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Pyrolysis and Gasification in a Bench-Scale High-Pressure Fluidized-Bed Reactor

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A bench-scale high-pressure fluidized-bed reactor designed for pyrolysis, gasification, and combustion experiments (up to 1000 °C, 40 bar) has been constructed and commissioned. The system is intended to generate fuel reactivity data rapidly and cheaply, under realistic experimental conditions; it is relatively simple to construct and capable of operation by a single researcher. The reactor body (Incoloy Alloy 800HT, 34 mm i.d., 504 mm long) serves as the resistance heater and is designed to withstand the reaction pressure, obviating use of a "cold" pressure casing. The reactor is lined with a loosely fitting quartz tube to limit corrosion and catalytic effects. Sample (up to 2000 mg) is held between two air actuated valves and injected batchwise ("single-slug") through a water-cooled probe. The design of the reactor allows determination of tar/oil and char yields. Exhaust gases are passed through a dryer before entering the analytical stage. The present report focuses on equipment design and preliminary data from pyrolysis and gasification experiments with Daw Mill coal (UK) at up to 1000 °C and 30 bar. Extents of gasification were calculated by subtraction of total volatile yields in CO_2 from mass loss during pyrolysis in helium, performed under otherwise identical conditions. Combustion reactivities of chars were determined in an atmospheric pressure TGA instrument. A number of design adjustments have been described, enabling total volatile yields from the FB reactor to match those from a high-pressure wire-mesh reactor. As expected, *tar* yields from the fluidized-bed reactor were significantly lower than those from the wire-mesh instrument, due to longer residence times of volatiles in the bed of solids and the reactor freeboard.

Introduction

Much of the fuel characterization data in the literature relating to gasification is based on TGA/DTA instruments,[1−6] capable of only relatively slow heating regimes (up to hundreds of K/min). Furthermore, many coal gasification studies have been carried out using chars prepared and gasified in separate experimental steps.[1,7−12] The two-step process affects the results of gasification reactivity experiments significantly: there is strong evidence showing that different results are obtained from chars prepared from the same coal under different pyrolysis conditions.[3,10,13−16] Peng et al.[16] found that the reactivities of in situ generated chars are up to 6 times higher than those of corresponding ex situ chars prepared by steam gasification at 1000−1300 °C. Given this sensitivity of pyrolysis yields and char reactivities to prior pyrolysis conditions, acquisition of realistic bench-scale conversion and reactivity data requires these steps to be carried out under conditions more akin to actual reaction conditions.

The present report describes the design and operation of a bench-scale high-pressure fluidized-bed reactor. The system is intended to generate fuel reactivity data rapidly and cheaply during pyrolysis, gasification, and combustion experiments at temperatures of up to 1000 °C and pressures up to 40 bar. It is relatively simple to construct and capable of operation by a single researcher. The mechanical design is relatively simple, featuring direct electrical heating of the reactor body to avoid use of a separate furnace and construction of the reactor body out of a high-strength alloy, resistant to creep at 1000 °C and 40 bar to obviate the use of a "cold" pressure casing. During routine operation, up to 2000 mg of sample, held between two air actuated valves is injected batchwise ("single-slug") through a water-cooled probe into the fluidized bed. In addition to gas analysis, the design of the reactor allows deter-

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mination of tar/oil and char yields with a repeatability of ±2%. A brief review of comparable bench-scale reactors would help place the present design in a more general framework.

Several, somewhat larger, *bench-scale* high-pressure fluidized-bed pyrolysis/gasification reactor systems have been reported in the literature. Morris and Keairns[17] have described a reactor made of Inconel 600 (35 mm i.d., 330 mm long). The reactor, the furnace heaters and surrounding insulation were placed inside a cold pressure casing, with the reactor body allowed to operate at high temperature at a minimal pressure differential with the surroundings. The bed material (char) was fluidized with nitrogen. Sample coal was held in a horizontal tube attached to a solenoid valve and injected into the reactor using a small cylinder of high-pressure nitrogen. Gas analysis data from experiments (up to 982 °C and 10 bar) using three separate coals have been reported. From descriptions, the apparatus appears relatively large and to require significant maintenance; the schematic diagram of the apparatus (cf. ref 17) suggests, furthermore, that the feed tube did not extend into the fluidized-bed of solids, implying the existence of a potential source of operating problems.

Adánez et al.[18] have described a stainless steel fluidized-bed reactor (AISI 304; 40 mm i.d., 500 mm long), its furnace and ancillary gas analysis equipment. Instead of a coal injection system, the reactor was initially charged with *char* (particle size range 100−630 mm) and heated in nitrogen flow at atmospheric pressure. When reaction temperature was reached, the reactor was pressurized and reactant gases were introduced. Gasification experiments with a lignite (1000 °C, 25 bar) have been reported. The temperature was determined by a single thermocouple placed inside the bed and the furnace temperature controlled manually using a variable voltage transformer. Gas pressure was regulated by means of a needle valve.

Another fluidized-bed pyrolysis/gasification reactor (1000 °C, up to 25 bar) equipped with on-line gas analysis instrumentation has been described by Hüttinger and co-workers.[19−21] The ceramic reactor and furnace ancillaries were enclosed in a bronze casing. From available diagrams, it appears the reactor did not have provision for injecting sample *into* the fluidizing bed; sample (200 mg) appears to have been injected downward in the reactor freeboard, onto a preheated fluidized-bed of alumina particles (60−65 mm). Details of the reactor construction (material, dimensions) have not been published and the apparatus has been described only in terms of a simple schematic diagram. It appears, nevertheless, that its combination of reaction conditions and size (i.d.) are closest to the reactor described in the present paper.

A larger scale apparatus with continuous feed has been described by Sue-A-Quan et al.[22,23] The reactor tube (Incoloy; 100 mm i.d., 1000 mm long) was centrally located in a refractory-lined steel pressure shell of 305 mm diameter. The central tube was heated electrically and the coal continuously fed (2−5 kg/h) by a star wheel feeder. Water, delivered by a diaphragm pump, was vaporized and superheated in coils immersed in a fluidized sand bed heated by a propane burner; its final temperature was adjusted by heat exchange with product gas from the reactor. Operating conditions have been reported as 900 °C and up to 18 bar. From descriptions, reactor design and operation appear complex.

A number of bench scale reactors with different configurations have already been developed at Imperial College for evaluating aspects of fuel behavior including reactivities, and volatile and tar release with char recovery for subsequent combustion tests. These include a high-pressure wire-mesh reactor with tar trapping capability and a steam injection facility[24−26] and a two-stage fixed-bed "hot-rod" reactor,[27] used for coal/biomass pyrolysis/gasification followed by hydrocracking of released volatiles. The effect of residence time on tar cracking reactions has been investigated in a variable freeboard-height atmospheric pressure fluidized-bed reactor.[28,29] Product distributions from differently configured reactors have been compared by using common coal samples at atmospheric pressure,[30] during hydropyrolysis,[31] and under CO_2-gasification conditions.[32]

This first report on the high-pressure fluidized-bed reactor focuses on equipment design and presents preliminary data from the pyrolysis and gasification of Daw Mill coal (UK), at up to 1000 °C and 30 bar. Extents of gasification were calculated by subtracting the amounts of volatiles released during pyrolysis in helium from sample mass loss during gasification in CO_2 (or steam), in experiments performed under otherwise identical conditions. Results have been compared with analogous data from a high-pressure wire-mesh reactor. Combustion reactivities of chars have been determined in an atmospheric pressure TGA apparatus.

Experimental Section

Fluidized-bed Reactor Assembly. Figure 1 presents a schematic diagram of the bench-scale high-pressure fluidized-bed reactor system, showing the gas supply system (1), the reactor (12), the coal injection probe (14), the tar trap assembly (15), and the product recovery train. A pressure-safety valve (20) is connected to the outlet line, to protect the reactor against overpressure. Exhaust gases pass from the reactor through a dryer into the product analysis train.

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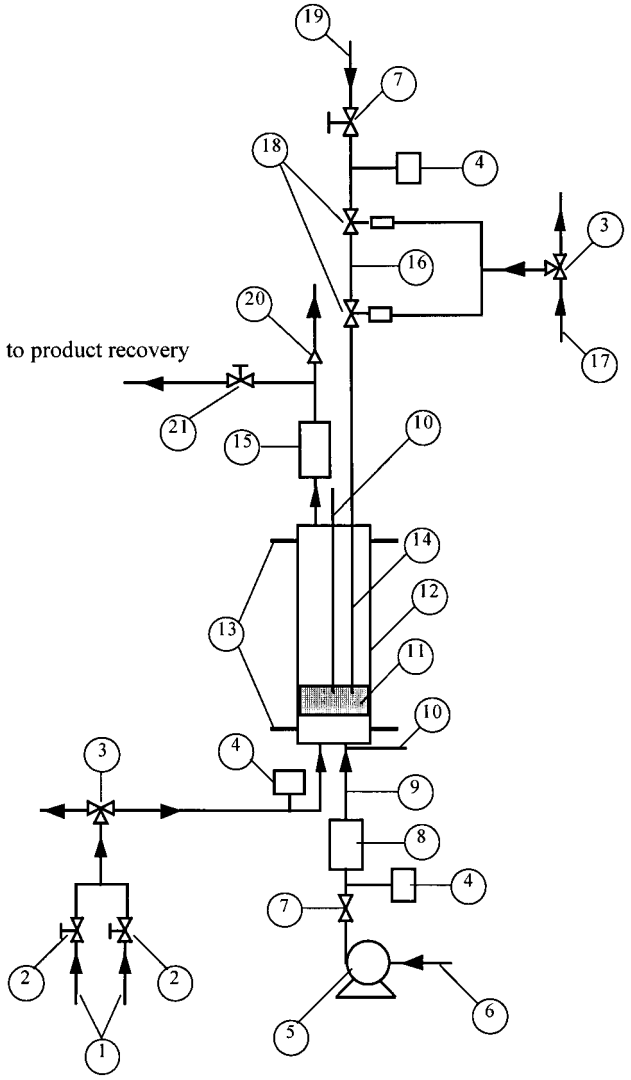

Figure 1. Schematic diagram of the high-pressure fluidized-bed reactor system: (1) high-pressure gas supply; (2) metering valve; (3) 3-way valve; (4) pressure transducer; (5) metering pump; (6) water supply; (7) valve; (8) steam generator; (9) heated line; (10) thermocouple; (11) sand bed; (12) reactor; (13) electrodes; (14) sample injection probe; (15) tar trap; (16) sample; (17) air supply; (18) air-actuated valves; (19) injection probe gas supply; (20) safety valve; (21) gas flow control valve.

Gas Supply System. High-pressure gas (1) is supplied from the bottom of the reactor; relative concentrations in gas mixtures are controlled by metering valves (2) in the inlet line where a pressure transducer (4) is used for tracking reactor pressure. The total flow of fluidizing gas is controlled downstream of the reactor at the let-down point by a fine metering valve (21). The flow is measured with a calibrated rotameter downstream of this valve. Water is supplied to the steam supply circuit by a calibrated high pressure liquid metering pump (5) (Magnus P4000/D; maximum pressure 400 bar). The steam generator (8) consists of an electrically heated 1 in. diameter, 25 cm long tube packed with ceramic spheres. The power supply is driven by a temperature controller and a K-type thermocouple connected at the exit of the generator. The steam-line into the reactor is trace-heated and the steam temperature at the reactor inlet monitored by a K-type thermocouple.

The Reactor. Figure 2 presents a diagram of the main reactor assembly, showing the reactor body (1) (Incoloy Alloy 800HT; 34 mm i.d., 504 mm long), which serves as the resistance heater and is designed to withstand the reaction

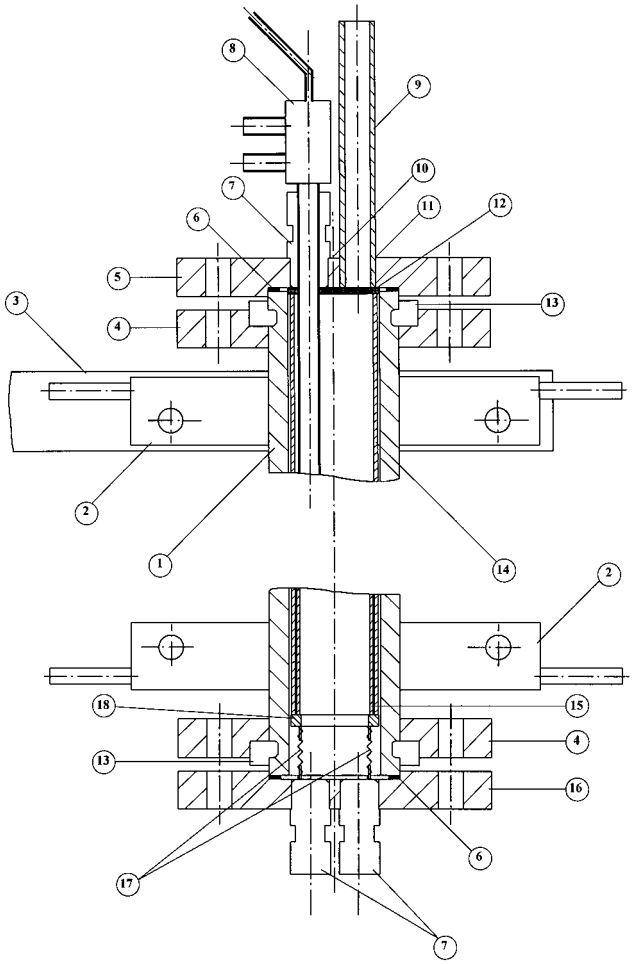

Figure 2. Main body of the reactor: (1) reactor tube; (2) electrode; (3) copper bar; (4) flange; (5) flange; (6) copper sealing ring; (7) male weld connector; (8) sample injection probe; (9) gas exit line; (10) position of male weld connector for thermocouple (not shown); (11) weld; (12) Kaowool-paper sealing ring, Kaowool, wire-mesh plates; (13) half-moon positioning ring; (14) quartz tube liner; (15) distributor disk supporting quartz tube; (16) flange; (17) springs; (18) spring-loaded ring.

pressure (40 bar maximum at 1000 °C), obviating use of a cold pressure casing.

Various materials of construction have been considered for the reactor tube. Stainless steels could not be used because of unsatisfactory creep resistance properties above 600−700 °C. Nimonic 105 and 115 alloys (Henry Wiggin Alloys) are more difficult to machine and were not available in the desired dimensions. Incoloy Alloy 800HT has high tensile strength and high creep resistance combined with resistance to high-temperature corrosion. These properties make it exceptionally useful for applications involving long-term exposure to elevated temperatures or corrosive atmospheres. Its chemical composition is given as Ni 30−35%, Cr 19−23%, Fe 39.5% minimum, C 0.06−0.10% maximum, Mn 1.5% maximum, S 0.015% maximum, Si 1% maximum, Cu 0.75% maximum, Al 0.15−0.60%, Ti 0.15−0.60% (aluminum + titanium 0.85−1.20%). Other properties and physical constants of the material are given in ref 33. Calculations according to BS 5500[34] and the High-Pressure Safety Code[35] have shown that the present reactor tube (34 mm i.d., 48.3 mm o.d., 504 mm long) can be

(33) Inco Alloys International Co., Incoloy Alloys 800 and 800HT, 1986.
(34) BS 5500, British Standards Institution, 1992.
(35) High-Pressure Technology Association, High-Pressure Safety Code, 1977.

used safely without undergoing creep rupture for 1000 h at 1000 °C and 39.9 bar.

Replacement of the central tube can be done with relatively little labor and other costs. Figure 2 shows that apart from smoothing surfaces and cutting grooves at either end, no machining was required on the main reactor tube. To improve simplicity and reliability, the flanges (AISI 316**)** were attached to the main body without recourse to welding: flanges (4, 5, 16) are passed over the body of the tube and fixed in-place by a pair of "half-moon" rings (13) (AISI 316) positioned in grooves cut at the top and bottom of the reactor. The inner and outer flanges were attached by eight bolts (10 mm diameter). The main seals were made by simple copper flat rings (6) (40.5 mm i.d., 48.5 mm o.d.; thickness 1.5 mm). The thickness of the flanges and of the positioning rings, the dimensions of the machined grooves on the reactor body, and the number and diameter of the bolts are based on BS 5500.[34]

All connections to the reactor were made through the top and bottom flanges. Gas and steam inlet lines are connected by two male welded connectors (7). The water-cooled coal injection probe (8) and the stem of the thermocouple sheath were sealed onto bored through male connectors, welded to the top flange. The main gas exit line (9) ($^1/_2$ in. diameter) is also welded onto the top flange. After the flanges were assembled, a tar trap assembly was connected to the gas exit line with a union fitting. All fittings and tubing used on the apparatus were made of AISI 316.

The reactor has been lined with a loosely fitting quartz tube (14) mounted with a ~3 mm thick quartz sintered disk (pore size 40−90 μm) serving as the support/gas-distributor plate. In the initial design, the disk was fused into the tube but this arrangement proved fragile, probably due to small differences between coefficients of thermal expansion. At present, the distributor plate is kept in position by means of a supporting smaller diameter quartz tube (15) inserted underneath the disk, pressing upward (through a quartz wool cushion) against a constriction in the liner. This arrangement appears to prevent loss of bed solids through the small gap between the disk and the wall of the lining. The construction of the bed does not allow gas passage around the periphery of the distributor plate: the distributor plate is pushed tightly against the liner constriction providing intimate contact.

The assembly is maintained under compression by a spring loaded ring located at the base of the reactor (see below). No difference was found in results between initial pyrolysis experiments carried out with the support-plate fused into the quartz liner (a fragile configuration, see above) and the present mode of operation.

The fluidized-bed material normally consisted of acid-washed sand; the temperature was measured by a 1.5 mm diameter type-K thermocouple (chromel/alumel) inserted inside the bed through the top flange. Due to constraints on the design of the pressure shell, thermocouple wires or other probes cannot be introduced radially; they must be introduced vertically downward from the upper flange. The cross-sectional area of the quartz tube is only about 6.5 cm^2; we have found that distortions of the bed due to additional detection equipment need to be minimized. Accordingly, a single thermocouple was used. The degree of temperature uniformity was investigated at atmospheric pressure where distortions would be expected to be more severe: when a temperature of 1000 °C was measured at the level of the bed where sample is injected, the bed temperature (bottom to top) was found to be between 990 and 1000 °C.

One important feature of the design emerged during commissioning runs. At 1000 °C, the cylindrical metal body expands axially by several millimeters more than the quartz liner. The pressure drop through the distributor plate being sufficient to raise the quartz liner assembly, the latter normally gets pushed against the top flange. However, unless an effective seal is maintained between the top of the liner and the top flange, gas is able to bypass the fluidized-bed, flowing through the annular space between the liner and the metallic reactor body. Figure 2 shows the positioning of a spring-loaded ring (18), located at the base of the reactor, pushing the liner against the top flange with layers of Kaowool paper (12) providing an effective seal between the liner and upper flange. A solids filter consisting of a layer of Kaowool between two layers of wire mesh is situated underneath the Kaowool paper sealing ring. The injection probe and the thermocouple are passed through holes in the mesh and Kaowool assembly. The Kaowool paper sealing ring has an additional third hole for the gas exit. The assembly is weighed before and after each experiment; the weight of captured solids is determined by weight difference. No sand or char particles have been found in the actual tar trap after experiments.

While the main purpose of the quartz liner (28.8 mm i.d., 32 mm o.d.) was to minimize corrosion and catalytic activity, the tube has proved otherwise useful: at the end of an experiment, the top flange is removed and the whole quartz-lining assembly can be taken out, complete with sand bed and chars, without having to dismantle the rest of the reactor.

The pressure drop across the reactor has been determined as 1470 Pa. Across the distributor disk alone, the pressure drop was 400 Pa. This gives a ratio of pressure drop across the distributor (400 Pa) over the pressure drop across the bed minus the drop across the distributor (1070 Pa) equal to 0.37. This value is within the recommended range of 0.2−0.4 verified by various analyses and experiments.[36]

Heating System. Electrical power for heating the reactor is supplied from a high-output transformer (2000 A, 1.5 V) to two copper electrodes (2; Figure 2) attached close to the top and bottom of the reactor. The two copper electrodes are split, with a semicircular hole cut in each half; the two halves are bolted together around the reactor body. The top electrode is connected to the transformer with copper bars (3) which serve to support the reactor in position. However, the bottom electrode is movable ("floating"), to accommodate thermal expansion of the reactor body and is connected to the transformer with 18 flexible copper cables (each capable of carrying 180 A). The electrodes are water-cooled to prevent heating and continuity is monitored by a flow sensor connected to the water outlet line. A continuous signal is logged via the data-logging card and the experiment aborted if the flow of water is interrupted.

A Eurotherm 94c temperature controller, attached to the Type-K thermocouple immersed in the fluidized-bed, is used for driving the power supply to the reactor. The controller is a PID device capable of communicating with a PC and the control parameters (PID parameters, set temperature, operating temperature, etc.) can be read and modified from the PC keyboard. The space available on the top flange does not allow the insertion of a second thermocouple inside the reactor, but the controller is able to use a single thermocouple for reading and logging as well as controlling the reactor temperature. For safety, the reactor external wall temperature is also continuously monitored by separate thermocouples.

Sample Injection. The coal is fed into the reactor through a water-cooled probe inserted from the top of the reactor (Figures 2 and 3). The sample is injected as a short pulse ("single slug") into the preheated bed of sand. It is initially placed in a tube (16; Figure 1) between two air actuated valves (18). With the reactor operating at the desired set of conditions, the valves are opened and gas is allowed to flow at a slight overpressure, carrying the sample into the sand fluidized-bed. The flow of the pressurized gas can be adjusted with a needle valve (7) situated upstream of the two air actuated valves and the pressure is measured by a pressure transducer (4). The coal injection probe (Figure 3a) consists of three

(36) Kunii, D.; Levenspiel, O. *Fluidization Engineering*, 2nd ed.; Butterworth-Heinmann: New York, 1991; pp 102−105.

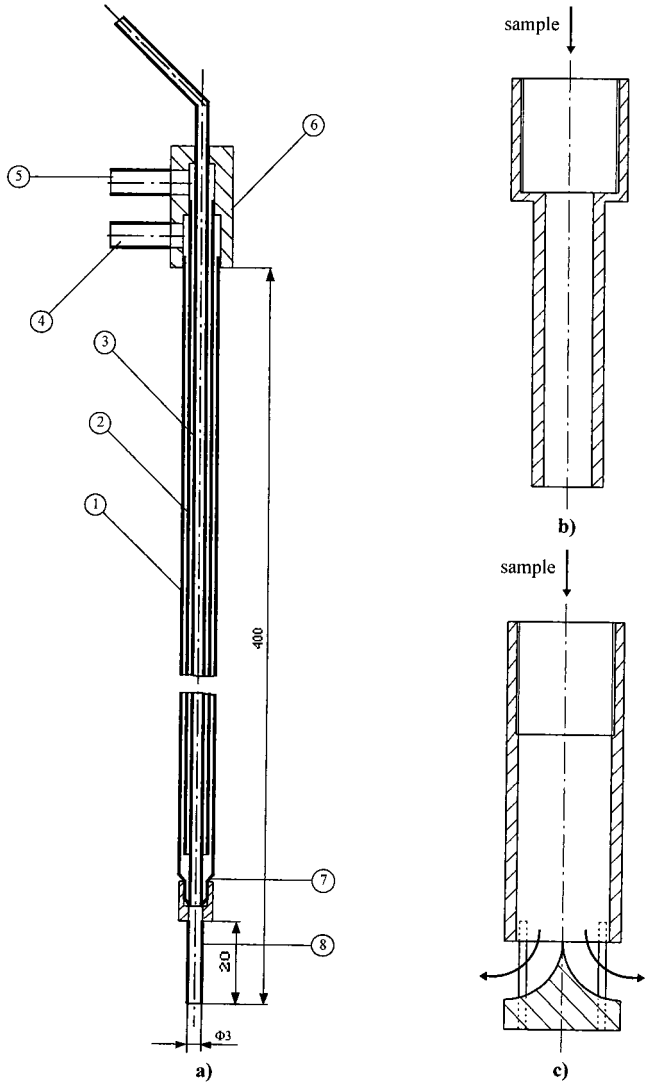

Figure 3. (a) Coal injection probe: (1) outer tube (o.d. $^5/_{16}$ in.); (2) middle tube (o.d. $^3/_{16}$ in.); (3) inner tube (o.d. $^1/_8$ in.); (4) water outlet tube; (5) water inlet tube; (6) hollow brass block; (7) stainless steel piece welded to outer and inner tubes; (8) tip. (b) Injection probe tip for axial injection. (c) Modified injection probe tip for radial injection.

concentric AISI 316 tubes (1, 2, 3; Figure 3a) silver-soldered into a hollow brass block (6). The coal is injected into the reactor through the inner tube (i.d. $^1/_8$ in.). Cooling water flows downward between the inner and the middle tube and then upward between the middle and the outer tube. A surge check valve in the water inlet line aims to prevent excessive water flow in the case of a water leak inside the reactor. Continuous signal from a flow sensor in the water outlet line is interrupted, aborting the experiment, if the flow of cooling water to the probe is discontinued. In order to minimize disturbance of the fluidized bed by insertion of the water-cooled probe, a 3 mm diameter tip (8) is threaded onto the exit from the probe, just above the bed. The (uncooled) tip extends into the bed when the bed expands during fluidization. During test runs, the straight hollow tip of the initial design (Figure 3b) serving to inject sample axially downward was modified in favor of a tip allowing nearly radial sample injection, serving to limit the level of coal agglomeration (Figure 3c).

Tar Traps. The tar trap assembly (Figure 4) consists of a $^1/_2$ in. diameter tube (2) packed with wire mesh (3) and cooled with liquid nitrogen (or a saline ice bath for operation under CO_2). After the trap, exhaust gas is passed through a small Soxhlet thimble (6) situated inside an AISI 316 filter housing (8), which is sealed with a copper ring (7). The thimble is also

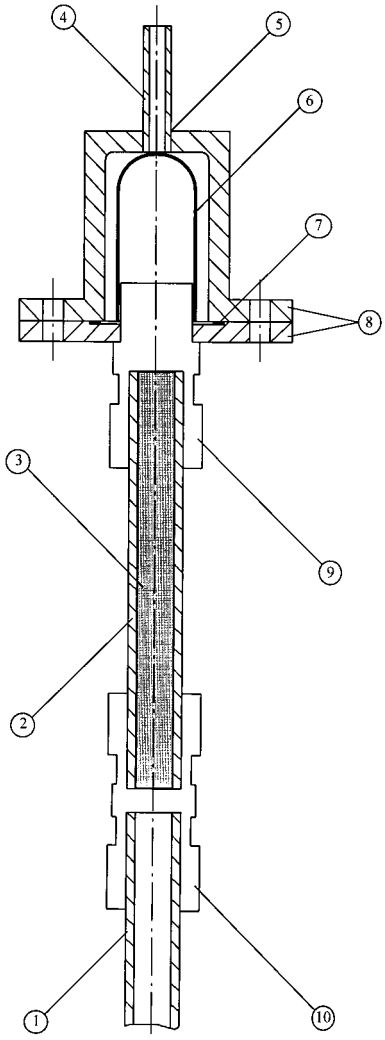

Figure 4. Tar trap assembly. (1) reactor gas exit line; (2) stainless steel tube (o.d. $^1/_2$ in.); (3) wire-mesh packing; (4) gas exit line; (5) weld; (6) Soxhlet thimble; (7) copper ring; (8) stainless steel housing; (9) male weld connector; (10) union fitting.

cooled with liquid nitrogen and is intended to collect any particles or tar carried over from the wire-mesh packed tube. To date, we have not found any tar condensation or particulates in the thimble assembly.

Gas Dryer. For accurate and reliable results, the gas analysis train requires a clean, dry sample. A Nafion gas sample dryer (Perma Pure Inc.) is used at the reactor gas outlet. This is a tube made of Nafion (a copolymer of tetrafluoroethylene (Teflon) and perfluoro-3,6-dioxa-4-methyl-7-octenesulfonic acid), which is highly resistant to chemical attack and can absorb up to 13 molecules of water for every sulfonic acid group in the polymer, without otherwise affecting the composition of analyte gases.

Data Acquisition. A PC and a 16-channel data acquisition card (Amplicon PC 26AT) were used for data logging and control. Software has been written for acquisition of signal through the card and for communicating with the reactor temperature controller. The fluidized sand bed temperature, the external reactor wall temperature, reactor pressure, steam temperature, steam pressure, dryer inlet temperature, and gas analysis data are routinely logged.

Experimental Procedure. Acid-washed sand (about 30 g; approximately 35 mm bed height prior to fluidization) was weighed using a Sartorius (BP 210 D; ±0.01 mg) balance and placed inside the reactor. The coal sample (about 50 mg) was then weighed and placed between the two air actuated valves.

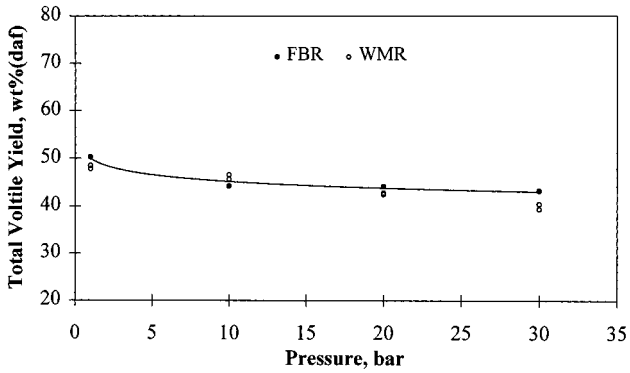

Figure 5. Pyrolysis total volatile yields from Daw Mill coal as a function of pressure: fluidized-bed reactor: 1000 °C, 60 s; wire-mesh reactor: 1000 °C, 1000 K/s, 60 s.

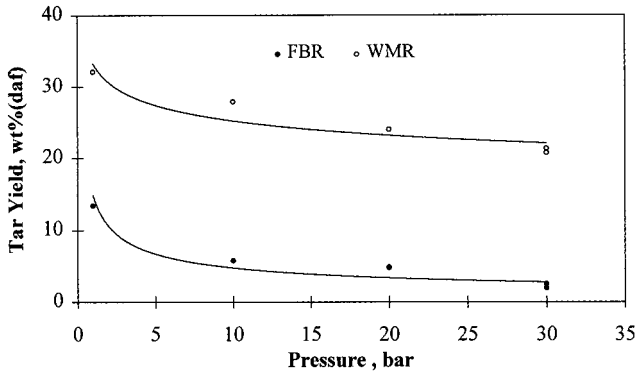

Figure 6. Pyrolysis tar yields from Daw Mill coal as a function of pressure: fluidized-bed reactor: 1000 °C, 60 s; wire-mesh reactor: 1000 °C, 1000 K/s, 10 s.

The thermocouple, the coal injection probe, and the tar trap were then assembled; gas pressure and flow rate were set. The tar trap assembly was cooled with liquid nitrogen or ice/NaCl bath for experiments with CO_2. The fluidizing velocity was set at 3 times the minimum fluidization velocity; hold time at peak temperature was 60 s. To inject sample, gas pressure in the injection circuit was adjusted to a slightly higher value than that of the reactor; after the experimental temperature was attained, sample was injected into the reactor and the two air-actuated valves immediately shut. At the end of the "holding" period, the reactor was allowed to cool: when experiments were carried out under a reactive gas atmosphere, the carrier gas flow was switched to He at the end of the intended reaction time.

After a run, the reactor was allowed to cool; the quartz liner and distributor plate assembly containing the sand and chars were taken out. Tar collected in the traps was washed out with a mixture of chloroform and methanol (4:1 v/v; Aristar grade, nonvolatile residues 8 ppm). Small amounts of tar were recovered from inner surfaces of the reactor and added to the total. The tar trap washing solvent was passed through the sand bed which acted as a filter and any possible fine particles in the tar trap were washed out and stayed in the sand bed. To date, we have not found any particles in the tar trap. Bed solids were washed with solvent, dried and weighed to determine sample weight loss. Tar/oil and char yields have been determined with a repeatability of ±2%.

It should be noted that 60 s represents the practical minimum for the residence time that can be used in the fluidized bed reactor whereas wire-mesh experiments can be (and usually are) conducted with shorter holding periods, typically 1−10 s. Both the start and the end point of experiments with the fluidized bed reactor are imprecise since the nature of the coal injection and coal distribution within the bed as well as the process of termination of reaction require finite time for completion. Reduction of the overall residence time would have the effect of magnifying the effect of these uncertainties.

Coal Samples. Daw Mill coal [% w/w daf: C 81.3, H 4.8, N 1.28, O 11.5, S 1.2, ash 4.7; ash composition (% ash): SiO_2 36.8, Al_2O_3 23.9, Fe_2O_3 11.2, CaO 12.0, MgO 2.5, Na_2O 1.5, K_2O 0.5, TiO_2 1.1, Mn_3O_4 0.4, P_2O_5 <0.3, SO_3 12.9] was used in experiments described below. The coal was ground and sieved to 106−150 mm, dried under vacuum at 35 °C for 16 h and then stored under nitrogen at −20 °C until required.

The sand used was provided by BDH Ltd. The particle size used was 150−300 μm. It is mainly composed of SiO_2 and the maximum impurities are as follows: hydrochloric acid-soluble matter 0.2%, loss on ignition 0.1%, chloride (Cl) 0.005%, and acid-soluble iron (Fe) 0.01%. The sand was washed with acid before use.

Extents of Coal Gasification and Char Combustion Reactivities. Gasification reactivity has been defined as the difference between sample weight loss from CO_2 (or steam) gasification and weight loss from pyrolysis under He, the two experiments performed under otherwise identical conditions; the reactivity has been expressed in terms of unit experimental residence hold time.

Relative combustion reactivities of residual chars[37] were determined with a Perkin-Elmer TGA7 1020 thermogravimetric analyzer (1−2 mg of char sample size), using simple isothermal combustion in air, at 500 °C. In this work, the relative combustion reactivity of char is defined as

$$R_{max} = -(1/W_o)(dW/dT)_{max}$$

where W_o is the initial sample weight (daf basis) and $(dW/dT)_{max}$ is the maximum weight loss rate in the rectilinear region of the TGA trace.

Results and Discussion

Sample Weight Loss and Tar Yield Determinations. Figure 5 presents sample weight loss data (Daw Mill coal) from pyrolysis experiments in helium carried out in the fluidized-bed reactor, at 1000 °C, between 1 and 30 bar (holding time 60 s). Results from experiments in a high-pressure wire-mesh reactor, conducted by heating at 1000 K/s to 1000 °C, with 60 s holding at peak temperature, have been included for comparison.

Pyrolysis total volatile yields from the two reactors were similar and were observed to decline with increasing pressure as a result of the physical suppression of volatiles release; our previous work suggests this to be due to suppression of *tar* evolution.[24] However, as shown in Figure 6, the eventual fate of tars released from coal particles was not the same in the two reactors, reflecting differences in their configurations. Tar yields from the fluidized-bed reactor were considerably lower compared to those from the wire-mesh reactor, due to tar cracking within the fluidized-bed as well as in the reactor freeboard.[28] The freeboard height is 325 mm, of which a 280 mm long section is placed below the top electrode. In He, with the fluidized-bed itself at 1000 °C, the temperature of the freeboard was measured as 960 °C, 50 mm below the electrode; further below, the temperature was uniform at 1000 °C. By contrast, in the wire-mesh reactor, tars released from coal particles are rapidly pushed out of the shallow reaction zone by a stream of carrier gas. Previous work by Tyler[38,39] and

(37) Cai, H.-Y.; Güell, A. J.; Chatzakis, I. N.; Lim, J−Y.; Dugwell, D. R.; Kandiyoti, R. *Fuel* **1996**, *75*, 15.
(38) Tyler, R. J. *Fuel* **1979**, *58*, 680.

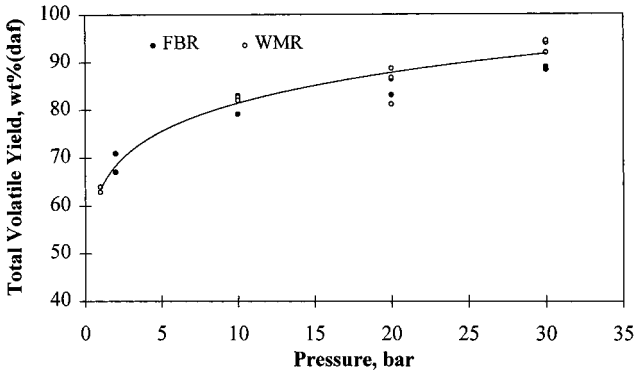

Figure 7. Gasification total volatile yields from Daw Mill coal as a function of pressure: fluidized-bed reactor: 1000 °C, 60 s; wire-mesh reactor: 1000 °C, 1000 K/s, 60 s.

in this laboratory[28] has shown, however, that tar *cracking* to lighter components does not alter total volatile yields. Results from the reactor described by Tyler[38] have been compared with those from a scaled-up reactor using three Australian coals[40] (atmospheric pressure; up to 900 °C). Good agreement was found between results from the two reactors (total volatiles, tar and hydrocarbon gas yields); the authors concluded that the small reactor could be used with confidence to investigate the behavior of a wide range of coals in this range of reaction conditions.

It may be noted that the wire-mesh reactor data shown in Figure 6 are from shorter (10 s) holding time experiments (1000 K/s to 1000 °C). We have previously shown that during experiments with peak temperatures at or above 700 °C, all recoverable tar is released during heatup,[30,41] so that the effect on pyrolysis tar yield of increasing the residence time from 10 to 60 s is negligible.

Figure 7 presents Daw Mill coal total volatile yields from the two reactors during *gasification* in CO_2 at 1000 °C. The fluidized-bed (FB) reactor data matched the data from the wire-mesh reactor at pressures up to between 10 and 20 bar. At 30 bar, conversion in the fluidized bed was found to be little changed from that at 20 bar, while the conversion in the wire-mesh (WM) reactor continued to rise. Lower conversions in the fluidized bed observed in the higher pressure range appears to be associated with more intense sample agglomeration observed to take place in this reactor and to increase with CO_2 pressure; agglomeration was much less intense during experiments at comparable helium pressures.

During the initial set of experimentation in this reactor, sample agglomeration had been observed to affect conversions at CO_2 pressures above 10 bar more severely than shown in later experiments (Figure 7), with conversions at 20 bar remaining near the 50% level. Since that stage, the extent of sample agglomeration was reduced considerably by (i) change of the sample injection probe tip to distribute sample nearly radially at the injection point, (ii) use of higher sample injection gas velocities, and (iii) use of bigger sand particles; 150−300 mm instead of 106−150 mm. The use of larger sand particles, up to 800−1000 mm, was also examined; no further improvement in terms of reduction in sample agglomeration was observed. It would appear that the 150−300 mm size range is optimum for the amount of sample and particle size used in the present experiments. Agglomeration was also found to be less intense when smaller amounts of coal were injected; less agglomeration was observed with 50 mg than with 200 mg of coal; mixing of coal with sand prior to injection was not found to reduce agglomeration significantly. The monitoring of extents of agglomeration was based on postoperation observations and total volatile yields measurements.

Table 1. Extents of Daw Mill Coal Gasification in the Fluidized-Bed Reactor (60 s) and the Wire-mesh Reactor (1000 K/s, 60 s) at 1000 °C as a Function of CO_2 Pressure

	gasification reactivities (wt %/min, daf)				
	1 bar	2 bar	10 bar	20 bar	30 bar
fluidized-bed reactor		18.7	36.8	40.7	45.5
wire-mesh reactor	15.3		36.4	41.2	53.6

It may be noted that smaller differences were observed during pyrolysis experiments compared to gasification runs, between results from the FB and the WM reactor. Chars from the pyrolysis experiments were clearly less agglomerated than those from gasification experiments. In parallel with this observation, comparison by SEM of pyrolysis (He) and gasification (CO_2) chars (from Daw Mill coal) prepared in the *wire-mesh* reactor have clearly shown greater fluidity in the presence of the CO_2. The effect of sample agglomeration on conversions in CO_2 appears to be related to the greater dependence of extents of gasification on exposure of reactive surfaces; in pyrolysis, heat transfer and volatile release (but not tar release) are less critically dependent on changes in morphology.

Extents of Gasification and Char Combustion Reactivities. Gasification reactivities of Daw Mill chars prepared in the two reactors are presented in Table 1. These reactivities have been calculated in terms of the difference in mass loss between gasification and pyrolysis (carried out under identical conditions) per unit time. Table 1 shows good agreement between reactivities in the two reactors at up to 20 bar. At 30 bar, char reactivities diverged significantly, reflecting the lower CO_2 conversion in the FB reactor (Figure 7), apparently due to greater extents of agglomeration. Overall, the gasification reactivities were found to increase with pressure, when the effect of agglomeration could be minimized: below 20 bar in the fluidized bed and over the whole pressure range in the wire-mesh reactor.

Figure 8 presents isothermal combustion reactivities of *pyrolysis* chars recovered from the fluidized-bed and wire-mesh reactor. The pyrolysis chars from both reactors showed a drop in reactivity between 1 and 10 bar with little change thereafter. The fluidized-bed reactor chars appeared to be somewhat more reactive than wire-mesh chars except at 10 bar but the differences were within experimental repeatability. Combustion reactivities of chars from the CO_2-gasification experiments (Figure 9) spanned a narrower range, from 0.8 to 1.2 wt %/min (daf), indicating little sensitivity to pressure. At all pressures, reactivities of chars from the fluidized-bed reactor were marginally higher than chars

(39) Tyler, R. J. *Fuel* **1980**, *59*, 218.
(40) Edwards, J. H.; Smith, I. W.; Tyler, R. J. *Fuel* **1980**, *59*, 681.
(41) Li, C.-Z.; Bartle, K. D.; Kandiyoti, R. *Fuel* **1993**, *72*, 3.

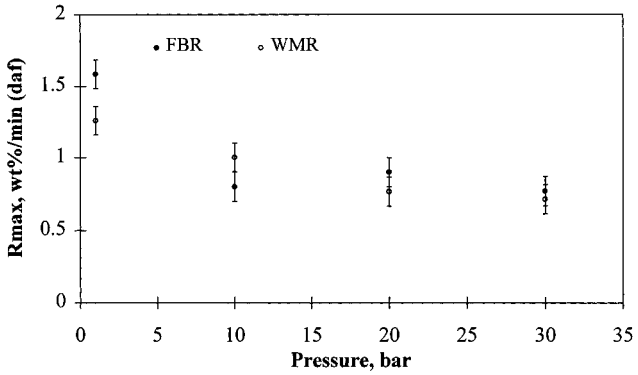

Figure 8. Combustion reactivities of Daw Mill pyrolysis chars as a function of pressure: fluidized-bed reactor: 1000 °C, 60 s; wire-mesh reactor: 1000 °C, 1000 K/s, 60 s.

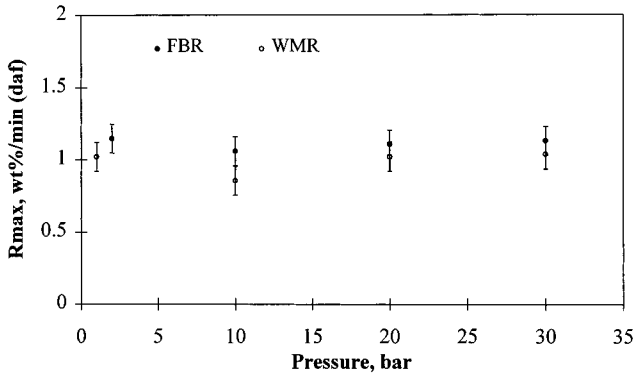

Figure 9. Combustion reactivities of Daw Mill gasification chars as a function of pressure: fluidized-bed reactor: 1000 °C, 60 s; wire-mesh reactor: 1000 °C, 1000 K/s, 60 s.

from the wire-mesh reactor, but again the differences were within experimental repeatability.

These results show that after 60 s, the residual char has been reduced to a relatively inactive state. As the residence time in CO_2 at high temperature is increased, a depletion of active sites on the char surface would be expected. However, the small differences in reactivity observed between pyrolysis and CO_2-gasification chars strongly suggest the low reactivities to be due to effects related to thermal annealing. In earlier work,[32] chars from experiments in the wire-mesh reactor with 10 s residence time showed more marked variation of reactivity with pressure.

Summary and Conclusions

A bench-scale high-pressure fluidized-bed reactor was constructed and commissioned for pyrolysis, gasification, and combustion experiments at temperatures up to 1000 °C and pressures up to 40 bar. The apparatus provides a rapid and inexpensive yet accurate technique for the characterization and screening of solid fuels—coals and biomass/waste feedstocks.

The reactor is relatively simple to construct and capable of operation by a single researcher. The reactor body (Incoloy Alloy 800HT; 34 mm i.d., 504 mm long) serves as the resistance heater and is designed to withstand the reaction pressure, obviating use of a cold pressure casing. The reactor is lined with a loosely fitting quartz tube to limit corrosion and catalytic effects. Sample (up to 2000 mg) is held between two air-actuated valves and injected batchwise (single slug) through a water-cooled probe. The system allows tar and char yield determinations and gas analysis; fuels can be tested for their gasification/combustion performance in commercial plants. In addition to greater ease of steam injection, the reactor has the advantage of operating with larger sample sizes than the wire-mesh reactor, providing larger samples of byproduct chars and tars for subsequent physical and chemical characterization.

The present report has focused on equipment design and preliminary data from pyrolysis and gasification experiments with Daw Mill coal (UK) at up to 1000 °C and 30 bar. Extents of gasification were calculated by subtraction of total volatile yields in CO_2 from mass loss during pyrolysis in helium, performed under otherwise identical conditions. Combustion reactivities of chars were determined in an atmospheric pressure TGA instrument. A number of design adjustments have been described, enabling total volatile yields from the FB reactor to match those from a high-pressure wire-mesh reactor. As expected, however, *tar* yields from the fluidized-bed reactor were significantly lower than those from the wire-mesh instrument, due to longer residence times of volatiles in the bed of solids and the reactor bed and freeboard.

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