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Development of a Bench-Scale High-Pressure Fluidized Bed Reactor and Its Sequential Modification for Studying Diverse Aspects of Pyrolysis and Gasification of Coal and Biomass

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This paper reviews the design, operation, and sequential modifications of a bench-scale high-pressure fluidized bed reactor system, capable of diverse pyrolysis and gasification applications, all based on the same hardware platform. The reactor is small: 34 mm i.d. and 504 mm high. The mechanical design is relatively simple and inexpensive, featuring direct electrical heating to avoid the use of a separate furnace. The reactor body is made of a high-strength alloy, with 1000 h creep resistance at maximum design conditions (1000 °C and 3.0 MPa). The design thus obviates the use of a "cold" pressure casing. The system can be operated by a single person and has demonstrated ability to generate fuel reactivity and product distribution data rapidly and cheaply, using a wide range of solid fuels. In batch operation, conversions achieved during coal pyrolysis and gasification experiments were comparable with results from a high-pressure wire-mesh reactor, indicating nearly single-particle behavior. The system has been modified for continuous feeding ($\sim$3 g min^{-1}), to study the effect of reaction conditions on the fate of fuel-N, during the gasification of coal and sewage sludge (to 3.0 MPa). The work showed that steam plays a primary role in the formation of NH_3 from both volatile-N and char-N. HCN concentrations were found to depend strongly on the residence time at temperature and on the extent of contact with heated bed solids. A quartz lining allowed the determination of extents of trace element emissions during gasification. Above 900 °C, enhanced depletion of Ba, Pb, and Zn in bed solids was accompanied by enrichment of fines, collected in a downstream filter. The system was subsequently modified to enable a slug of coal to be injected and bed solids discharged (1–3.0 MPa) from the fluidized bed under controlled conditions and precise solid residence times in the bed. The reactivities of the chars were measured as a function of "residence time at temperature" and were observed to decrease with increasing temperature, time, pressure, and particle size. At 1000 °C, coal char reactivities were found to diminish by nearly a factor of 4 within 10 s. The study confirmed and extended prior work carried out in a high-pressure wire-mesh reactor. The system was subsequently configured for pyrolyzing waste plastic material at low temperatures. Altering the electrode positions enabled changing the position of the heated zone, enabling trouble-free injection of polymer samples at temperatures up to 600 °C. The aim of these experiments was to investigate the potential to produce liquid fuel precursors from pure and mixed waste plastics. In its latest incarnation the system has been further modified for performing oxy-fuel gasification experiments.

Introduction

There has been interest in the use of fluidized bed technology to gasify solid fuels for many decades. The Winkler gasifier was developed in the 1920s to gasify lignite at atmospheric pressure and was one of the first processes to use fluidized bed technology.[1] Other air-blown fluidized bed gasifiers have been developed since the 1970s to gasify coal and other fuels for power generation at elevated pressures. Several low–medium temperature gasification technologies have been developed and moved toward the commercial scale. These include the KRW gasifier (USA)[2] and the air-blown gasification cycle (ABGC) (UK).[3] These developments were intended as more efficient and cleaner power generation technologies, particularly due to their

ability to suppress sulfur and trace element emissions. However, they have not yet progressed beyond the demonstration scale. The ash agglomerating fluidized bed coal gasification process has been under research and development by Institute of Coal Chemistry, CAS in China. By the end of 1989, a pilot plant (24 tons coal/day) was set up and put into operation. Tests with air/steam, enriched air/steam, oxygen/steam blown modes were carried out. A wide variety of feedstocks, including lignite, bituminous coal, sub-bituminous coal, anthracite, and petroleum coke were successfully gasified. An industrial demonstration gasifier with 100 tons coal per day was constructed in Chenggu Fertilizer Plant, Shaanxi, in 2001. This gasifier has been successfully run with a long continuous operating time.[4]

Within the context of selecting and developing new technologies, bench-scale reactors have been widely used for rapid and inexpensive determinations of fuel reactivities and product distributions, under conditions simulating those in pilot and

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(1) Elliot, M. A. *Chemistry of Coal Utilisation*; John Wiley and Sons: New York, *2nd Supplementary Volume*, 1981.

(2) US Dept of Energy, Pinon Pine Power Project, Clean Coal Topical Report No. 8, December 1996.

(3) Dawes, S. G.; Mordecai, M.; Brown, D.; Burnard, G. K. The Air Blown Gasification Cycle. *Proceedings of the 13th International Conference on Fluidized Bed Combustion*, Orlando, FL, May 1995.

(4) Fang, Y. T.; Huang, J. J.; Chen, H. S.; Chen, Z. H.; Wang, Y. The Research and Development of Pressurized Ash Agglomerating Fluidized Bed Coal Gasification. Presented at the 6th World Congress of Chemical Engineering, Melbourne, 2001.

commercial-scale plants. A number of bench-scale reactors with different configurations have already been developed at Imperial College London for evaluating aspects of fuel behavior including reactivities and volatile and tar release with char recovery for subsequent characterization. These include atmospheric pressure and high-pressure wire-mesh reactors with tar trapping capabilities, and steam injection facilities; the surprisingly diverse applications of wire-mesh reactors have been recently reviewed.[5] A two-stage fixed-bed "hot-rod" reactor has also been used for coal/biomass pyrolysis/gasification followed by hydrocracking of released volatiles.[6,7] The effect of residence time on tar cracking reactions has been investigated in a variable freeboard-height atmospheric pressure fluidized-bed reactor.[8] Product distributions from differently configured reactors have been compared by using common coal samples at atmospheric pressure, during pyrolysis and hydropyrolysis, as well as under CO_2 and steam-gasification conditions. The capabilities, construction, and product distributions from several distinct types of bench-scale thermochemical reactors have been collected in a recent book.[9]

The present report reviews the design, operation, and successive reconfigurations of a bench-scale high-pressure fluidized-bed reactor, developed at Imperial College London. The reactor is small: 34 mm i.d. and 500 mm high. The system was intended for studying different aspects of the pyrolysis and gasification of solid fuels in fluidized beds. It was initially built as a batch system capable of operating up to 30 bar and 1000 °C, with "single-slug" injection of sample particles. Conversions achieved during coal pyrolysis and gasification experiments were found to be comparable with results from a high-pressure wire-mesh reactor, indicating nearly single-particle behavior. The system was found capable of generating pyrolysis and gasification reactivity data rapidly and cheaply. It is relatively simple to construct and capable of operation by a single researcher. The design uses direct electrical heating of the reactor body to avoid the use of a separate furnace. The construction of the reactor body out of a high-strength alloy, resistant to creep over the maximum experimental conditions for over 1000 h, serves to avoid the use of a "cold" pressure casing. These features make the system far less bulky and cheaper to construct compared to many high-pressure fluidized-bed systems.

After the batch-reactor phase, the equipment was modified to incorporate a spouted base and a continuous fuel feed (∼3 g min⁻¹), to enable studies in support of the ABGC (British Coal) gasifier. One of the studies focused on the effect of gasification conditions on the fate of fuel-N, during coal and sewage sludge gasification (to 3.0 MPa),[10] involving an investigation of NH_3 and HCN formation and destruction reactions. The quartz lining of the reactor allowed the reliable determination of extents of trace element emissions during gasification.[11] In another study, with the same configuration of the reactor, at near atmospheric pressure, the gasification of sewage sludge (reactivity, N release, and trace element partitioning) has been studied to assess the

performance of sewage sludge under conditions that represented those in a combined heat and power plant.

The reactor was subsequently modified to enable a slug of coal to be injected and discharged from the fluidized bed under controlled conditions and precisely controlled residence times. The work aimed to determine changes in the reactivity of the char as a function of residence time at temperature in fluidized bed gasifiers, as a function of particle size, pressure, and composition of ambient atmosphere.[12,13]

Following a relatively minor reconfiguration, the reactor was also used to investigate the potential for producing liquid fuel precursors from the pyrolysis of pure and mixed waste plastics. Altering the electrode positions enabled trouble-free injection of polymer samples at temperatures up to 600 °C. The equipment is currently undergoing yet another reconfiguration to enable gasification to be studied in CO_2-O_2 mixtures, as part of an EU funded project.

A brief review of comparable bench-scale reactors would help place the present design in a more general framework.

Comparable Laboratory-Scale Fluidized Bed Designs in Outline. Several, somewhat larger, *bench-scale* high-pressure fluidized bed pyrolysis/gasification reactor systems have been reported in the literature. While this short survey does not claim to be exhaustive, we have attempted to cover most relatively small scale *high-pressure* systems used and reported in the literature during the last two decades or so.

Morris and Keairns[14] 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 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.[15] 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 μm) 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, 2.5 MPa) 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 2.5 MPa) equipped with online gas analysis instrumentation has been described by Hüttinger and co-workers.[16–18] The

(5) Gao, L.; Wu, L.; Paterson, N.; Dugwell, D. R.; Kandiyoti, R. *Int. J. Oil, Gas Coal Technol.* **2008**, *1*, 152–179.

(6) Pindoria, R. V.; Lim, J.-Y.; Hawkes, J. E.; Lazaro, M.-J.; Herod, A. A.; Kandiyoti, R. *Fuel* **1997**, *76*, 1013–1024.

(7) Pindoria, R. V.; Megaritis, A.; Herod, A. A.; Kandiyoti, R. *Fuel* **1998**, *77*, 1715–1726.

(8) Stiles, H. N.; Kandiyoti, R. *Fuel* **1989**, *68*, 275–282.

(9) Kandiyoti, R.; Herod, A. A.; Bartle, K. D. *Solid Fuels and Heavy Hydrocarbon Liquids: Thermal Characterization and Analysis*; Elsevier Science: Amsterdam, 2006; ISBN: 0-08-044486-5.

(10) Paterson, N.; Zhuo, Y.; Dugwell, D.; Kandiyoti, R. *Energy Fuels* **2005**, *19*, 1016–1022.

(11) Reed, G. P.; Paterson, N.; Zhuo, Y.; Dugwell, D. R.; Kandiyoti, R. *Energy Fuels* **2005**, *19*, 298–304.

(12) Cousins, A.; Paterson, N.; Dugwell, D. R.; Kandiyoti, R. *Energy Fuels* **2006**, *20*, 699–704.

(13) Cousins, A.; Paterson, N.; Dugwell, D. R.; Kandiyoti, R. *Energy Fuels* **2006**, *20*, 2489–2497.

(14) Morris, J. P.; Keairns, D. L. *Fuel* **1979**, *58*, 465.

(15) Adánez, J.; Miranda, J. L.; Gavila'n, J. M. *Fuel* **1985**, *64*, 801.

(16) Hüttinger, K. J. *NATO ASI Series, Series C. Math. Phys. Sci.* **1988**, *244*, 433.

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 deep). 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.[19,20] The reactor tube (Incolloy; 100 mm i.d., 1000 mm long) was contained within a refractory lined pressure shell (0.3 m diameter). The reactor was heated electrically and the coal (1− 3 mm) continuously fed (2−5 kg/ h) by a star wheel feeder. The maximum operating pressure was 1.4 MPa. 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 recent applications have involved the pyrolysis and gasification mainly of various types of biomass and lignites, occasionally also processing coals. All of these systems appear to have used larger equipment with attendant larger operating costs and larger operating teams called upon to run these systems. Ashman and co-workers at the University of Sydney have reported the gasification of Victorian lignite has in a laboratory-scale fluidized bed gasifier.[21] Their reactor is 200 mm (i.d) and operates at atmospheric pressure. The Institute of Chemical Process Fundamentals in Prague has recently completed a project on the "Gasification of biomass/coal in a fluidised bed" and has reported on the gasification of coal and polyethyleneteraphthalate in a fluidized bed reactor.[22] Their reactor is 1300 mm tall and 94 mm (i.d) and operates at atmospheric pressure and temperatures less than 1000 °C. ECN in The Netherlands also operates a laboratory-scale fluid bed gasifier and this is 6 m tall and 74 mm (i.d), expanding to 108 mm in the freeboard. It has been used for ash agglomeration and other studies with biomass/wastes.[23] At the Iowa State University, "Combustion and Gasification Laboratory" a 7 kW (approximately equal to a feed rate of 12 g min^{-1}) bubbling fluidized bed gasifier has been used for studying conversion of biomass into energy, fuels, and commodity chemicals.[24] In Japan, Noda and co-workers have worked on the gasification

characteristics of biomass cracking with catalyst derived from clay minerals. A "laboratory scale" fluidized bed gasifier (43 mm id, 250 mm tall), operating at 650 °C and atmospheric pressure was used for the catalytic gasification of cellulose by steam.[25]

More recently, collaboration between Imperial College London and Taiyuan University of Technology (Shanxi Province, China) has led to the construction and operation of a system with similar design and the same dimensions. One application at TUT has involved the characterization of tar from sawdust gasified in the pressurized fluidized bed.[26]

This paper reviews the basic design and successive reconfigurations of the bench-scale fluidized-bed reactor, used for performing several distinct types of pyrolysis and gasification experiments, and using a range of solid fuels.

Experimental Section

Bench-Scale High-Pressure Fluidized Bed Reactor: the Batch Reactor Configuration. The reactor has a direct electrically heated Incolloy 800 HT body. The initial batch configuration of the reactor featured a flat distributor plate supporting a fluidized bed.[27] Up to 2000 mg of sample, held between two air-actuated valves was injected ("single slug") through a water-cooled probe. The design allows the determination of tar/oil and char yields with a repeatability of ±2%. Apart from gas analysis, total tar and solids capture and characterization could be done routinely.

Figure 1 presents a schematic diagram of the bench-scale high-pressure fluidized-bed reactor system.

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) at 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; max. pressure 40.0 MPa). The steam generator (8) consists of an electrically heated 25 mm 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) (Incolloy Alloy 800HT: 34 mm i.d., 504 mm long), which serves as the resistance heater and is designed to withstand the reaction pressure (4.0 MPa max 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. Incolloy 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[28] Its chemical composition is given as Ni 30−35%; Cr 19−23%; Fe 39.5% min; C 0.06−0.10% max; Mn 1.5% max, S 0.015% max; Si 1% max; Cu 0.75% max; Al 0.15−0.60%, Ti

(17) Azuma, T.; Hegermann, R.; Hüttinger, K. J. *Erdöl Kohle Erdgas Petrochem.* **1991**, *44* (7/8), 301.

(18) Hüttinger, K. J.; Nattemann, C. *Fuel* **1994**, *73* (10), 1682.

(19) Sue-A-Quan, T. A.; Cheng, G.; Watkinson, A. P. *Fuel* **1995**, *74* (2), 159.

(20) Sue-A-Quan, T. A.; Watkinson, A. P.; Gaikwad, R. P.; Lim, C. J.; Ferris, B. R. *Fuel Process. Technol.* **1991**, *27*, 67.

(21) Ashman, P. J.; Kosminski, A.; Button, S. J.; Mullinger, P. J. Gasification of Victorian lignite in a laboratory scale fluidised bed gasifier. *Proceedings of the 5th Asia Pacific Conference on Combustion ASPACC 05*, Adelaide, Australia, July 2005; pp 113−116.

(22) Pohorely, M.; Voseckey, M.; Hejdova, P.; Puncichar, M.; Skobilia, S.; Staf, M.; Vosta, J.; Koutsky, B.; Svodoba, K. *Fuel* **2006**, *85* (17−18), 2458−2468.

(23) http://www.ecn.nl/en/bkm/products-services/experimental-facilities/
wob/.Also: Van der Drift, A.; Olsen, A. Conversion of Biomass Prediction and Solution Methods for Ash Agglomeration and Related Problems; ECN-C-99-090, contract JOR3-95-0079.

(24) http://www.me.iastate.edu/research/combustion-and -gasification-laboratory.

(25) Noda, R.; Itoh, T.; Kurita, M.; Tanaka, N.; Horio, M. Paper on *Gasification-the clean choice for carbon management*, 8−10 April 2002, Noordwijk, The Netherlands.

(26) YuHong, Q.; HaiFeng, H.; ZhiBin, W.; Jie, F.; Wenying, L.; KeChang, X. *Biomass Bioenergy* **2007**, *31*, 243–249.

(27) Megaritis, A.; Zhuo, Y.; Messenbock, Rv.; Dugwell, D. R.; Kandiyoti, R. *Energy Fuels* **1998**, *12*, 144.

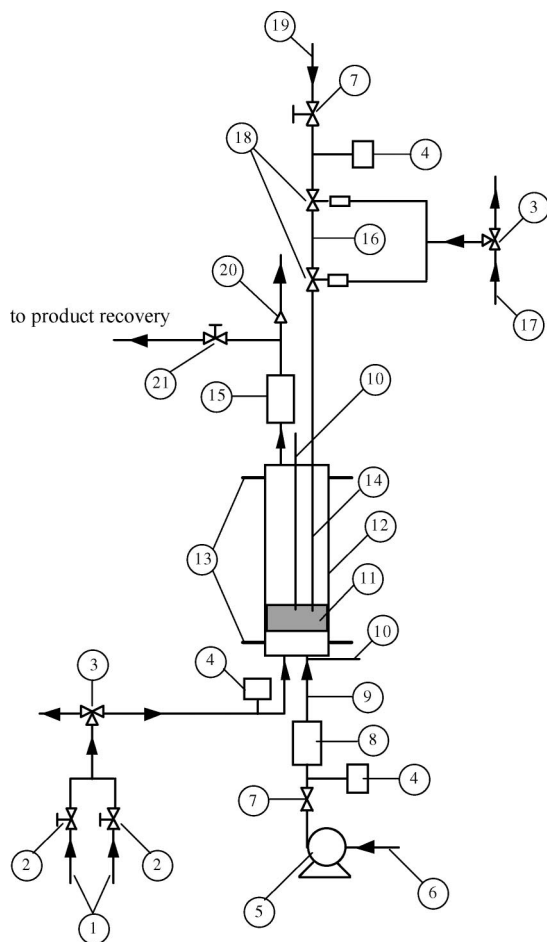(28) Inco Alloys International Co., Incolloy Alloys 800 and 800HT, 1986.

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) injection probe gas flow control 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. Reprinted from ref 27. Copyright 1998 American Chemical Society.

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[29] and the High Pressure Safety Code[30] have shown that the present reactor tube (34 mm i.d.; 48.3 mm o.d.; 504 mm long) can be 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 cost. 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 (stainless steel, AISI 316) have been 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 8 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.[29]

All connections to the reactor are made through the top and bottom flanges. Gas and steam inlet lines are connected by two

(29) BS 5500, British Standards Institution, 1992.
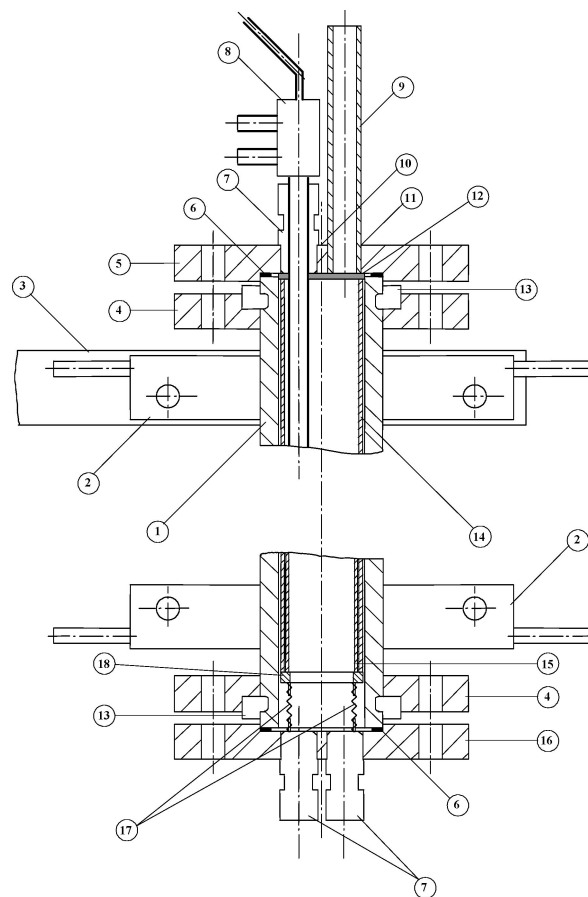(30) High Pressure Safety Code, High Pressure Technology Association, 1977.

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. Reprinted from ref 27. Copyright 1998 American Chemical Society.

male welded connectors (7). The water-cooled coal injection probe (8) and the stem of the thermocouple sheath are sealed onto bored-through male connectors, welded to the top flange. The main gas exit line (9) (12.5 mm 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 a loosely fitting quartz tube liner (14) mounted with a ~3 mm thick quartz sintered disk (pore size 40−90 μm) serving as the support/gas-distributor plate. The presence of the liner avoids any catalytic effects caused by the metal reactor wall and also protects it from any corrosion/erosion effects. 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 of the quartz tube and sintered disk. 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).

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 cm²; 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 has been 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.[31]

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 (8; Figure 2). 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; Figure 1) situated upstream of the two air-actuated valves and the pressure is measured by a pressure transducer (4). The coal injection probe (8; Figure 2, not shown in detail) consists of three concentric AISI 316 tubes silver-soldered into a hollow brass block. The coal is injected into the reactor through the inner tube (i.d. 3 mm). Cooling water flows downward between the inner and the middle tube, 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 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 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 (cf. original publication for details).

Tar Traps. The tar trap assembly consists of a 12.5 mm diameter tube packed with wire mesh 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 inverted Soxhlet thimble situated inside an AISI 316 filter housing, which is sealed with a copper ring (cf. original publication for details). The thimble is also cooled with liquid nitrogen and is intended to collect any particles or tar carried over from the wire-mesh packed tube.

Bench-Scale High-Pressure Fluidized Bed Reactor: Continuous Injection and Operation As Spouted Bed. The spouted reactor base design enables coal to be fed continuously at high velocity through a spout jet sited at the apex of an inverted cone shaped base.[32] The design mimics the hydrodynamic behavior in the pilot scale ABGC gasifier operated by British Coal. The flow scheme for this version of the equipment is shown in Figure 3.

A 28 mm (i.d.) quartz liner has been fitted within the pressure tube and this has been modified to give the inverted conical section at its lower end, with a hole at the apex. The angle of the cone is similar to that of the base in the pilot scale ABGC gasifier. The spout jet, which feeds the coal and spout gas into the bed, fits into the hole at the base of the cone. The head flange of the reactor contains the gas exit tube, which conveys the gas through a cooled section equipped with tar, steam, and particulate filters. A needle valve is used to control the reactor pressure.

The continuous fuel feed system consists of twin feed hoppers (capacity 60 g coal each) with isolating valves, which feed into a common hopper. From the common hopper, the fuel is fed through a calibrated metering valve, which is driven by a variable speed dc motor. The metered fuel falls into an ejector, through which the spout gas mixture is passed at high velocity. This entrains the fuel and conveys it through a 1.5 m long, 2 mm (i.d) pipe to the spout jet. The jet itself is 6 mm (i.d.). The coal feed rate was set up before each test using the calibrated rotary valve. The actual rate of feeding was determined from the initial and final hopper weights. Typically, the average fuel feed rate was 2.5 g min⁻¹. A hydrogen analyzer was incorporated into the exit gas analysis sample train, and the variation of this component gives an indication of the stability of

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

(32) Zhuo, Y.; Paterson, N.; Dugwell, D. R.; Kandiyoti, R. *Energy Fuels* **2002**, *12*, 127–135.
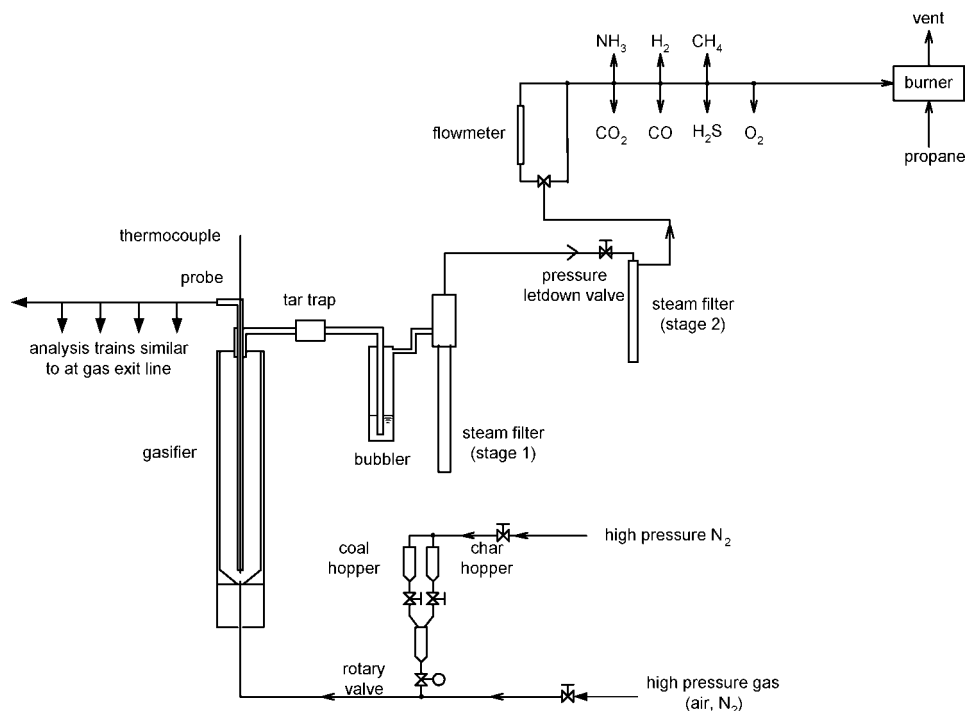
Figure 3. Schematic diagram of spouted bed reactor system.

the fuel feed. Data suggests that the fuel feed rate may have fluctuated by approximately ±10% of the average value during each test.

The batch feed system (for use with the spouted bed configuration) is comprised of a small pressure vessel, which contains the sample of fuel (less than 2 g). This is assembled on the reactor, such that the outlet valve faces downward. It is pressurized before a test to approximately 0.1 MPa above the intended test pressure and the fuel sample is fed by simply opening the air-actuated isolating valve between the vessel and the reactor. In this way it can feed batch samples into either the freeboard or the spout line.

The steam generator consists of an electrically heated pipe, packed with ceramic beads, and a water metering pump. The temperature of the steam at the outlet of the generator is determined by the operating pressure. It is set to be 20 °C above the boiling point of water under the test pressure. The flow rate of water for the steam generator was set using a calibrated HPLC pump and is used to calculate the input flow rate of steam. It is mixed with the preheated air/N_2/coal stream just before the gasifier base flange.

Exit Gas Analysis. CO_2, CO, CH_4, H_2, and O_2 were determined in the exit gas using continuous, infrared gas analyzers, a thermal conductivity analyzer, and a paramagnetic analyzer. During tests with air/N_2 mixtures, the NH_3 was sampled from a side stream of gas before the pressure control valve by bubbling a measured volume of gas through a series of bubblers, containing deionized water. The collected NH_3 was determined by ion chromatography or using an ion-selective electrode. During tests with steam injection, the concentration of NH_3 was determined from the concentration measured (by ion chromatography) in the water present in the condensate traps, plus the much lower concentration present in the gas upstream of the condensate traps. The tar concentration in the exit gas could be determined from the analysis of the material condensed in the condensate traps. HCN can also be collected using a similar set of bubblers, but containing 10% NaOH solution and the solution is analyzed using a cyanide ion specific electrode.

Measurement of the Exit Gas Flow Rate and Air Input Rate. The exit gas flow rate was estimated from the reading of the calibrated rotameter and the volume flow rate of gas used by side stream sampling equipment. The air input rate was calculated from the CO_2 and CO concentrations in the fuel gas and its volumetric flow rate. This assumes that the O in the CO_2 and CO originates in the input air. The coal:air ratio was determined from the average coal feed rate and the calculated mass flow of air.

Operation of the Gasifier. *Tests with Continuous Feed.* Crushed Coalite was used as the initial bed material, as it has a low volatile matter content (approximately 9%). This avoided problems of tar evolution and condensation at low temperature, which would have caused operating difficulties if coal were present during initial start up. The feed was switched to coal after the initial bed had been heated to approximately 750 °C, which ensured the effective pyrolysis of the released volatiles. The bed temperature was controlled by adjusting the air/N_2 ratio in the fluidizing gas. Care was needed in the adjustment of the input air to avoid temperature excursions. With a significant carbon reservoir in the bed, the rate of heat release was potentially high and this could lead to rapid temperature excursions (up and down) when adjusting the inlet gas mixture composition to achieve the desired steady state conditions, particularly at high pressure. The small diameter of the reactor meant that the particle size and superficial fluidizing velocity were lower than those used at the larger scale. In the laboratory-scale reactor, the fuel particle size was in the 200−300 μm range and the fluidizing velocity was between 0.1 and 0.2 m s^{-1}, which compares with values of up to 3 mm and 0.8 m s^{-1} in the pilot-scale gasifier developed by British Coal. Typical test duration was 10−15 min. During this time, analyses were conducted on the gas in the spout and downstream of the gasifier. There was no char off-take through the base, so that bed material built up during the test. Sinter formed on the base during most tests with coal; this limited the maximum test time to less than 30 min.

Tests with a Batch Feed. Sand was used as the bed material and this was fluidized and heated to the required test temperature before injecting the batch of fuel.

Modification of Reactor to Produce Char Samples under Closely Controlled Conditions. The continuously fed gasifier required modification[33] to enable the preparation of char samples under strictly controlled conditions, so that the variation in char reactivity with conditions of formation could be measured. It was converted from the continuous mode of operation to batch feed, while retaining the glass liner with the inverted cone shaped base. The initial bed material inside the reactor was changed from char to acid-washed sand to enable char derived from the coal sample alone to be collected after each test. There was a requirement for a rapid start and end to each test, so that the char formation time was accurately known. This was achieved by installing the batch

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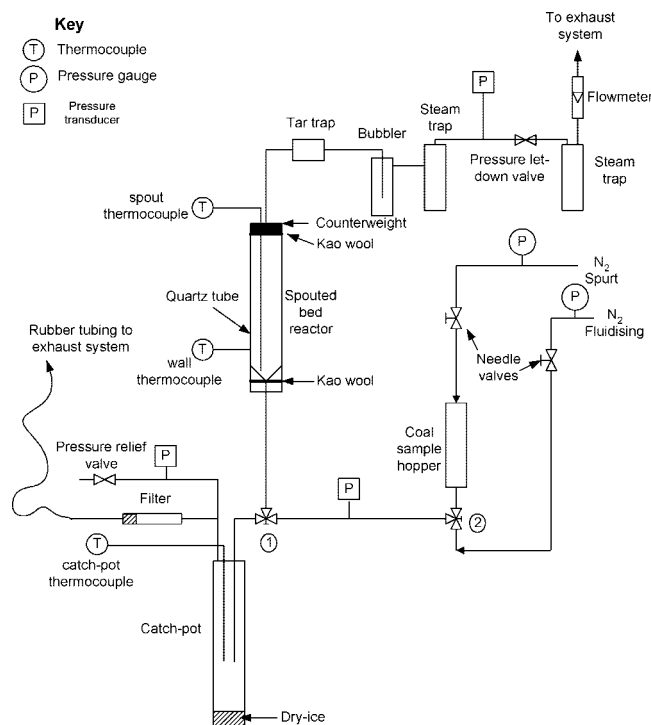(33) Cousins, A. Ph.D. Thesis, University of London, 2005.

Figure 4. Schematic diagram of the equipment to collect char samples.

Figure 5. Pyrolysis of waste plastics.

method for feeding the coal into the spout of the reactor and developing a very rapid method for draining the sand/char bed from the reactor at the end of an experiment. A flow scheme of the modified reactor setup is shown in Figure 4.

Feeding Method. A three-way valve was installed in the gas line feeding into the reactor (valve 2, Figure 4). The third valve port was connected to a pressurized coal feed capsule, which enabled the coal sample to be injected rapidly into the reactor.

Draining Method. The tests had to be terminated and the bed containing the char cooled rapidly so that the formation time was accurately defined. This was achieved by the use of another three-way valve (valve 1, Figure 4). This valve was placed directly below the reactor, with the reactor inlet pipe being connected to the common port on the valve. One arm of the valve was then connected to the gas supply, with the other connected to a cooled (using dry ice), vented catchpot, at atmospheric pressure. During a test, valve 1 was positioned so that the fluidizing gases could enter the reactor. After the desired test time, this valve was switched so that the reactor was connected to the catchpot and the pressure used to eject the bed into the catchpot very rapidly.

At the end of each test, the bed was removed and the mixture separated into char and sand using their density difference. The technique involved placing the bed into chloroform, which has a density that is intermediate between sand and char. The sand sank, whereas the char floated. The char sample was obtained by filtration through a 63 μm mesh filter.

Pyrolysis of Waste Plastics in an Atmospheric Pressure Fluidized Bed. The experimental configuration has recently been further modified to pyrolyze waste plastics with the objective of optimizing the tar yields to obtain a potential liquid fuel. The feeding system was changed to batch operation, where a maximum of 10 g of sample could be placed into a stainless steel feed hopper. Valve 2 shown in Figure 5 was closed and a 1 g sample was placed in the hopper. Any air contained in the dead space above the hopper was purged with N_2 and the hopper was sealed using eight bolts in a stainless steel cap, which compressed a rubber O-ring. The hopper was then attached to the inlet gas stream shown in Figure 5. Fluidizing of the reactor commenced using N_2 as the process gas, with an operating temperature of 450 °C and atmospheric pressure (the pressure drop across the system was 0.5 bar). The heating rate was 10 °C min^{-1}. However, in this reactor setup, the lower electrode

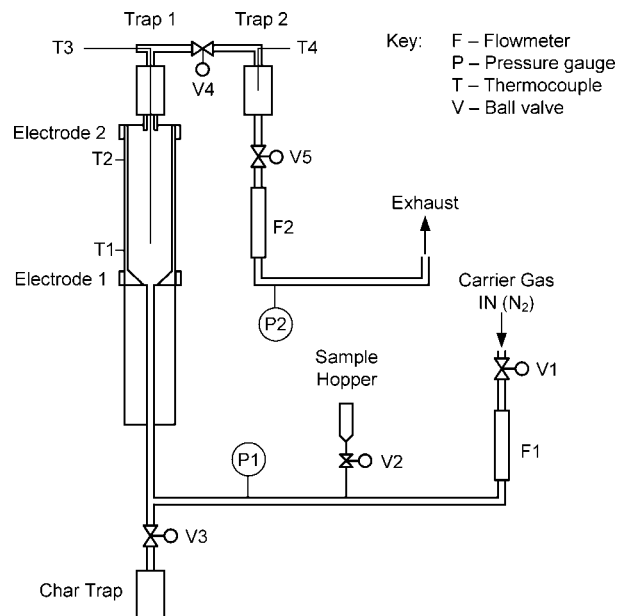was placed at the top of the spout rather than at the bottom of the main reactor body. This prevented preheating and melting before the fuel could exit the spout, into the fluidized bed. The bed material was acid-washed sand sieved in the range <200 μm and >150 μm. The sand had been heated in a muffle furnace overnight at 900 °C to ensure any impurities that could affect the reaction products and char measurements were removed. When the system was at steady state the sample was introduced by opening valve 2. The sample was removed from the hopper into the N_2 stream by a combination of gravity and the feed hopper/spout line pressure differential. The reaction products were chars, permanent tars, volatile tars, and permanent gases. To collect the tars and gases, a sequential tar-trap system was used as in Figure 5. Tar trap 1 was cooled in liquid N_2 and was attached as close to the reactor body as possible (3 cm apart). This captured *all* the reaction products. Once the experiment was finished, trap 1 was allowed to reach room temperature while trap 2 was kept under liquid N_2. Any tars volatile at room temperature, as well as permanent gases, was volatilized from trap 1 and carried through and condensed in trap 2. Trap 2 could then be isolated by closing V4 and V5, trapping the volatile products for subsequent analysis. The bed material and char were collected by draining them into the catchpot after the test had ended.

Product Quantification and Characterization. As the products of interest were the tars, it was important that the char be quantified, but not necessarily characterized. Therefore, there was an element of flexibility in how the chars were treated. First of all, the sand bed was washed with $CHCl_3$, followed by *n*-heptane to collect any tars which had condensed on the sand. The solution was filtered to separate the solids from the tar/solvent solution. The sand bed was allowed to dry in ambient conditions for weighing. The solvent was carefully evaporated for subsequent quantification of tar. It was not possible to accurately quantify char production by taking the mass of sand before and after the experiment due to elutriation of a tiny quantity of sand from the bed into the exit gas. Measurements were therefore taken by combusting the postexperiment solvent-washed sand at 900 °C in a muffle furnace overnight. The loss in mass after this combustion was the mass of char produced during the experiment (assuming that the inert content of the original plastic was negligible).

The tars collected in trap 1 were removed by dissolution of the trap contents in $CHCl_3$, followed by *n*-heptane. The two solutions underwent gentle evaporation at ambient conditions until the solvents had volatilized to leave the tar as a residue. This procedure was also followed for the sand as described above. Additionally, a quantity of sand could also be seen to have collected on the quartz liner. The quartz liner was therefore also washed in the solvents,
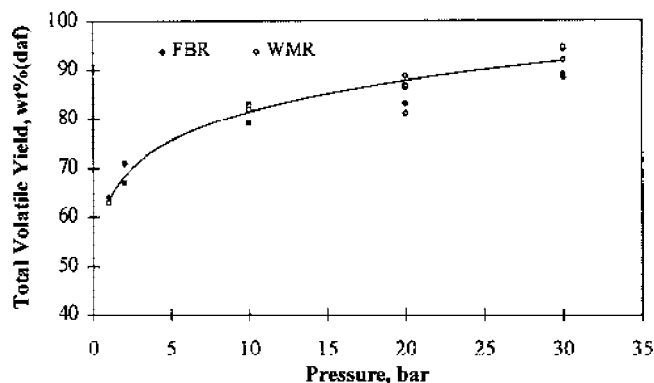
Figure 6. Total volatile yields from Daw Mill coal as a function of pressure in the fluidized bed and wire-mesh reactors.
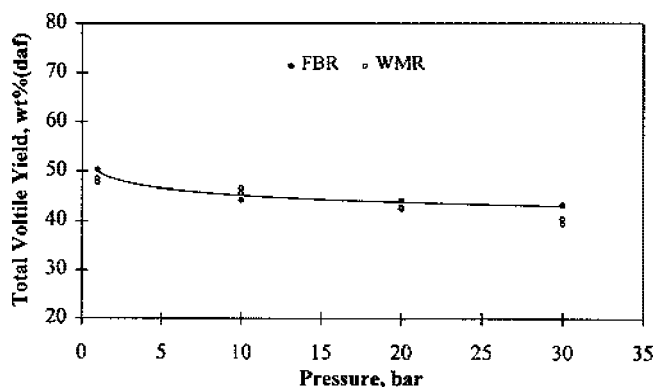

Figure 7. Pyrolysis volatile yield as a function of pressure with the fluidized bed and wire-mesh reactors.

and the total tar produced was the sum of the quantity in the trap, on the walls of the quartz liner, and condensed on the sand bed. Finally, the thimble filter placed at the top of the tar trap was also washed to check if any tars had not been caught by trap 1. Eight tar products were therefore obtained from the $CHCl_3$ and *n*-heptane washings in four reactor locations for each experiment. Where tars were detected, these were individually analyzed using a gas chromatograph and an SEC for characterization.

The volatile tars and permanent gases in trap 2 could be characterized by sampling directly from trap 2 and inserting the gas directly into a gas chromatograph. Volatiles at ambient temperature and permanent gases were quantified by difference, from the mass of tar and char produced.

Results and Discussion

Initial Studies Using the Batch Fed Reactor. When first built, the reactor was set up using the batch feeding system. Pyrolysis and gasification studies were done using Daw Mill coal at up to 1000 °C and 3 MPa.[34] Tar yields and total volatile yields were measured as a function of pressure and the results compared with those obtained in a wire-mesh reactor operated under similar conditions (temperature 1000 °C, pressure 0.1−3 MPa, heating rate 1000 °C s⁻¹, hold time 60 s). The heating rate in the fluid bed is not known with certainty, but is likely to be greater than 1000 °C s⁻¹. The WMR operates with a specific heating rate and therefore a rate of 1000 °C s⁻¹ was used in this comparison. The results are shown in Figure 6, 7, and 8.

The data in Figure 6 (tests done in CO_2) shows that the total volatile yields (i.e., conversion by pyrolysis and gasification) in both reactors were similar for comparable reaction conditions.
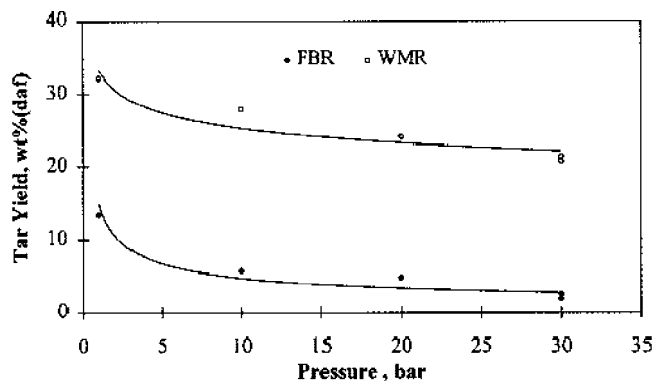
(34) Megaritis, A.; Zhuo, Y.; Messenbock, R.; Dugwell, D. R.; Kandiyoti, R. Pyrolysis and Gasification in a Bench Scale High Pressure Fluidised Bed Reactor. *Energy Fuels* **1998**, *12*, 144.

Figure 8. Pyrolysis tar yields from Daw Mill coal as a function of pressure in the fluidized bed and wire-mesh reactors.

Table 1. A Comparison of the Experimental and Calculated Conversions during Co-Gasification Tests with the Fluidized Bed[a]

temp, °C	% coal in mixture	total volatile yield, %		tar yield, %	
		calcd	exptl	calcd	exptl
850	48.4	61.8	61.4	3.4	1.9
1000	47.7	86.0	86.7	3.3	3.4

[a] Pressure 2 MPa; hold time 60 s; fluid gas 100% CO_2.

The values were calculated from the weight of char remaining in the reactor after each test. The conversion increases with increasing pressure, but the extent of increase declined at the higher end of the pressure range studied. Figure 7 shows the volatile yields in He, where the conversion is due to pyrolysis alone. Again, the results are similar to each other and show a slight decrease in conversion as the pressure was raised. This decrease is due to the suppression of volatile release from the particles by the effect of the increased external pressure and causes the deposition of secondary char within the fuel particles.

The difference between the sets of data shown in Figures 6 and 7 represents the conversion due to gasification in CO_2. The extent of reaction increased with increasing pressure, but the rate of increase declined at the higher end of the pressure range. The tar yields are shown in Figure 8. The yield from the fluid bed was much lower than from the wire-mesh reactor. This is explained by the longer time at temperature and increased contact between the evolved volatiles and bed particles in the fluid bed compared with the wire-mesh reactor. This enabled the breakdown of the primary released volatiles by thermal degradation. The batch fed reactor was also used to study the coprocessing of coal and biomass under both pyrolysis and gasification conditions.[35] Table 1 shows data obtained using Polish coal and a forest residue under gasification conditions.

The calculated data shown in the table was derived from results of tests with the individual components of the mixture and the composition of the mixture. It is the result that would be expected if there were no synergistic effects when the components were treated together. These values are very similar to actual experimental values obtained with the mixtures. This shows the absence of synergistic effects when cogasifying in the fluid bed and is consistent with the relatively poor contact between particles in the bed.

Ammonia Formation during Gasification Tests with Coal in the Spouted Bed Gasifier.[36] The equipment was modified to enable the study on ammonia formation to be done.

(35) Collot, A.-G.; Zhuo, Y.; Dugwell, D. R.; Kandiyoti, R. Copyrolysis and cogasification of coal and biomass in bench scale fixed and fluidised bed reactors. *Fuel* **1999**, *78*, 667.

(36) Zhuo, Y.; Paterson, N.; Avid, B.; Dugwell, D. R.; Kandiyoti, R. *Energy Fuels* **2002**, *16*, 742–751.

Table 2. Effect of Steam Input, Operating Temperature, and Coal/Air Ratio on NH₃ Concentrations in the Product Gas[a]

	% steam (by vol)	press. (MPa)	coal[b] feed rate) g min⁻¹	coal:air ratio (mass)	temp (°C)	dilution factor	NH₃ (adjusted for dilution by N₂) vpm,[c] av
no coal feed	0	1.25	0	−	850	6.06	49
	10.1	1.32	0	−	860	2.84	1297
	16.4	1.30	0	−	890	2.36	2294
effect of % steam	6.0	1.33	2.1	0.32	795	2.59	2820
	14.3	1.31	2.2	0.28	800	2.21	5131
effect of temp	6.0	1.33	2.1	0.32	795	2.59	2820
	6.1	1.26	2.0	0.25	837	2.20	1460
effect of coal:air	6.1	1.26	2.0	0.25	837	2.20	1460
	6.5	1.35	2.2	0.46	841	3.10	3720
	6.3	1.36	2.2	0.80	830	4.78	5290

[a] Data corrected for start-up NH₃ formed fresh Coalite bed. Gas analysis adjusted for dilution by N₂. [b] Daw Mill coal (1.3% N). [c] vpm = volume parts per million.

Table 3. Nitrogen Concentrations in Final Bed Chars

fluidizing gas (vol %)	N concn in final bed char (wt % (db))
air/N₂	0.8
air/N₂	1.0
air/N₂/steam (6%)	0.7
air/N₂/steam (14%)	0.4

It was converted to the spouted base configuration and operated with a continuous coal feed. When fluidizing mixtures of air/N₂ are used, the NH₃ concentrations in the exit gas may be understood in terms of the breakdown of volatile fuel-N compounds. Between 35% and 45% of the fuel-N was found in the recovered chars. In air/N₂, the residual char-N does not appear to be released unless N-bearing parts of the solid matrix are consumed by reaction. Table 2 shows that the addition of steam resulted in large increases in the NH₃ concentration of the exit gas, compared with operation in air/N₂. The amounts of nitrogen in the NH₃ were greater than the N content of evolving volatiles. Thus, much of the new NH₃ appears to have been formed by reaction with *char*-N. A large effect of steam to form ammonia had not been anticipated in these experiments, although the reactivity of char-N in the presence of high-pressure hydrogen had been noted during earlier hydropyrolysis experiments.[37]

The effect of steam on the char bed was examined further by varying the proportion of inlet steam during tests with a Coalite char bed, in the absence of the coal feed. Steam was varied from 0% to 10% and 16% by volume. The amount of NH₃ increased from 50 to 2300 vpm (volume parts per million) over this range, in proportion to the amount of added steam. Table 3 presents N analyses of selected residual char beds from tests where coal was used as the feed. The data show that steam caused a reduction in the N concentration of final bed chars. The overall effect of added steam on enhancing NH₃ formation and its preferential reaction with char nitrogen are clear.

The proportion of the total NH₃ formed from the volatile-N and char-N can be assessed from the results of tests with and without steam addition in Table 4.

The NH₃ content was found to increase substantially as the coal:air ratio was increased during tests in air/N₂ as well as in air/N₂/steam. Assuming that primary decomposition mechanisms remained unaltered by the presence of steam, it was calculated that the total NH₃ formed by pyrolysis (i.e., that released in the absence of steam) rose from 20 to 37%, as the coal:air ratio was raised. The amount of NH₃ formed from char-N by the action of steam also increased with the coal:air ratio, but the

Table 4. Proportions of NH₃ Formed by Pyrolysis and from Char Nitrogen

coal:air ratio (mass)	steam addition (vol %)	measd NH₃ vpm (% of total NH₃ during tests with steam)	diff in NH₃ (with steam − without steam), vpm (% of total NH₃)
0.25	6.1	1460 (100)	1173 (80)
0.24	0	287 (20)	
0.45	6.5	3720 (100)	2336 (63)
0.45	0	1384 (37)	

proportion of the total NH₃ decreased from 80 to 63%. These data indicate that, during tests with steam in the air-blown gasifier, the majority of the NH₃ is produced from char-N. The effect of temperature on NH₃ production was studied between 850 and 980 °C, in the presence of S sorbent, at a nominal pressure of 1.3 MPa and a coal:air ratio of 0.3. Figure 9 shows the NH₃ concentration measured at the exit of the bench-scale fluidized bed, as a function of temperature. The NH₃ concentration peaked at approximately 880 °C, indicating the temperature where NH₃ formation and destruction reactions were evenly balanced. NH₃ destruction is likely to result from decomposition to N₂ and H₂, as the composition tends toward low gas phase equilibrium values.

Gasification of Sewage Sludge.[38] In an EU funded project, the spouted bed gasifier was used to study the formation of NH₃ and HCN during the gasification of sewage sludge. The work was done under conditions that simulated those in a gasifier operating as part of a combined heat and power plant, at near-atmospheric pressure. The configuration of the equipment was the same as that used in the previous study. However, in this work there was no initial bed as one of the objectives was to measure the partitioning of trace elements and the presence of an initial bed material would have complicated the analysis and evaluation of the data. A shallow char bed therefore built up in the reactor during these tests. Dried pellets of sewage sludge were gasified in air/N₂ and air/steam/N₂ mixtures to identify the effects of temperature and steam on HCN and NH₃ concentrations and on the partitioning of trace elements.

Higher concentrations of NH₃ (and HCN) were observed when steam was present (i.e., consistent with the work with coal, described above). The mechanism of the effect is not obvious, but gives rise to increasing concentrations of potential NOₓ precursors. The concentration of HCN showed a somewhat different pattern to that of NH₃ formation. As mentioned earlier,

(37) Wu, F.; Guell, A. J.; Li, C-Z.; Madrali, E. S.; Cai, H.-Y.; Dugwell, D. R.; Kandiyoti, R. *Proc. ICCS, Banff*, 1993; p 307.

(38) Paterson, N.; Zhuo, Y.; Reed, G. P.; Dugwell, D. R.; Kandiyoti, R. Presented at the *7th European Biosolids, Organic Residuals Conference, and Exhibition*, Wakefield, England, Nov 18−20, 2002; Vol. 2; ISBN 1-903958-06-7; Session 10, Paper 071.
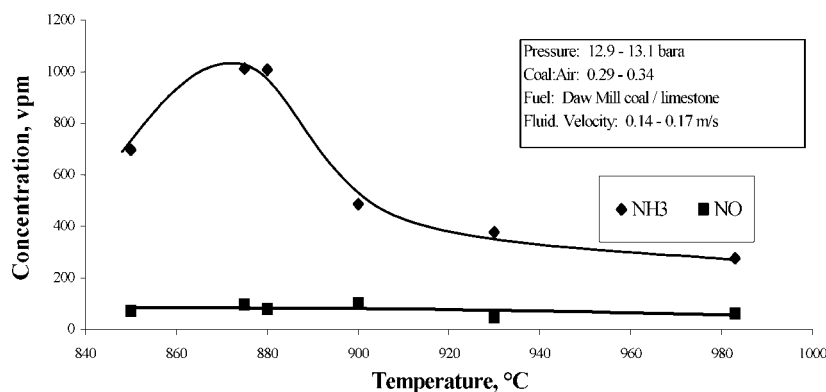
Figure 9. NH$_3$ Concentration in the exit gas as a function of the temperature.

Table 5. Concentration of HCN in the Fuel Gas during Tests with Sewage Sludge

temp (°C)	% added steam	feed rate (g min^{-1})	press. (MPa)	HCN concentration (vpm)		
				sample 1	sample 2	av
820	0	2.6	0.32	2900	1100	2000
890	0	2.4	0.36	3700	2100	3000
930	0	2.4	0.39	4200	3100	3600
770	36	1.9	0.26	5870	−	5870
850	44	2.0	0.19	7830	−	7830
930	39	1.8	0.25	6390	−	6390
940	47	2.1	0.25	9480	−	9480
970	31	1.6	0.23	2740	−	2740
970	35	1.6	0.24	3390	−	3390

the bench-scale fluidized bed reactor has no char discharge facility. Instead, the char bed builds up during a test. With sewage sludge, measured HCN concentrations were observed to decrease as the experiment progressed and depths of char increased. The growing height of bed appears to have provided an effective environment for the reaction of HCN to form NH$_3$. This result was consistent with data obtained in the pilot-scale spouted-bed gasifier, where only low concentrations of HCN were measured in the exit fuel gas, after longer residence times in the char bed, compared to the laboratory-scale reactor. In our bench-scale experiments, the concentration of HCN was observed go through a maximum at around 930 °C and to decrease rapidly thereafter (Table 5). The increase of HCN with temperature indicates the intensity of tar cracking reactions taking place in contact with bed solids. The data shows that, above about 930 °C, its destruction by secondary reactions becomes increasingly rapid. NH$_3$ formation reactions would also be promoted by the increasing amounts of H$_2$ liberated through the cracking of the sewage sludge volatiles.

The results from sewage sludge gasification indicate that more complete tar cracking leads to progressively greater proportions of H$_2$ in the product gas (Figure 10).

In this hydrogen-rich environment, very high (superequilibrium) NH$_3$ concentrations were reached at low temperatures (above 9000 vpm at about 780 °C), in the presence of steam. From these high values, NH$_3$ concentrations in the exit gas decreased with increasing temperature (Table 6), both in the presence and absence of steam in the spout gas. This appears to result from the faster approach to equilibrium with rising temperature, effectively decomposing NH$_3$ to N$_2$ and H$_2$. The effect was sufficiently important to have masked the increase in NH$_3$ formation from HCN at higher temperatures.

The concentration of HCN formed from coal was also measured using the bench-scale reactor, using air/N$_2$ mixtures. These tests required an initial char bed in the reactor (for operational reasons), and consequently, the effect of residence time in the char bed on HCN concentration could not be
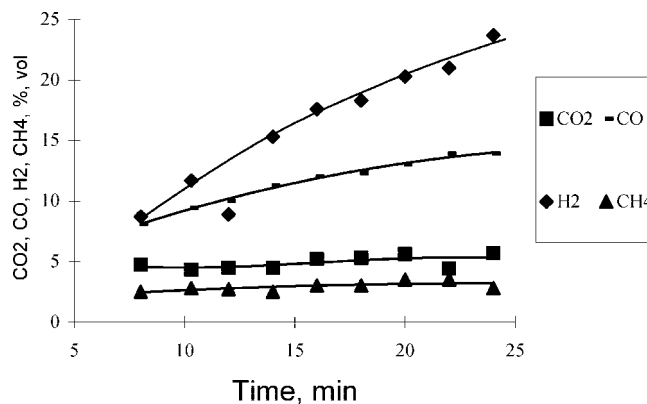

Figure 10. Gas composition (950 °C).

Table 6. Concentration of NH$_3$ in the Fuel Gas during Tests with Sewage Sludge in Air/Steam/N$_2$ Mixtures

temp (°C)	press. (MPa)	feed rate (g min^{-1})	NH$_3$ (ppm, by vol)
770	0.26	1.9	9680
850	0.19	2.0	8120
930	0.25	1.8	4380
940	0.25	2.1	6600
970	0.23	1.6	3490
970	0.24	1.6	5160
980	0.21	0.9	3900

monitored. The concentration of HCN in the exit gas was observed to decrease at temperatures above 900 °C. This is thought to be a result of the increased H$_2$ concentration released by pyrolysis, which would enhance the rate of decay of HCN to NH$_3$.

Trace Elements in Output Solid Streams during Sewage Sludge Gasification.[39] Gasification and pyrolysis processes have attracted considerable interest from water utilities as technologies for sewage sludge disposal. However, elements such as Ba, Cu, Hg, Pb, and Zn are present in sewage sludges at levels significant to the disposal of the residual solid streams from the gasifier. Measurements of trace element concentrations by ICP-AES have been used to determine (i) the retention of selected elements in the solid streams, (ii) their relative depletion from the coarser bed residue, and (iii) any enrichment in the fines carried to the gas cleaning system. The effect of gasifier bed temperature and type of sewage sludge was investigated. The depletion of trace elements from the bed char relative to the feed is a useful indicator of the volatility of individual elements; these may

(39) Reed, G. P.; Zhuo, Y.; Paterson, N.; Dugwell, D. R.; Kandiyoti, R. Presented at the *7th European Biosolids, Organic Residuals Conference*, Wakefield, England, Nov 18−20, 2002; Vol. 2; ISBN 1-903958-06-7; Session 10, Paper 070.
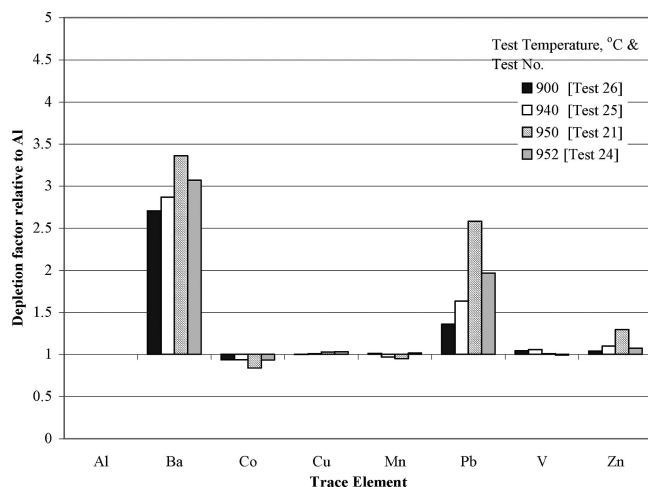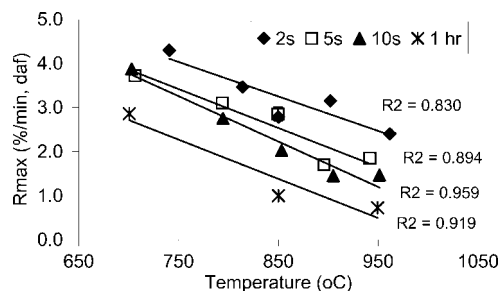
Figure 11. Trace element depletion.

Figure 12. R_{max} as a function of temperature at 1.3 MPa N_2.

normalized relative to a nonvolatile element such as Al using the following expression:

$$\text{trace element depletion factor}_{Al} = \frac{[TE]feed/[Al]feed}{[TE]bed/[Al]bed} \quad (1)$$

where TE and Al are the measured trace element and aluminum concentrations

Results indicated that gasifier bed temperatures in excess of 900 °C enhanced the depletion of Ba, Pb, and Zn from the bed residue (Figure 11) and their enrichment in the fines. Mercury and selenium capture required low-temperature filters operating below 120 °C. It was also found that thermodynamic modeling is not always helpful in predicting outcomes of experiments, due to either limitations of databases or problems arising from kinetic constraints. Parallel cocombustion experiments have suggested that the presence of chlorine somewhat enhances the volatility of lead and cadmium.

Reactivity of Char Formed in the Spouted Bed.[12,13] The modified fluidized bed reactor has been used to form and collect char samples within the operating window of air-blown fluidized bed gasifiers. Changes in reactivity with conditions of char formation have been measured using a TGA method and visual changes identified by SEM. Increasing the temperature, pressure, and particle size each had a negative impact on the char reactivity. The effects are illustrated in Figures 12 and 13, which show the char reactivity as a function of variations in the operating conditions. Initial rapid reductions in reactivity occur as part of the pyrolysis of the coal volatiles, and this is thought to result from the deposition of secondary char within the primary char. Longer time scale decreases in reactivity seem to result from the development of graphitic structures within the solid. Char samples prepared in the fluidized bed reactor with residence times of 2, 10, and 3600 s were studied by X-ray diffraction. The XRD results are shown in Figure 14. The peaks present in the 2 s spectrum were noted to be SiO_2, thought to
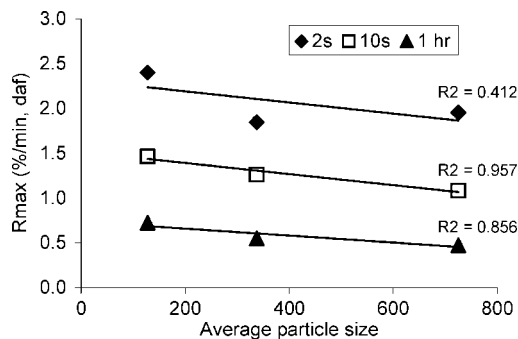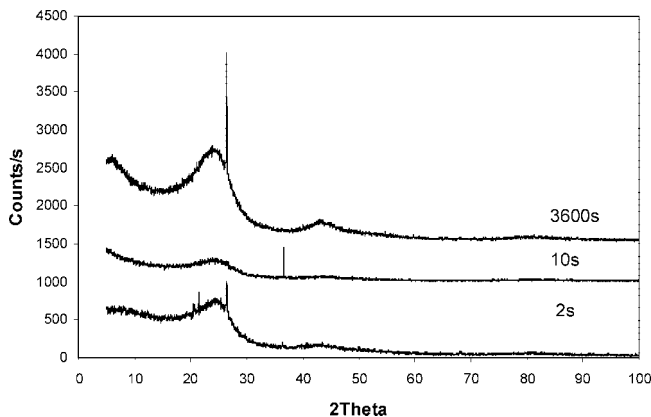

Figure 13. Effect of coal particle size on R_{max} at 950 °C and 1.3 MPa N_2.

Figure 14. XRD pattern for char samples prepared in the reactor at 950 °C and 1.3 MPa.

Table 7. TGA Reactivity of Pilot-Scale Bed Chars Derived from Different Coals

parent coal	R_{max} (% min^{-1})[a]
Daw Mill	0.31
El Cerrejon	0.25
Reitspruit	0.17
Illinois No. 6	0.51
Drayton	0.30

[a] R_{max} is the maximum rate of reaction in air, at 500°C, estimated from the TGA trace.

be introduced from the bed material. The peak in the 10 s spectrum was not found to correspond to any structures in the database and hence thought to be an anomaly. The peak in the 3600 s spectrum however, corresponded to graphite. This data shows that no significant graphitic material formation occurs in the short residence time chars and therefore cannot explain the early loss in reactivity. However, there may be a movement toward the graphitic structures in the char and these would be less reactive. This is thought to explain the decrease in reactivity that occurs over longer timescales in the gasifier.

TGA reactivity measurements (Table 7) on chars formed in the bed of a pilot-scale gasifier (char particle size 1200 μm and long residence time) are about 50% lower than those measured for laboratory-scale chars formed from 600−850 μm coal and a 60 min residence time. This suggests that the laboratory test can produce chars that approach the reactivity of chars formed in the larger scale process.

Pyrolysis of Waste Plastics in an Atmospheric Pressure Fluidized Bed. Four individual plastics and a mixture in their equal proportions were investigated: polyethylene (PE), polypropylene (PP), polystyrene (PS), and poly(vinyl chloride) (PVC). Particle sizes were 150, 200, 200, and 250 μm, respectively. Tar yields would be affected by their residence time in the

Table 8. Product Distribution of Tars, Chars, and Gases from Pyrolysis of Plastics

material	tar (%)	char (%)	gas + volatiles[a] (%)
PE	69.5	negligible	30.5
PP	64.2	negligible	35.8
PS	68.7	negligible	30.1
PVC	62.2	1.2	37.8
mixture (1:1:1:1)	68.8	negligible	31.2

[a] Calculated by difference.

Table 9. Product Distribution of Tars between Different Reactor Regions

	bed + wall tar (%)	trap 1 tar (%)	thimble tar (%)
PE	12.2	78.8	0
PP	10.3	85.4	4.3
PS	3.4	86.6	0
PVC	1.2	98.8	0
mixture (1:1:1:1)	8.7	91.3	0

reactor at the chosen reactor conditions. An increased residence time could increase cracking of tars but also could enhance recombination reactions of volatile products, thus increasing tar yield. A systematic approach was therefore taken to investigate this phenomenon by starting with the minimum possible residence time. No operating problems were noted during the tests, apart from a slight gluing effect within the bed with the PE feed.

Table 8 shows the mass balance obtained for the four individual plastic samples and the equal-parts mixture, while Table 9 shows the mass distribution of the tars between the different components of the reactor. Each experiment was repeated three times and standard deviations for the masses obtained varied from 9 to 16%.

Tar yields were fairly high and shown to be comparable to other studies found in literature for this type of system.[40–42] PVC was the only plastic shown to produce char in detectable quantities. Taking into consideration the relative standard deviation of the experiments, it is not possible to state if the results from pyrolyzing the plastics mixture show any synergy with respect to tar yield. The characterization of the tars showed that PE tar contained a distribution of straight chain hydrocarbons, up to a chain length of C60 (peaking at around C30), while the other tars were much more complex.

When considering the distribution of tars in different regions of the reactor, it may be concluded that trap 1 worked very effectively in condensing the volatile reaction products. In the case of PP, some tar was shown to have passed through trap 1 to the final collection thimble. Further washing of the stainless steel tubing post-thimble did not show further condensation of tars, so it may be concluded that this system setup was fit for purpose. Collecting the tars in different reactor regions also enabled the analysis of variations in tar quality at these points. It was found that the sand and wall tars were identical to each other, but contained generally heavier components to the tars collected in Trap1.

Conclusions

The design, operation, and several modifications of a bench-scale high-pressure fluidized bed reactor system have been reviewed. The design is capable of diverse pyrolysis and gasification applications, all based on the same hardware platform. The reactor is small, and the mechanical design is relatively simple and inexpensive, featuring direct electrical heating to avoid the use of a separate furnace. The reactor body (34 mm i.d. and 504 mm high) is made of a high-strength alloy, with 1000 h creep resistance at maximum design conditions (1,000 °C and 3.0 MPa). There is therefore no need to use a "cold" pressure casing. The system is quite compact, can be operated by a single person, and has demonstrated ability to generate fuel reactivity and product distribution data rapidly and cheaply, using a wide range of solid fuels. Using the various possible reconfigurations, the reactor has provided a greater understanding of air-blown fluidized bed gasification.

A study of the release of fuel-N from both coal and sewage sludge has shown that high NH_3 concentrations can be formed in the gasifier and the presence of steam causes substantial increases in the amount formed. This must be stripping the N from both the volatiles and from the char. NH_3 is also destroyed in the gasifier by the decay to N_2 and H_2: this results in lower exit NH_3 concentrations from longer residence time commercial-scale gasifiers. HCN is formed readily from the volatiles of both coal and sewage sludge but decomposes to produce NH_3 in the presence of H_2. Increasing the depth of the char bed enhances the destruction of the HCN.

The fate of trace elements was also measured during tests with sewage sludge. Results indicated that gasifier bed temperatures in excess of 900 °C enhanced the depletion of Ba, Pb, and Zn from the bed residue and their enrichment in the fines.

Mercury and selenium were released and their subsequent capture required low-temperature filters operating below 120 °C.

The reactor was modified to enable char samples to be prepared and collected under controlled conditions. The reactivities of the chars were measured as a function of "residence time at temperature" and were observed to decrease with increasing temperature, time, pressure, and particle size. At 1000 °C, coal char reactivities were found to diminish by nearly a factor of 4 within 10 s. The study confirmed and extended previous work carried out in a high-pressure wire-mesh reactor. There appears to be an initial decrease in reactivity during pyrolysis and a further longer- term decrease caused by graphitisation.

The pyrolysis of plastic waste materials has been studied using the reactor with a batch feed system at atmospheric temperature and a relatively low temperature. The data shows complete conversion of the materials to tar, low boiling point organics, and gas. The tar formed the greatest proportion of product (in the range 60−70%) for all of the wastes tested. Further work is planned in this area.

(40) Miskolczi, N.; Bartha, L.; Deák, G.; Jóver., B. Thermal degradation of municipal plastic waste for production of fuel-like hydrocarbons. *Polym. Degrad. Stab.* **2004**, *86*, 2, 357–366.

(41) Hwang, E.-Y.; Kim, J.-R.; Choi, J.-K.; Woo, H.-C.; Park., D-W. performance of acid treated natural zeolites in catalytic degradation of Polypropylene. *J. Anal. Appl. Pyrol.* **2002**, *62* (2), 351–365.

(42) Gao, Z.; Kaneko, T.; Amasaki, I.; Nakada, M. A kinetic study of Thermal degradation of polypropylene. *Polym. Degrad. Stab.* **2003**, *80* (2), 269–274.

Abbreviations

ABGC = air-blown gasification cycle
KRW = Kellog Rust Westinghouse
CAS = Chinese Academy of Sciences
EU = European Union
AISI = American Iron and Steel Institute
ECN = Energy Research Centre of The Netherlands
TUT = Taiyuan University of Technology

BS = British Standard
PID = proportional integral derivative
SEC = size exclusion chromatography
ICP-AES = inductively coupled plasma, atomic emission spectrometry
TGA = thermogravimetric analyzer
XRD = X-ray diffraction