	29.9 ± 0.1	5.6 ± 0.1	10.4 ± 0.5	16 ± 1.3	87 ± 0.1	0.00	1.6 ± <0.05
0 g (empty)	0.9 ± 0.1	23.3 ± 0.6	1.6 ± 0.2	28.5 ± 0.5	5.6 ± 0.1	11.8 ± 0.1	16.7 ± 3.1	88.4 ± 2.9	N/A	N/A

^aFirst stage: feed = beechwood, superficial velocity = 0.1 m s⁻¹, inlet pressure = 2.2 bar, temperature = 500 °C. Second stage: superficial velocity = 1.6 m s⁻¹, inlet pressure = 2.1 bar, temperature = 1000 °C, packed bed = spruce char of variable amount, char size (diam.) = 212–500 μm. Values shown ±SD

Table 6. Product Distribution with Char of Different Particle Sizes in the Second Stage^a

char size (μm)	as % of initial biomass feed (of 1 g), dry basis							total identified	2nd stage char wt loss (g)	2nd stage char wt loss (%)
	tar	1st stage char	lights	CO	CH ₄	CO ₂	H ₂ O			
212–500 (8.3 g to full)	0.2 ± <0.05	23.9 ± 0.4	0.0 ± <0.05	49.5 ± 1.0	2.3 ± 0.1	0.2 ± <0.05	0.0 ± <0.05	76.1 ± 1.2	0.68	8.2 ± <0.05
850–1180 (7.3 g to full)	0.3 ± <0.05	23.9 ± <0.05	0.1 ± <0.05	49.7 ± 0.1	2.0 ± <0.05	0.2 ± <0.05	0.0 ± <0.05	76.2 ± 0.1	0.50	6.9 ± <0.05
2000–3000 (5.4 g to full)	0.3 ± 0.1	23.8 ± <0.05	0.1 ± <0.05	49.6 ± 0.9	2.1 ± 0.1	0.7 ± <0.05	0.0 ± <0.05	76.5 ± 0.8	0.32	6.1 ± 0.1

^a1st stage: feed = beechwood, superficial velocity = 0.1 m s⁻¹, inlet pressure = 2.2 bar, temperature = 500 °C. 2nd stage: superficial velocity = 1.6 m s⁻¹, inlet pressure = 2.1 bar, temperature = 1000 °C, packed bed = oak char, char size = variable. Values given ±SD.

reforming reactions even at the higher superficial velocity of 1.6 m s⁻¹.

3.3. Effect of the Amount of Char in the Second Stage. Most of the experiments carried out with char in the second stage employed a completely filled reactor (4 g char used). A suite of tests was also done with the second stage part filled (2 and 0.3 g char were used) to simulate a decrease in the depth of the reduction zone in the downdraft gasifier. This investigation gave an insight into the effect of the residence time on tar cracking and product distribution in the reduction zone. The results are shown in Table 5.

The amounts of tar recovered were similar when the reactor was half-filled or completely filled with char. This suggests that there was a sufficient residence time with the half-filled reactor to enable the cracking reactions to be completed under the experimental conditions used. On the other hand, the amounts

of tar recovered were similar when the second stage was empty and with only 0.3 g of char present. These tests demonstrate that under the present reactor conditions there is a narrow range of tar-char contact time (bed height) in which tar cracking effectively occurs in the gasifier.

Table 5 also shows that a 50% decrease in the residence time in the char bed had no significant effect on the release of CO and CH₄, while further decreases in residence time did have an effect. The results with a shallow char bed were similar to those obtained with an empty second stage and the trend is similar to that found with the tar emission. The CO content showed a large increase as the weight of char increased from 0.3 to 2 g but did not increase further when the char weight was increased to 4 g. This can be explained by the extent of reaction with the 2 g bed being sufficient to remove most of the CO₂ and steam from the gas. An increase in the char bed weight resulted in a

Table 7. Identified Components as a Function of Type of Char in the 2nd Stage^a

char type (source)	as % of initial biomass feed (1 g), dry basis								2nd stage char wt loss (g)	2nd stage char wt loss (%)
	tar	1st stage char	lights	CO	CH ₄	CO ₂	H ₂ O	total identified		
oak char 8.3 g (full)	0.2 ± <0.05	23.9 ± 0.4	0.0 ± <0.05	49.5 ± 1.0	2.3 ± 0.1	0.2 ± <0.05	0.0 ± <0.05	76.1 ± 1.2	0.68	8.2 ± <0.05
spruce char 4.0 g (full)	0.2 ± <0.05	23.2 ± 0.2	0.0 ± <0.05	49.2 ± 0.4	3.1 ± <0.05	0.1 ± <0.05	0.0 ± <0.05	75.9 ± 0.2	0.20	5.1 ± 0.1
pine bark 4.7 g (full)	0.2 ± <0.05	23.7 ± 0.4	0.0 ± <0.05	49.5 ± 0.3	2.5 ± <0.05	0.1 ± <0.05	0.0 ± <0.05	76.1 ± 0.7	0.20	4.3 ± 0.1

^a1st stage: feed = beechwood, superficial velocity = 0.1 m s⁻¹, inlet pressure = 2.2 bar, temperature = 500 °C. 2nd stage: superficial velocity = 1.6 m s⁻¹, inlet pressure = 2.1 bar, temperature = 1000 °C, packed bed = variable, char size = 212 – 500 μm. Values given ±SD.

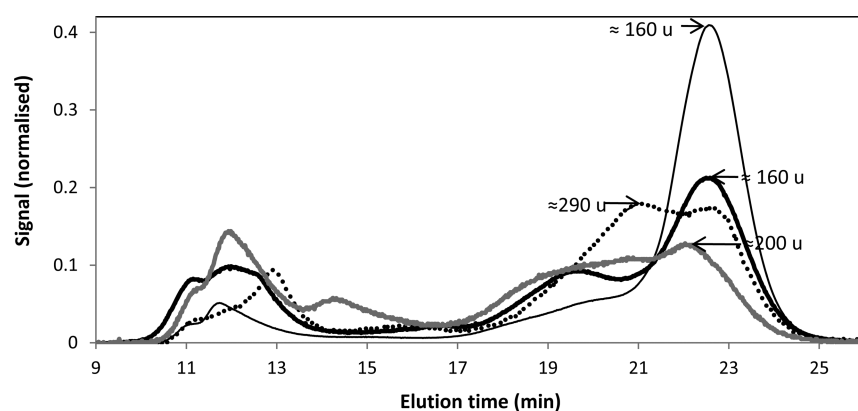


Figure 4. SEC analysis of tar recovered as a function of the type of char bed in the 2nd stage of the hot rod reactor. SEC was performed with a Mixed D column. All chromatograms have been area normalized. 1st stage: feed = beechwood, superficial velocity = 0.1 m s⁻¹, inlet pressure = 2.2 bar, temperature = 500 °C. 2nd stage: superficial velocity = 1.6 m s⁻¹, inlet pressure = 2.1 bar, temperature = 1000 °C, packed bed = 8.3 g of oak char/4.7 g of pine char/4.0 g of spruce char, char size = 212 – 500 μm. Results are for pine char (thick black line), oak char (broken black line), spruce char (thick gray line), empty (thick black line).

decrease in the CO₂ and steam released. The larger rate of decrease was between bed weights of 0.3 and 2 g, with only minor further decreases to near zero, when the bed weight was further doubled. An increase in the char bed weight from zero to 2 g also led to a decrease in the amount of light hydrocarbons released. An increase in the bed weight to 4 g removed the final trace of the light hydrocarbons. It was also found that C₂H₄ makes up the highest fraction (~98%) of the light hydrocarbons released, independent of the length of the char bed.

3.4. Effect of Packing the Second Stage with Chars of Different Particle Sizes. The second stage of the hot rod reactor has a diameter of 12 mm, which imposes a restriction on the size of the char particles that can be packed into the reactor. In this investigation the maximum char size used was 3 mm, while the minimum was 212 μm. Although char particles in downdraft gasifiers can have particle size distributions extending to larger sizes, the present study gives an insight into the trends that can be expected with different char sizes. Char was used in three size ranges: 212–500 μm, 850–1180 μm, and 2000–3000 μm. The results are shown in Table 6.

The data in Table 6 show that the amount of tar recovered was relatively constant over the char size range. Therefore, it seems that, under the investigated conditions, the size of the char had no significant effect on the extent of tar cracking and amount of emitted tar. The temperature used will have ensured a high level of tar cracking, so it is possible that a limiting value

was reached with each particle size. What is important to point out is that the use of the larger size range did not appear to reduce the effectiveness of the bed as a cracking medium. The amounts of CH₄ and CO released were relatively constant with the change in char size range. This shows that the reactivity of the bed for all of the reactions was maintained with the larger size range. The concentration of light hydrocarbons released increased slightly from zero with the increase in char size range from 212–500 to 850–1180 μm, with no further increase with the larger size range 2000–3000 μm. Nevertheless, the actual amount of hydrocarbons released for all char sizes was near zero. The low amount of light hydrocarbons reflects the effectiveness of reforming of the hydrocarbons by steam and CO₂ at 1000 °C. A higher amount of CO₂ was released in the presence of the larger char particle sizes, while the steam reacted completely with all three size ranges. This may be reflecting the lower reactivity of the char with CO₂ compared to steam.

3.5. Effect of Packing the Second Stage with Char from Different Sources. Most of the experiments used char derived from oak in the second stage. A limited suite of tests were done to assess whether chars from different woods affected the performance of the second stage (char reduction zone). Chars with a particle size range between 212 and 500 μm were used with a char bed height of 180 mm. An attempt to use the char remaining from the first stage was also made. However, due to the small size of the feed (106–150 μm); this

char caused a high pressure drop in the reactor system, which prevented a comparative test to be done. The performances obtained with oak, spruce, and pine bark chars are compared in Table 7. The densities of the chars were different, and therefore, different weights of each char were needed to provide the same depth of bed in the reactor.

The recovered amounts of tar, lights, CO, CO₂, and steam were independent of the type of char used. The concentration of CH₄ was slightly higher with spruce char, which may indicate an effect on the cracking pathway.

The tars produced with different types of second stage char were characterized by SEC. Figure 4 shows the SEC chromatograms. All the tar samples recovered showed a bimodal molecular size distribution. A peak, which represents molecules excluded from the column porosity, appears at short elution times. Another peak, which represents molecules that were retained and resolved by the column, appears at longer elution times. A valley of low intensity separates the two peaks. The molecular mass of the recovered tars, based on the maxima of their retained peaks, was estimated and presented in the figure. Figure 4 shows that the presence of char affected the tar molecular size distribution markedly, and the type of char had a less significant effect on the distribution. When char is present in the second stage, the size distribution of the tars shifts from longer elution (smaller molecular size material) to shorter elution times (larger molecular size material). It is inferred that the presence of char affects the mechanism of the cracking reactions, and this results in (i) depletion of lighter molecular mass material cracking to lighter gases and (ii) larger molecular mass tar molecules forming through condensation reactions on heated solid surfaces.

On comparison of the molecular weight distribution of the tars in the retained region, it would seem that the tar recovered in the presence of pine char was shifted toward smaller values compared to the tars recovered in the presence of spruce and oak chars. It may be that pine char did not allow as much condensation of the small tars on the char surface, so that the tars remained relatively small. The results from SEC showed that when the second stage is packed with different chars, the structures of the tars recovered are different. Therefore, even though the type of char does not have a measurable effect on the amount of tar recovered, the SEC analysis shows that the type of char has an impact on the structures of the tars.

3.6. Effect of Adding O₂ at the Inlet of the Second Stage. The effect of adding a limited amount of O₂ (2% O₂ in He) to the flange at the entry to the second stage has been studied. This addition of oxygen just above the char-packed region simulates the throat and the char reduction zone of the downdraft gasifier. In the previous parts of this study, an inert gas (He) was added through the flange nozzles. Therefore, while previous experiments focused on high temperature pyrolysis/gasification/reforming, these experiments added combustion to the reactions. Experiments were carried out with a beechwood sample in the first stage and three different second stage conditions were investigated, as shown in Table 8.

The above reactor conditions were chosen because investigations in the absence of O₂ concluded that with an empty second stage at 800 °C pyrolysis was dominant, while with the second stage at 1000 °C gasification and reforming also played important roles. The role was further enhanced by the presence of the char bed. The results obtained are shown in Table 9.

Table 8. Reactor (Second stage) Conditions for Tests with O₂ Addition^a

condition	second stage feed	temp. (°C)
1	empty	800
2	empty	1000
3	spruce char (2 g)	1000

^a1st stage: feed = beechwood, superficial velocity = 0.1 m s⁻¹, inlet pressure = 2.2 bar, temperature = 500 °C. 2nd stage: superficial velocity = 1.6 m s⁻¹, inlet pressure = 2.1 bar, temperature = variable, packed bed = variable.

The addition of O₂ had a significant effect on the tar recovered when the second stage was empty. At temperatures of 800 and 1000 °C, the tar recovered significantly decreased when O₂ was added due to the partial combustion of the tar, in line with work previously reported.^{13,30} However, the effect of O₂ seems insignificant when the second stage was half filled with char at 1000 °C, as the amounts of tar recovered were similar in the absence and presence of O₂. Although the tar reacts with O₂ within the empty reactor stage, when the reactor is part filled with hot char the O₂ is preferentially scavenged by the char bed and is not available to combust the tar. Increasing the temperature from 800 to 1000 °C, in the presence of O₂ and an empty second stage, decreased the amount of tar recovered. In comparison, it seems that addition of a limited amount of O₂ at a temperature of 800 °C decreased the tar content to a lower value than increasing the temperature from 800 to 1000 °C in the absence of O₂.

The release of CH₄ decreased when O₂ was added. This was evident at both 800 and 1000 °C in both the absence and presence of char. This is expected as CH₄ is consumed by combustion with O₂. When the temperature was increased from 800 to 1000 °C (with an empty second stage), in the presence of O₂, the CH₄ released stayed relatively constant. This is different to what was observed in the absence of O₂, when with an increase in temperature, the CH₄ release increased due to enhanced tar cracking. In the presence of O₂, it seems that combustion counterbalances the impact of this effect.

The amount of light hydrocarbons decreased for all the investigated conditions in the presence of O₂; this must be as a result of combustion. However, when O₂ was added to the second stage, there was a slight change in the composition of the light hydrocarbons. Although C₂H₄ was still the dominant product, there were traces of some higher hydrocarbons present, such as C₄H₁₀ and C₅H₁₂, which were not present in the absence of O₂.

The presence of O₂ did not have a significant effect on the amount of CO released when the second stage was empty at 800 °C, while at 1000 °C there was a minor decrease. In the presence of char, the amount of CO release increased significantly when O₂ was added. This is attributed to enhanced gasification and combustion of the char bed. The amount of CO increased when the temperature was raised from 800 to 1000 °C in the presence of O₂. This is similar to the finding on the impact of temperature in the absence of O₂. However, the extent of the increase was greater.

The proportion of CO₂ increased significantly in the presence of O₂ at temperatures of 800 and 1000 °C and with an empty second stage. This is expected and consistent with combustion reactions of CO, light hydrocarbons (including CH₄) and tars to produce CO₂. When the second stage was packed with char, the CO₂ released is the balance between CO₂

Table 9. Identified Components in Experiments with Addition of O₂ through the Flange Nozzles at the Entry to the Second Stage^a

temp. (°C)	identified components (g)							estimated amount of O ₂ used (g)	2nd stage char wt loss (g)	2nd stage char wt loss (%)
	tar	lights	CO	CH ₄	CO ₂	H ₂ O	total identified (g) **			
800 °C (O ₂ present)	0.006 ± 0.001	0.014 ± 0.003	0.20 ± 0.017	0.027 ± 0.002	0.355 ± 0.007	0.43 ± 0.025	0.95 ± 0.035	0.32 ± 0.02	N/A	N/A
800 °C (O ₂ absent)	0.046 ± 0.001	0.026	0.204 ± 0.005	0.040 ± 0.003	0.102 ± 0.001	0.28 ± 0.025	0.92 ± 0.026	N/A	N/A	N/A
1000 °C (O ₂ present)	0.002	0.003	0.25 ± 0.020	0.030 ± 0.004	0.31 ± 0.011	0.31 ± 0.013	0.85 ± 0.031	0.30 ± 0.03	N/A	N/A
1000 °C (O ₂ absent)	0.009 ± 0.001	0.016 ± 0.002	0.285 ± 0.005	0.056 ± 0.001	0.118 ± 0.001	0.17 ± 0.031	0.88 ± 0.029	N/A	N/A	N/A
1000 °C, half filled char (O ₂ present)	0.002	0.000	1.41 ± 0.019	0.012 ± 0.001	0.461	0.000	0.86 ± 0.015	1.27	0.96	47.8 ± 0.4
1000 °C, half filled char (O ₂ absent)	0.002	0.001	0.495 ± 0.008	0.027 ± 0.004	0.003 ± 0.001	0.000	0.76 ± 0.010	N/A	0.16	7.8

^aTest conditions are summarized on Table 8. Values are shown ± SD. ** = include remaining char in the 1st stage and correction (subtraction) for mass of O₂ used.

formed by combustion reactions and the CO₂ consumed by gasification. Temperature also seemed to have an effect on the CO₂ released with a char bed. As temperature was increased from 800 to 1000 °C, in the presence of O₂, the CO₂ release decreased, which is consistent with increased gasification at the higher temperature.

The amount of H₂O produced increased significantly at temperatures of 800 and 1000 °C when O₂ was added as a result of combustion reactions of H₂, light hydrocarbons, and tars to produce H₂O. However, when the second stage was packed with char, H₂O was not recovered, even in the presence of O₂, showing the reactivity of the char bed with H₂O.

3.7. Effect of Type of Feedstock. First, different biomasses (beechwood, palm fiber, and olive bagasse) and a sewage sludge sample were pyrolyzed in the first stage only (tar production zone). Second, the different feeds were pyrolyzed in the first stage with the second stage installed. The data obtained are shown in Table 10.

The amounts of tar at the outlet of the first stage varied with the feedstock and with its original volatile matter content (values given in italics in Table 10). In general, less than half of the original volatile matter was emitted as tar (the lowest proportion was with sewage sludge). The second stage temperature was 1000 °C for this suite of tests, in order to optimize the extent of tar destruction reactions. Cracking of the tars at high temperature (1000 °C) in the presence of char decreased the amounts of tar recovered by 99.3%, 99.3%, 98.9%, and 98.3% for beechwood, palm fiber, olive bagasse, and sewage sludge, respectively. The char-packed second stage was efficient in removing the tars formed in the first stage for the fuels studied. The extent of tar cracking did not seem to be very dependent on the type or amount of tar generated in the first stage.

The tars recovered from the different feeds were characterized by SEC. Figures 5 and 6 show the results of the analysis.

The SEC analysis of the tars at the exit of the first stage (as shown in Figure 5) suggest that there were no significant differences between the molecular masses of the tars generated by the different feeds. However, differences are apparent in the molecular weight distributions of the tars recovered after the tar cracking (second) stage, as shown in Figure 6.

The tars recovered from palm fiber and sewage sludge appeared similar to each other and seemed larger than those at the outlet of the first stage of the reactor. The distribution of the tars from these feeds show a shift toward shorter elution times (i.e., larger size) in the retained region, compared to the distribution of the tars from beechwood and olive bagasse.

Beechwood and palm fiber released larger amounts of CH₄, while sewage sludge released the least. This matches the amount of tar generated in the first stage, which is similar for beechwood and palm fiber and lower for sewage sludge, as CH₄ is mainly released from tar cracking.

Beechwood released the largest amount of CO; palm fiber and olive bagasse released similar amounts of CO, while sewage sludge released the lowest amount. CO must be mainly formed by the reforming of hydrocarbons and gasification of C in the second stage. In all cases, the CO₂ and steam entering the second stage completely reacted, which indicates that this pathway produced most or all the observed increase in the CO contents in the second stage. Tar cracking reactions could have been a complementary source of CO. The O/C ratio in the feeds (Table 1) was about 0.91, 0.85, 0.84, and 0.48 for

Table 10. Product Distribution with Different Feedstocks^a

feed type	as % of initial biomass feed (of 1 g), dry basis									
	tar	1st stage char	lights	CO	CH ₄	CO ₂	H ₂ O	total identified	2nd stage char wt loss (g)	2nd stage char wt loss (%)
beechwood (1st and 2nd stages)	0.2 ± <0.05	23.7 ± 0.4	0.0 ± <0.05	49.5 ± 0.3	2.5 ± <0.05	0.1 ± <0.05	0.0 ± <0.05	76.1 ± 0.7	0.20	4.3 ± 0.1
beechwood (1st stage only)	33.4 (75)	24.5 ± 0.8	1.4 ± 0.2	2.4 ± 0.2	0.5 ± 0.0	7.2 ± 0.4	20.8 ± 1.2	90.3 ± 0.6	N/A	N/A
palm fiber (1st and 2nd stage)	0.2 ± 0.1	29.2 ± 0.8	0.2 ± <0.05	42.1 ± 0.7	2.7 ± 0.2	0.2 ± <0.05	0.0 ± <0.05	74.7 ± 1.2	0.20	4.2 ± <0.05
palm fiber (1st stage only)	34.7 (69)	30.9 ± 0.5	1.5 ± 0.2	2.4 ± 0.2	0.5 ± <0.05	8.4 ± 0.3	25.0 ± <0.05	103.4 ± 1.3	N/A	N/A
olive bagasse (1st and 2nd stages)	0.3 ± 0.1	34.6 ± 0.4	0.1 ± <0.05	42.7 ± 0.5	2.3 ± <0.05	0.1 ± <0.05	0.0 ± <0.05	80.0 ± <0.05	0.20	4.3 ± 0.5
olive bagasse (1st stage only)	25.0 (67)	34.1 ± 1.1	3.9 ± 0.5	1.7 ± 0.1	0.6 ± 0.1	9.7 ± 0.5	22.5 ± <0.05	97.5 ± 1.2	N/A	N/A
sewage sludge (1st and 2nd stages)	0.4 ± <0.05	42.7 ± 0.4	0.1 ± <0.05	27.2 ± 0.7	1.9 ± <0.05	0.1 ± <0.05	0.0 ± <0.05	72.5 ± 0.2	0.18	3.9 ± <0.05
sewage sludge (1st stage only)	23.9 (50)	42.9 ± 0.2	2.3 ± <0.05	0.5 ± <0.05	0.4 ± 0.1	3.4 ± 0.3	20.0 ± <0.05	93.4 ± 0.6	N/A	N/A

^a1st stage: feed = variable, superficial velocity = 0.1 m s⁻¹, inlet pressure = 2.2 bar, temperature = 500 °C, 2nd stage: superficial velocity = 1.6 m s⁻¹, inlet pressure = 2.1 bar, temperature = 1000 °C, packed bed = pine char 4.7 g, char size (diam.) = 212–500 μm. Values given ±SD. Values in *italics* represent the initial volatile matter of the feed stock; these values were taken from Table 1.

beechwood, palm fiber, olive bagasse, and sewage sludge, respectively, and this order corresponds to the amounts of CO produced from the feeds. It was observed that the larger the O/C ratio, the larger the amount of CO produced.

The amounts of light hydrocarbons (except CH₄) varied with the feeds: with beechwood no light hydrocarbon was detected, while with palm fiber, olive bagasse, and sewage sludge small amounts were released. The data is consistent with the reforming of the hydrocarbons at 1000 °C.

3.8. Measurement of the H₂ Concentration. The results of all of the above studies show mass balance closures in the range 75–90%. One important contributor to the missing material was H₂. It was not feasible to measure this component routinely during the study, because He was used as the sweep gas through the reactor. This meant that the normal method of detecting H₂ by thermal conductivity could not be used due to the similar thermal conductivities of He and H₂. Therefore, some modifications were made to the experimental procedure to enable the contribution of H₂ gas to the balance to be assessed. A limited number of tests were done using Ar sweep gas (instead of He) and ice/salt/H₂O as the tar trap coolant (instead of liquid N₂). The experiment was only carried out using one experimental condition and the results are shown in Table 11.

The amount of char produced when Ar was used to sweep the volatiles out of the reactor was slightly higher than when He was used. The thermal conductivity of Ar is much lower than that of He, so this may have influenced the heat transfer during the biomass pyrolysis in the first stage, resulting in slightly less pyrolysis and therefore more residual char. Moreover, the amount of tar recovered after thermal cracking and reduction reactions in the char-packed second stage was not affected by the carrier gas used. This may be because the presence of char and the very high temperature of 1000 °C in the second stage were sufficient to crack the tars to a similar degree regardless of the sweep gas.

The profiles for CH₄, CO, and H₂ release with time, as the first stage temperature was ramped to 500 °C, while the second char packed stage was at 1000 °C, are shown in Figure 7. In Ar as sweep gas, the release of H₂ started at a similar time (temperature) as the release of CH₄ and CO, although it was completed over a slightly longer time scale. The figure shows that the volume (%) of H₂ in the gas stream is significant, even though the actual amount (in mass), as shown in Table 11, is relatively small. It increased the proportion of initial biomass that was accounted for by approximately 3%. The volume of H₂ was less than that of CO but was significantly more than that of CH₄.

4. CONCLUSIONS

A laboratory scale, two stage reactor has been developed to simulate aspects of a downdraft gasifier. The reactor has been used to study the effect of the conditions in the throat and char reduction zone of a downdraft gasifier on the reduction in the tar concentration and on the suite of other gaseous products formed. In general, between 75 and 90% of the first stage biomass was accounted for as residual char in the first stage and gaseous and condensable species at the outlet of the second stage. The measurement of H₂ increased the recovery by about 3%. The remaining material is thought to be low boiling hydrocarbons lost during the tar separation procedure and soot not quantified during the tests. The recovery was higher during tests with the first stage (at 500 °C), as a high concentration of

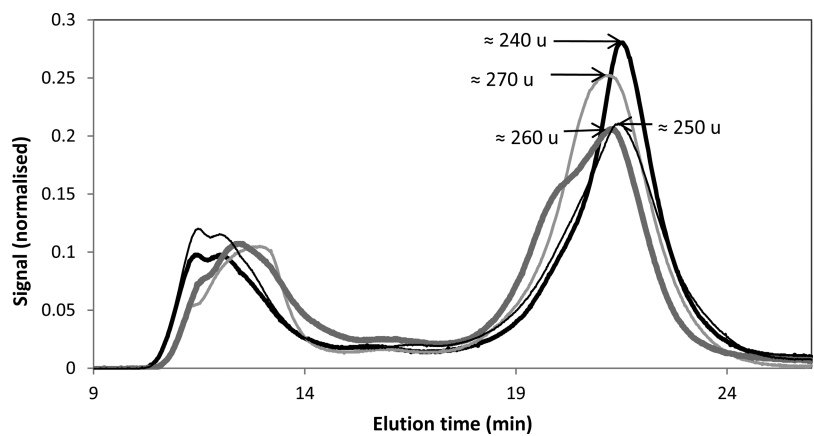


Figure 5. SEC analysis of tar recovered from various feeds after pyrolysis in the single stage reactor. SEC was performed with a Mixed D column. All chromatographs have been area normalized. Single stage: superficial velocity = 0.1 m s⁻¹, inlet pressure = 2.2 bar, temperature = 500 °C, heating rate = 1 °C s⁻¹. Results are for palm fiber (thick black line), sewage sludge (medium light gray line), beechwood (thick dark gray line), olive bagasse (thin black line).

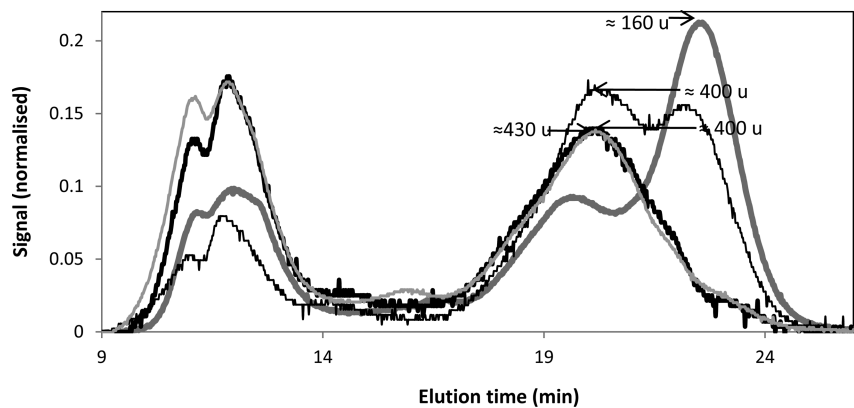


Figure 6. SEC analysis of tar recovered after tar cracking of tars from various feeds. SEC was performed with a Mixed D column. All chromatographs have been area normalized. 1st stage: feed = variable, superficial velocity = 0.1 m s⁻¹, inlet pressure = 2.2 bar, temperature = 500 °C. 2nd stage: superficial velocity = 1.6 m s⁻¹, inlet pressure = 2.1 bar, temperature = 1000 °C, packed bed = pine char 4.7 g, char size (diameter) = 212–500 μm. Results are for palm fiber (thick black line), sewage sludge (medium light gray line), beechwood (thick dark gray line), olive bagasse (thin black line).

Table 11. Measurement of H₂ and Other Components using Ar as Sweep Gas^a

as % of initial biomass feed (of 1 g), dry basis										2nd stage char wt loss (g)	2nd stage char wt loss (%)
sweep gas	coolant	tar	1st stage char	lights	CO	CH ₄	CO ₂	H ₂ O	H ₂		
He	liquid N ₂	0.2 ± <0.05	23.2 ± 0.2	0.0 ± <0.05	49.2 ± 0.4	3.1 ± <0.05	0.1 ± <0.05	0.0 ± <0.05	*	0.20	5.1 ± 0.1
Ar	ice + H ₂ O + salt	0.2 ± <0.05	24.9 ± 0.5	*	54.5 ± 2.2	2.7 ± 0.1	*	*	3.1 ± <0.05	0.27	6.7 ± 0.2

^a1st stage: feed = beechwood, superficial velocity = 0.1 m s⁻¹, inlet pressure = 2.2 bar, temperature = 500 °C. 2nd stage: superficial velocity = 1.6 m s⁻¹, inlet pressure = 2.1 bar, temperature = 1000 °C, packed bed = 4 g of spruce char, char size (diam.) = 212–500 μm, carrier gas = variable. Values shown ±SD. * = unable to quantify.

tar was formed. These tars were cracked in the second stage to lighter products. Some of these were lost under the conditions used to isolate and measure the residual tar and hence recoveries calculated from data at the outlet of the second stage were lower.

The study shows that tar cracking at high temperatures results in the formation of mainly CO and CH₄; and cracking is influenced by superficial velocity such that higher superficial velocity favors higher CO, CO₂, and tar release. This is a residence time effect; the higher the velocity, the lower the time

available for cracking to occur and equilibrium positions (products) to be attained. Therefore, temperature and residence time are two of the main factors that determine the extent of tar destruction. It is also important to note that tar cracking (destruction) is enhanced by the presence of a char bed. Under the optimum conditions, 99% of the tar could be removed by reactions in the second stage. Chars of different biomass (source) showed similar extent of tar destruction, although the actual structure of the residual tars recovered (after cracking) varied. Different biomass feeds have their

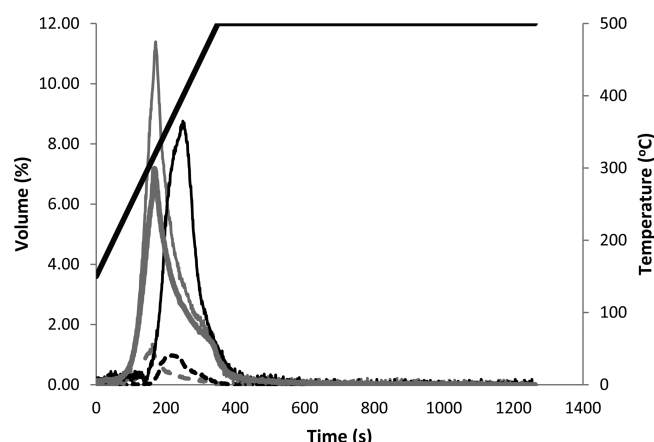


Figure 7. Tar cracking products (CH_4 , CO and H_2) released as a function of inert sweep gas flowing downward in the reactor. Each product is shown as a percentage of the initial biomass weight, dry basis. 1st stage: feed = beechwood, superficial velocity = 0.1 m s^{-1} , inlet pressure = 2.2 bar, temperature = 500°C , sweep gas = variable. 2nd stage: temperature = 1000°C , inlet pressure = 2.1 bar, carrier gas = variable. Results for CH_4 (argon) (broken thick gray line), CH_4 (helium) (broken thick black line), CO (argon) (solid medium gray line), CO (helium) (solid medium black line), H_2 (argon) (solid thick gray line), temperature (solid thick black line).

particular pyrolysis characteristics and generate particular amounts and composition of primary tar, char, and volatiles. Nevertheless, regardless of the initial amount and type of tar generated by the feed, it was possible to decrease tar content by in excess of 98%, such that the tar recovered was near zero for all the investigated feeds. The high level of tar destruction led to an increase in gas release as CO , CO_2 , H_2O , and light hydrocarbons.

The effect of addition of O_2 to the flange at the entry to the second stage (simulating the throat of a downdraft gasifier) depended on the second stage conditions. With an empty second stage, the O_2 reduced the tar content at the exit of that stage. With char in the second stage, the addition of O_2 did not have any impact at 1000°C as the extent of tar cracking was very high and the char bed reacted with the O_2 .

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Notes

The authors declare no competing financial interest.

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