

2. THERMOCHEMICAL CALCULATIONS FOR REPRESENTATIVE GASIFIER SYSTEMS

As stated in Sect. 1, the initiation of carbon deposition and metal dusting requires a carbon activity greater than unity. For this reason, the product gas chemistries of eight representative gasifier systems were examined with respect to the chemical activity of carbon. A principal concern is the change in carbon activity brought about by reduction in the gas temperature downstream from the outlet of the gasifier reaction vessel; such cooling may accompany filtration and sulfur removal functions. The selected systems and their nominal gas compositions are listed in Tables 1 and 2, which present input data for air-blown and oxygen-blown systems, respectively.

The principal components of the product gas include CO, CO₂, H₂, H₂O, CH₄, and, in the case of air-blown gasifiers, N₂. Minor species include H₂S, NH₃, and COS. A series of thermochemical calculations, based on the SOLGASMIX¹⁰ computer program, was made to examine essentially all of the possible chemical interactions among these species as a function of temperature at representative system pressures. The calculations assumed that the mole fractions of the elemental constituents (C, H, O, S, and N) in the compounds composing the reference product gas do not change from point to point in the system, and therefore do not vary with the gas temperature. This assumption appears valid given the conditions of forced convective

Table 1. Gas composition and pressures of reference air-blown gasifiers

| Gas component | Concentration (vol %) | | | | |
|-----------------------|---------------------------------|-----------------------------------|----------------------------------|-----------------------------------|----------------------------------|
| | M. W. Kellogg/ Piñon Pine | Foster Wheeler/ Wilsonville | M. W. Kellogg/ Wilsonville | Foster Wheeler/ Four Rivers | Tampella U-Gas/ Toms Creek |
| CO | 23.89 | 18.05 | 18.43 | 16.50 | 26.0 |
| CO ₂ | 5.44 | 8.79 | 8.10 | 9.00 | 5.0 |
| H ₂ O | 5.50 | 9.11 | 8.07 | 9.50 | 14.0 |
| H ₂ | 14.57 | 16.57 | 13.70 | 12.90 | 5.0 |
| CH ₄ | 1.35 | 3.97 | 0.36 | 1.40 | 2.2 |
| N ₂ | 48.65 | 42.68 | 51.30 | 50.50 | 47.5 |
| H ₂ S | 0.03 | 0.05 | 0.02 | 0.04 | 0.006 |
| NH ₃ | 0.02 | 0.32 | 0.01 | 0.19 | 0.15 |
| Ar/other | 0.56 | 0.48 | 0.02 | | |
| Gas pressure (bar) | 20.26 | 14.19 | 20.68 | 14.18 | 22.65 |

Table 2. Gas compositions and pressures of reference oxygen-blown gasifiers

| Gas component | Concentration (vol %) | | |
|--------------------|-----------------------|-----------------------|--------|
| | Shell | British Gas/ Lurgi | Texaco |
| CO | 62.9 | 54.1 | 46.5 |
| CO ₂ | 1.3 | 3.2 | 15.3 |
| H ₂ O | 0.2 | 0.0 | 0.0 |
| H ₂ | 30.8 | 27.7 | 35.9 |
| CH ₄ | 0.035 | 7.0 | 0.0 |
| N ₂ | 4.4 | 6.8 | 2.0 |
| H ₂ S | 0.4 | 0.0 | 0.3 |
| Ar/other | | | 0.1 |
| Gas pressure (bar) | 28.58 | 22.05 | 35.13 |

flow in a closed piping system and limited reaction of the gas with its containment system. Based on these calculations, the following generalizations can be applied to all gasifier systems and their attendant product gas compositions:

1. The equilibrium gas composition and, accordingly, the carbon activity are determined by three principal chemical reactions:



Thus changes in the carbon activity of the product gas as a function of temperature (at a given system pressure) are controlled by the temperature dependencies of the standard free energies of these three reactions.

2. For a given gas composition, the effect of increasing the system operating pressure is to increase the effective carbon activity of the gas by reaction 1 and to decrease it by reaction 3.
3. Nitrogen is an intrinsic gas species in air-blown gasifiers. By diluting the product gas, N₂ can indirectly affect the carbon activity. For example, proportional reductions in the CO and CO₂ partial pressures brought about by the presence of N₂ will decrease the carbon activity through reaction 1, while the decreases in the CH₄ and H₂ partial pressures will increase the carbon activity through reaction 3. However, even in air-blown gasifiers, N₂ of itself is not sufficiently reactive to interact significantly with carbon or hydrogen; that is, gaseous products such as NH₃ are relatively unstable.

4. Even at the H_2S concentrations associated with the highest sulfur coals, the sulfur availability is too small to affect the concentration of the principal carbon- or hydrogen-containing species. Therefore, the carbon activity is unaffected by the presence of H_2S .

For air-blown gasifiers, the calculations indicated that the gas compositions exiting the gasifier reactor (Table 1) are at equilibrium with respect to the exit gas temperature. The carbon activity at this point is less than unity. Typically, as the gas is cooled under equilibrium conditions, the CO and H_2 concentrations decrease while the CO_2 , H_2O , and CH_4 concentrations increase, and these changes are accompanied by a significant increase in the carbon activity. The temperature at which the carbon activity reaches unity is process- and fuel-dependent, but for the air-blown gasifiers examined, it ranged from a low of $770^\circ C$ ($1420^\circ F$) to a high of $880^\circ C$ ($1620^\circ F$).

In the case of oxygen-blown gasifiers, where the initial CO content was 54 vol % or greater, calculations showed that the carbon activity of the gas was already higher than unity at the reference reactor outlet temperature. Again, cooling under equilibrium conditions resulted in a decrease in the CO and H_2 concentrations and an increase in CH_4 , CO_2 , and H_2O levels, while the carbon activity remained at unit activity. For the Texaco gasifier, in which the initial CO content was only 46.5 vol %, the carbon activity was more typical of an air-blown system, and unit carbon activity was not established until the temperature had dropped to $870^\circ C$ ($1600^\circ F$).

The formation of CH_4 is promoted by decreasing temperature, and, in effect, CH_4 becomes a sink for carbon as the temperature is lowered. Accordingly, reaction 3 acts to offset the increase in carbon activity with decreasing temperature resulting from reaction 1. However, without the action of an effective catalyst, reaction 3 is relatively sluggish and tends to be ineffective at temperatures below $800^\circ C$ ($1470^\circ F$). Accordingly, calculations of the CH_4 gas concentration assuming equilibrium conditions for reaction 3 can be expected to give unrealistically high CH_4 concentrations at lower temperatures. To examine this effect, another series of calculations was made in which reaction 3 was excluded, and the CH_4 concentration was assumed to remain unchanged as the product gas was cooled. An unexpected finding in these latter calculations was that excluding reaction 3 had only a small effect on the temperature at which unit carbon activity was reached, and this temperature in some cases even decreased slightly. (This result appears to be associated with the relatively high H_2 level in the product gases compared with the level of CH_4 and the combined role of H_2 in reactions 2 and 3.) However, once the temperature dropped below the unit carbon activity threshold, the elimination of reaction 3 significantly increased the carbon activity (or availability of solid carbon) upon further cooling.

The significant findings of these calculations relative to carbon deposition are summarized in graphical form in Figs. 1 through 4. The results could be presented either in terms of the effective carbon activity of the gas excluding carbon in solid form or, as selected here, in terms of the availability of solid carbon in the gas, assuming no carbon had deposited at temperatures higher than the reference temperature. Figures 1 and 2 compare the carbon availability (moles of carbon/100 moles of gas) for selected air-blown gasifier systems (Table 1) with and without CH_4 formation, respectively, and Figs. 3 and 4 compare the same calculations for oxygen-blown gasifiers (Table 2). The temperatures at which the respective plots intersect the abscissa represent those at which unit carbon activity is initially achieved. In the case of oxygen-blown systems with initial CO concentrations of 60% or greater, the carbon availability is several times higher than that of all other systems. The Texaco (oxygen-blown) gasifier, with an initial CO concentration of 46.5%, has a relatively low carbon availability compared with air-blown systems when equilibrium CH_4 levels are assumed, but the carbon availability is significantly higher if CH_4 formation is excluded. The central conclusion to be drawn from these plots is that, from a thermodynamic standpoint, the potential for carbon deposition will exist for all gasifier systems at some temperature below that attained in the reaction vessel. This potential arises from the relatively high CO concentration in the product gas. Based on equilibrium calculations, H_2 will act to offset the extent of carbon deposited through the generation of CH_4 , but this reaction is very sluggish at the temperatures at which carbon deposition will occur. The temperature at which deposition becomes possible is directly proportional to the CO content of the gas and may increase or decrease slightly with higher H_2 contents.

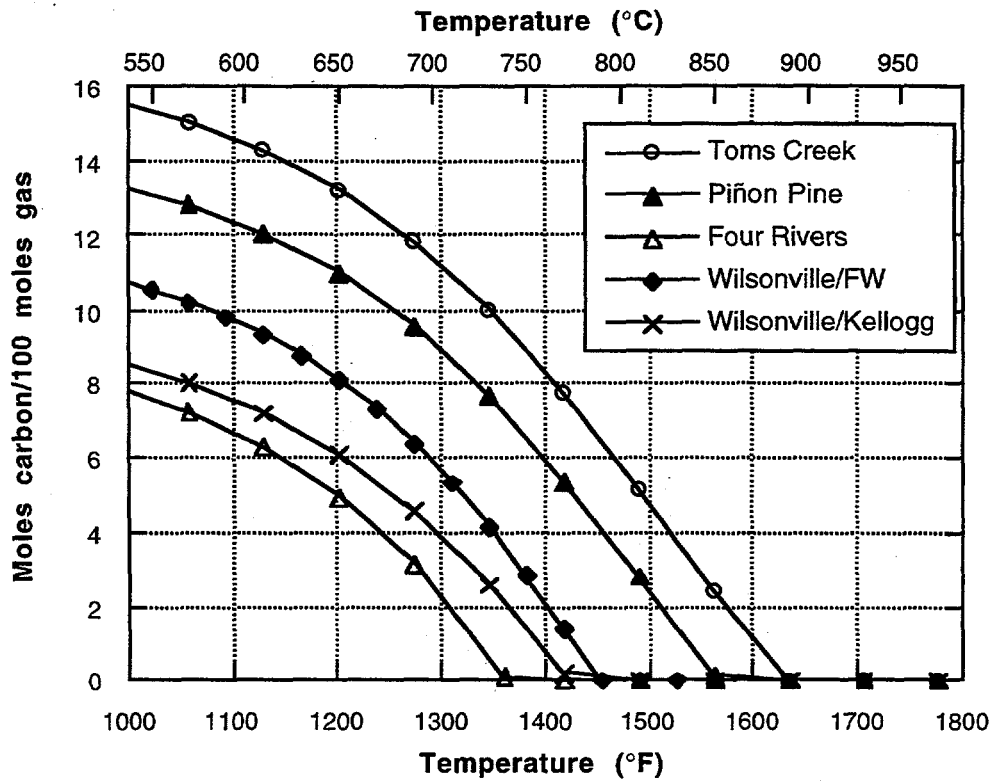


Fig. 1. SOLGASMIX-calculated equilibrium levels of solid carbon showing temperature at which unit a_c is achieved for various air-blown gasifiers.

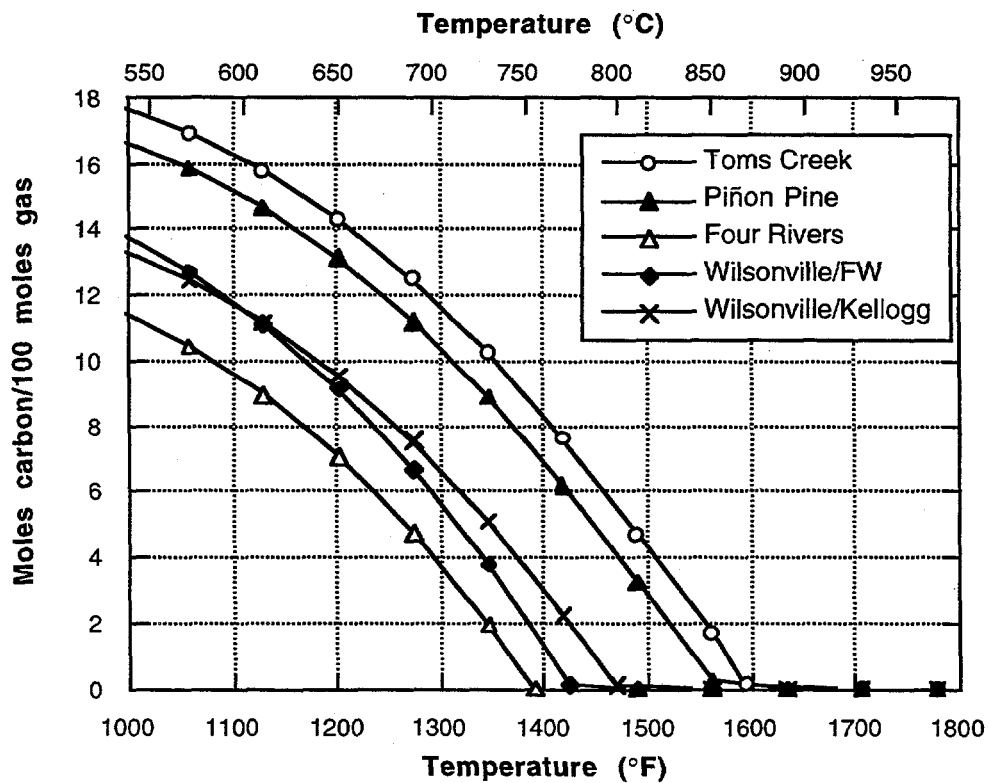


Fig. 2. SOLGASMIX-calculated equilibrium levels of solid carbon showing temperature at which unit a_c is achieved for various air-blown gasifiers under the assumption of no methane formation.

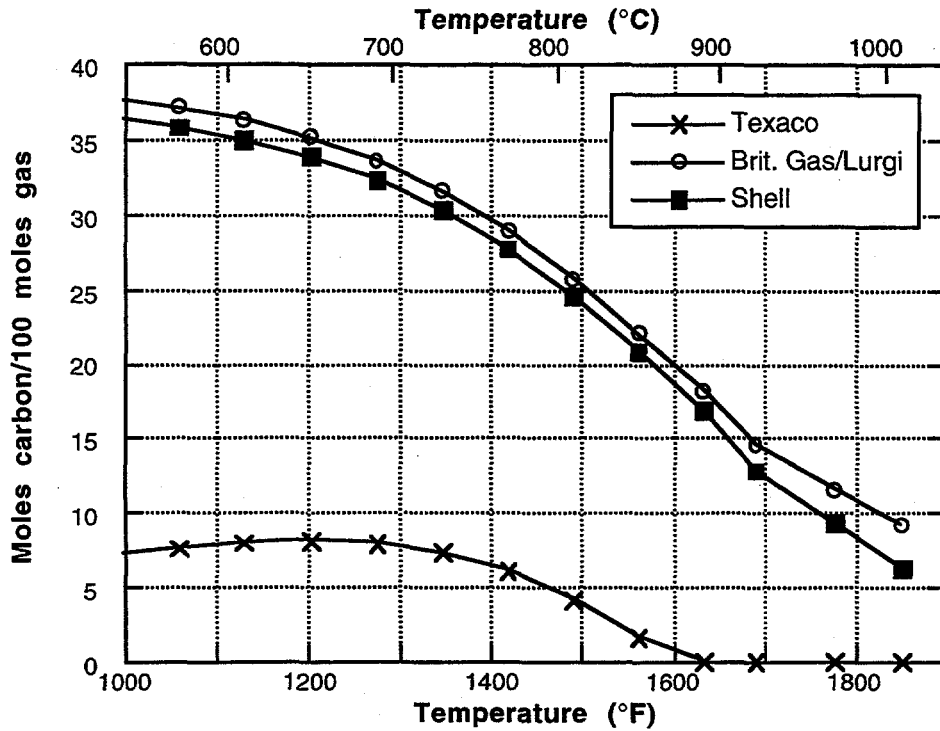


Fig. 3. SOLGASMIX-calculated equilibrium levels of solid carbon showing temperature at which unit a_c is achieved for various oxygen-blown gasifiers.

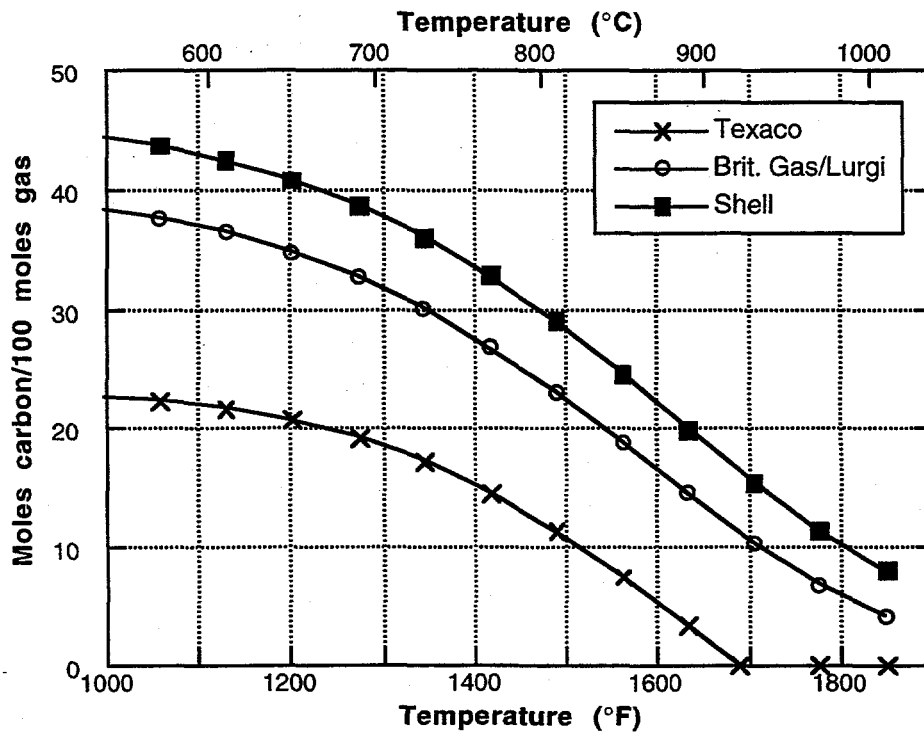


Fig. 4. SOLGASMIX-calculated equilibrium levels of solid carbon showing temperature at which unit a_c is achieved for various oxygen-blown gasifiers under the assumption of no methane formation.

Because the formation of a metastable carbide (Fe_3C , for steels) is a necessary condition for metal dusting, determination of solid-phase stabilities in different gasifier environments is an important aspect of evaluating the potential for degradation of exposed materials. Accordingly, equilibrium calculations were performed to determine the phase stability of iron-containing reaction products in contact with the product gases of air- and oxygen-blown gasifiers at 600 and 800°C (1110 and 1470°F), respectively. The Piñon Pine and Foster Wheeler/Wilsonville reference gas compositions in Table 1 were arbitrarily selected from the air-blown category, while the Shell gasifier composition in Table 2 was selected from the oxygen-blown class. The phase-stability relationships were initially determined under equilibrium considerations that limited the carbon activity to that of the most stable carbon-containing phase. Since the carbon activity of graphite ($a_c = 1$) is below that of the most stable carbide, Fe_3C , the formation of graphite supersedes that of Fe_3C under equilibrium conditions. However, if the deposition of solid carbon from the product gas is relatively sluggish, such that the carbon activity of the gas can build up above that of graphite, then Fe_3C formation becomes thermodynamically possible, particularly at lower temperatures. Accordingly, a second series of phase stability calculations was carried out in which solid carbon formation was suppressed. The H_2S concentrations used in the calculations were those listed for the given gasifiers in Tables 1 and 2. Note that the H_2S concentration can vary depending on the coal source and hot-gas cleanup system and that such changes will significantly affect the relative stability of iron sulfide in the system.

When graphite was allowed to form, phase stability calculations for both air-blown gasifiers indicated that iron oxide (FeO) predominated as the most stable iron-containing phase at 800°C (1470°F), and both iron sulfide ($\text{Fe}_{0.877}\text{S}$) and iron oxide were stable phases at 600°C (1110°F). Under these same conditions, only the $\text{Fe}_{0.877}\text{S}$ phase was stable in the case of the oxygen-blown Shell gasifier. When the formation of solid carbon was suppressed but CH_4 formation (reaction 3) was allowed, the results for the air-blown gasifiers were unchanged: FeO and $\text{Fe}_{0.877}\text{S}$ were the principal phases at 600°C (1110°F), and FeO alone was predominant at 800°C (1470°F). However, if the reaction to form CH_4 was suppressed along with the one to form solid carbon, then Fe_3C and $\text{Fe}_{0.877}\text{S}$ became the predominant phases at 600°C (1110°F) for both air-blown gasifiers. At 800°C (1470°F), Fe_3C was the predominant phase in the case of the Piñon Pine gasifier, while $\text{Fe}_{0.877}\text{S}$ and FeO were predominant in the case of the Foster Wheeler/Wilsonville gasifier. When the formation of graphite was suppressed in the case of the oxygen-blown Shell gasifier, the $\text{Fe}_{0.877}\text{S}$ phase remained stable and the Fe_3C phase did not appear even when the CH_4 reaction was suppressed. Only by lowering the H_2S content of the gas to below 0.20 vol % at 600°C (1110°F) and 0.32 vol % at 800°C (1470°F) could stability be conferred to the Fe_3C phase, where it coexisted with $\text{Fe}_{0.877}\text{S}$. At H_2S concentrations below 0.09 vol % at 600°C (1110°F) and 0.20 vol % at 800°C (1470°F), Fe_3C became the predominant phase. Similar calculations indicated that nitrogen-containing reaction products with iron would not be expected to form under equilibrium conditions even for air-blown gasifiers. A summary of the phase-stability relationships for these three gasifiers is shown in Table 3.

For the air-blown gasifiers, the appearance of the Fe_3C phase coincided with the disappearance of the iron oxide phase, which was a result of the oxygen activity of the system being reduced by the relatively high carbon activity. These phase stability calculations indicate that the formation of Fe_3C is precluded thermodynamically under conditions where an oxide can form, a finding that suggests that an FeO scale should be effective in mitigating metal dusting. The sulfide reaction product in the air-blown gasifiers was found to coexist with either the oxide or the carbide. However, in the oxygen-blown Shell gasifier, the oxide was not thermodynamically stable, and, because of the relatively high H_2S concentration (1.4 vol %), the sulfide existed to the exclusion of the carbide. It follows that at higher H_2S concentrations the sulfide can act effectively to exclude formation of Fe_3C in the same manner as an oxide, while at lower H_2S levels, where it coexists with the carbide, its effectiveness as a barrier to Fe_3C will depend on the relative nucleation and growth rates of the carbide vis-a-vis the sulfide. Because the reaction rate to form iron sulfide is significantly faster than that of iron oxide at 600°C (1110°F),¹¹ the stability of iron sulfide in this temperature range, as shown by these calculations, could be a significant factor in inhibiting the formation of Fe_3C . A general conclusion from these stability calculations is that removal of H_2S by a hot-gas cleanup system may have less effect on the formation

Table 3. Predominant solid-state phases of iron when exposed to reference product gas components

| Gasifier system | Temperature (°C) | Predominant phases | | |
|--------------------------------|------------------|--------------------|------------------------------|--|
| | | Fully equilibrated | Carbon deposition suppressed | Carbon deposition and CH ₄ formation suppressed |
| Piñon Pine (M. W. Kellogg) | 600 | Graphite, FeO, FeS | FeO, FeS | FeS, Fe ₃ C |
| | 800 | Graphite, FeO | FeO | Fe ₃ C |
| Foster Wheeler/ Wilsonville | 600 | Graphite, FeO, FeS | FeO, FeS | FeS, Fe ₃ C |
| | 800 | FeO | FeO | FeO, FeS |
| Shell (oxygen-blown) | 600 | Graphite, FeS | FeS | FeS ^a |
| | 800 | Graphite, FeS | FeS | FeS ^b |

^aFe₃C is also stable if H₂S < 0.2 vol %.

^bFe₃C is also stable if H₂S < 0.32 vol %.

of Fe₃C (and therefore on metal dusting) in the two air-blown gasifier environments, where the iron oxide phase can exist and is unaffected by the removal of sulfur, than in the Shell product gas environment, where iron sulfide provides the only significant potential barrier to Fe₃C formation.

Kinetic effects can be expected to play an important role relative to carbon deposition in gasifier systems, considering that deposition is possible only at reduced gas temperatures. (These effects, particularly those associated with H₂S and NH₃, are discussed in Sect. 3.) In fact, on the basis of the reactions 1, 2, and 3, it appears more fruitful to approach the problem of controlling carbon deposition in gasifiers by inhibiting the kinetics of the reactions rather than by altering the concentrations of major gas species. An example is the effect of adding steam to one of the reference air-blown product gases, namely, the Piñon Pine reference composition (Table 1). Equilibrium calculations were made in which the concentration of steam was doubled from the initial level of 5.5 vol % to a level of 11 vol % without changing the relative concentrations of the other gases. Even such a large steam injection did not eliminate the potential for carbon deposition, although it did lower the temperature at which unit carbon activity is achieved from 850°C (1560°F), the temperature shown in Fig. 1, to 798°C (1468°F). Accordingly, the injection of steam does not eliminate the possibility of carbon deposition, although by lowering the threshold temperature for solid carbon formation it could possibly inhibit the reaction based on kinetic effects.

Another aspect of increasing the steam content of the product gas is the effect on corrosion products formed by reaction with the containment material. By increasing the oxygen potential of the gas, steam injection could promote the formation of oxide reaction products, which may serve to prevent development of Fe₃C. Accordingly, the effect of doubling the steam content of the Piñon Pine gasifier to 11% was also examined from the standpoint of its effect on the phase stability of iron-containing reaction products. As already shown, if the formation of solid carbon is suppressed, the predominant phases formed in the nominal Piñon Pine product gas, containing 5.5% H₂O, are FeO and Fe_{0.877}S at 600°C (1110°F) and FeO at 800°C (1470°F). Increasing the H₂O content to 11% in this case did not change the stable ensembles at either

temperature. In the case where the formation of both solid carbon and CH_4 (reaction 3) is suppressed, increasing the H_2O content to 11% has no effect at 600°C (1110°F) but is beneficial at 800°C (1470°F). Both $\text{Fe}_{0.877}\text{S}$ and Fe_3C are retained as the predominant phases at 600°C , while at 800°C , the Fe_3C phase, predominant in the nominal atmosphere, is, in fact, supplanted by FeO . It appears that H_2O additions could provide an overriding effect on iron carbide formation at higher temperatures, where the carbon activity of the gas is more moderate, but very large additions would be required at lower temperatures to offset the larger carbon activities that can accrue if solid carbon deposition and CH_4 production fail to keep pace with carbon-forming reactions (such as reaction 1).