Development of analytical techniques and scrubbing options for contaminants in gasifier streams intended for use in fuel cells

Final Report

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Chariton Valley Biomass Power Project

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Executive summary

One goal of the Chariton Valley Biomass Power Project is the development of an integrated switchgrass gasifier/fuel cell (IGFC) power plant. Phase I of this activity involved testing the gasification of switchgrass in a 4.5 tonne/day (5 ton/day) fluidized bed reactor on the campus of Iowa State University (ISU). Simulation of the IGFC was performed by FuelCell Energy (formerly Energy Research Corporation) based on the results of the gasification tests at ISU. Further development of an IGFC power plant and eventual construction of such a plant will require additional equipment to couple the two technologies.

Gas generated during gasification of switchgrass contains contaminants detrimental to the operation and/or useful life of the fuel cell. Successful integration of gasifiers with fuel cells mandates the conditioning of the producer gas to levels stipulated by fuel cell manufacturers. This report brings together the different aspects associated with IGFC power plant.

Although no testing of an IGFC has taken place, manufacturers and fuel cell experts have estimated the impacts of certain contaminants on the performance and expected life cycle of a fuel cell. Carbon monoxide is the primary contaminant for use in a proton exchange fuel cell. Phosphoric acid fuel cells are sensitive to sulfur, chloride, ammonia, and carbon monoxide. Molten carbonate and solid oxide fuel cells suffer adverse affects from sulfur and chloride.

Detection and quantification of the contaminants in the producer gas requires carefully designed sampling and analytical techniques. Every gas species of interest has unique characteristics for sampling, transport, and detection. Although methods have been identified, much more testing needs to be done to confirm the accuracy of the various methods. Presently it appears direct gas stream analysis with Drager tubes is the method of choice for determination of hydrogen sulfide. Analyses of ammonia by fluorometric or ion electrode methods appear to be the most promising. Ion mobility spectroscopy and Drager tubes offer two potential methods of analyses for hydrogen chloride. Hydrogen cyanide is a difficult species to measure and at this time no methodology has been chosen.

Other contaminants include particulate and tar (condensable hydrocarbons). Hot gas cleanup technology removes contaminants while preserving the sensible energy in the producer gas. However, hot gas cleanup technology is not commercially available for biomass applications. Ceramic filters are susceptible to breakage due to thermal and mechanical shock and exhibit intolerance to certain minerals. Metal filters are an alternate hot gas cleanup technology but have not yet been fully developed. Tarry substances in the gas stream may plug both ceramic and metal filters if not operated at sufficient temperatures. Alternatively, soot may form if the filters are operated at too high of temperatures. Moving bed filters are able to capture particles on granular material at elevated temperatures. Its capability for removing trace contaminants, however, is essentially unexplored.

The use of a catalytic reactor downstream of the gasification reactor has proved an effective approach to elimination of tar. A variety of catalysts have shown significant ability to destroy tar in gasifier streams. These catalysts include dolomite, nickel and alumina based catalysts, and various proprietary catalysts.

Testing of a moving bed granular filter to remove dust from hot producer gas has demonstrated promising results. A filter of 0.914 m (36 in.) diameter was able to remove 97 - 98% of the 60 g/m^3 dust loading from a 345 nm^3/h (200 ft^3/min) gas flow. Pressure drop never exceeded 80 mm water (3.0 in) water in these tests. Most of the dust penetrating the filter was 2 – 3 μm in size. Virtually none of the exiting dust was from the silica pebbles used as granular media in the filter, as confirmed by elemental analysis of dust entering and exiting the filter. However, we do not appear to have operated under steady state conditions of the filter; additional testing is required.

A tar cracking system consisting of a guard bed and catalytic reactor was designed for the purpose of improving the quality of producer gas from an air-blown, fluidized bed biomass gasifier. All three metal catalysts (ICI 46-1, Z409, and RZ409) proved effective in eliminating heavy tars (>99% destruction efficiency) and increasing hydrogen concentration by 6-11 vol-% (dry basis). Space velocity had little effect on gas composition while increasing temperature boosted hydrogen yield and reduced light hydrocarbons (CH_4 and C_2H_4), thus suggesting tar destruction is controlled by chemical kinetics.

More research and development is needed before integration of a gasifier to a fuel cell can be attempted. Although the moving bed granular filter and catalytic reactors show great promise for gasifier stream conditioning, the gas quality is still not sufficient for direct use in a fuel cell. Testing and development of the moving bed granular filter and the catalytic reactors will continue. Gas analytical techniques will be tested and implemented for further characterization of the producer gas.

Introduction

One goal of the Chariton Valley Biomass Power Project is the development of an integrated switchgrass gasifier/fuel cell (IGFC) power plant. Phase I of this activity involved testing the gasification of switchgrass in a 4.5 tonne/day (5 ton/day) fluidized bed reactor on the campus of Iowa State University (ISU). Simulation of the IGFC was performed by FuelCell Energy (formerly Energy Research Corporation) based on the results of the gasification tests at ISU. Further development of an IGFC power plant and eventual construction of such a plant will require additional equipment to couple the two technologies.

Currently, the low Btu gas produced by the biomass gasifier is unsuitable for conversion in a fuel cell without treatment. Generally, the presence of particulates, tars, and many other elements (including chlorine, arsenic, selenium, sulfur, zinc, and lead) will lead to degradation and fouling of the catalyst used in the fuel cell. Therefore it is critical to remove the producer gas contaminants prior to use in a fuel cell.

Commercial equipment used for removal of contaminants either does not exist, does not address removal of all contaminants, or is still in the developmental stage. In a few cases there may be equipment currently available for purchase to remove a specific contaminant. Therefore, further development and testing of clean-up technology is necessary to move this project forward.

Background

There are numerous ways to convert biomass into alternative forms of energy. The different conversion methods are accompanied by a plethora of conversion technologies. Thermal conversion systems present opportunities to convert biomass feedstocks or other fuels into heat, gaseous fuels, liquid fuels, or chemicals. The coupling of a biomass thermal conversion system to prime movers like internal combustion engines, fuel cells, and combustion turbines require the transformation of the solid fuel into gaseous or liquid fuels.

As stated earlier, one goal of the Chariton Valley Biomass Power Project is the integration of a switchgrass gasifier with a fuel cell to generate power and heat. Testing and development of the gasifier portion of the system at Iowa State University have utilized a atmospheric pressure fluid bed reactor in which to perform the gasification. As fuel cells typically operate at or near atmospheric pressure, it is logical to avoid the pitfalls of a pressurized gasification system. The fluid bed reactor has several advantages over other conversion technologies. Fluid beds offer fuel flexibility, relative ease of operation, and are easily scaled to different sizes. However, the fluid bed reactor does not come without its own set of difficulties. Particulate and tar loading in the combustible gas is problematic and present significant gas cleaning challenges. The operating conditions within the reactor may also be constrained by fuel characteristics that impose limitations on operating temperatures within the reactor. Nonetheless, fluid bed reactors present an attractive conversion technology that should be further developed.

Gasifier system

A pilot-scale fluidized bed reactor, illustrated schematically in Figure 1, was used to perform the experiments. The system is rated at 800 kW (2.8 MMBtu/hr) thermal input, which corresponds to an average throughput of 180 kg/hr (400 lb/hr) of solid biomass fuel at a heating value of 16,000 kJ/kg (7000 Btu/lb). The nominal gas generation rate is 340 nm^3/h (200 ft^3/min).

The feed system consists of a live bottom hopper that utilizes a single screw to meter fuel. The metering auger discharges into a high-speed auger that injects the material into the fluid bed. The metering hopper can be charged while operating to enable continuous operation. The bed is fluidized with air at an equivalence ratio between 0.25 and 0.30, which results in a reactor temperature range of 700-760ºC (1290-1400°F). The feed rate of biomass during operation is in the range of 160 – 200 kg/h (350-450 lb/h).

The fluidized reactor is a 46 cm (18 in) diameter cylindrical steel vessel standing 4.3 m (14 ft) tall. The reactor is lined with castable ceramic to insulate the vessel. Fluidization air enters the reactor through an array of nozzles that evenly distribute air to the bottom of the bed. Bed media consists of sand mixed with limestone. The limestone comprises about 5-20% of total bed weight and acts to minimize agglomeration of bed material arising from alkali in the biomass feed. Particulate-laden producer gas exits the reactor through the freeboard and passes through a cyclone that removes much of the particulate matter larger than 10 µm in size. Details on the operation of the biomass gasifier can be found in Smeenk and Brown [1].

Quality of combustible gas for use in fuel cells

The authors are unaware of any system, commercial or research, consisting of a biomass gasifier coupled to a fuel cell. Conceptually such integration has several benefits including high fuel to electric efficiency, the potential for reduced emissions, and opportunity for distributed generation. Operationally, integration is perceived to be difficult for several reasons including low energy content of the combustible gas, contaminants in the gas, and in some cases the high temperature of the gas.

The knowledge and experience of various fuel cell manufacturers has enabled the preliminary establishment of fuel quality standards. The current understanding of the fuel quality issues has been collected and presented [2-3]. Table 1 is a culmination of this information. Blanks in the table represent contaminants that do not affect the particular fuel cell.

Table 1. Contaminants for various fuel cell systems.

		Contaminant Tolerance Level			
Fuel Cell Type	Operating Temperature	H_2S	HCl	NH_3	CO
Proton Exchange	70-90 ºC (160-195 ºF)	-	-	-	10 ppm
Phosphoric Acid	160-210 ºC (320-410 ºF)	50 ppm	4 ppm	0.2	1%
Molten Carbonate	600-700 ºC (1110-1290 ºF)	0.5 ppm	1 ppm	1%	-
Solid Oxide	800-1000 ºC (1470-1830 ºF)	1 ppm	1 ppm	0.5%	-

Analytical procedures for quantification of contaminants in producer gas

Methods for determining H_2S, NH_3, HCl, and HCN in gasifier streams are being determined. The gas matrix involved greatly complicates these determinations and makes suitable analytical methods difficult to find in some cases. For most of the trace gases of interest, it should be noted that a variety of instrumental methods for on-line analyses are available but are not discussed here. The cost, size, or difficult operating procedures make utilization of these instruments in this application undesirable. For example, an on-line NH_3 analyzer based on UV absorption with a photo diode array is commercially available. However, it comes in a six-foot tall rack and weighs 270 kg (600 lb). The cost of the analyzer is also significant. Such analyzers were avoided for several reasons. The intent is to develop suitable analytical methods for the species of interest that could be performed routinely with a minimum of training, a minimum of instrument maintenance, and a minimum of expense. Analytical approaches considered for each gas of interest are discussed separately below.

Hydrogen Sulfide (H_2S)

Many analytical methods for determination of H_2S have been tested. Direct gas stream analysis using Drager tubes appears to be the most promising method. This method is discussed in detail as well as several other less successful methods.

H_2S – Drager tubes

Drager tubes are small glass tubes filled with a chemically sensitive material that changes color when the gas species of interest is present in the gas stream. A sample pump draws a measured volume of gas through the glass tube enabling determination of the gas species concentration. Drager tubes are relatively inexpensive and allow reasonable sample rates. The tubes are typically accurate to approximately 25% and there is no sensitivity to relative humidity, a major advantage over other methods, specifically the chemically impregnated tapes used with the Zellweger analyzer (discussed below). Readings are linear with H_2S concentration.

There do not appear to be any significant interference gases for the sample streams of interest. Organic vapors in the sample gas have little or no effect on the H_2S reading and the organic vapors themselves do not give a reading. Because of gas density issues, the H_2S reading will be biased high by approximately one percent for each percent of hydrogen in the gas stream. The tubes cost approximately $5 each and have a typical shelf life of 2-3 years (compared to several months for the Zellweger cassettes). Tubes are available for H_2S concentrations ranging from 0.1 ppm to 1% or more.

The solubility of H_2S in water necessitates the avoidance of upstream moisture condensation when sampling gasifier streams to enable accurate analysis. In the proposed sampling scheme, particulate matter will first be removed with a high-temperature filter maintained above 400°C (750°F). Next, heavy tars will be removed by condensation at 100°C (212°F). A modified pressure cooker has been developed, but not yet tested, to enable condensation of tars without the use of an impinger train. The use of an impinger train would likely result in condensation of moisture and subsequent capture of H_2S in the moisture.

A boiling water bath in the pressure cooker will provide a constant temperature of 100°C (212°F). The gas sample will flow into a large stainless steel beaker, which will reduce the gas velocity and initiate dropout of tars. The sample will then pass through a stainless steel coil (inside the pressure cooker) consisting of 3.6 m (12 ft) of 9.5 mm (0.375 in) outer diameter tubing. This is intended to provide enough residence time at 100°C (212°F) to complete the removal of heavy tars. The inner diameter of the steel tubing was chosen such that tars are not expected to plug the lines during a given sampling run. However, it is likely the tubing will need to be rinsed of tars between each run. Because H_2S tends to be reactive with steel, all of the steel in the pressure cooker that contacts the sample has been coated with several microns of amorphous silica.

After heavy tar removal, the sample gases will pass through a heated Perma Pure drier. The Perma Pure cannot be operated in the normal manner (i.e., heated only to the Perma Pure inlet) because too many light hydrocarbons are likely to condense and plug the walls of the Nafion tubing. Therefore, the entire Perma Pure will be heated by housing it in an oven. Heating will prevent many of the light hydrocarbons from condensing, but will also result in incomplete drying of the gas stream and variable RH. In fact, the moisture dew point may be as high as 50-60°C (120-140°F). The variable RH may slightly affect (perhaps by 10%) the concentration determined by the Drager tube. Heated tubes could potentially be used to avoid this problem. According to manufacturer specifications, the tubes can be used up to 40°C. At higher temperatures, the chemicals may be affected and lead to erroneous results. The additive uncertainties in the analysis may result in an accuracy of ±40% (probably worst case). However, tracking of relative H_2S concentrations should be reliable if proper sampling techniques are utilized.

H_2S – chemically impregnated tapes

A Zellweger Analytics Model 7100 Toxic Gas Monitor was considered for on-line H_2S analyses. This method is based on passing sample gas through chemically impregnated tapes. Presence of the analyte gas causes a color change on the tape, which is then measured by monitoring the reflectivity of the tape. The change in reflectivity is related to analyte concentration. The colorimetric cassette tapes have a short shelf life (typically several months) and cost approximately $50 for a few days of testing.

The colorimetric tapes exhibit excellent linearity and precision even at concentrations of 0-5000 ppb when the relative humidity (RH) is in the proper range. Additionally, this method is very sensitive to small changes in H_2S levels. Typical gases found in a producer gas matrix do not impose significant interference. The dynamic range is very narrow (e.g., 0-50 ppm) for the "high level" calibration. The dynamic range is 0-5000 ppb for the "low level" calibration. However, for the "low-range" calibration, readings are only statistically meaningful to the second figure (e.g., 1100 ppb versus 1200 ppb). Being able to differentiate between 1000 and 1500 ppb will probably not be an important issue in field-testing. At H_2S levels of about 50 ppb or less, the analyzer response time is approximately 10 minutes, but a shorter response time is realized at higher H_2S concentrations.

The H_2S readings (both high and low calibrations) are very sensitive to the RH of the gas stream, which greatly complicates both calibration and sample analysis. The RH of the calibration gas must match (very closely) the RH of the sample gas. The optimum RH (for best accuracy) has a narrow window of only about 10% RH (absolute). Also, the optimum RH is sensitive to the H_2S concentration as well as some instrument variables. This problem is less severe for H_2S than for other gases such as HCN. The analyzer does an excellent job under certain conditions, but does not do very well under other conditions. It is probably best used to simply detect the presence of H_2S (and trigger a built in audible and/or visual alarm if desired). It may also be used to track relative H_2S concentrations at a specific (controlled) RH level in the sample gases. The overall utility of this method is considered marginal for the accurate determination of H_2S in the application of interest.

H_2S – ion chromatography

Water solutions could potentially be used to collect H_2S, which is very water soluble, with subsequent analysis by ion chromatography (IC). However, the IC manufacturer discourages the use of aqueous samples derived from a producer gas matrix because of significant levels of water-soluble organic materials (light hydrocarbons) in the samples. The organic materials would likely cause analytical problems and potentially damage system components.

H_2S – misc. methods

A variety of titrimetric procedures are available, but have not been explored. An ion selective electrode looks like an attractive alternative to ion chromatography, since it is highly specific and very sensitive. However, sulfide tends to be very unstable in solution and is difficult to preserve.

H_2S – lead acetate solution

Bubbling gases into a lead acetate solution to form lead sulfide yielded promising results. After a sampling time of only two minutes in the laboratory, 10 ppm H_2S could easily be detected due to the decrease in sample transmittance from the formation of microcrystalline lead sulfide (black). However, the lead solutions are a hazardous waste and direct gas stream analyses are preferred to wet chemical approaches.

H_2S – commercial instruments

Other instrumental approaches are possible for continuous, on-line H_2S measurement. H_2S in gasifier streams is typically determined by gas chromatography (GC) with a flame-photo detector (FPD). Several vendors of different instruments have verbally agreed to free instrument loans for our evaluation of the analyzers for our specific applications. However, the significant cost of these instruments is unacceptable when satisfactory results and low cost analyses are available with Drager tubes.

H_2S – sample conditioning and transport

The transport of H_2S through a Perma Pure drier was investigated. When using a 2-ppm H_2S stream at a flow rate of 1 L/min, H_2S successfully passed through the drier (i.e., all the H_2S was retained in the sample gas). Successful results were achieved for counter-current purge flow rates of 2 and 10 L/min.

H_2S – sample line issues

During laboratory testing, no significant wall effects were observed when H_2S was passed through Teflon lines at room temperature, even for H_2S in the 0-5000 ppb range. Laboratory tests showed that a stream of 25 ppm H_2S (in nitrogen) could be successfully transported through stainless steel (type 316) lines at 25 and 200°C (77 and 390 °F). However, major H_2S losses were observed at 400°C. Using electropolished stainless steel or superalloy Inco Alloy C276 did not alleviate the loss of H_2S at the higher temperature. However, using stainless steel with an interior coating of amorphous silica (Silcosteel from Restek Corporation) proved successful at 400°C (750 °F). It is highly recommended that all sample transport lines and other sampling components above 200°C (390 °F) be made of Silcosteel. Below that temperature, Teflon should be used to help ensure effective sample transport over a wide range of H_2S concentrations. Additionally, blending 10 ppm or 250 ppb H_2S with 1000 ppm NH_3 did not affect the H_2S concentration (i.e., the NH_3 and H_2S did not react to form ammonium sulfide compounds).

Ammonia (NH_3)

Analyses of NH_3 by fluorometric or ion electrode methods appear to be the most promising. Drager tubes may also be an option. Each method requires further investigation.

NH_3 – chemically impregnated tapes

The Zellweger analyzer was tested for its suitability for performing NH_3 analyses. There was no interference from most matrix gases. However, severe interference from CO (not in the literature from the vendor) at the concentrations anticipated for gasifier streams renders this method unsuitable for NH_3 analyses in gasifier streams. Even if the CO were not a problem, the instrument reading was strongly influenced by the RH of the gas stream, as appears to be the case with all the detection tapes for this analyzer.

NH_3 – ion chromatography

The previous discussion regarding H_2S analyses by IC pertains to NH_3 analyses as well. Concerns regarding the presence of light hydrocarbons in the liquid sample matrix and collection of NH_3 in water impingers (or simply collecting aqueous condensate) prohibit the determination of NH_3 by IC.

NH_3 – fluorometric measurement

A fluorometric method investigated for the determination of NH_4 in aqueous solutions appears promising. The method is based on reacting NH_4 with orthophthaldialdehyde to form a highly fluorescent compound and subsequent measurement with a fluorometer. The fluorometer is not much larger than a toaster, requires virtually no maintenance, and is simple to use. The approach is found to be extremely sensitive with a detection limit of less than 1 ppb in solution. Under the conditions studied, a linear range of 0-200 ppb is possible. Based on analyses of actual field samples obtained during biomass gasification, autofluorescence (fluorescence of the matrix itself) was not a problem. The severity of any matrix effects still requires investigation.

NH_3 – ion electrode

A promising alternative (yet to be tested) to the fluorometric determination of NH_4 in aqueous solutions involves the use of a specific ion electrode. Based on catalog information, there do not appear to be any significant interference gases for the sample matrix involved. The method is very sensitive and has a detection limit of about 10 ppb in solution. This approach offers the advantage of immediate determination, in contrast with the fluorometric method, which requires an "incubation time". A specific ion electrode costs approximately $500 and requires the use of a suitable meter. This approach may be explored in the future.

NH_3 – Drager tubes

The use of Drager tubes for performing NH_3 determinations is being explored. There do not appear to be any significant interference gases in the anticipated sample gas matrix. However, tar vapors (atmosphere above dichloromethane containing dissolved tars) give a significant positive response, suggesting tars may cause interference. Vapors from pure dichloromethane do not give any response by themselves. This phenomenon requires further exploration before the utility of Drager tubes for determining NH_3 in gasifier streams can be fully assessed.

NH_3 – sample conditioning and transport

A humidified stream of 500 ppm NH_3 flowing at 1 L/min could not be passed through a laboratory-scale Perma Pure moisture removal system. In fact, there was no trace of NH_3 in the sample gases exiting the drier, even though the NH_3 level entering the drier was 10 times the amount necessary to saturate the analyzer. No NH_3 was detected in the countercurrent purge gas stream (flowing at 2 and 10 L/min). The Nafion tubing in the Perma Pure drier contains sulfonic acid groups, and it is likely that those sulfur-containing species are reacting with the NH_3. This demonstrates that a Perma Pure drier should probably not be used for field sampling of NH_3.

NH_3 – sample line issues

Laboratory tests demonstrated that NH_3 is successfully transported through stainless steel (type 316) tubing at 25, 200, and 400 °C (77, 390, and 750 °F). Thus, it does not appear necessary to use Silcosteel for transport of NH_3 in the temperature range and concentration range of interest. In addition, the coexistence of NH_3 and HCl would lead to the formation of solid ammonium chloride if the sample temperature drops to near room temperature.

Hydrogen cyanide (HCN)

HCN is the most difficult trace gas of interest to determine. No analytical method is clearly the best option. Fluorometric analysis may work although much more testing needs to be done.

HCN – chemically impregnated tapes

The manufacturer of the Zellweger analyzer notes that the HCN tapes are extremely sensitive to RH. Additionally, the optimum RH being is dependent on the analyte concentration. In other words, the reading is very sensitive to RH, but the optimum RH that must be used to get accurate readings depends on the HCN concentration. The readings obtained with the tape had a relative standard deviation of 15% for a 50-ppm HCN stream. This uncertainty (which in itself is very acceptable) must be combined with the large uncertainties due to the effects of RH.

H_2S is an interference gas, although it takes 5-10 ppm H_2S to give a reading of 1 ppm HCN. H_2S alone gives a false positive signal, but when H_2S is combined with HCN, the H_2S actually leads to signal suppression. Thus, there are numerous problems in using this particular analytical approach. The H_2S can be removed by using a scrubber (based on lead acetate) supplied by the vendor. However, it would cost about $100 a day to use their non-regenerable scrubbers. Homemade scrubbers would cost approximately $5 each, but in view of all the other analytical uncertainties that result in semi-quantitative analyses at best, it is probably best to simply analyze the unscrubbed gases. The analyses would only be semi-quantitative and could be used (if desired) to indicate the absence or presence of significant levels of HCN.

HCN – ion chromatography

As with the other water-soluble species, IC is probably not an option for analysis of HCN because of the problems associated with water-soluble organics.

HCN – Drager tubes

Drager tubes cannot be used because CO and H_2 are major interference gases. It would be difficult to remove those gases without affecting trace levels of HCN.

HCN – other analytical methods

UV or visible light absorption won't work because HCN has no significant absorption bands in those regions. The use of ion selective electrodes is possible, but suffers from severe interference by sulfide and chloride ions. The sulfide can easily be removed by adding lead carbonate. The effect of lead carbonate on chloride removal is uncertain at this time.

HCN – fluorometric analysis

A fluorometric method for determining cyanide in aqueous solutions will be tested, since that method is reportedly highly sensitive and very selective. Although there are essentially no interference gases, the presence of sulfide causes an analytical error due to a decrease in the pH of the sample. This problem can be avoided by checking the pH of the sample solutions. If the pH is indeed a problem, then a phosphate buffer can be used to eliminate the problem. The necessary optical kit for the fluorometric determination of HCN has been installed in the fluorometer. It must be noted that cyanide samples degrade very quickly, and analyses should be performed immediately. Difficulties in working with cyanide in solution require immediate sample preservation. In addition, immediate sample pretreatment (PRIOR to sample preservation) to remove sulfide may be required, since sulfide quickly converts cyanide to thiocyanate (SCN). If these steps are not taken, it is reported that the rate of cyanide loss can be as high as 50% per hour.

HCN – sample conditioning and transport

Testing suggests transport of a 100-ppm stream of HCN through a Perma Pure drier at a flow rate of 1 L/min is possible without loss of analyte. Purge gas flow rates of 0, 2, and 10 L/min were tested.

HCN – sample line issues

The transport of a 60-ppm HCN stream (in nitrogen) was studied in stainless steel and Teflon sample lines. Laboratory tests suggest that HCN could be successfully transported through stainless steel (type 316) lines at 25, 200, and 400°C (77, 390, and 750°F). Thus, it does not appear to be necessary to use Silcosteel for transport of HCN in the temperature range and HCN concentration range of interest.

Hydrogen Chloride (HCl)

Ion mobility spectroscopy (IMS) and Drager tubes offer two potential methods of analysis. However, our current IMS system is in need of repair and has a narrow dynamic range. An IMS analyzer capable or measuring up to 100 ppm is available commercially. This instrument offers dual-range that enables measurement on the order of parts-per-billion. Drager tubes have demonstrated susceptibility to interference gases.

HCl - chemically impregnated tapes

After considering all the information presented here, this method does not appear to be a good analytical choice for determining HCl in gasifier streams. However, it may be suitable to detect the presence of HCl and trigger an internal alarm if HCl is detected. The Zellweger instrument (described earlier) has three separate instrument calibrations available for HCl: 1) high-level (0-50 ppm), 2) high-level with low humidity, and 3) low-level (0-5000 ppb). The low-level tapes should not be used in the field with this analyzer. The long response time (up to 10 minutes) and stringent RH requirements limit its usefulness. In addition, this tape is more susceptible to chemical interference than the high-level HCl tape.

The measured concentration is very sensitive to RH of the sample gas. For example, the signal obtained for a 20 ppm HCl gas stream is ten times higher at 60% RH than at 80% RH. A very narrow RH range of 40-60% is needed to obtain reasonable results. Additionally, the narrow analytical range of only 0-50 ppm HCl limits its usefulness. The use of dry HCl tapes with dry HCl streams enables the instrument to track changes in concentration well and achieve a linear response over the analytical range of the instrument. For a 40 ppm HCl stream (dry), the relative standard deviation for multiple readings was about 5%. Although better results are obtained with dry gases, the analytical range is still only 0-50 ppm. The difficulty associated with preparing a dry sample also limit its applicability. Drying the sample gases with a Perma Pure is not very effective since it must be operated at elevated temperatures to keep most of the light hydrocarbons in the vapor phase.

Contrary to vendor claims, laboratory tests indicate that H_2S is an interference gas. At 50% RH, a 100 ppm H_2S stream gave a reading of 15 ppm. Thus, there is roughly a 7:1 rejection ratio for H_2S based on these tests. Although this might at first appear to be only a minor interference, it must be kept in mind that gasifier streams could have H_2S levels that are much (e.g., five-fold or more) higher than the HCl concentrations, in which case it would be a major interference gas. Although HCN and NH_3 do not present interference problems (do not give a ready in themselves), the vendor notes that either one of those gases can desensitize the HCl tape and result in lowered readings.

HCl – ion chromatography

Water solutions could potentially be used to collect HCl since it is highly water-soluble followed by IC analysis. However, the same restrictions on use of IC in gasifier streams noted earlier apply here. The hydrocarbon content in the sample would likely interfere with the analyses and would probably damage the instrument.

HCl – misc. methods

Ion selective electrodes do not appear promising for HCl analyses because sulfide and cyanide ions (among others) strongly interfere. A variety of titrimetric procedures could potentially be used, but have not been explored.

HCl – Drager tubes

Overall, Drager tubes work well. The tubes are typically accurate to approximately 25% and there is no sensitivity to RH (RH of 0-90%). Tubes are available for concentrations of 0.2 to 75 ppm, but require a correction factor for concentrations between 20 and 75 ppm. For gasifier sample streams, there do not appear to be any significant interference gases. HF imposes only a minor interference. However, tar vapors (atmosphere over tars in dichloromethane) appear to suppress the HCl reading significantly. Therefore, it is not certain whether Drager tubes are the best approach for HCl analyses. Further testing is needed to determine the applicability of Drager tubes.

HCl – commercial analyzers

A variety of instrumental approaches are possible for continuous, on-line measurement. One potential instrument for determination of HCl levels greater than 1 ppm involves gas filter correlation IR. The gas stream would have to be oxidized to eliminate the severe interference from methane. Oxidation would eliminate NH_3, which otherwise would combine with HCl upon cooling to form solid ammonium chloride. At least one vendor that supplies gas filter correlation IR has verbally agreed to a free instrument loan so we can evaluate the analyzer for our specific applications. Unfortunately, the cost of such an instrument is considerable. Another potential analytical method involves ion mobility spectroscopy (IMS), which is an atmospheric time-of-flight analyzer. However, it is more difficult to operate and maintain than IR-based analyzers. Our existing IMS could potentially be used, although it is in need of repair. A new IMS analyzer (with a range of 0-100 ppm) would cost on the order of $25,000, which eliminates the purchasing of a new analyzer as a viable option at this time.

HCl – sample conditioning and transport

Tests were performed to determine whether low levels of HCl could be successfully transported through a Perma Pure drier. A 45-ppm HCl stream (humidified) flowing at 1 L/min was passed into a small, laboratory-scale Perma Pure drier. Gases exiting the drier were analyzed continuously with the Zellweger Toxic Gas Analyzer. Purge gas flow rates of

10 and 20 L/min were tested. Results of the tests indicated that the HCl stream could be passed through the drier without any detectable losses of HCl from the sample gas.

HCl – interference gases

The effect of blending NH_3 with HCl on the HCl concentration was examined. If gases are allowed to cool, ammonium chloride will form and may deposit as a solid powder. In addition to potentially clogging sample transport lines, this obviously constitutes a loss of analyte. When a stream of 50 ppm HCl was blended with 50 ppm NH_3, the HCl readings on the Zellweger analyzer disappeared within several minutes. The HCl readings were fully restored within minutes after shutting off the NH_3 flow. The temperature necessary to prevent the formation of ammonium chloride varies, depending on the absolute and relative concentrations of NH_3 and HCl in the gas stream. The formation of ammonium chloride remains an area of concern; regardless of the type of sampling/analytical technique used. In previous work, catalytic oxidation of the gas stream was employed to destroy the hydrocarbons and NH_3, which made the detection of HCl relatively simple. In that work, IMS was used for the detection system. A variety of technical issues still remain before that approach could be used routinely.

HCl – sample line issues

Tests were performed to study the transport of HCl through various types of sample lines. A nitrogen stream containing 50 ppm HCl was used. Materials tested were PFA Teflon, 316 stainless steel, electropolished stainless steel, Silcosteel, and superalloy Inco Alloy C276. Sample transport in a 316 stainless steel gas line was poor at room temperature, but was somewhat better with the Inco Alloy C276. However, at room temperature, the HCl stream was transported most effectively using Silcosteel or electropolished stainless steel (electropolishing greatly reduces surface area and provides a chromium enrichment on the surface). In both cases, sample transport appeared to be nearly as effective as when using Teflon tubing. At temperatures of 200 and 400°C (390 and 750°F), HCl was effectively transported in all the metal lines tested. Therefore, as with NH_3 and HCN (but unlike H_2S), Silcosteel is probably not necessary for the effective transport of HCl at the 50-ppm level. However, sample lines below 200°C (390°F) should be made of Teflon or Silcosteel. As was the case with the other gases tested, only nitrogen was used as the carrier gas. It is possible that different results could be observed when using a more complex gas matrix (i.e., closer to a real gasifier stream) that provides a highly corrosive environment.

Overview of cleaning technology

Gas cleaning at elevated temperature is desirable in order to retain the sensible energy of the gas. Proven gas cleanup systems, typically oil or water scrubbers, cool the gas to near ambient temperatures. While wet scrubbers are an effective way to remove all contaminants, a significant efficiency penalty occurs if the heat cannot be recovered. Heat exchangers prior to the scrubber are likely to clog. Wet scrubbing also generates an additional waste stream.

Hot gas cleanup technology removes contaminants while preserving the sensible energy in the producer gas. However, hot gas cleanup technology is not commercially available for biomass applications. Ceramic filters are susceptible to breakage due to thermal and mechanical shock and exhibit intolerance to certain minerals. Metal filters are an alternate hot gas cleanup technology but have not yet been fully developed. Tarry substances in the gas stream may plug both ceramic and metal filters if not operated at sufficient temperatures. Alternatively, soot may form if the filters are operated at too high of temperatures. Moving bed filters are able to capture particles on granular material at elevated temperatures. Its capability for removing trace contaminants, however, is essentially unexplored.

Moving bed granular filter

Squires and Pfeffer [4] were among the first to consider the use of granular beds for control of fly ash emissions. Reported collection efficiencies were as high as 99.8%. Lippert and coworkers [5] reported collection efficiencies of essentially 100% for fixed beds operated at superficial velocities less than 0.4 m/s. Significantly, they attributed these outstanding results to the formation of a dust cake at the surface of the beds, a result confirmed by tests with Plexiglas models operated at ambient conditions. It was hypothesized that dust bridges the gaps between individual media granules and the collection mechanism shifts from interception deep within the bed to impaction at the freeboard-bed interface.

The use of moving beds as filters dates back to the 1940's [6]. Some of the earliest designs employed cross-flow configurations. The Dorfan Impingo filter [7], offered commercially in the 1950's, used 1.3 cm to 3.8 cm pebbles enclosed in 30 cm thick panels. Several decades later, the Combustion Power Company developed a cross-flow filter in which the gas flowed radially outward through an annular moving bed of 3 mm to 6 mm pea gravel [8]. Plugging of the screens that enclosed the granular media was often a problem in this design. Combustion Power Company went on to develop a screenless MBGF to avoid plugging problems. The resulting design appears to be the first parallel flow MBGF. Granular material was fed to the surface of the bed through a complex of eight, gravity-fed pipes. Collection efficiency was 99% for particles greater than 4 μm diameter and exceeded 93% for smaller particles. Some of the literature published on this filter suggests that most of the dust capture occurred in a zone very close to the injection point of gas into the bed.

Based on observations by other researchers that formation of a dust cake is important to efficient dust collection for fixed bed granular filters, we have developed a new concept for a MBGF that makes use of this phenomenon. The goal is to establish a quasi-steady dust cake that is continuously or periodically renewed on the upstream side of the dust cake and swept away on the downstream side.

In the proposed filter, granular material moving downward by gravity spills from a centrally located dipleg to form an interfacial region where dust cake forms and most particulate removal occurs. The lower edge of the filter cake is dispersed by the downward flow of granular material while the upper interface is continuously covered by a fresh layer of granular material cascading from the dipleg above the interface. In this fashion, the interface establishes a dust cake of quasi-steady thickness, which is controlled to give high collection efficiency and acceptable pressure drop.

In a recent paper [9], we describe three innovations in development of a new MBGF: a *tangential gas inlet*, a *flow straightening section*, and a *screened gas disengagement section*. As illustrated in Figure 2, the gas enters the filter through a *tangential inlet*, which imparts a cyclonic motion to the gas flow. Inside the filter, the gas swirls downward towards the interface between the gas and granular bed. By imparting cyclonic flow, the momentum of the gas is preserved, reducing pressure drop normally associated with sudden expansion into a filter. However, bed granules and dust cake on the surface of the bed would be disturbed unless the radial component of the gas flow is redirected in the axial direction before the gas reaches the bed surface.

A *flow straightening section*, consisting of evenly spaced fins projecting radially about the circumference of the annular space above the surface of the bed, accomplishes this redirection. The flow-straightening section also evenly distributes the gas flow over the surface of the interface region, which is important to the efficient utilization of the filter media. Gas cleaning is hypothesized to occur primarily at this interface. The accumulation of dust particles on the granules and in the voids between granules forms a thin dust cake, which aids in the capture of dust particles in the gas flow.

The *gas disengagement region* requires a special configuration to allow high gas flows through the filter. The upward flowing gas induces a drag on the granules that causes the bed to expand and eventually fluidize, an undesirable behavior that limits gas throughput for the filter. We have designed a gas disengagement section consisting of a small diameter feeder tube conveying granular material to a larger diameter downcomer. At low gas velocities, the granules from the feeder tube spread out into a conical pile much like the one in the engagement section. However, at high gas velocities, these particles expand upward against an annular porous plate or screen that prevents their continued expansion. The screen allows gas to exit the filter while retaining granular material.

Catalytic destruction of tars

The use of a catalytic reactor downstream of the gasification reactor has proved an effective approach to catalytic tar destruction [10]. A variety of catalysts have shown significant ability to destroy tar in gasifier streams. These catalysts include dolomite [11-12], nickel- and alumina-based catalysts [13], and various proprietary catalysts [14-15]. System variables such as biomass composition, residence time, and reactor temperature play important roles in the successful application of these catalysts.

The use of a guard bed of inexpensive catalytic material upstream of a metallic catalyst bed has been demonstrated to improve the life of the metallic catalysts [16]. The inexpensive mineral catalyst converts many of the heavy tars, while the metallic catalyst serves to “polish” the gas stream, reducing tar concentrations to very low levels. Lifetime tests have not been reported for catalysts protected by guard beds, but Milne et al. [17] recommend this approach to catalytic tar destruction.

Discussion of equipment and methodologies

Tar and particulate determination

The sampling systems upstream and downstream of the MBGF (designated as the inlet and exit sampling systems, respectively) are designed to separately capture particulate and tar as well as measure gas composition. As illustrated in Figure 3, each sampling system consists of a sample probe, a heated sintered-metal particulate filter, an impinger train to collect tar, a vacuum pump with a bypass control valve, and a rotameter. Additionally, gas exiting the vacuum pumps can be directed to a Varian Model CP2003 Micro-Gas Chromatograph for determination of gas composition. Figure 4 is similar to Figure 3 but includes the sampling system for the catalytic reactors.

Accurate quantification of particulate loading in the producer gas entering and exiting the MBGF mandates the use of isokinetic sampling. The velocity in the producer gas duct downstream of the MBGF was measured with an S-type pitot tube [18] from United Sensor Corporation. This velocity was temperature corrected to the positions of inlet and exit particulate sampling. Isokinetic sampling was obtained by matching the velocity at the tip of the sampling probe with the velocity in the producer gas duct. The average gas velocity in the probe was calculated by dividing the volumetric flow rate in the sampling line, as measured with a Dwyer VFB series rotameter, by the cross-sectional area of the sampling probe. The by-pass valve across the vacuum pump was used to control volumetric flow rate.

Particulate matter in the sampling lines was collected with sintered metal filters sized appropriate to the dust loading at the inlet and exit of the MBGF. The inlet sampling system employed a Mott Hyline Series cylindrical sintered metal filter of 0.06 m (2.5 in) diameter and 0.23 m (9 in) length, designed with a cut size of 0.5 μm. The exit sampling system employed a Mott 6300 Series sintered metal filter, which consists of seven individual porous cups with total surface area of 0.006 m^2 (10 in^2). These filters were operated in ovens maintained at 450 °C to prevent condensation of high molecular weight tars, which would have plugged filter pores as well as made it difficult to distinguish between tar and particles. In addition, sample lines upstream of the impinger trains were heated to 450 °C with Cole Palmer 12.5 cm (0.5 inch) dual-element heating tapes.

Different methods were employed to collect tar in the inlet and outlet sampling systems. The inlet sampling system provided quantitative measurement of various tar fractions by means of six glass impinger bottles filled with glass beads and dichloromethane solvent [19]. The first four bottles were immersed in an ice bath while the last two bottles were immersed in an acetone/dry ice bath. The first and sixth bottles were filled with glass beads, while the second, third and fourth bottles were filled with dichloromethane. The fifth bottle was filled with both glass beads and dichloromethane. The exit sampling system simply captured tar without quantification by means of four impinger bottles filled with glass wool and immersed in an ice bath. For both systems, gas leaving the impinger trains passed through vacuum pumps before exiting through wet test meters to accurately determine the total (dry) gas volume sampled.

In preparation for a test, the impinger bottles for both upstream and downstream sample lines were packed, greased, and inspected before installation. The weight of both inlet and exit sampling filters were recorded prior to installation into the sampling systems. Sampling did not commence until the MBGF was preheated to 450°C (840°F), which was accomplished by operating the gasifier in combustion mode at 790°C (1450°F) for an hour or more. During this interval granular material was not removed from the MBGF, which helped reduce heat-up time. In addition, this start-up procedure helped establish a filter cake in the gas-contacting region, which was important in quickly achieving steady-state pressure drop across the MBGF. Once the MBGF reached 450°C (840°F) granular material was removed from the filter at the desired rate.

At this point the impinger baths were filled with water/ice or acetone/dry ice mixtures as specified previously and the gasifier was gradually transitioned to gasification mode (achieved by increasing the flow rate of fuel to the gasifier). When all of the desired operating conditions were reached sampling commenced by turning on the vacuum pump and adjusting the flow rate through the isokinetic sample lines.

Upon completion of testing, nitrogen was injected into the sample lines just downstream of the sample probe in an effort to flush dust that may have settled in the sample lines and capture it in the sampling filters. Following this injection, all valves were closed, the vacuum pump shut off, power to heat tapes turned off, and the gasifier transitioned back to combustion mode by decreasing fuel flow rate. After the system cooled off, sampling filters were removed and weighed to determine the amount of particulate matter captured.

Particulate concentrations at the inlet and outlet of the MBGF, C_{inlet} and C_{exit}, respectively, were calculated by dividing the weight change in the appropriate filter by the total gas flow through the sampling line. The particulate collection efficiency, η, of the MBGF was determined from the relationship:

$$\eta = 1 - \frac{C_{exit}}{C_{inlet}}$$

Particles collected in the sampling filters were subjected to scanning electron microscopy (SEM) with energy-dispersive spectroscopy for bulk elemental determination. The SEM was also used to estimate the mean particle diameter of the dust.

At the completion of a test, dichloromethane was rinsed through sample lines connected to the impingers to remove any tar condensed in them. This rinse liquid and impinger liquid were combined and stored in sample bottles until the tar analysis was performed. This analysis began by filtering out solids and then decanting water from the mixture. The volume of the remaining dichloromethane/tar solution was measured followed by distillation at 75ºC (170°F) for 30 minutes to separate heavy tar from the solution. The result was three fractions of tar: light tar (still dissolved in the dichloromethane), heavy tar (the distillation residue), and soluble tar (dissolved in the decanted water). Each tar fraction was sent out for total organic carbon (TOC) analysis, which was used to estimate the weight of tar in the light tar and soluble tar fractions by assuming the average molecular formula for these fractions was $(CH_2)_n$. The weight of heavy tar was determined directly by weighing the distillate.

Moving Bed Granular Filter

The filter, illustrated in Figure 2, consists of five major sections: a cyclonic inlet, a flow straightening section, an interfacial gas contacting region, a granule downcomer, and a gas disengagement section. The cyclonic gas inlet imparts a radial component to the gas flow for the purpose of reducing entrance pressure losses. This inlet consists of a 0.914 m (36 in) diameter cylinder of 0.762 m (30 in) length constructed of mild steel. Once inside the MBGF, the hot gas swirls radially downward until it reaches a flow straightening section. This section serves to redirect the gas uniformly and perpendicularly into the gas-contacting region while preventing entrainment of deposited dust. Each of the 80 flow straighteners is 0.076 m (3 in) long and 0.06 m (2.6 in) wide. The majority of the dust is filtered from the gas flow in this interfacial region while further dust removal occurs downstream. After negotiating the interfacial region, the flow of clean gas is directed upward through the granule downcomer until it reaches the disengagement section. The disengagement section consists of a 0.76 m (30 in) diameter cylinder of 0.61 m (24 in) length constructed of mild steel. In this section the clean gas passes through a stainless steel mesh screen, which retains granular material and prevents the moving bed from fluidizing. Without this screen, granules would tend to be entrained in the exiting gas stream.

Granular material is gravity fed to the filter from a feed hopper above the filter by means of a 0.07 m (3 in) diameter delivery pipe that passes through the center of the mesh screen (gas does not flow into the delivery pipe because the feed hopper is sealed). The capacity of the filter is 0.45 m^3 (15.9 ft^3) while that of the hopper is 0.73 m^3 (25.8 ft^3). Dust-laden granular material exiting the bottom of the filter is augured into a barrel for subsequent disposal. Granular bed material used for testing were 3 mm diameter, smooth (non-porous) silica pebbles obtained from American Materials Corp. of Eau Claire, Wisconsin.

Catalytic reactors

The tar cracking system consisted of a guard bed reactor of dolomite stone and a metallic catalyst reactor in series. The guard bed was designed to capture fine particulate as well as steam-reform heavy tars and absorb hydrogen sulfide. The metallic catalyst bed, which is susceptible to coking during the destruction of heavy tars and poisoning by hydrogen sulfide, was designed to convert lighter tars into carbon monoxide and hydrogen. The two reactors, which were identical in construction, were operated as fixed beds.

Each reactor has an internal diameter of 22 mm (0.875 in) and can be filled to various depths to achieve space velocities between 1500 h^{-1} and 6000 h^{-1}. Each was mounted in an electrically heated oven to maintain a desired temperature for each experiment. Two thermocouples were mounted in each reactor: one at the center of the fixed bed, which was moveable for obtaining longitudinal temperature profiles, and the other at the perimeter of the bed.

Three kinds of commercial steam reforming, Ni-based catalysts were evaluated in our tests. The Imperial Chemical Industry produced ICI46-1 while Z409 and RZ409 are products of Qilu Petrochemical Corp., P.R. China. The compositions of the catalysts are listed in Table 2. All three catalysts contain alkali additives, such as potassium, calcium and magnesium oxides, which eliminate the formation of coke on the catalyst by converting carbon-to-carbon monoxide by the following reaction:

$$C + H_2O \rightarrow CO + H_2$$

Although the potassium promoter might be expected to readily diffuse out of the catalyst, it is in the form of potassium aluminosilicate, which releases the potassium very slowly, resulting in long service life.

Catalysts are usually activated before use by exposure to a reducing environment, typically a mixture of N_2 and H_2 at 750-850ºC (1380-1560°F) for several hours. However, in our experiments, catalysts ICI46-1 and Z409 were not reduced. RZ409 is a reduced form of Z409 prepared by the manufacturer. The as-received catalysts were in the form of 15 mm rings. The rings were crushed and sifted to obtain 0.9-2.0 mm diameter particles for use in our reactors. The pore size distributions of the crushed and sieved catalyst particles were obtained by mercury porosimetry. Typical characteristics for catalysts used in steam reforming are: specific surface area of 16-23 m^2/g; total pore volume of 0.14-0.18 cm^3/g; and average pore diameter of 200-500Å.

Table 2. Chemical Composition of Tested Catalysts

Catalyst	Active Component	Promoter	Carrier	Preparation
ICI46-1	NiO	CaO, K2O	SiO2, Al2O3	Not reduced
Z409	NiO	MgO, K2O, FeOx	SiO2, Al2O3	Not reduced
RZ409	NiO	MgO, K2O, FeOx	SiO2, Al2O3	Reduced

Discussion of Results

The experiments employed a mixture of waste seed corn and waste soybeans as fuel, both of which are waste streams of interest to one segment of the agricultural processing industry. Feed rates of 150-180 kg/hr (325-400 lb/hr) were common. The gasifier operating temperature was commonly set at 730 ºC (1350 ºF).

Particulate and the moving bed granular filter

The MBGF has been successfully operated for over 150 hours on producer gas at a nominal flow rate of 345 nm^3/h (200 scfm) with dust loadings on the order of 60 g/m^3 (26 gr/ft^3) and “heavy” tar loading of about 85 g/m^3. Operations have been trouble free, producing continuous removal of dust from producer gas at temperatures exceeding 510 ºC (950 ºF). These high temperatures prevent tar from condensing on the granular media, yielding dry, non-sticky dust in the granular media exiting the MBGF.

Pressure drop across the MBGF as a function of time is illustrated in Figure 5 for two trials of the filter representing different granular media flow rates 3.3 kg/h (10 lb/hr) and 6.6 kg/h (15 lb/hr). Pressure drop was in the range of 60 – 65 mm (2.4 in of water) water early in the test while the gasifier was being preheated by combustion. Once the reactor was transitioned to gasification, the pressure drop increased to the range of 75 – 80 mm water (3 in of water); this increase is the result of higher gas flow rate during gasification compared to combustion. The trends toward constant pressure drop with increasing time suggest an approach toward steady state. However, post analysis of results indicated that dust loading in the gas inlet was equivalent to 12 – 13 kg/hr (26 – 28 lb/hr), which is lower than the apparent media removal rate; therefore, it does not appear that we were removing material from the bed fast enough to achieve steady operating conditions. Additional testing will be required.

Detailed gas and particulate analyses were performed for the test operated at a granular media flow rate of 3.3 kg/h (10 lb/hr). The composition of the producer gas in this test is reported in Table 3, which is typical of air-blown gasification. We were not able to obtain gas composition at the exit of the MBGF although no change was expected for the non-porous silica rock employed at granular media in these trials. Dust collection efficiency was 97 - 98 %, although these values were not obtained under steady-state operating conditions.

Table 3. Composition of producer gas

Constituent	H_2	CO	CH_4	C_2H_4	CO_2	N_2
Vol-%	11.7	10.2	4.4	2.8	14.8	50.4

Scanning electron micrographs of dust collected at the inlet and exit of the filter were prepared to compare the size of particles at the two locations. Figure 6 shows that dust at the inlet contains large quantities of particles in the size range of 25 – 30 μm. At the outlet, there are few particles as large as 10 μm and most appear to be in the size range of 2 – 3 μm.

Elemental analyses of the inlet and exit streams to the MBGF, illustrated in Figure 7, show no dramatic change in dust composition. Of particular significance in the elemental analysis is the absence of silicon enrichment in the exit dust, which might be expected if the silica pebbles were releasing fine dust to the gas stream as it passed through the filter. Granular media must be non-friable to be effective in the MBGF.

Tar and the catalytic reactors

Typically, the producer gas had total tar concentration of 108.9 g/nm^3 of which about 80% was heavy tar (as defined above). The carbon associated with tar in the producer gas was distributed among the three tar fractions as follows: 27.8 g/nm^3 from the heavy tar; 13.6 g/ nm^3 from the light hydrocarbons; and 5.7 g/nm^3 from the soluble tar fraction. Thus, the carbon concentration for the combined tar fractions was 47.1 g/nm^3, which represents a steam/TOC ratio of 2.8.

For all catalysts and operating conditions tested, no visible tar was observed in the lines after the catalytic reactor or in the impingers. The dichloromethane recovered after these tests was clear with no hint of color, indicating the absence of heavy tar at the exit of the catalytic reactor system.

Quantitative analysis of tar in the producer gas exiting the catalytic reactor system was performed for only one test: the ICI 46-1 catalyst operated at 800ºC (1470ºF) with a space velocity (SV) of 3000 h^{-1} and a steam/TOC ratio 2.8. Analysis confirmed that no measurable heavy tar was present in the exit stream. However, 6.8 g/nm^3 of light tar and 0.7 g/nm^3 of soluble tar were detected, which represents 7.5g/nm^3 of total tar at the exit to the catalytic reactor system. Although this may appear to be a relatively large concentration, it includes organic compounds that are not considered "tar" in many applications since they are not condensable. Furthermore, it represents a 95% reduction in total tar and greater than 99% reduction in heavy tars. The total concentration of carbon associated with tar in the producer gas was 6.4 g/nm^3, which represents a carbon conversion efficiency of 86%.

Gas samples were taken before the guard bed and after the catalytic reactor to provide information about overall system performance. Gas sampling was done every half-hour after steady operation of the gasifier and catalytic reactors were achieved. Gas samples were analyzed off-line by gas chromatography using a Varian Micro-GC CP-2003 Quad equipped with Molsieve 5A BF, Poroplot Q, and CP-Sils CB columns and a thermal conductivity detector with argon as carrier gas for the first column and helium as carrier gas for the second and third columns. The first column gave H_2, O_2, N_2, CH_4, and CO concentrations; the second and third columns yielded CO_2, C_2H_4 and some light hydrocarbons.

The effects of space velocity and catalytic bed temperature on gas composition (H_2, CO, CO_2, CH_4, and C_2H_4) for each of the three catalysts are presented in Figures 8 – 13. In all tests, the inlet temperature to the tar destruction system was 650°C (1200ºF). In these figures "GB Inlets" refers to the concentration of a gas species at the guard bed inlet (upstream of the tar destruction system) and "CR Outlet" refers to the concentration of a gas species at the catalytic reactor outlet (downstream of the tar destruction system). In general, H_2 and CO_2 increase while CO decreases in the producer gas as it passes through the tar destruction system, as expected for steam reforming reactions acting in tandem with the water-gas shift reaction. Concentrations of CH_4 and C_2H_4 decrease in the producer gas. The decrease in CH_4 was about 0.2-1.0 vol.% while the decrease in C_2H_4 was about 0.5-1.5%. Although these low molecular weight hydrocarbons can be products of steam reforming of tar, they are also susceptible to further steam reforming to CO and H_2. The ICI46-1 catalyst showed no deactivation during 12 hours of testing while the Z409 and RZ409 catalysts showed no deactivation during 18 hours of testing.

The effect of space velocity on hydrogen concentration in the producer gas is illustrated in Figure 8 for catalysts ICI46-1, Z409 and RZ409 (T_{CR} = 800°C; Steam/TOC = 2.8). There was little evidence that decreasing space velocity significantly increases hydrogen production (observed variations are within the uncertainty of hydrogen measurements). The effects of space velocity on CO and CO_2 concentrations in the producer gas are illustrated in Figure 9 for catalysts ICI46-1, Z409 and RZ409. For space velocities less than 4500 h^{-1} there is no effect on CO concentration.

The concentration of CO_2 is not substantially influenced by space velocity in the range of 1500 – 6000 h^{-1}. The effects of space velocity on CH_4 and C_2H_4 concentrations in the producer gas are illustrated in Figure 10 for catalysts ICI46-1, Z409 and RZ409. No definitive trends are evident for CH_4 while C_2H_4 clearly decreases as space velocity decreases. These observations indicate that tar destruction is not mass-transfer limited.

The effect of catalytic bed temperature on hydrogen concentration in the producer gas is illustrated in Figure 11 for catalysts ICI46-1, Z409 and RZ409 (SV = 3000h^{-1}; Steam/TOC = 2.8). As expected, hydrogen production increases with increasing reaction temperature although the increase is less than 25% in going from 740°C to 820°C (1360°F to 1510°F). The effects of catalytic bed temperature on CO and CO_2 concentrations in the producer gas are illustrated in Figure 12 for catalysts ICI46-1, Z409 and RZ409. Carbon monoxide increases while CO_2 decreases with increasing temperature. The strongest effect is observed for catalyst Z409 where CO increases 40% during a temperature increase from 740°C to 820°C (1360°F to 1510°F). The large uncertainty in the data points for catalyst ICI46-1 at 820°C (1510°F) obscures the strength of the temperature effect for this catalyst. The effects of catalytic bed temperature on CH_4 and C_2H_4 concentrations in the producer gas are illustrated in Figure 13 for catalysts ICI46-1, Z409 and RZ409. No definitive trends are evident for CH_4 while C_2H_4 clearly decreases, especially for the Z409 and RZ409 catalyst which resulted in reduction greater than 85% for an increase in temperature from 740°C to 820°C (1360°F to 1510°F). These observations indicate that the rate of tar destruction is controlled by chemical kinetics.

Conclusions

Significant progress was made toward meeting the goals set out for this research project. Much has been learned about gas quality issues associated with the integration of a biomass gasifier with fuel cells or other prime movers. The design, installation, and testing of a moving bed granular filter and catalytic tar reactors are steps forward in the conditioning of the gas stream for use in a fuel cell. Analytical procedures needed to characterize the gas have been instituted for some contaminants while other procedures are yet to be tested.

Testing of a moving bed granular filter to remove dust from hot producer gas has demonstrated promising results. A filter of 0.914 m (36 in.) diameter was able to remove 97 - 98% of the 60 g/m^3 dust loading from a 345 nm^3/h (200 ft^3/min) gas flow. Pressure drop never exceeded 80 mm water (3.0 in) water in these tests. Most of the dust penetrating the filter was 2 – 3 μm in size. Virtually none of the exiting dust was from the silica pebbles used as granular media in the filter, as confirmed by elemental analysis of dust entering and exiting the filter. However, we do not appear to have operated under steady state conditions of the filter; additional testing is required.

A tar cracking system consisting of a guard bed and catalytic reactor was designed for the purpose of improving the quality of producer gas from an air-blown, fluidized bed biomass gasifier. All three metal catalysts (ICI 46-1, Z409, and RZ409) proved effective in eliminating heavy tars (>99% destruction efficiency) and increasing hydrogen concentration by 6-11 vol-% (dry basis). Space velocity had little effect on gas composition while increasing temperature boosted hydrogen yield and reduced light hydrocarbons (CH_4 and C_2H_4), thus suggesting tar destruction is controlled by chemical kinetics.

Much more research and development still needs to be done. Although the moving bed granular filter and catalytic reactors show great promise for gasifier stream conditioning, the gas quality is still not sufficient for direct use in a fuel cell. Testing and development of the moving bed granular filter and the catalytic reactors will continue. Gas analytical techniques will be tested and implemented for further characterization of the producer gas.

References

1 Smeenk, J. and Brown, R. C., "Experience with atmospheric fluidized bed gasification of switchgrass," BioEnergy '98 Conference, Madison, WI, October 4-8, 1998.

2 Dayton, D.C., Bain, R. and Ratcliff, M., "Fuel Cell Integration-A Study of the Impacts of Gas Quality and Impurities," National Renewable Energy Laboratory, NREL/MP-510-30298.

3 Fuel Cell Handbook, Fifth Edition, Oct. 2000 (CD-ROM), US Department of Energy National Energy Technology Laboratory, Morgantown, WV/Pittsburgh, PA.

4 Squires, A.M. & Pfeffer, R. (1970) *Panel bed filters for simultaneous removal of fly ash and sulfur dioxide: 1. Introduction.* J. Air Pollut. Control Assoc. **20**, 534-538.

5 Lipert, T. E. et al. (1981) Testing and verification of granular bed filters for removal of particulates and alkalies. High Temperature, High Pressure Particulate and Alkali Control in Coal Combustion Process Streams. In: *Proceedings U.S. DOE Contractors' Meeting*, CONF-810249, pp. 471-489.

6 Hall, H. J. & J. C. Munday (1946) *Purification of gases*. U.S. Patent 2,411,208.

7 Dorfan M. I. (1952) *Method and apparatus for suppressing steam and dust rising from coke being quenched.* U.S. Patent 2,604,187.

8 Saxena, S. C. et al. (1985) Particulate removal from high temperature, high pressure combustion gases, Prog. Energy Combust. Sci. **11**, 193-251.

9 Brown, R. C., Smeenk, J., and Wistrom, C., "Design of a moving bed granular filter for biomass gasification," Proceedings of the Progress in Thermochemical Biomass Conversion Conference, Tyrol, Austria, September 17-22, 2000.

10 Kurkela, E., Stahlberg, J., Laatikainan, J., Simell, P., "Development of Simplified IGCC-Processes for Biofuels," Biores. Technology, 46, pp. 37-47.

11 Alden, H., Espenas, B.G., Rensfelt, E., "Conversion of Tar in Pyrolysis Gas from Wood Using a Fixed Dolomite Bed," Research in Thermochemical Biomass Conversion, ed. by A.V. Bridgewater and J.L. Kuester, London: Elsevier Applied Science, pp 987-1001.

12 Simell, P. and Bredenburg, J.B., "Catalytic Purification of Tarry Fuel Gas," Fuel 69 (10), 1990, pp. 1219-1225.

13 Wiant, B.C., Bachovchin, D.M., and Onischak, M., "Biomass Gasification Hot Gas Cleanup Demonstration Program Status," Bioenergy '94—Sixth National Bioenergy Conference, 1994, pp. 471-478.

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14 Bain, R. and Overend, R.P., “New Gasification Technology Offers Promise for Biomass Power Plants,” Power Engineering, August 1996, p. 4.

15 Paisley, M.A., “Catalytic Hot Gas Conditioning of Biomass Derived Product Gas,” Developments in Thermochemical Biomass Conversion, Vol. 2, edited by A.V. Bridgewater and D.G.B. Boocock. London: Blackie Academic & Professional, 1997, pp. 1209-1223.

16 Narvaez, I., Corella, J., and Orio, A., “Fresh Tar (from a Biomass Gasifier) Elimination over a Commercial Steam-Reforming Catalyst: Kinetics and Effects of Different Variables of Operation,” Ind. Eng. Chem. Res., 36, 1997, pp. 317-327.

17 Milne, T. A., Abatzoglou, N., and Evans, R.J., “Biomass Gasifier ‘Tars’: Their Nature, Formation, and Conversion,” NREL/TP-570-25357, 1998.
18 Pitot-Static Tubes Method. ASHRAE. Equation 5, page 14.16.

19 Albrecht, J., Deutsch, S., Kurkela, E., Simell, P., Sjostrom, K. 1998. “Provisional Protocol For The Sampling And Analysis of Tar and Particulates In The Gas From Large-Scale Biomass Gasifiers. Prepared by a working group of the biomass gasification task of the IEA Bioenergy Agreement.”

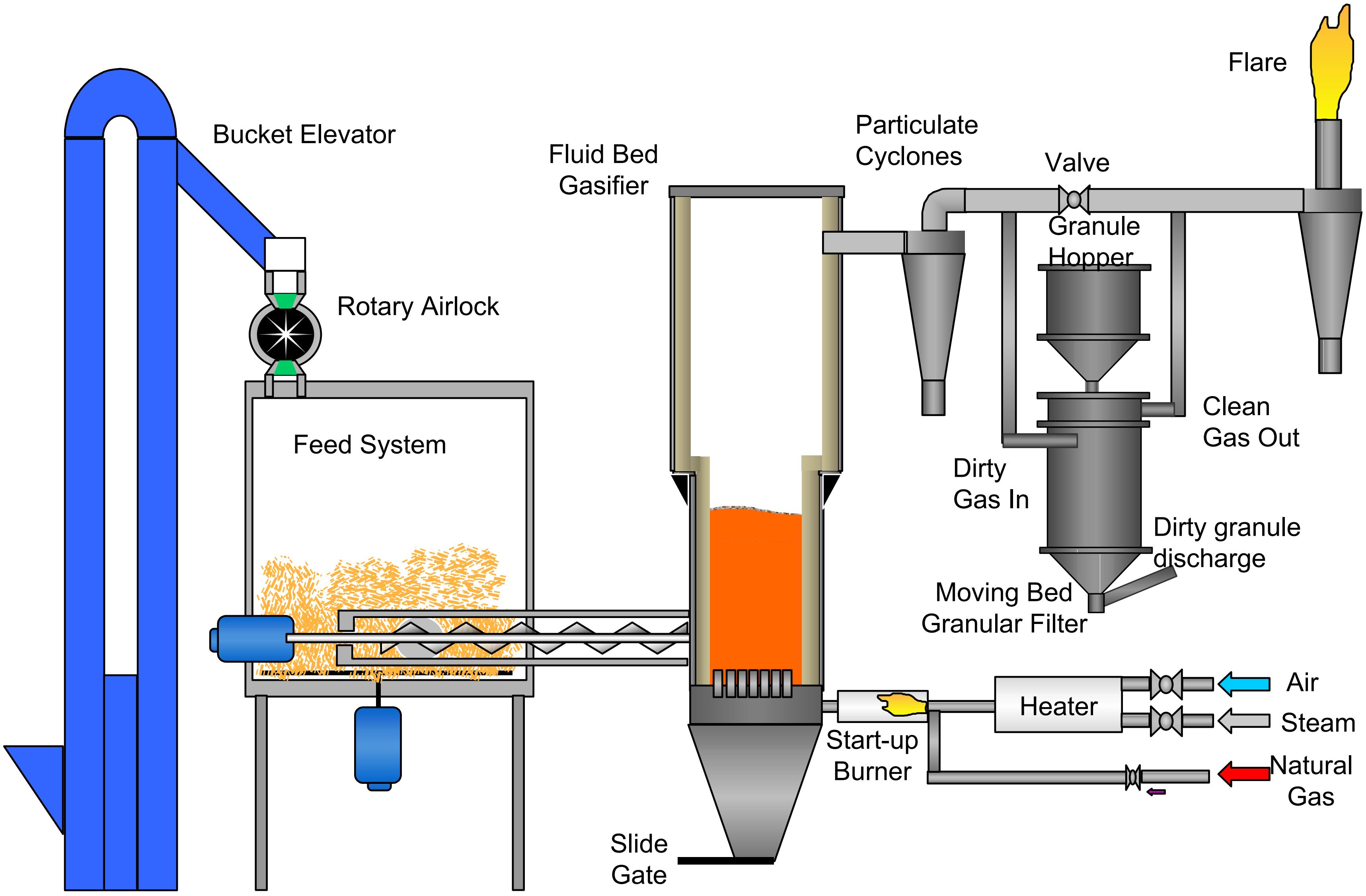


Figure 1. Schematic of fluid bed gasifier and moving bed granular filter.

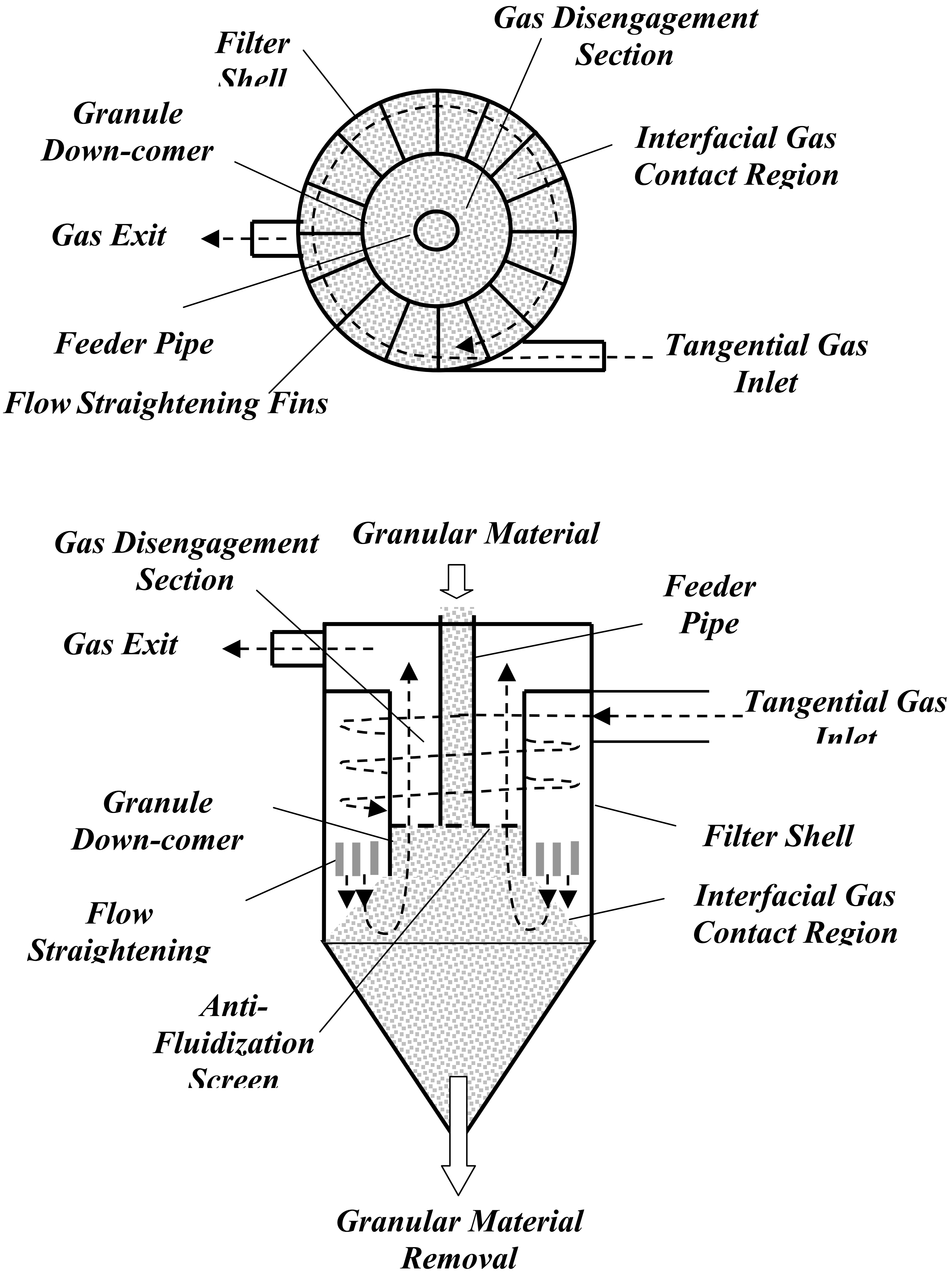


Figure 2. Operating principle of moving bed granular filter

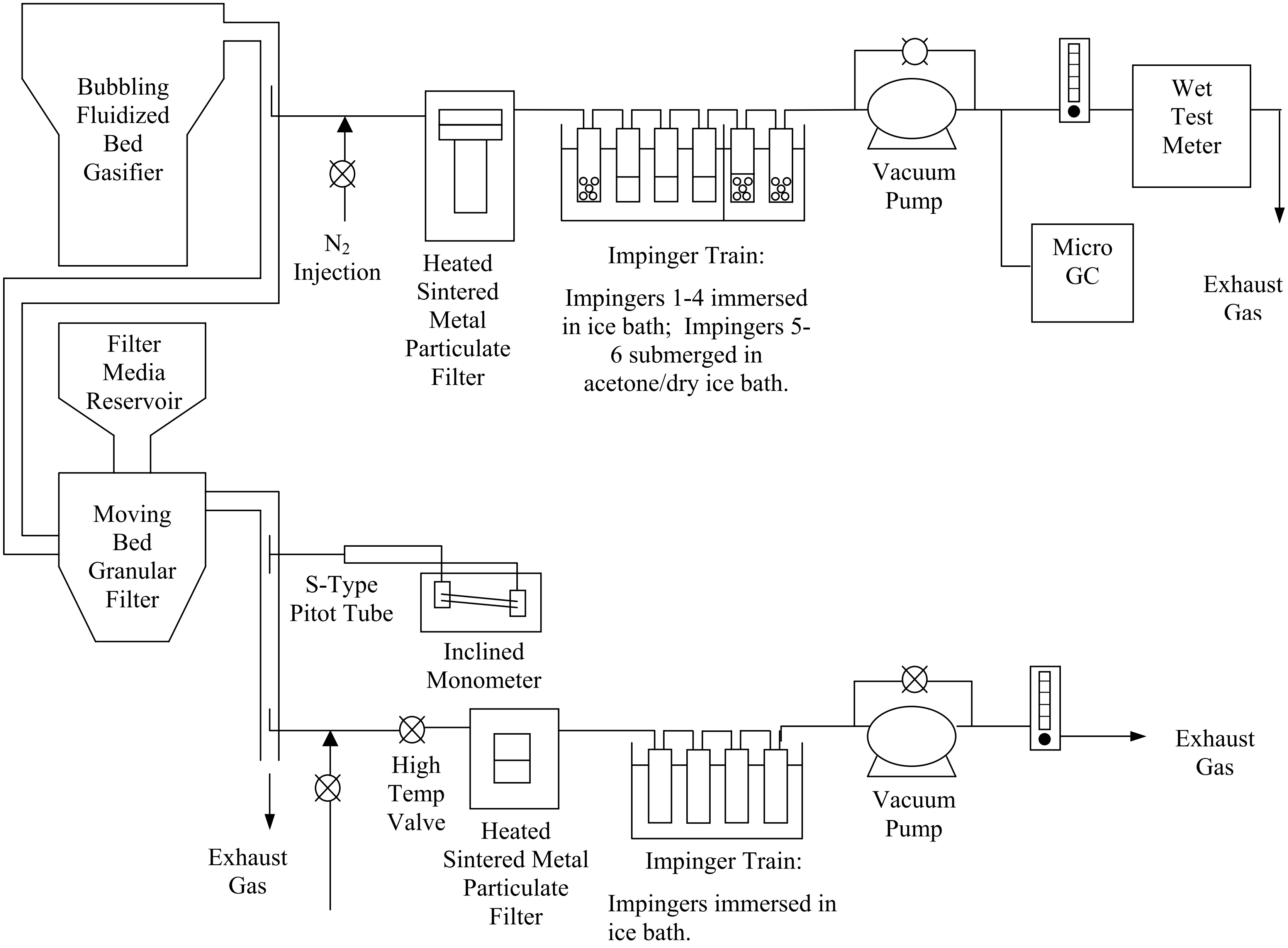


Figure 3. Schematic of particulate sampling systems.

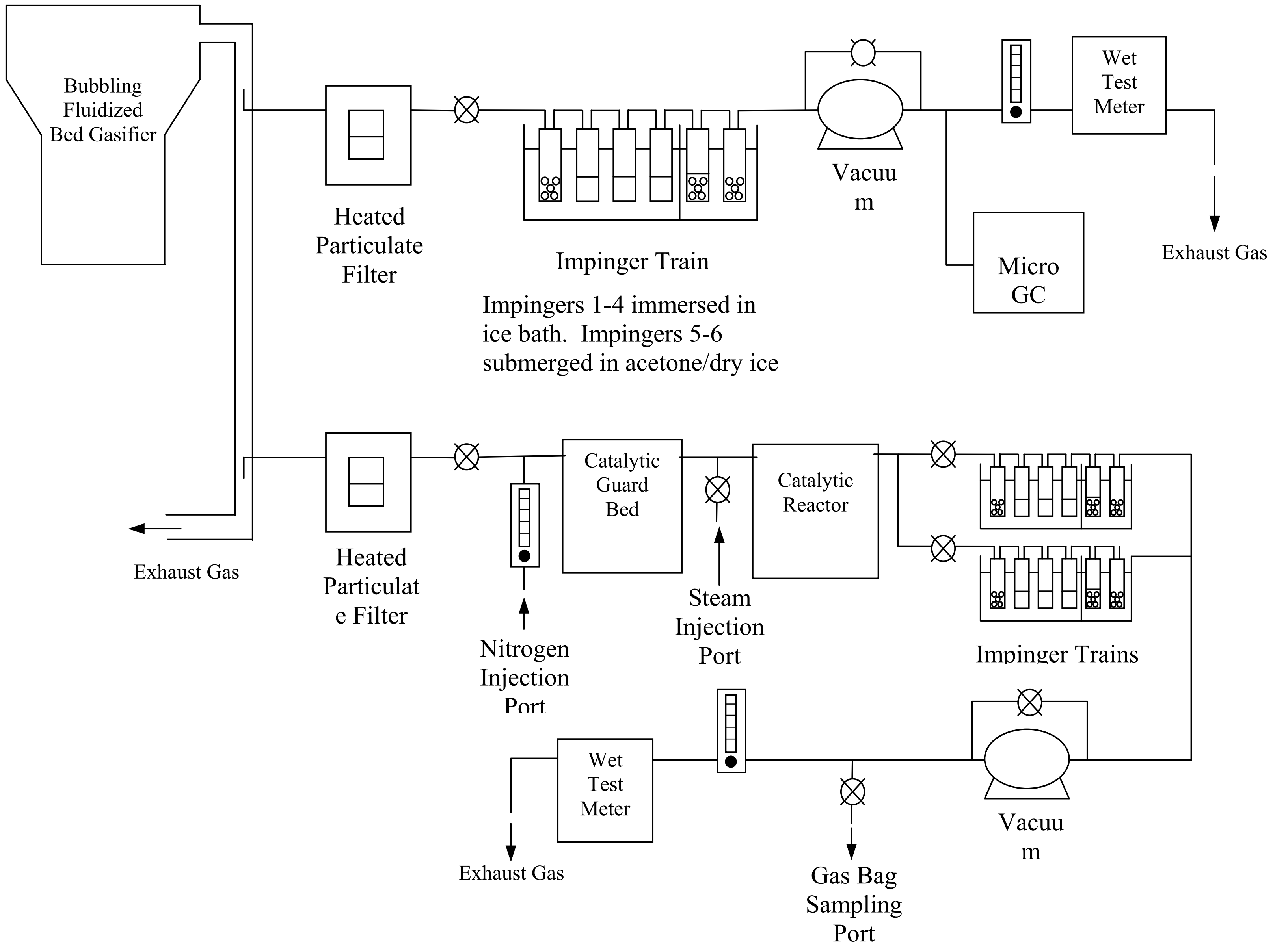
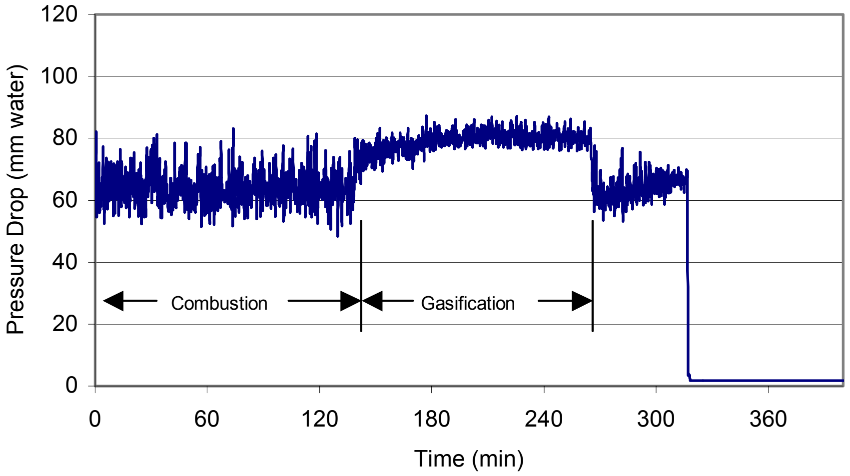


Figure 4. Schematic of experimental system to investigate catalytic tar cracking.



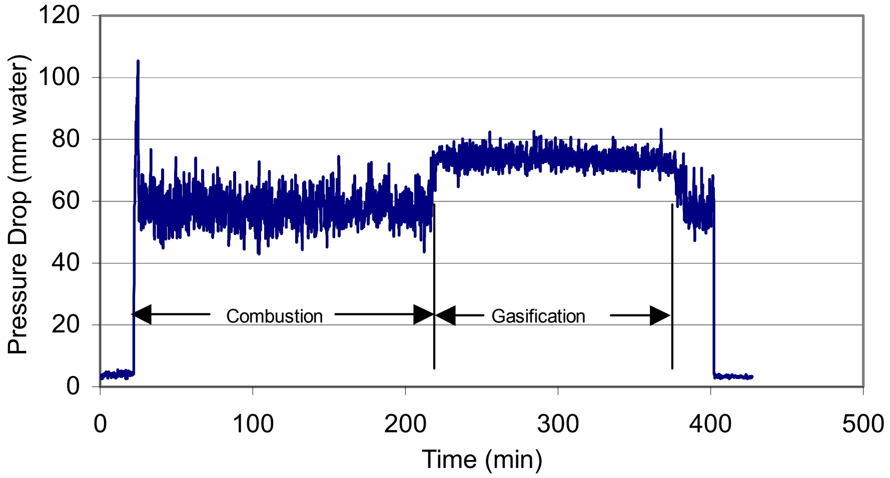


Figure 5. Pressure drop through the moving bed granular filter (80 scfm, 650 C) for various granular flow rates (a) 10 lb/h and (b) 15 lb/h.

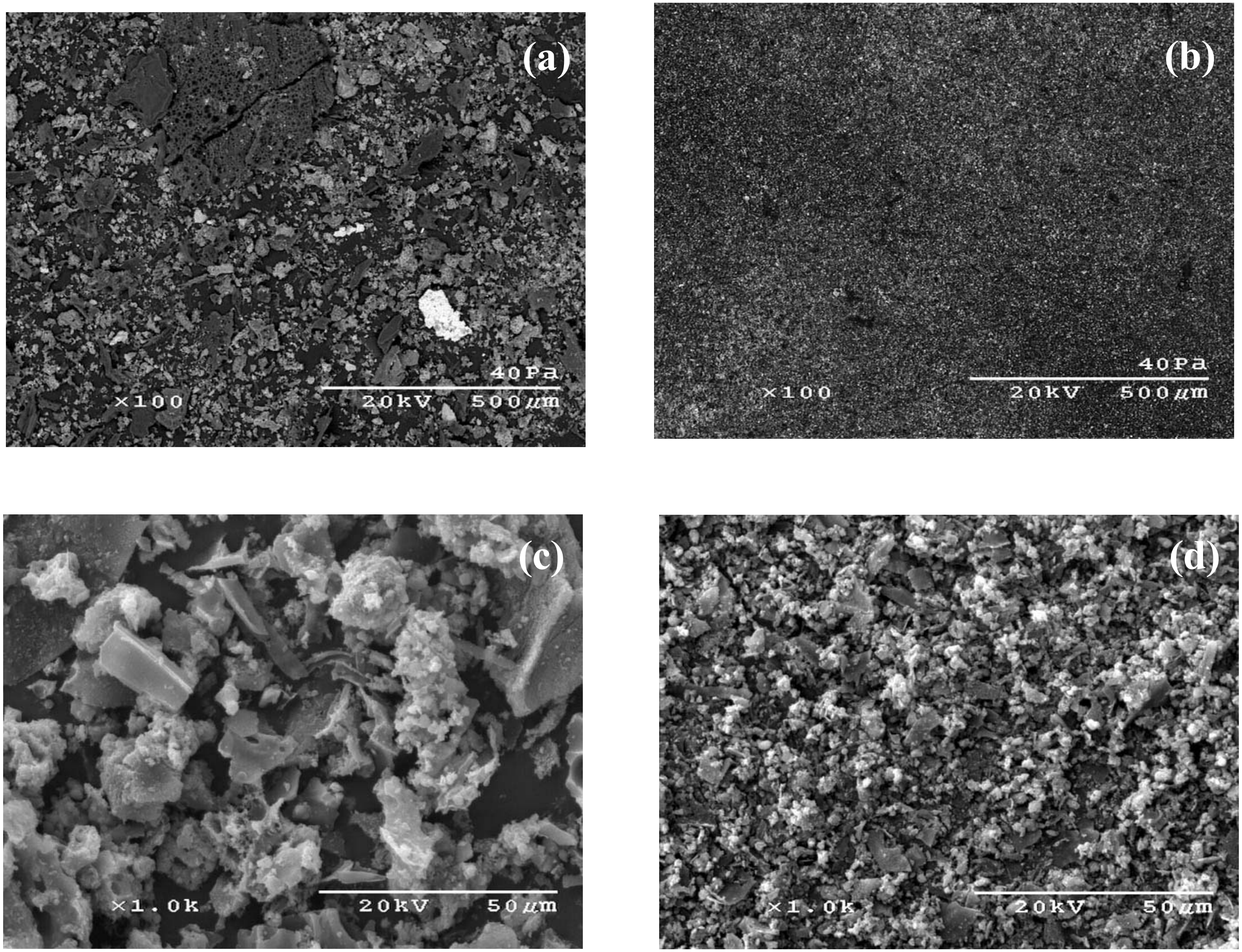


Figure 6. Scanning electron microgaphs of isokinetically sampled dust from producer gas. (a) Upstream of the MBGF at 100x magnification, (b) Downstream of the MBGF at 100x magnification, (c) Upstream of the MBGF at 1000x magnification, (d) Downstream of the MBGF at 1000x magnification.

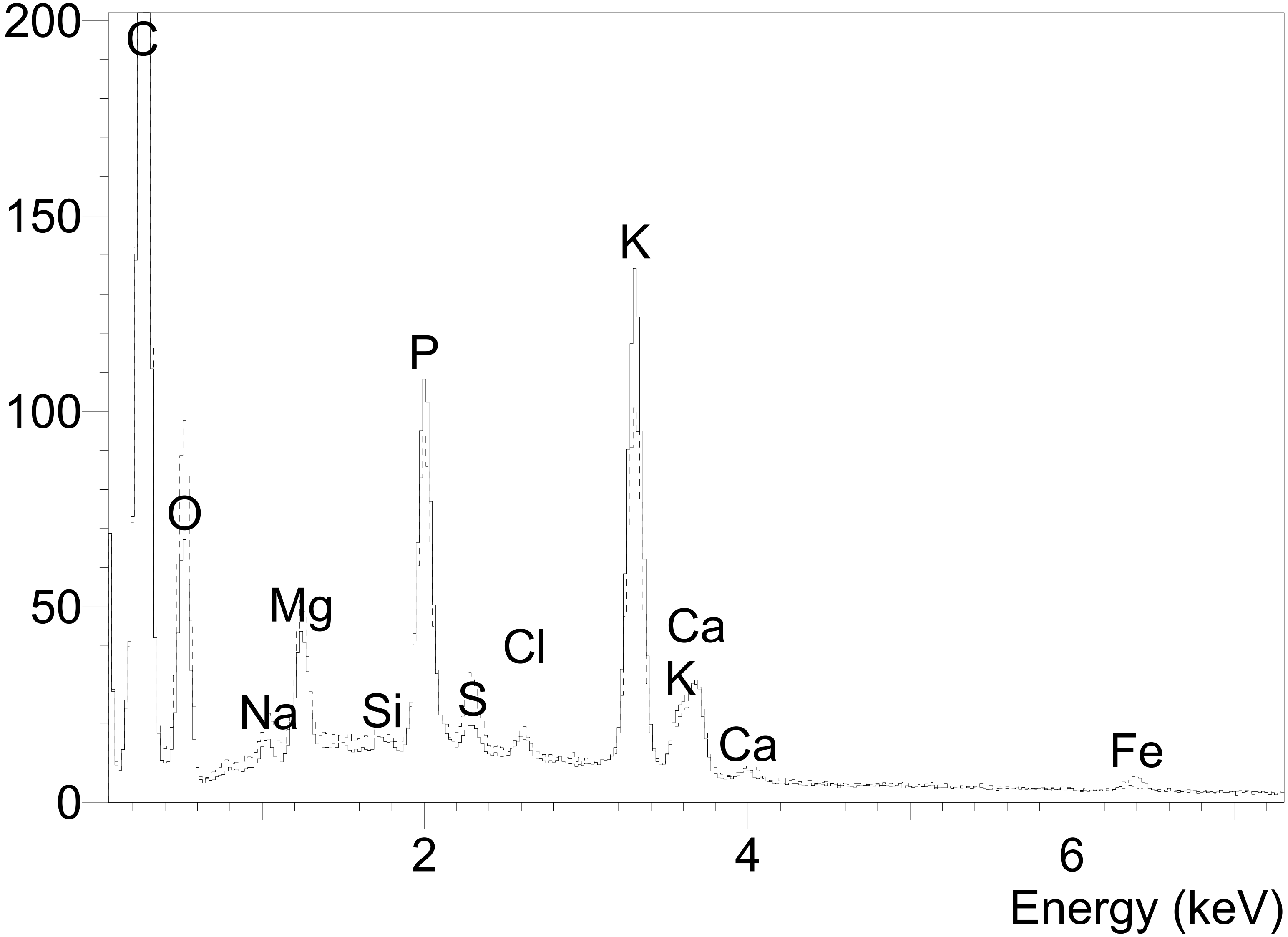


Figure 7. Elemental composition of dust in producer gas (solid line – inlet stream; dashed line – exit stream).

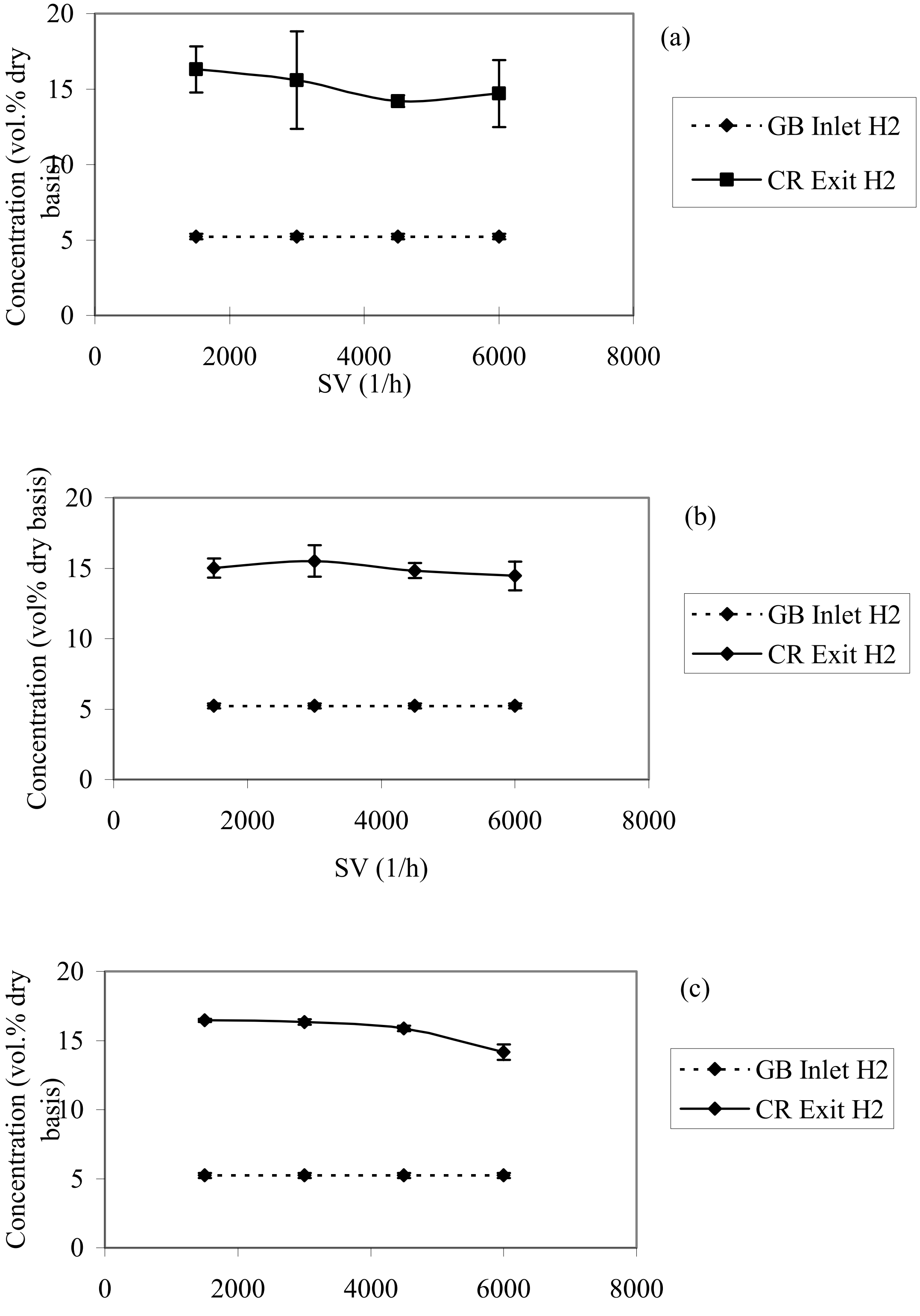


Figure 8. H_2 concentration in producer gas at the inlet of the guard bed and the exit of catalytic bed as a function of space velocity: T_{GB} = 650°C; T_{CR} = 800°C; Steam/TOC = 2.8. (a) ICI46-1, (b) Z409, (c) RZ409.

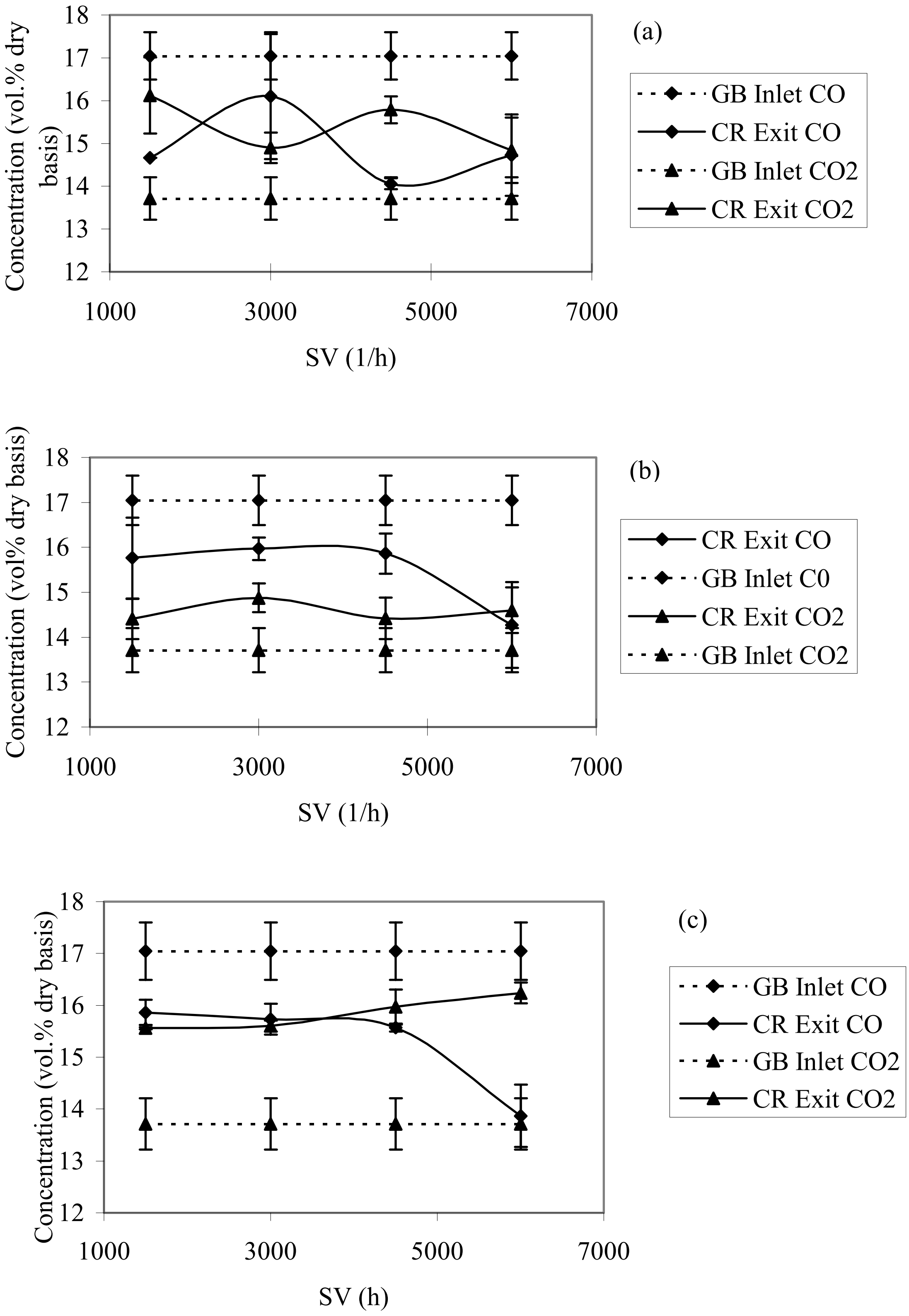


Figure 9. CO and CO_2 concentrations in the producer gas at the inlet of the guard bed and the exit of catalytic bed as functions of space velocity: T_{GB} = 650°C; T_{CR} = 800°C; Steam/TOC = 2.8. (a) ICI46-1, (b) Z409, (c) RZ409.

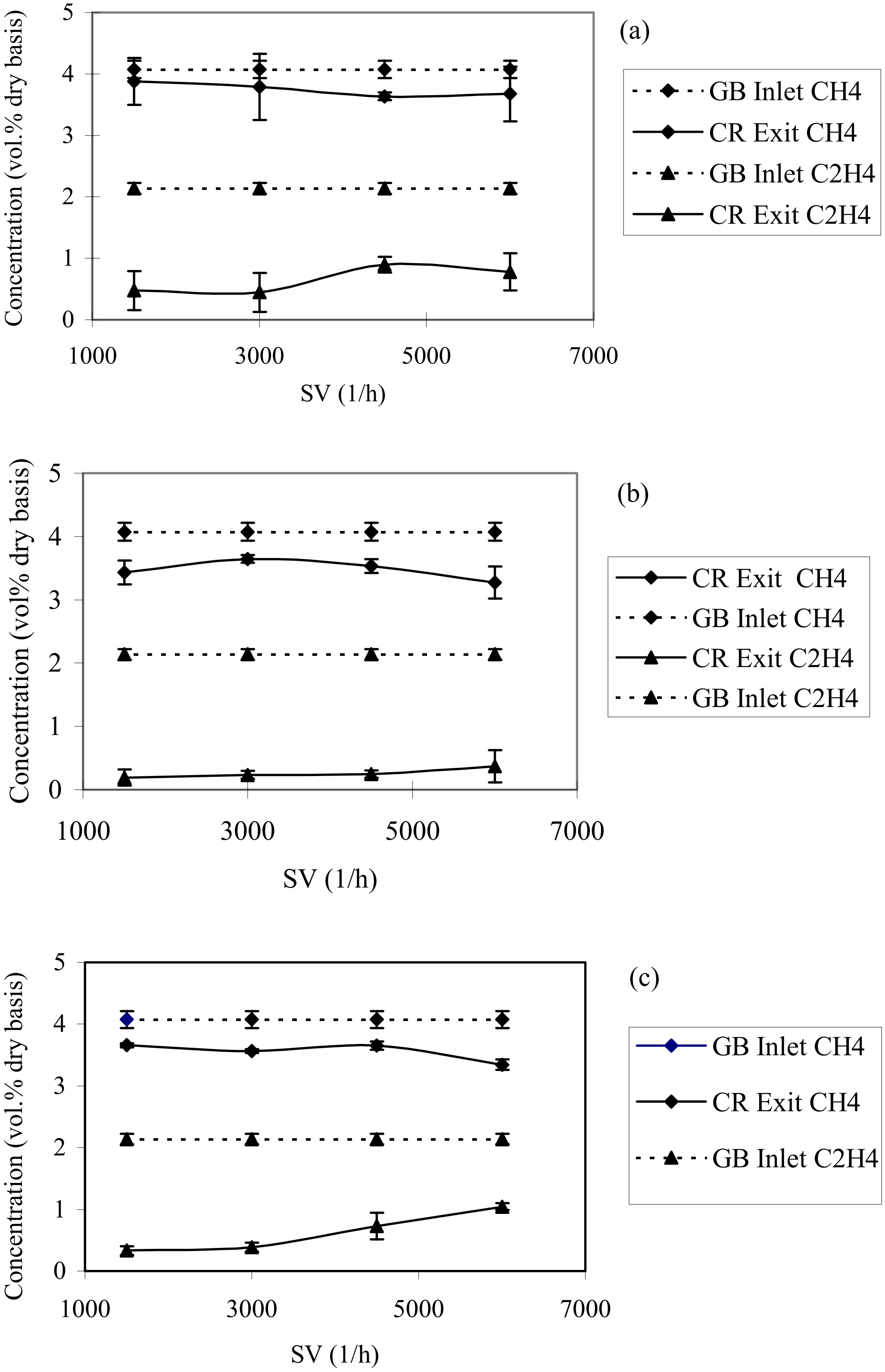


Figure 10. CH_4 and C_2H_4 concentrations in the producer gas at the inlet of the guard bed and the exit of catalytic as functions of space velocity: T_{GB} = 650°C; T_{CR} = 800°C; Steam/TOC = 2.8. (a) ICI46-1, (b) Z409, (c) RZ409.

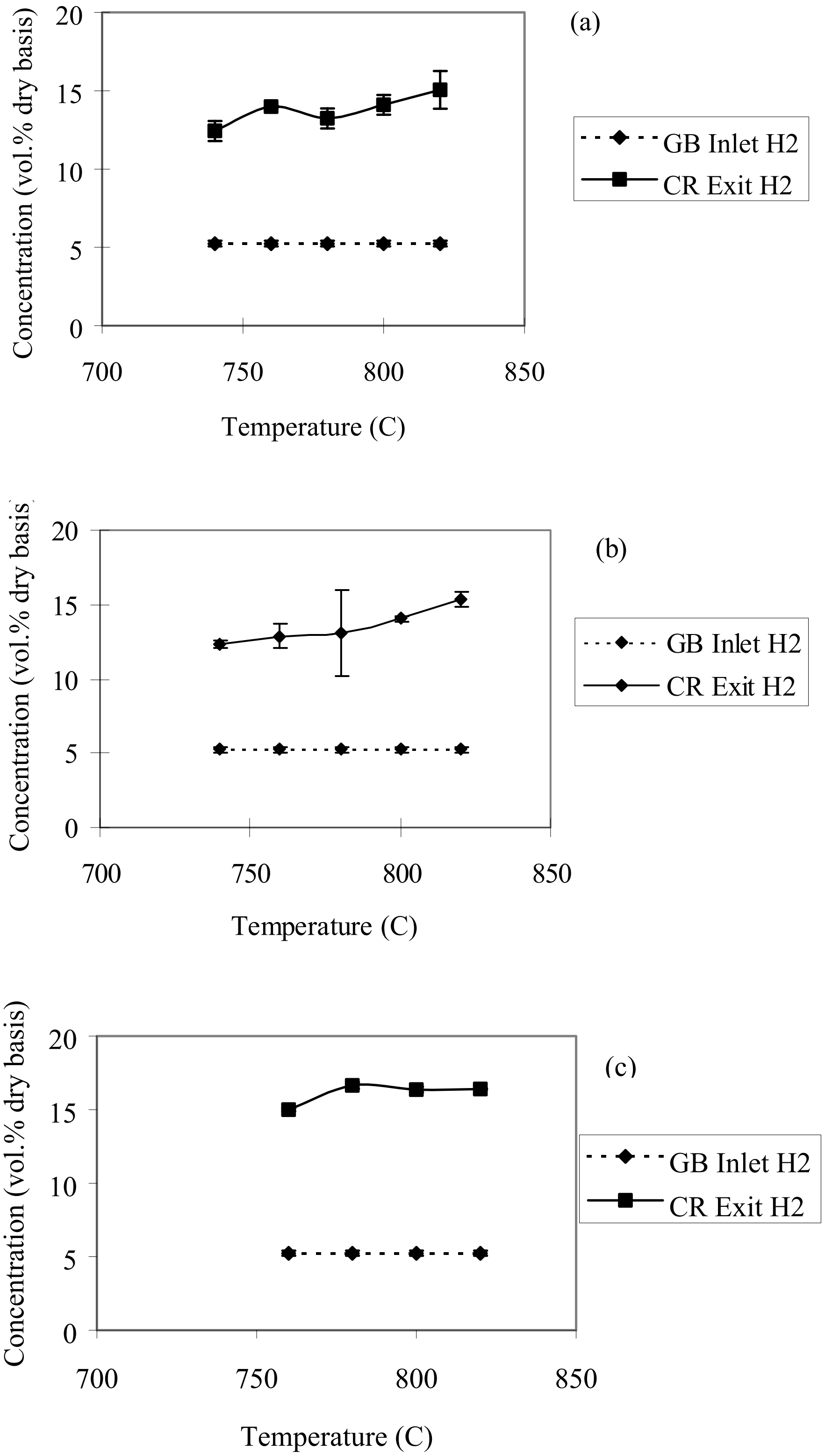


Figure 11. H_2 concentration in the producer gas at the inlet of the guard bed and the exit of catalytic bed as a function of catalytic bed temperature: $T_{GB} = 650°C$; $SV = 3000h^{-1}$; Steam/TOC = 2.8. (a) ICI46-1, (b) Z409, (c) RZ409.

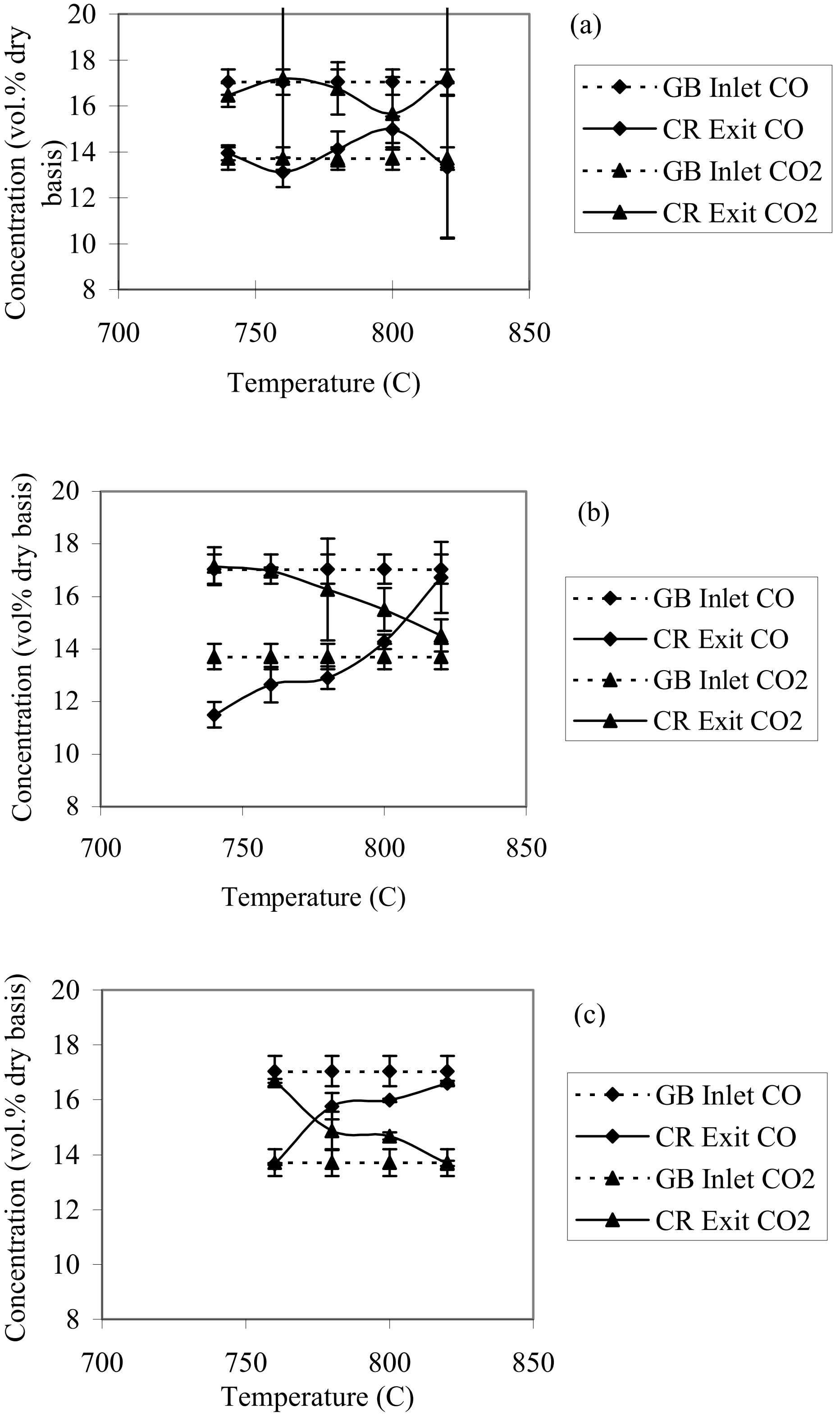


Figure 12. CO and CO_2 concentrations in the producer gas at the inlet of the guard bed and the exit of catalytic bed as functions of catalytic bed temperature: T_{GB} = 650°C; SV = $3000h^{-1}$; Steam/TOC = 2.8. (a) ICI46-1, (b) Z409, (c) RZ409.

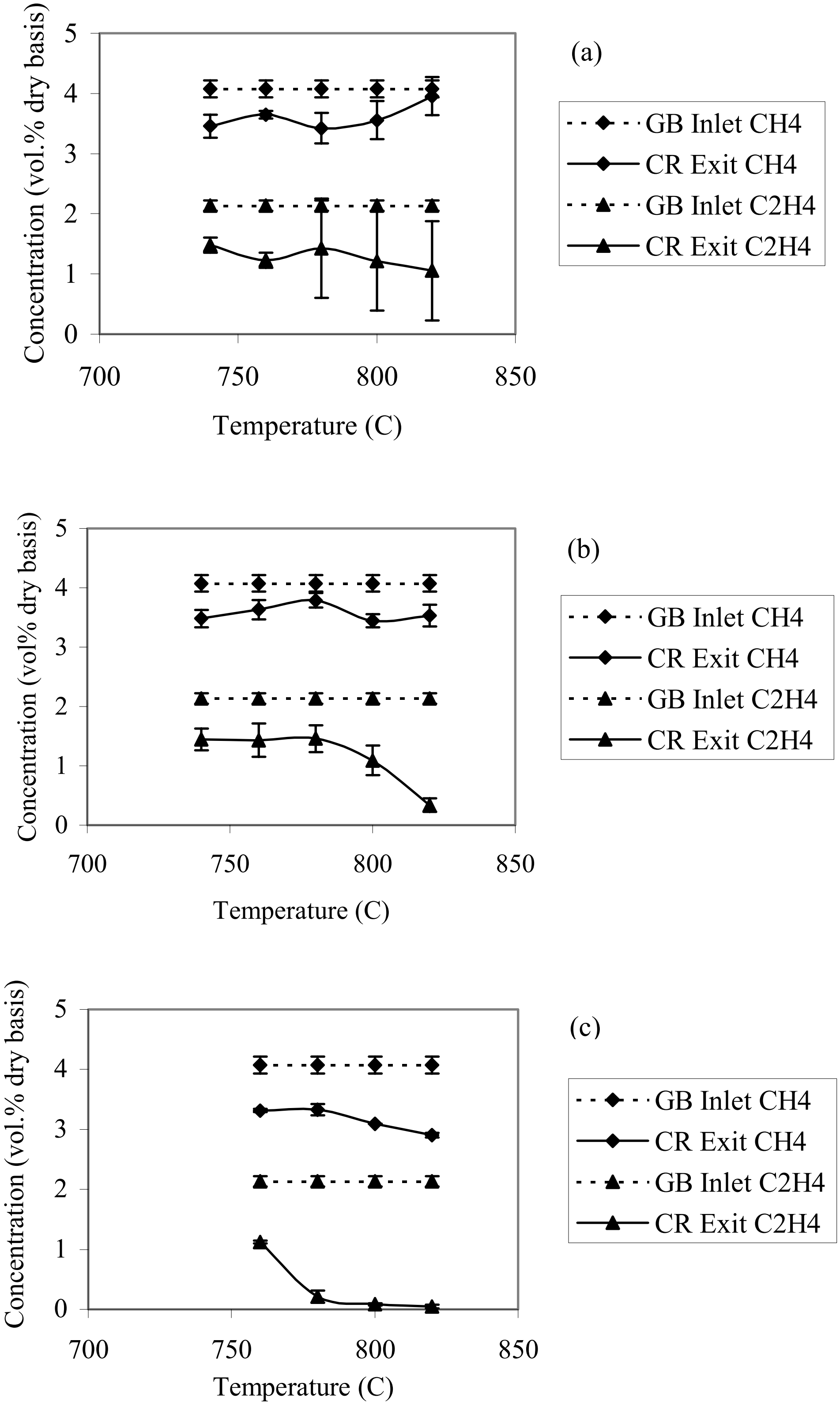


Figure 13. CH_4 and C_2H_4 concentrations in the producer gas at the inlet of the guard bed and the exit of catalytic bed as functions of catalytic bed temperature: T_{GB} = 650°C; SV = $3000h^{-1}$; Steam/TOC = 2.8. (a) ICI46-1, (b) Z409, (c) RZ409.