

AN ANALYSIS OF THE POTENTIAL FOR DEPOSITION, EROSION, OR CORROSION IN GAS TURBINES FUELED BY THE PRODUCTS OF BIOMASS GASIFICATION OR COMBUSTION

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ABSTRACT

Fuel gas produced by gasifying biomass feedstocks will be expected to meet the general specifications for corrosive and particulate impurities set by the gas turbine manufacturers before being approved for use. The extent to which impurities are present in the fuel gas will be a function of the process used to produce the gas, as well as the type of feedstock from which the gas is derived. Experiences from various biomass gasification trials and hot gas filtration testing to assess the types and amounts of impurities that are likely to be present in the delivered gas during normal operation of the gasification/hot gas cleanup process and upset conditions are reviewed. Overall, it appears that biomass fuels can be separated into two classes: those derived from grass-based biomass and those from wood. Of these, the grasses have the potential to be the more troublesome since they contain the largest amounts of alkalis and total solids and have a significant excess of chlorine over sulfur species. A possible mitigating factor is that it may be possible to lower the alkali metal species (Na + K) to levels considered acceptable by operating the filters at temperatures below 500°C. There is concern that larger amounts of particulate matter than allowed in current gas turbine fuel specifications may pass through the hot gas clean-up systems in biomass gasification processes. These particles may also carry condensed alkali deposits. Therefore, it is considered essential that detailed characterization of the size and type of these particles be obtained so that their potential to cause deposition, erosion, or corrosion problems can be better assessed.

BACKGROUND

The fact that there is no penalty from carbon emissions resulting from the use of biomass as a fuel has led to its consideration as a primary energy source in many scenarios for greenhouse gas mitigation. As a solid fuel, biomass has many

of the drawbacks of coal in that it is almost as variable in composition and properties, while its calorific value is significantly lower (by approximately 20 percent) which implies low energy densities. There are also economic problems associated with its seasonal nature, as well as transport and storage peculiarities. The processing of biomass into pyrolysis gases or liquids are two routes by which it could be used as a fuel for land-based gas turbines, assuming that acceptably clean fuels can be produced. The issues involved in the use of fuels derived from coal or biomass in power generation gas turbines have been addressed by a number of authors [see, for instance, Wenglarz, et al., 1995; DeCorso, et al., 1996; Moses and Bernstein, 1996]. The main area of unknown appears to center around the combustion characteristics of these fuels and the tendency for deposition, erosion, or corrosion (DEC) on the turbine airfoils. There have been few reported trials of burning these fuels in gas turbine engines [Kasper, et al., 1983; Patnaik et al., 1998], so that resolution of these problems has been slow.

The processes developed to gasify coal for use in power generation gas turbine systems (integrated gasification combined cycle/IGCC) provide a route for producing gaseous fuels from biomass, in which biomass could be used as the sole feedstock or mixed with other fuels. In fact, the experience gained in the European APAS Clean Coal Technology Programme [see, for instance, Madsen and Christensen, 1994] suggests that co-firing biomass with a solid fuel such as coal will be the preferred route for some fuels and gasification technologies; for instance, the low sintering temperature of straw results in difficulties in fluidized-bed gasifiers. The goal of these IGCC process development efforts is to meet the same product gas specifications that have been established by the gas turbine

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manufacturers for conventional fuels, and which must be met by users in order to maintain the manufacturers' warranties. Obviously, the levels and, to some extent, the types of species that enter the turbine will depend on the source of the fuel and the characteristics of the conversion process and clean-up system employed. In any practical IGCC system, there will be contact of the turbine hot gas path components not only by those fuel contaminants that normally pass through the hot gas clean-up system but also by contaminants that escape clean-up as a result of degradation in the performance of the fuel clean-up systems or as a result of process malfunctions. Even though such occurrences may be sporadic and possibly of short duration, the potential for the initiation of DEC problems must be known.

The extensive body of research on the causes of degradation of combustion turbines burning conventional fuels and the remedial measures possible provides a starting point for considering the implications of using coal- or biomass-derived fuels in gas turbines. In this analysis, gasification [which includes the pyrolysis stream in an advanced pressurized, fluidized-bed combustor (PFBC)] is considered as the route for using biomass as a fuel for gas turbines, since the resulting gas could be directly fired in a conventional gas turbine (with some modifications). The gasification processes of most interest for highly-efficient systems such as the U. S. Department of Energy's Vision 21 [Ruth, 1999] are oxygen-blown, since these have the best potential for minimizing emissions of NO_x , but air-blown processes have received the most attention with biomass fuels so far. Combustion of biomass is also considered as a possible route for firing gas turbines, and the scenario of interest involves direct expansion of the products of combustion in a gas turbine, as in a PFBC. Biomass could also be used in the indirect firing of a gas turbine, which would involve the use of a heat exchanger between the combustion gas and a clean working fluid, so that any corrosion threat from the fuel is to the heat exchanger surfaces and not the gas turbine. This scenario has been examined recently by Tariq et al [1997], and is not discussed further here.

POTENTIAL HOT GAS PATH PROBLEMS

The nominal environment experienced by the hot gas path components of a gas turbine consists of combustion products in a large excess of air at high temperature and high pressure, flowing at high velocity. These conditions are expected to lead to thermal oxidation of the surfaces of metallic parts touched by the gas and, since oxidation is a thermally-activated process, the rate of oxidation is expected to increase exponentially with increasing temperature. Hence, the turbine components must be capable of forming a protective surface oxide. In practice, a major factor limiting the useful lifetime of these components is loss of such protective oxide scales through corrosion attack or mechanical damage.

Corrosion in land-based gas turbines may occur as a result

of deposition of molten salts (hot corrosion) derived from contaminants in the fuel or combustion air. The departure from the experience of conventionally-fueled land-based turbines expected with the use of biomass-derived fuels is from the expected presence of different amounts and proportions of species with the potential for causing DEC problems. These fuel-derived contaminants will be added to the usual air-borne contaminants at some point in the gasification or combustion process. Deposits may form on the airfoil surfaces by condensation of vaporized salts or by impingement of partially molten ash particles. For deposition by the condensation route, the salt species of interest must remain above their dewpoints throughout the fuel delivery path, so that there will be an increased threat from this source when hot gas clean-up systems are used. Conversely, cold gas clean-up (or water quench) systems would be expected to produce gas with a much reduced threat for DEC problems. Since the tendency is for increasing airfoil surface temperatures, condensation in the turbine likely will not occur until the later stages of airfoils, although there may be locations on the forward rows where the surface temperature falls below the condensation temperature at some part of the turbine duty cycle. Deposition by impingement requires some mechanism for allowing the build-up of solid deposits upstream of the turbine, and a scenario for their periodic release [Bornstein, 1996]. Typically, the first rows of vanes and blades are most subject to direct impingement since the particles are broken up and redistributed by impact and by centrifugal forces in the turbine.

Depending on its composition, deposited material may lead to corrosion or simply build up and degrade the aerodynamic profiles or block the flow paths (fouling). The presence of molten deposits of mainly sodium sulfate in land- (or marine-) based gas turbines can give rise to a form of rapid attack (termed 'Type 1 hot corrosion'), particularly in the temperature range 800-950°C (1472-1742°F), in which the protective surface oxide is essentially dissolved, leading to rapid attack of the exposed substrate alloy. Scale loss by spallation may be induced by thermal cycling (as a consequence of the duty cycle of the turbine, or from uneven temperature distribution in the combustor), or by mechanical means (such as erosion).

Biomass Fuels

A sampling of the reported compositions of a range of biomass materials considered for use as fuels is shown in Table I; similar data for Illinois No. 6 coal are included for comparison. One problem in reporting these data is that, since biomass fuels are typically not washed, there may be variable amounts of earth or other adventitious material adhering to them, which is probably responsible for some of the differences in compositions reported for nominally similar fuels. In order to make meaningful comparisons among the various types of biomass, the amounts of the elements of interest were calculated

on the common basis of *gram-atoms per GigaJoule* (gat/GJ, based on the calorific value of the fuel), and these are listed in Table II. Since the calorific value and ash content were not reported by all sources, where values had to be assumed to permit calculation of the values shown in Table II; the actual values of the parameters used in the calculations are also listed.

From the data in Table II it is clear that, in terms of amount of the ash contained in the biomass-derived fuels, there is an obvious difference between the fuels derived from grass (wheat, rice, corn, bagasse) and those from wood. While the wood-derived fuels contain significantly less ash than coal, straw from various sources contains a similar amount or more ash than coal. The wood-derived fuels contain smaller amounts of alkali metals than coal, with the notable exception of poplar, for which high levels of Na and K are reported, especially for hybrid poplar [Tariq et al., 1997]. In contrast, cultivated grasses, wheat and rice straw, and corn cobs all have significantly higher levels of K and, in some cases Na than coal, while corn stalks have high levels of Na, Ca, and Mg. In addition, high chlorine levels have been reported for some wheat straw [Kurkela, 1996]. It is likely that the high levels of alkali metals in these cultivated crop wastes derive from the use of chemical fertilizers and insecticides [Tariq et al., 1997]; the alkali levels in bagasse, for instance, are obviously lower. In addition to alkali metals, sulfur is a major contributor to fireside corrosion in coal combustion, but it is conspicuously absent, or present at very low levels in both woody- and grassy-biomass fuels.

The exact species formed from the ash constituents when these fuels are gasified or combusted depends on the prevailing temperature and oxygen partial pressure, which will change as the gas travels through the process. The partitioning of the sulfur and chlorine among the alkali species, for example, may be inferred from detailed thermochemical calculations, assuming equilibrium conditions are established among the ash components and the product gas at the prevailing temperature. For instance, in an IGCC system the sulfur species would be present as sulfides rather than sulfates (alkalis and alkaline earths as sulfides; Fe as FeS_x), whereas the Al- and Si-containing species probably would be present as oxides. Hence, the gas delivery system from the gasifier to the turbine combustor [including the hot gas clean-up (HGCU unit)] would encounter the contaminants in their reduced states. Obviously, the extent to which the formation of solid particles occurs, and the composition of the particles and the surrounding gas will depend on the extent to which interactions occur in the gas path between the gasifier and components of interest which, in turn, depends on features specific to a given process. These uncertainties highlight the importance of measurements of gas and deposit compositions as a function of location in such process streams.

Since all these contaminant species will pass through the highly oxidizing conditions of the gas turbine combustor before

entering the turbine hot section, for the purposes of analyzing the potential for DEC problems, the simplifying assumption is made that they are present in their highest oxidation states.

For the purposes of this paper, the sources of biomass have been arbitrarily divided into 'grass', typified by the wheat straw data of Kurkela [1996] and 'wood,' typified by the pine bark data from the same author. The compositions of the ashes from these fuels are compared to that from coal in Table III. Assuming that all the species will be available for reaction and that the alkalis and alkali earths in excess of the amounts required to combine with the sulfur and chlorine species will be present as oxides (rather than hydroxides), the relative amounts of sulfates, chlorides, alkali and non-alkali oxides were estimated, as shown in Table III. It is immediately obvious that, whereas coal has an excess of the sulfur required to convert all the alkali metal content to sulfates, the grass and wood fuels have a large excess of (Na+K).

If the amount of volatile/condensable solids is taken as a measure of the potential for deposition to occur, and the amount of non-volatile solids represents a measure of the potential for erosion, and if the corrosion potential is represented by the amount of alkali sulfate species, the values summarized in Table IV give an idea of the relative DEC potential of these fuels. Corrosion data from waste-fired boilers [Krause, 1979], in which the occurrence of accelerated attack was associated with nominally oxidizing conditions where chloride-rich rather than sulfate-rich deposits could form, suggested that the criterion for the formation of chloride-rich deposits is a sulfur to chlorine ratio in the fuel of less than 4:1. On this basis, the ratio of sulfur to chlorine species might also be used as an indicator of the potential for forming unusually corrosive deposits in the turbine, given that there is a sufficient (Na+K) in biomass to react with the sulfur and chlorine contents.

Biomass Gasification

The real potential of these fuels to promote DEC in the downstream gas turbine depends on the fate of the species of interest in the gasification (or combustion) process and in the associated gas clean-up steps, as discussed above. In the gasification process, the impurities in the fuels will enter the product gas in an oxidation state corresponding to the prevailing temperature, oxygen partial pressure and total pressure. The fraction of the total impurity species entering in the fuel and air that leave the gasifier in the product gas stream will depend on the particular gasification process. In coal gasification, the major part of the alkalis from the coal is removed in the bottom ash. In contrast, in biomass gasification, essentially all the alkalis are taken into the product gas stream and so must be removed by the filters.

The product gas exiting the gasifier typically encounters cyclone separators and is then cooled in heat exchangers before

encountering particle removal and desulfurization systems, after which it is fed to the turbine. As the product gas is cooled, reactions among the vaporized salts and gaseous species will occur and, at the point in the gas path where the gas encounters surfaces at temperatures below the condensation temperature of the various vapor species, they will deposit.

In gasification trials with coal, peat and wood waste, Kurkela, et al. [1993] found that the concentration of vapor-phase alkalis could be reduced to approximately 0.1 ppmw by operating the ceramic filter below 500°C. The concentration of Na and K species in the gas leaving the cyclones (upstream of the heat exchanger) decreased rapidly with decreasing temperature (870 to 770°C); for gas from sawdust the Na levels ranged from 0.30 to 0.19 ppmw, and the K levels were 0.30 to 0.15 ppmw.

Downstream of the ceramic filter, where the gas temperature ranged from 508 to 439°C, the levels of Na and K were 0.06-0.04 and 0.08-0.04 ppmw, respectively (Na+K = 0.08-0.14 ppmw). Apparently, the alkali phases tended to condense onto gas-borne particulates during gas cooling, so that a major fraction of them were removed with the dust cake. A mass balance over the filters indicated that, for sawdust gasification, the bulk of the Na+K from the fuel was removed in the filter dust (and bottom ash, depending on the gasifier set point). Similarly, Nieminen, et al., [1996] found the (Na+K) content of the gas downstream of the candle filters in the VTT Process Development Unit to be 0.4 to 0.5 ppmv when the filters were operated in the range 396 to 413°C (745 to 775°F) at a pressure of 4.8 bar. They also measured 28-87 ppmv H₂S, 3-9 ppmv COS, and 0.3-0.6 ppmv Cl in the gas after the filters.

According to the various specifications for gas turbine fuels, summarized in Table V, the observed HGCU unit performance on the gasification product gas from biomass fuels meets the levels listed for natural gas (0.2-0.5 ppmw) for normal operation. It seems clear that, by judicious adjustment of the filtration temperature, the bulk of the vapor phase (Na+K) can be removed from the gas stream by causing it to deposit onto particulate matter in the gas, or onto the filter cake, so that it is removed with the filter dust. While this is good news as far as turbine deposition or corrosion problems are concerned, the relatively large amount of alkali species (and the total amount of solids) to be removed by the filters may be a concern in terms of filter cleaning and solids handling. These quantities (expresses as alkali/total solids, kg/h based on the gasification of an amount of biomass with an energy content equivalent to 10 MW) for wood-derived gas are: 2/22, and for grass-derived gas: 6/184.

This scenario requires that, for successful operation of the gas turbine, the leakage of alkali-laden dust particles through the filters is minimal. The experience of Kurkela, et al. [1993] when gasifying coal or peat was that the concentration of particles following two cyclones in series was in the range 5-30 g/m³n, while downstream of the following ceramic hot gas

filter system it was less than 3-10 mg/m³n. This represents a removal efficiency of 99.94-99.97 percent. Measurements by Nieminen, et al., [1996] showed that the 7.3 to 22 x 10³ ppmw particles in the inlet gas could be reduced to 3.8 to 29 ppmw in a HGCU system consisting of two levels of cyclones followed by candle filters, a particle removal efficiency of 99.95 to 99.87 percent. Using data from Table IV, these removal efficiencies suggest that, for the gasification of an amount of biomass with an energy content equivalent to 10 MW(th), 30 to 130 x 10³ mg/h of particulate matter could pass through a ceramic candle-based filter HGCU unit in a grass-fired system, and 1 to 5 x 10³ mg/h for a wood-fired system.

The experience of Newby, et al. [1999] with a multi-element candle filter system (10-14 candles) on gasification pilot plants has been very positive. In 20 to 30-hour tests on the product gas stream from a pressurized, air-blown, fluidized-bed gasifier using bagasse there was no detectable dust loading in the filter outlet when operated at 860-899°C/18.9 bara (1580-1650°F/260 psig) or at 538-666°C/14.5-17.9 bara (1000-1230°F/195-245 psig) with the upstream cyclone disabled (particle loading 980-2900 ppmw, mean particle size 10.8 µm). In the lower-temperature test, the alkali level ranged downstream of the filter from 0.7 to 1.0 ppmv. The 14-element filter test unit was also operated for approximately 150 hours on a slip stream of the gasification plant in Paia, Hawaii, filtering the product of approximately of a 10-tons per day of bagasse. No problems were experienced with the performance of the filters in this test.

If the levels of particulate matter in gas from wood or grass gasification measured by Kurkela, et al. [1993] and Nieminen, et al., [1996] are taken to represent the worst-case scenario, it can be seen by comparison with the particle loading limits set by major gas turbine manufacturers shown in Table VI that these levels are significantly higher than acceptable limits. Compared to the General Electric specification for low-Btu gas, the levels in wood-derived gas are up to a factor of 2.2 higher, whereas the levels from grass gasification may range from 13 to 58 times this specification. Whether or not these particles will result in DEC problems in the turbine will obviously depend on their size, size distribution, and composition after passing through the turbine combustor. For instance, Stringer and Drenker [1981] suggested that, in view of the relative large difference in erosion damage caused by particles of different sizes, specification of both the particle size and loading would be more appropriate. They suggested limits of: <0.1 ppm of particles >20 µm; <1 ppm 10-20 µm; and <10 ppm 4-10 µm; particles smaller than 4 µm were assumed to pass through the turbine without striking the components. Clearly, however, the fuel gas delivery system connecting the HGCU unit to the turbine combustor will most likely be subjected to interactions with these species in the oxidation state in which they leave the filters and should be constructed accordingly.

One problem for filtration systems in biomass gasification systems is the production of relatively large amounts of tar, and the possibility of this condensing as the gas is cooled; for woody biomass, tar condensation occurs over the range 200 to 500°C. This can lead to rapid blinding of filters. Kurkela, et al [1993] found that with gas derived from sawdust the filter was blinded in less than 5 h when operated at 700°C. However, when dolomite or coal was added to the gasifier and the filter was operated at less than 600°C, a steady pressure drop was measured and blinding was not observed. They measured vapor phase alkali metals and particulate concentrations after the second cyclone and after the ceramic filter. Sampling at the second location proved very problematic: although the particulate concentration was 10 mg/m³n, the concentration of heavy tars ranged to over 1,000 mg/m³n, part of which condensed on the probe, and part may have created artificial soot particles. The tar concentrations in coal gasification were much lower, and such problems were not encountered.

In work carried out as part of the European JOULE II program, Nieminen et al. [1996] used a small scale PFBC (2.5-10 bar; bed temperature 700-1000°C) gasifier (air- or steam-blown) to test the susceptibility to blinding of standard rigid filter types. Ceramic filters were tested at 400-700°C: no increase in pressure drop was detected, and the dust cake was loose. Tests of metallic filters at 400-500°C also showed little blinding but some corrosion. In tests of SiC-based filter materials at 650°C with alkali chlorides in a reducing gas (and without particles present to avoid any mitigating influence of dust), K, Na, Cl and Fe were enriched on the surfaces of the filter materials. Some changes in phase and composition were observed in the surfaces. Mullite-based materials were least affected.

Rensfelt [1997] introduced a dolomite-containing CFB immediately downstream of the gasifier to catalytically crack the tars to simpler compounds (at approximately 900°C). This process allowed conventional gas cleaning equipment to be used.

Biomass Combustion

An alternative route for using biomass fuels in high-efficiency power generation processes is through combustion in, for instance, a PFBC where the flue gas is expanded through a turbine. For the gas turbine involved, the PFBC replaces the conventional combustor, and the air from the compressor flows through the PFBC before entering the hot section of the turbine. Any impurities entering with the combustion air are mixed with those from the fuel in the combustion process, so that the only source of corrosive, erosive or fouling species that enter the expander turbine is the flue gas. In transiting the circuit from the combustor exit to the turbine inlet the species entering an expander turbine will have had time to equilibrate to the temperature and oxygen potential of the flue gas, hence no

further chemical changes are expected. Hence, The types and forms of potentially harmful species that enter the expander turbine will be exactly the same as those in the gas leaving the clean-up system.

A question that arises is the extent to which the filtration characteristics of ceramic candle filters might differ when filtering gasifier product gas (reducing gas composition, mainly sulfide, chloride, and oxide species) and a combustor flue gas (oxidizing gas composition, mainly sulfate, chloride, and oxide species). In cases where a topping combustor is not employed, the filters in a HGCU system on a biomass combustor most probably will be run hotter than those on a gasifier to maximize the expander inlet temperature. Since the gas from a gasifier will be combusted prior to entering the turbine, it should be possible to run the HGCU system cooler than in the case of a PFBC expander without a large impact on overall system efficiency, if this will benefit filter operation. Experience with coal-fired gas turbines showed that, provided the ash particles were sufficiently fine and enough time was provided to allow completion of the combustion of the flyash particles, the use of relatively simple filtration devices (cyclones) allowed the flue gas to be successfully expanded through a conventional gas turbine with a minimum of DEC problems [Australian Coal-Burning Gas Turbine Project, 1973]. However, rapid deposition and fouling of the turbine resulted if the entering flyash was not fully burnt out.

OVERALL IMPLICATIONS FOR BIOMASS-FUELED GAS TURBINES

The amounts of *alkali metal species* in biomass fuels are such that there is concern that the various gas cleaning options must function efficiently at all times on IGCC and PFBC plants. Grass-based fuels appear to pose the greatest threat of DEC, since they contain the largest amounts of alkalis and total solids and have a significant excess of chlorine over sulfur species, which is taken as an indicator that chloride species could be stable in any deposits formed. A possible mitigating factor is that operation of filter systems at temperatures where the alkali vapors will condense has been shown to lower the levels of alkali metal species (Na + K) to concentrations considered to be acceptable in other fuels by gas turbine manufacturers. The removal of the alkali species in the filter dust, however, places a large burden on the HGCU system in terms of filter cleaning and solids handling. In some circumstances, it may be necessary to consider using the filter system as a chemical and physical clean-up device by introducing, for instance, sorbent or diluent material into the gas upstream of the filter to lower the levels of alkalis and other contaminants, and to improve the properties of the filter cake when potentially sticky deposits are possible.

In some gas turbine fuel and air specifications, the potential for hot corrosion attack is related to the ratio of K to Na in the fuel, air, or in the combustion gas entering the turbine. The

nominal ratio for sea salt, which is the most common source of these alkalis in conventional fuels (and in aerosol form in the combustion air), is 0.036. For coal, the ratio is 1.4 (see Table III), while for woody biomass the value is 9.8, and for grassy biomass 24. In the specification published by the General Electric Company [General Electric, 1994], the turbine inlet limit for (Na+K) is 20 ppbw when $K/Na = 0.036$, which falls to < 6 ppbw for $K/Na > 1$. Obviously, the potential contaminants from biomass-derived fuels can be considered to pose a considerable hot corrosion threat to gas turbine hot gas path components.

There is concern that the amount of *particulate matter* found to escape the HGCU systems in biomass gasification trials may be significantly larger than current gas turbine fuel specifications. These particles may also carry condensed alkali deposits. Therefore, it will be necessary to obtain information on the size and type of these particles before more detailed analysis can be made of their DEC potential. Although the predominant particle size may be smaller than that at which impingement and/or deposition are considered to be likely (4 μm), the particle loading may be higher than acceptable.

The scenarios for gasification- and combustion-based systems are slightly different. In a biomass-fired IGCC system, contaminants with potential to cause DEC problems in the turbine hot gas path will enter the system in the combustion air (as in conventionally-fired land-based gas turbines), as well as in the fuel gas, depending on the efficiency of the HGCU system. All of these contaminants will be oxidized in the combustion process (some solid particles may not be fully oxidized depending on their size and residence time in the flame) before they enter the hot gas path. In a biomass-fired combustion system, such as a PFBC, all the contaminants in the combustion air will pass through the combustion process, and those retained in the flue gas will have been equilibrated with those from the fuel and will pass through the HGCU system before entering the expander turbine in the same state as they left the HGCU system.

The major departure from conventional experience involves the presence of potentially corrosive species derived from the fuel that are different in composition and proportions than encountered in conventional gaseous or liquid fuels. If any release of solid particles and vapor species occurs from the hot gas cleanup system, these species will enter the combustion chamber of the turbine without any modification. So far, there have been few reports of examination of turbine components after exposure to biomass-derived fuels. Patnaik et al. [1998] described corrosion tests using a fuel made from the fast pyrolysis of waste wood suspended in approximately 20 wt. percent water. The ash composition is given in Table I. Tests were run in a flame tunnel in which the fuel was burned and in a laboratory furnace where specimens were coated with actual deposits taken from the surfaces exposed in the flame tunnel.

The tests consisted of 50 h in the flame tunnel followed by 1000 h in a furnace (with the surface deposits maintained undisturbed) and furnace exposures in contact with the ash for various times.

The materials tested were Ni-based superalloys with either a pack diffusion aluminide coating or a thermal barrier coating (TBC) with an MCrAlY bond coating. Severe corrosion attack was observed on the MCrAlY and base metal after the flame tunnel + furnace test and after the furnace-only tests, where the specimen temperature was 850°C. The form of attack was thought to be Type I hot corrosion, despite the relatively low sulfur level in the fuel. Micrographs of cross sections of the corroded alloys showed morphologies which resembled Type I hot corrosion, but no analysis was presented of the internal corrosion zone (which would have consisted of chromium sulfides if the attack were Type I hot corrosion). The majority of the deposits were found to consist mostly of calcium sulfate ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$, gypsum) with lesser amounts of $\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (syngenite), along with spherical silica grains.

Leyens et al. [1999a,b] have recently reported systematic laboratory tests intended to explore the hot corrosion behavior of gas turbine alloys exposed to molten salts containing the species expected from biomass-derived fuels. A transition in the composition of simple sulfate deposits from Na-rich to K-rich resulted in a decrease in the corrosion of a typical NiCoCrAlY coating composition when the K:Na atomic ratio of the salt was greater than 0.06. When the sulfur level of the salt was reduced below that required for stoichiometric sulfates (the excess alkali was included as hydroxide, neutralized by nitric acid), the corrosion rates for deposits containing sodium alone were reduced, whereas in the presence of potassium, the rates slightly increased. The influence of additions of alkaline earths, or of chlorides is the subject of continuing research. Nevertheless, it is clear that despite the lack of sulfur in biomass-derived fuels, there is the potential for the corrosive components expected to be present in the fuel gas to lead to severe attack of protective oxide scales through fluxing, if conditions are such that they can be deposited in the molten state. There is an obvious need to develop an understanding of the mode and rate of the corrosive attack from the range of contaminant compositions possible in these fuels to provide confidence in the applicability of fuel specifications and guidance for the selection of the appropriate protective coatings.

SUMMARY

Overall, it appears that biomass fuels can be separated into two classes, those derived from grass-based biomass and those from wood. Of these, the grasses have the potential to be the more troublesome. Since the impurities of interest here are present in the fuel gas stream, those that are not removed in the hot gas cleanup system in gasification-based systems will pass directly into the combustion chamber of the turbine, and their oxidation products will have direct access to the turbine hot

section components. Solid particles may pass through the combustion chamber and directly impact the components. Gasification tests with biomass generally have shown that despite the very high concentration of alkalis in the raw product gas, cooling and filtration at about 500°C can reduce the level to less than 1 ppmw, similar to that considered acceptable (in other fuels) for use in gas turbines. It is probable that a substantial proportion of the chlorine compounds in the raw product gas also will be removed in the filter dust, but this will depend on the specific fuel and the gasification process. Any role played by condensable species depends on their contacting surfaces at temperatures below their dewpoints. Hence, while the first stages of advanced land-based gas turbines may not operate at sufficiently low temperatures for any significant time, deposition may be possible on the third and fourth stages, which typically are not particularly troubled by hot corrosion attack.

For biomass-fired combustion systems, the contaminants in the combustion air will pass through the combustion process and will be equilibrated with those from the fuel before entering the HGCU system. In the case of an unfired expander, condensable vapors or solid particles that escape the HGCU system will enter the turbine section without any further change in composition or state, and so may present somewhat different DEC threats than in the case of a fired (topped) expander or a turbine burning biomass-derived fuel gas.

It appears that larger amounts of particulate matter than allowed in current gas turbine fuel specifications may pass through the HGCU systems in biomass gasification processes. These particles may also carry condensed alkali deposits. Therefore, it is considered essential that detailed characterization of the size and type of these particles be obtained so that their potential to cause DEC problems can be better assessed.

The types or relative levels of corrosive species in these fuels are significantly different from those in conventional fuels, and there is at present no rational basis for alloy or coating selection or modification to provide an acceptable measure of inherent protection to the gas turbine. Hence, there is a need to develop an understanding of any differences in mode or rate of attack, as well as the temperature range of susceptibility, so that the potential consequences of the resulting interactions with the different classes of alloys and coatings used in the hot gas path can be quantified. An effort to measure the gas and deposit compositions in the biomass-derived fuel as a function of location in the process stream from the gasifier to the turbine would be a significant step toward resolving some of these issues.

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Table I. Biomass Feedstock Analyses

<u>Content</u>	<u>Illinois#</u>	<u>Peat</u>	<u>Peat</u>	<u>Pine</u>	<u>Sawdust</u>	<u>Sawdust</u>	<u>Sawdust</u>	<u>Pine</u>	<u>Pine</u>	<u>Pine bark</u>	<u>Forest</u>	<u>Waste</u>	<u>Waste</u>	<u>Birch</u>
	<u>6 coal</u>	<u>(fuel)</u>	<u>(surface)</u>	<u>sawdust</u>			<u>(conifers)</u>	<u>chips</u>	<u>chips</u>		<u>residues</u>	<u>wood</u>	<u>wood*</u>	
	Kurkela, 1996	Kurkela, 1996	Kurkela, 1996	Kurkela, 1996	Kurkela, et al., 1993	Kurkela, et al., 1993	Rudiger, et al., 1995	Reinoso, et al., 1995	Kurkela, 1996	Kurkela, 1996	Kurkela, 1996	Kiel, et al., 1995	Patnaik, et al., 1998	Chen, et al., 1999
LHV (dry) MJ/kg	25.2	21	18.5	19	—	19.1	—	19.56	18.9	20.1	19.70	—	19.8	19.22
Moisture, wt%	2-5	15-19	9-16	6-16	4.0-11.3	6.4-15.5	22.7	—	6-7	5-7	9-12	7.8	20.4	—
Volatile matter (wt%, dry)	33.8	68.3	72.2	83.1	83.0	82.8-83.1	83.1	75.56	81.5	71.8	76.7	78.8		na
Fixed C (wt%, dry)	53	27.4	25.1	16.8	16.8	16.9	16.9	21.41	18.1	26.6	21.2	21.1		na
<u>Ultimate analysis</u>														
<u>(wt% dry)</u>														
C	64.6	54.5	51.2	51.0	50.3	51.2	50.8	51.28	50.5	53.9	52.3	52.3		49.0
H	4.2	5.6	5.6	6.0	6.0	6.1	6.5	4.69	6.1	5.8	6.0	5.0		6.1
N	1.3	1.8	0.9	0.1	0.1	0.1	0.2	0.51	0.2	0.4	0.6	0.2		0.1
S	2.9	0.20	0.10	0.01	nd	<0.01	0.10	0.15	0.03	0.03	0.0	0.1	0.03	<0.01
O	13.8	33.6	39.5	42.8	43.4	42.5	42.4	40.34	42.8	38.3	39.0	42.4		44.5
Ash	13.2	4.30	2.70	0.10	0.2-0.34	0.08-0.23	0.60	3.03	0.40	1.60	2.1	0.1	0.06	0.40

Table I (continued). Biomass Feedstock Analyses

<u>Content</u>	<u>Wheat</u> <u>straw</u>	<u>Wheat</u> <u>straw</u>	<u>Wheat</u> <u>straw</u>	<u>Straw</u> <u>pellets</u>	<u>Eucalyp-</u> <u>tus</u>	<u>Switch</u> <u>grass</u>	<u>Oats</u>	<u>Oats</u>	<u>Miscan-</u> <u>thus</u>	<u>Miscan-</u> <u>thus</u>	<u>Miscan-</u> <u>thus</u>	<u>Rapeseed</u>	<u>Rapeseed</u>	<u>Salix</u>
	Kurkela, 1996	Rudiger, et al., 1995 (MAF)	Rudiger, et al., 1995	Kiel, et al., 1995	Kurkela, 1996	Dayton, et al., 1995	Rudiger, et al., 1995 (MAF)	Rudiger, et al., 1995	Rudiger, et al., 1995 (MAF)	Rudiger, et al., 1995	Chen, et al., 1999	Rudiger, et al., 1995 (MAF)	Rudiger, et al., 1995	Chen, et al., 1999
LHV (dry) MJ/kg	17.2	—	—	—	18.5	—	—	—	—	—	16.52	—	—	18.72
Moisture, wt%	6-7	7.4	8.1	4-5	8.16	13.2	9.8	—	6.4	—	na	89.6	na	—
Volatile matter (wt%, dry)	75.8	81.2	76.4	80.4	79.19	79.7	81.2	na	89.6	na	10.4	na	na	na
Fixed C (wt%, dry)	18.1	18.8	18.9	18.8	16.22	20.2	18.8	na	10.4	na	na	na	na	na
<u>Ultimate analysis (wt%</u>														
<u>dry)</u>														
C	46.1	50.5	48.0	47.0	51.2	46.9	47.8	45.1	53.3	50.9	47.3	63.1	60.7	47.4
H	5.6	4.8	4.6	4.9	6.0	5.8	6.6	6.2	4.6	4.4	6.2	9.6	9.2	6.1
N	0.5	0.8	0.8	0.8	0.2	0.6	1.1	1.0	0.5	0.5	0.7	3.3	3.2	0.4
S	0.08	0.1	0.1	0.14	0.0	0.11	0.20	0.2	0.3	0.3	0.11	0.40	0.4	0.40
O	41.7	43.0	40.9	42.5	41.8	42.0	44.3	41.8	41.1	39.3	42.9	23.6	22.7	43.3
Ash	6.10	6.0	5.7	4.70	0.8	4.59	5.60	5.6	4.9	4.90	2.77	3.80	3.80	2.46

Table II. Summary of Trace Element Contents of Fuels

Element (gat/GJ)	Illinois Coal	Peat (fuel)	Peat (surface)	Wheat Straw	Wheat Straw	Wheat Straw	Rice Straw	Rice Husks	Bagasse	Corn Cob	Corn Stalk	Pine	Pine Bark	Pine Bark
	Kurkela, 1996	Kurkela, 1996	Kurkela, 1996	Tariq, 1997	Anson, 1999	Kurkela, 1996	Tariq, 1997	Tariq, 1997	Anson, 1999	Anson, 1999	Anson, 1999	Anson, 1999	Tariq, 1997	Kurkela, 1996
Al	16.89	5.39	2.98	1.8	2.4	0.53	0.0	1.9	4.9	0.0	4.9	1.2	2.2	0.83
Ca	4.31	6.28	2.62	3.0	13.0	5.13	3.8	4.0	1.1	0.2	10.4	11.5	3.6	5.76
Fe	8.16	3.78	1.52	0.3	1.7	0.32	0.2	0.7	2.5	0.0	0.7	0.6	0.3	0.03
Mg	0.86	1.52	1.56	2.2	4.5	1.75	1.8	0.9	1.1	2.8	18.6	0.2	1.3	0.88
Na	2.26	0.68	0.89	10.7	2.8	0.63	6.8	2.3	0.4	0.3	26.9	0.2	0.3	0.13
K	3.08	0.58	0.9	15.8	38.6	15.24	11.2	0.5	1.2	11.8	0.1	0.7	1.0	1.28
Si	46.62	14.65	12.73	21.2	55.6	34.34	32.9	4.7	10.8	11.6	27.7	7.1	5.2	0.17
Ti	0.5	0.11	0.08	—	—	0.01	—	—	—	—	—	—	—	0.01
Cl	1.35	0.36	0.27	—	—	4.73	—	—	—	—	—	—	—	0.15
S	35.96	2.98	1.69	1.9	0.0	1.45	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.47
P	—	—	—	1.0	0.0	—	0.0	0.0	0.0	0.0	0.0	0.0	0.0	—
CV (LHV) (MJ/kg)	25.2	21	18.5	17.2 ^a	17.2 ^a	17.2	17	18	18 ^a	18 ^a	18 ^a	19.0 ^a	20.1	20.1
Ash (% dry)	13.2	4.3	2.7	5.9	12.5	6.1	6.0	6.0	2.5	2.5	7.5	2.5	1.6	1.6
Ash (kg/GJ)	5.24	2.05	1.46	3.43	7.27	3.55	3.53	3.33	1.39	1.39	4.17	1.32	0.80	0.80
Ash (kg/h)*	189	74	53	123	262	128	127	120	50	50	150	48	29	29

^a used CV value from different author for similar material.

* for an amount of biomass with an energy content equivalent to 10 MW

Table II (continued). Summary of Trace Element Contents of Fuels

Element (gat/GJ)	Pine sawdust	Pine waste	Spruce Bark	Birch	Poplar	Hybrid Poplar	Maple	Oak	Oak Bark	Furniture Wood Waste	Forest Residues	Forest Residues	Softwood	Hog Wood Fuel
	Kurkela, 1996	Tariq, 1997	Tariq, 1997	Tariq, 1997	Anson, 1999	Tariq, 1997	Anson, 1999	Tariq, 1997	Tariq, 1997	Tariq, 1997	Tariq, 1997	Kurkela, 1996	Tariq, 1997	Tariq, 1997
Al	0.02	4.6	1.7	0.1	0.3	0.0	1.7	0.0	0.0	0.1	0.7	0.4	2.2	4.6
Ca	0.4	1.1	3.6	1.7	11.0	3.4	21.0	2.4	0.2	0.1	8.6	5.3	11.7	9.9
Fe	0.01	2.4	0.6	0.0	0.1	0.2	0.5	0.0	0.0	0.0	0.2	0.2	1.6	0.7
Mg	0.15	1.1	0.8	0.6	1.4	1.6	10.4	0.4	2.5	0.0	2.0	1.0	4.1	17.6
Na	0.005	0.3	2.1	0.1	0.1	6.1	0.0	0.0	0.2	0.0	0.7	0.3	2.5	25.5
K	0.14	1.1	0.4	0.5	5.6	10.1	2.7	0.0	10.6	0.0	1.9	2.0	34.9	0.1
Si	0.07	10.2	4.3	0.1	0.6	29.4	3.5	0.1	10.4	0.5	3.1	4.6	50.4	26.3
Ti	0.001											0.01		
Cl	0.02											0.3		
S	0.16	0.0	0.2	0.1	0.0	0.0	0.0	0.0	0.2	0.0	0.4	0.6	0.0	0.3
P		0.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.1		0.1	0.7
CV (LHV) (MJ/kg)	19	19	20	19.22	19 ^a	19.0	19 ^a	19.0	20	19.5	19.90	19.70	19	19.0
Ash (% dry)	0.2	1.6	1.6	0.4	2.5	0.4	4.0	0.4	1.6	0.1	2.1	2.1	0.3	1.6
Ash (kg/GJ)	0.09	0.84	0.80	0.21	1.32	0.21	2.11	0.21	0.80	0.06	1.06	1.07	0.16	0.84
Ash (kg/h)*	3	30	29	8	48	8	76	8	29	2	38	39	6	30

^a used CV value from different author for similar material.

- for an amount of biomass with an energy content equivalent to 10 MW

Table III. Detailed Comparisons of Coal, Grass, and Wood

Element, gat/GJ	Coal	Wheat Straw	Pine Bark
	Kurkela, 1996	Kurkela, 1996	Kurkela, 1996
Al	16.89	0.53	0.83
Ti	0.50	0.01	0.01
Fe	8.16	0.32	0.03
Mg	0.86	1.75	0.88
Ca	4.31	5.13	5.76
Na	2.26	0.63	0.13
K	3.08	15.24	1.28
Si	46.62	34.34	0.17
S	35.96	1.45	0.47
Cl	1.35	4.73	0.15
<hr/>			
K/Na	1.4	24	9.8
Ca+Mg as sulfates, gat/GJ	5.17	0.72	0.24
Na+K as sulfates, gat/GJ	5.34	1.46	0.48
Excess alkali, gat/GJ	0.00	21.66	7.70
Excess S, gat/GJ	34.83	0.00	0.00
Sulfates, kg/h*	45	9	3
Ca+Mg as chlorides, gat/GJ	0.00	2.37	0.06
Na+K as chlorides, gat/GJ	0.00	4.73	0.03
Chlorides, kg/h*	0	40	1
Solids (Al,Si,Fe oxides) g/GJ	6,694	2,807	103
Oxides (except alkalis), kg/h*	241	101	4
Alkali oxides, kg/h*	0	34	14

* for an amount of biomass with an energy content equivalent to 10 MW (th).

Table IV. Summary of Relative Potential for Deposition, Erosion, or Corrosion from Biomass Fuels; Amounts Before Filtration

DEC Potential	Species	Coal	Grass	Wood
Deposition	volatile solids, kg/h*	45	83	18
Erosion	non-volatile solids, kg/h*	241	101	4
Corrosion	total (Na+K) sulfates	23	6	2
	S:Cl	45:0	1:4.4	3:1

*data for an amount of biomass with an energy content equivalent to 10 MW(th).

Table V. Representative gas Turbine Fuel Specifications [after Moses and Bernstein, 1996]
(quantities in ppmw, except as noted)

Specification	Fuel	Na+K	Ca	Pb	S	Ash
ASTM	liquid	0.5	0.5	0.5	—	0.01-0.03%
OEM 1, aeroderivative	liquid	0.1-0.2	2.0	1.0	1.0%	0.01%
OEM 2, aeroderivative	natural gas	0.2	—	—	no limit (alkali metal sulfates < 0.6)	—
OEM 3, heavy duty	petroleum	1.0	2.0	1.0	—	—
OEM 4, heavy duty	natural gas	0.5	10.0	—	no limit	—
OEM 5, general	—	1.0	1.0	1.0	—	—
General Electric Co.*	fuel	0.072	0.48	0.24	7.2	7.2

*The General Electric Co., 1994.

Table VI. Particle Loading Specifications for Gas Turbines

Manufacturer	Maximum Particle Loading	
	<u>ppmw</u>	<u>(mg/h)</u> ***
Westinghouse	0.4	124
Brown-Boveri	0.6	185
General Electric Co.*	7.2**	2,223
Natural gas [Moses and Bernstein, 1996]	30	927
Westinghouse (PFBC projection)	4-36	1,236-11,123
Ingersoll-Rand (expanders on catalytic crackers)	125	38,600
<u>Potential Particle Loading</u>		
Coal		
Grassy biomass		30,000-130,000
Wood biomass		1,000-5,000

*The General Electric Co., 1994.

**for low-Btu gas; no more than approx. 1 wt.% can exceed 10 μ m

***based on a gaseous fuel flow with an energy content equivalent to 10 MW(th), assuming a gas calorific value of 10 MJ/kg.