MINIMIZING FOULING AND CORROSION BY IONIC LIQUIDS FORMED IN THE COMBUSTION OF BIOMASS

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ABSTRACT

The combustion of biomass produces ionic liquids which are the probable cause of fouling and corrosion in combustion systems. Calculations of the combustion products of aspen wood at ten atmospheres indicate that a molten potassium sulfate rich liquid forms at high temperatures and is completely crystallized before 1015.3°C. A second liquid rich in calcium and potassium carbonates forms at 909.7°C and cristyllizes completely by 802.5°C. This undesirable molten carbonate presents a problem for the combustor and any equipment downstream. Addition of sulfur (or SO$_2$) to the combustor eliminates the carbonate rich phase and raises the temperature below which no liquid is present to 912.3°C by the formation of a calcium-potassium sulfate rich liquid. The combustion of wheat straw produces a liquid silica-potassium rich silicate containing small quantities of chlorides, sulfates and carbonates at high temperatures which persists to temperatures below 500°C. Mixing the wheat straw with alumina rich mixed paper waste and silica raises the temperature below which no liquid is present to 837°C. Solution theories for the prediction of the properties of multicomponent molten salts and silicates are a key factor in defining the probable cause of fouling and corrosion and in deducing possible solutions to these problems.

INTRODUCTION

Biomass is a possible alternative to fossil fuels which does not lead to a net increase of CO$_2$ in the atmosphere and produces a non-polluting ash which may be returned to the soil as a fertilizer. However, the combustion of biomass produces molten salts and/or silicates which are the probable root cause of fouling and corrosion in combustion systems. In order to minimize the problems of fouling and corrosion we need to determine the chemistry of these liquids and deduce a means for ameliorating the problems which arise because of them. To do this, we utilize the Conformal Ionic Solution Theory for molten reciprocal salt systems (1) and the Modified Quasichemical Theory (2) for molten silicates which permits one to predict the properties of...
multicomponent molten salts and silicates from the subsidiary binaries and, for silicates, also ternaries. These theories are combined with a large database for binary molten salt solutions, binary and ternary molten silicate solutions, solid solutions and over 6000 solid, liquid and gaseous species. All this information is contained in the FACT computer system (3) which also uses the CHEMSAGE algorithm for minimizing the total free energy of a chemical system (4) to calculate the equilibrium chemistry. In this paper, we discuss calculations for two typical kinds of biomass. The first is aspen wood with a composition given in Table I which contains no silica and produces molten carbonate-sulfate salts as combustion products. The second is wheat straw with a composition given in Table II which is high in silica and potassium which produces very low melting silicates as combustion products.

Table I. Composition of aspen wood (wt %)

| Element | Weight % |
|---------|----------|
| C       | 51.57    |
| H       | 6.27     |
| N       | 0.47     |
| O       | 39.52    |
| P       | 0.0085   |
| K       | 0.0810   |
| Ca      | 0.1524   |
| Mg      | 0.0256   |
| Al      | 0.001008 |
| S       | 0.025040 |
| B       | 0.000360 |
| Mn      | 0.001008 |
| Fe      | 0.001872 |
| Zn      | 0.00245  |
| Cu      | 0.000216 |
| Na      | 0.000432 |

Zn (0.00245 wt %) and Cu (0.000216 wt %) were not included as they form a small amount of benign oxides and Na (0.000432 wt %) was left out because it was overshadowed by potassium which is present in much greater abundance. 188 gm O and 619 gm N were added to 100 gm of aspen wood.

COMBUSTION OF ASPEN WOOD (5)

Because aspen wood has been considered for use in driving a turbine, we will discuss calculations for the combustion of aspen wood in an excess of oxygen at 10 atmospheres. (5) It has been shown that, at this pressure, the calculation of the inorganic chemistry of combustion indicates that a molten potassium sulfate rich liquid is formed at high temperatures, begins to crystallize at 1024.9°C and is completely crystallized at 1015.0°C to form a slightly contaminated (mole fraction 0.998) \( \text{K}_2\text{SO}_4 \) solid. A second liquid rich in calcium and potassium carbonates forms at 909.7°C and crystallizes completely by 802.5°C to a potassium sulfate-carbonate solid solution and CaCO₃.

In this paper we will examine the addition of sulfur (or SO₂) to aspen wood. The problem is the carbonate rich liquid. It is formed because the moles of potassium is larger than twice the moles of sulfur in aspen wood (Table I). As a consequence, after the potassium, sulfur and oxygen react to form a sulfate rich liquid, there is a significant amount of basic KOH vapor molecules left in the gas phase as well as solid CaO to react with the weakly acidic CO₂ molecules at low temperatures. The result is a carbonate rich
liquid which is likely to be deleterious to the combustor and to pose a definitive threat to the operation of a downstream turbine. Since $\text{SO}_2 + \frac{1}{2}\text{O}_2$ is a stronger acid than $\text{CO}_2$, addition of sulfur (or $\text{SO}_2$) will help to eliminate the molten carbonate phase by forming relatively high melting sulfates at higher temperatures. It is hoped that the separation of the consequent solids can be accomplished by a cyclone and/or filter system to effectively remove these solids well enough to operate a turbine using the combustion effluents with no significant corrosive or erosive effects.

![Table II. Elemental composition of 100 moles of wheat straw and 80 moles of waste paper.](image)

| Element | Wheat Straw | Waste Paper |
|---------|-------------|-------------|
| C       | 27.2655     | 24.59998    |
| H       | 49.0240     | 40.49816    |
| N       | 0.4747      | 0.06157     |
| O       | 22.1420     | 14.17705    |
| S       | 0.0425      | 0.02432     |
| Si      | 0.6528      | 0.23988     |
| Al      | 0.0228      | 0.52877     |
| Ti      | 0.0008      | 0.02752     |
| Fe      | 0.0078      | 0.00517     |
| Ca      | 0.0298      | 0.06853     |
| Mg      | 0.0387      | 0.03005     |
| Na      | 0.0406      | 0.00874     |
| K       | 0.1923      | 0.00173     |
| Cl      | 0.0542      | --------    |

Calculations were performed at 10 atmospheres at 25° intervals between 1200°C and 600°C for 100 g of the composition of aspen wood given in Table I with 0.115 g of S added. In Table III, one can see that a sulfate rich liquid is already present at 1200°C and, at equilibrium, disappears at 912.3°C to form the solid stoichiometric compounds $\text{CaSO}_4$ and $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ by a peritectic reaction. The second solid, $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$, decomposes to a $\text{K}_2\text{SO}_4$ rich (0.998 $\text{K}_2\text{SO}_4$ at 800°C) solid solution and $\text{CaSO}_4$. If a large fraction of the solid $\text{CaO}$, which is present at very high temperatures, precipitates in the high temperature region of the combustor, the liquid sulfate would be much higher in potassium, would have a higher liquidus temperature and thus would crystallize earlier at a higher temperature. Careful design for this separation might be possible and could improve the efficiency of the combustor. In Table IV, the mole fractions of the important gas species in the 30.769 moles of gas are given. The most important results are the low values for KOH and $\text{SO}_2$ mole fractions at 600°C which are both $<10^{-9}$. Thus we have managed to reduce the KOH content in the gas by the addition of sulfur and prevented the formation of a deleterious molten carbonate without having a significant amount of $\text{SO}_2$ as an environmental pollutant. Other acidic additives might further broaden the range of temperatures in which no ionic liquid is present. In addition to the above gaseous and
solution phases there are a number of stoichiometric solids formed which are exhibited in Table V and a spinel solid solution formed exhibited in Table VI.

### Table III. Mole fractions of components and number of moles of molten and solid salt solutions produced in the combustion of 100 gm of aspen wood with 0.115 gm of S added at 10 atmospheres.

| T(°C) | 1200 | 1100 | 912.3 | 800 | 600 |
|-------|------|------|-------|-----|-----|
| CaSO₄ (lq) | 0.771 | 0.730 | 0.536 | ----- | ----- |
| K₂SO₄ (lq) | 0.215 | 0.258 | 0.462 | ----- | ----- |
| CaCO₃ (lq) | 1.04E-2 | 8.98E-3 | 1.08E-3 | ----- | ----- |
| K₂CO₃ (lq) | 2.91E-3 | 3.17E-3 | 9.36E-4 | ----- | ----- |
| moles | 3.41E-3 | 3.64E-3 | 0 | 0 | 0 |
| K₂SO₄ (ss) | ----- | ----- | ----- | 0.998 | 1.000 |
| CaSO₄ (ss) | ----- | ----- | ----- | 1.92E-3 | 3.91E-4 |
| K₂CO₃ (ss) | ----- | ----- | ----- | 4.18E-5 | 7.41E-5 |
| CaCO₃ (ss) | ----- | ----- | ----- | 8.04E-8 | 2.90E-8 |
| moles | 0 | 0 | 0 | 1.04E-3 | 1.04E-3 |

lq refers to the liquid solution and ss refers to the solid solution

Note that there is no solid solution at 912.3°C because the stable solids are CaSO₄ and K₂Ca₂(SO₄)₃.

### Table IV. Mole fractions of gaseous species formed during the combustion of 100 gm of aspen wood with 0.115 gm S added, at 10 atmospheres.

| T(°C) | 1100 | 1000 | 900 | 800 | 700 | 600 |
|-------|------|------|-----|-----|-----|-----|
| NO | 2.84E-4 | 1.53E-4 | 7.37E-5 | 3.11E-5 | 1.10E-5 | 3.05E-6 |
| OH | 9.02E-6 | 2.95E-6 | 7.99E-7 | 1.69E-7 | 2.62E-8 | 2.64E-8 |
| KOH | 4.25E-6 | 6.50E-7 | 1.19E-7 | 2.51E-8 | 2.81E-9 | ----- |
| SO₂ | 4.40E-6 | 1.13E-6 | 5.99E-8 | ----- | ----- | ----- |
| NO₂ | 3.11E-6 | 2.49E-6 | 1.93E-6 | 1.42E-6 | 9.80E-7 | 6.24E-7 |
| KBO₂ | 7.49E-7 | 9.57E-8 | 6.31E-9 | ----- | ----- | ----- |
| K₂SO₄ | 3.45E-7 | 1.04E-7 | 1.81E-8 | 1.64E-9 | ----- | ----- |
| SO₃ | 2.14E-7 | 1.07E-7 | 1.24E-8 | ----- | ----- | ----- |
| HBO₂ | 1.26E-7 | 4.47E-8 | 5.88E-9 | ----- | ----- | ----- |
| O | 3.91E-8 | 6.83E-9 | ----- | ----- | ----- | ----- |
| H₂BO₃ | 2.07E-7 | 2.65E-7 | 1.58E-7 | 8.49E-8 | 3.95E-8 | 1.51E-8 |
| N₂O | 4.83E-8 | 2.69E-8 | 1.36E-8 | 6.12E-9 | 2.34E-9 | ----- |
| Ca(OH)₂ | 4.02E-9 | ----- | ----- | ----- | ----- | ----- |
| Mg(OH)₂ | 2.45E-9 | ----- | ----- | ----- | ----- | ----- |

The fractional partial pressures and total number of moles of the major species are essentially constant at all temperatures at N₂ = 0.7186, CO₂ = 0.1395, H₂O = 0.1011, O₂ = 0.0406 and 30.769 moles.

----- denotes <10⁻⁹ mole fraction in the gas phase.
Table V. Moles of solid compounds produced in the combustion of 100 gm of aspen wood with 0.115 gm of S added at 10 atmospheres.

| T(°C) | Moles of Compounds |
|-------|--------------------|
|       | MgO | CaO | CaSO4 | Ca3Ho13P3 | Ca2Al2O5 | Ca2Fe2O5 | Mn3O4 | Mg3B2O6 | K2Ca2(SO4) | CaFe2O4 | MnO3 | MgFe2O4 | CaCO3 |
| 1200  | 1.05 E-3  | 5.85 E-4 | 6.23 E-4 | 9.15 E-5 | 1.87 E-5 | 1.67 E-5 | 6.12 E-6 | 1.04 E-5 | 1.03 E-3 | 2.36 E-6 | 3.00 E-6 | 4.72 E-5 | 1.26 E-3 | 3.33 E-3 |
| 1100  | 1.05 E-3  | 5.85 E-4 | 1.58 E-3 | 9.15 E-5 | 1.26 E-3 | 1.67 E-5 | 1.27 E-6 | 1.40 E-5 | 1.31 E-5 | 1.31 E-5 | 7.09 E-6 | 1.67 E-5 | 1.26 E-5 | 3.33 E-3 |
| 1000  | 1.01 E-3  | 6.23 E-4 | 1.26 E-3 | 9.15 E-5 | 9.15 E-5 | 1.44 E-5 | 1.75 E-6 | 1.60 E-5 | 1.26 E-5 | 1.26 E-5 | 8.35 E-6 | 1.67 E-5 | 1.03 E-3 | 1.03 E-3 |
| 900   | 1.00 E-3  | 1.01 E-3 | 3.33 E-3 | 9.15 E-5 | 9.15 E-5 | 9.15 E-5 | 1.87 E-5 | 1.60 E-5 | 1.26 E-5 | 1.26 E-5 | 8.35 E-6 | 1.67 E-5 | 1.03 E-3 | 1.03 E-3 |
| 700   | 9.86 E-4  | 9.86 E-4 | 9.86 E-4 | 9.15 E-5 | 9.15 E-5 | 9.15 E-5 | 1.87 E-5 | 1.60 E-5 | 1.26 E-5 | 1.26 E-5 | 8.35 E-6 | 1.67 E-5 | 1.03 E-3 | 1.03 E-3 |
| 600   | 9.70 E-4  | 9.70 E-4 | 9.70 E-4 | 9.15 E-5 | 9.15 E-5 | 9.15 E-5 | 1.87 E-5 | 1.60 E-5 | 1.26 E-5 | 1.26 E-5 | 8.35 E-6 | 1.67 E-5 | 1.03 E-3 | 1.03 E-3 |

Table VI. Spinel solid solutions formed during combustion of aspen wood with added sulfur at 10 atm.

| T(°C) | MnAl2O4 | MgAl2O4 | FeAl2O4 |
|-------|---------|---------|---------|
| 1100  | 0.778   | 0.222   | 4.7 E-5 |
| 1000  | 0.701   | 0.299   | 1.3 E-5 |
| 900   | 0.586   | 0.414   | 7.9 E-5 |
| 800   | 0.409   | 0.591   | 2.2 E-5 |
| 700   | 0.223   | 0.777   | 4.3 E-6 |
| 600   | 0.088   | 0.912   | 4.8 E-7 |

Moles of spinel are constant at all temperatures at 1.87 E-5.

COMBUSTION OF WHEAT STRAW

Wheat straw is a common waste which is a potential source of energy that does not contribute to the greenhouse effect. However, combustion of wheat straw leads to problems with fouling and corrosion of combustors and power systems (6). This has led to the derating of experimental combustors in several European countries (6). In order to understand this problem, we have performed calculations of the inorganic chemistry of 100 moles of wheat straw using the composition given in Table II. The most striking result is given in Table VII which gives the compositions (mol%) and moles of a silicate melt which is present at 1200°C and persists to temperatures below 500°C. The melt is largely composed of silica and potassium oxide (88-94 mole%) with lesser amounts of the oxides of Ca, Na, Mg, and Al. The Cl, S04, and CO3 designate the sums of the concentrations of the anions in salts of these ions with K, Ca, Na, and Mg. These were combined to simplify the Table with an insignificant loss of information.
Table VII. Composition of molten condensates in wheat straw combustion effluents (mol %)

| T°C | 1200 | 1000 | 800  | 600  | 500  |
|-----|------|------|------|------|------|
| SiO2 | 80.91 | 82.65 | 80.49 | 77.82 | 76.28 |
| K2O | 9.66 | 11.23 | 11.15 | 11.79 | 11.71 |
| CaO | 2.92 | 0.49  | 0.64  | 0.82  | 0.85  |
| Na2O | 2.57 | 2.81  | 4.24  | 4.89  | 5.66  |
| MgO | 2.46 | 1.11  | 0.37  | 0.06  | 0.02  |
| Al2O3 | 1.47 | 1.61  | 2.67  | 3.78  | 4.51  |
| Cl | 0.61 E-3 | 4.46 E-3 | 65.59 E-3 | 0.50  | 0.50  |
| CO2 | 0.51 E-3 | 89.93 E-3 | 0.39  | 0.35  | 0.33  |

Obviously, wheat straw produces deleterious molten silicates in a combustor and this is the root cause of the problems which led to derating of combustors by lowering the operating temperature. Any methods for converting these liquids to solids might help to make the efficient combustion of wheat straw for power production feasible.

One possible additive is alumina which tends to form some relatively high melting aluminosilicates. Rather than use alumina directly, we chose to use an alumina rich mixed waste paper with a composition given in Table II. Aluminum is the most abundant element in this waste after H, C and O. Calculations were made for 100 elemental moles of wheat straw, 80 elemental moles of mixed waste paper, 148.5 moles of O, 558.6 moles of N and 0.5 moles of SiO2. The silica was added because of a flaw in the computer program for silicates with high alumina content. The silica addition helped to circumvent this flaw which didn't allow the calculation to converge and which we

Table VIII. Molten silicate compositions (mol%) produced in the combustion of 100 moles of wheat straw mixed with 80 moles of mixed waste paper and 0.5 moles of SiO2.

| T°C | 1150 | 1050 | 950  | 850  | 837  |
|-----|------|------|------|------|------|
| SiO2 | 72.80 | 78.88 | 82.06 | 81.62 | 81.29 |
| Al2O3 | 13.60 | 10.75 | 9.00  | 8.73  | 8.80  |
| K2O | 5.60 | 5.68  | 5.04  | 4.84  | 4.85  |
| Na2O | 1.45 | 2.04  | 2.37  | 3.45  | 3.68  |
| CaO | 3.81 | 1.85  | 1.30  | 1.22  | 1.22  |
| MgO | 2.72 | 0.80  | 0.23  | 0.12  | 0.12  |
| Cl | 8.32 E-5 | 8.54 E-5 | 1.06 E-4 | 3.90 E-4 | 5.13 E-4 |
| SO4 | 9.53 E-6 | 3.75 E-5 | 3.03 E-4 | 2.17 E-2 | 4.39 E-2 |
| CO3 | 1.00 E-8 | -------- | -------- | -------- | -------- |
| Moles | 1.693 | 1.052 | 0.946 | 0.769 | 0.000 |
hope to correct in the near future. Equilibrium compositions were calculated at 25° intervals between 550°C and 1150°C. Some of the results for the molten silicate are exhibited in Table VIII. The liquid contains considerably more alumina than do the liquids produced by wheat straw alone. The liquid crystallizes completely at 837°C, thus significantly raising the temperature below which there is no liquid present. The 392.8 moles of residual gases are not displayed and tend to be acidic. Tables IX and X exhibit the stoichiometric solids and the ideal solid plagioclase solution. Clearly, the use of additives shows promise for improving the performance of biomass as a source of energy. When the flaw in the current program is corrected, we can aggressively examine the ability of a number of additives to optimize the performance of wheat straw.

| Table IX. Moles of stoichiometric solids formed in the combustion of wheat straw mixed with waste paper and 0.5 mole SiO₂. |
|---|---|---|---|---|---|---|
| T(°C) | 1050 | 950 | 850 | 750 | 650 | 550 |
| K₂Al₂Si₆O₁₈ | 0.0420 | 0.0672 | 0.1060 | 0.0833 | 0.0765 | ------ |
| Mg₂Al₅Si₆O₁₈ | 0.0297 | 0.0333 | 0.0342 | 0.0344 | 0.0344 | 0.0344 |
| Fe₂O₃ | 0.0065 | 0.0065 | 0.0065 | 0.0065 | 0.0065 | 0.0065 |
| Al₂Si₂O₅ | 0.0109 | ------ | ------ | ------ | ------ | ------ |
| Al₂SiO₅ | ------ | 0.0366 | 0.0394 | 0.0372 | 0.1024 | 0.1040 |
| SiO₂ | ------ | ------ | 0.2920 | 0.3415 | 0.3994 | 0.3241 |
| CaSO₄ | ------ | ------ | ------ | 0.0651 | 0.0668 | ------ |

| Table X. Mole % and number of moles of hypothetical ideal plagioclase solid solution formed in combustion of 100 moles of wheat straw mixed with 80 moles of waste paper and 0.5 moles SiO₂. |
|---|---|---|---|---|---|---|---|
| T(°C) | 1150 | 1050 | 950 | 850 | 750 | 650 | 550 |
| CaAl₂Si₂O₈ | 89.69 | 79.81 | 70.62 | 49.44 | 38.06 | 16.60 | 11.47 |
| K₂Al₂Si₂O₈ | 9.84 | 18.90 | 25.79 | 33.54 | 42.85 | 58.75 | 70.59 |
| NaAl₂Si₂O₈ | 0.47 | 1.30 | 3.59 | 17.02 | 19.09 | 24.64 | 17.94 |
| Moles | 0.038 | 0.096 | 0.122 | 0.193 | 0.258 | 0.200 | 0.275 |

CONCLUSIONS

Calculations of the inorganic chemistry of the combustion of aspen wood and wheat straw have defined the root causes of fouling and corrosion. Calculations of the influence of additives have demonstrated potential improvements in performance of the combustion products. Further calculations will be needed to find additives which might provide optimal performance beyond these promising results. These calculations were made possible by theories of molten salts and silicates which permit one to make reliable
calculations of the thermodynamic properties of multicomponent solutions from properties of the lower order binary and (for silicates only) ternary systems.

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REFERENCES

1. M. Blander and S. J. Yosim, J. Chem. Phys., 39 2610 (1963)
2. M. Blander and A. D. Pelton, Geochim. Cosmochim. Acta, 51 85-95 (1987)
3. C. W. Bale, A. D. Pelton and W. T. Thompson, Facility for the Analysis of Chemical Thermodynamics, CRCT, Ecole Polytechnique de Montreal, P. O. Box 6079, Station “Downtown”, Montreal, Quebec H3C3A7, Canada
4. G. Eriksson and K. Hack, Metall. Trans., 21B 1013 (1990)
5. M. Blander, K. W. Ragland, R. L. Cole, J. A. Libera and A. D. Pelton, Biomass and Bioenergy, 8 29-38 (1995)
6. T. R. Miles, T. R. Miles Jr., L. L. Baxter, R. W. Bryers, B. M. Jenkins and L. L. Oden, Alkali Deposits Found in Biomass Power Plants: A Preliminary Investigation of Their Extent and Nature, Summary Report, NREL/TP-433-8142, National Renewable Energy Laboratory, Golden, CO, U. S. A.