

Low-temperature corrosion caused by alkali phosphate containing particulates in biomass conversion

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ABSTRACT

Maximizing energy recovery by keeping flue gas temperatures as low as possible is of great industrial interest. In biomass fired boilers lowest temperature is often determined by hygroscopic deposits. While it is well known that in fossil fuel combustion the limiting factor in lowering flue gas temperatures is the sulfuric acid dew point; in biomass combustion the situation is different. Recent studies have shown that virtually no sulfuric acid is present in the flue gas in biomass combustion, because of the presence of alkaline ash that effectively captures any SO₃ formed and relatively low combustion temperatures. Low-temperature corrosion is still a problem in biomass combustion and one possible explanation is the presence of hygroscopic salts in deposits. Hygroscopic salts absorb moisture from the flue gas to form a wet deposit leading to wet corrosion at a much higher temperature than the pure water dew point. Low-temperature corrosion caused by deposition of hygroscopic particulate matter on surfaces may occur well above 100°C if the moisture content of the fuel is high enough. In this work we have studied phosphates and their ability to absorb water. The work reveals interesting new findings on the absorption of water from the flue gas and the resulting corrosion.

Keywords: *Low-temperature corrosion, biomass, particulate matter, deposits, deliquescence*

BACKGROUND

Efficient use of energy in flue gases is of great importance in biomass boiler operation. Recovering the heat in the flue gases is a prerequisite when developing competitive thermal biomass conversion processes. One easy way is to lower the boiler exit flue gas temperature since every 10°C drop in temperature could potentially increase the boiler thermal efficiency by 0.5%. Lowering the temperature of the flue gases can lead to corrosion of cooler surfaces, here referred to as low-temperature corrosion. One of the concerns with respect to lowering the flue gas temperature is the sulfuric acid dew point. If the temperature of heat exchangers is lower than the sulfuric acid dew point it may lead to severe corrosion [1]. However, recent studies in biomass boilers have shown that sulfuric acid is virtually not present, and is not the limiting factor in lowering flue gas temperatures [2-5]. It has been found that hygroscopic salts can lead to the absorption of water and subsequent corrosion at relatively high temperatures (>100°C) [2-6]. In a study of low-temperature corrosion in a bubbling fluidized bed boiler burning biomass, it was concluded that the limiting factor in lowering flue gas temperatures was the presence of hygroscopic deposits [2]. Furthermore, it has been shown in small grate-fired biomass boilers that hygroscopic salts caused corrosion with material temperatures of up to 100°C [5]. Hygroscopic CaCl₂ and ZnCl₂ and the subsequent formation of a wet deposit were suggested to be the cause of corrosion in these boilers.

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The use of low-grade biomass fuels, such as agricultural fuels, has become increasingly popular in energy production. Combustion of pyrolysis oil and char from the pyrolysis of agricultural residues to substitute fossil fuels is also increasing. Agricultural fuels contain phosphorus, which form particulate matter containing phosphates. These phosphates may cause low-temperature corrosion in boilers by forming hygroscopic deposits. Hygroscopic salts will absorb moisture from the flue gas at a temperature higher than the pure water dew point. When the temperature of the flue gas is sufficiently lowered, the solid salt will begin to absorb water. As the temperature is lowered further, enough water will be absorbed that the salt is fully dissolved. The temperature at which the salt is fully dissolved at a given vol% water, is referred to as the deliquescent temperature. The deliquescent temperature is different for different salts and salt mixtures. Almost all of the work on the deliquescent properties of salts has been done in the field of atmospheric chemistry (e.g. [8] and [9]). However, no systematic work has been done on the deliquescent properties of salts in combustion related conditions and very little has been done in the area of corrosion due to the absorption of water by hygroscopic salts [6][10]. Two phosphates that may form in thermal conversion of biomass containing potassium and phosphorous are K_3PO_4 and KH_2PO_4 [11]. In this study, the absorption of water by these phosphates is studied and the deliquescent temperatures are determined for three different levels of water vapor.

EXPERIMENTAL

The temperature of deliquescence was studied in a reactor shown in Fig. 1a. About 50 mg of salt (K_3PO_4 and KH_2PO_4) was placed on a sample holder and inserted in the reactor. The reactor was heated to 200°C with nitrogen flowing through it. The deliquescent temperature was determined at three different water vapor concentrations: 15, 25 vol%, and 50 vol%. The higher water vapor concentrations were chosen to be representative of conditions during soot-blowing in a biomass boiler when the water vapor concentration can locally be very high. The rest of the gas consisted of N_2 , and the total flow was 2 NI/min.

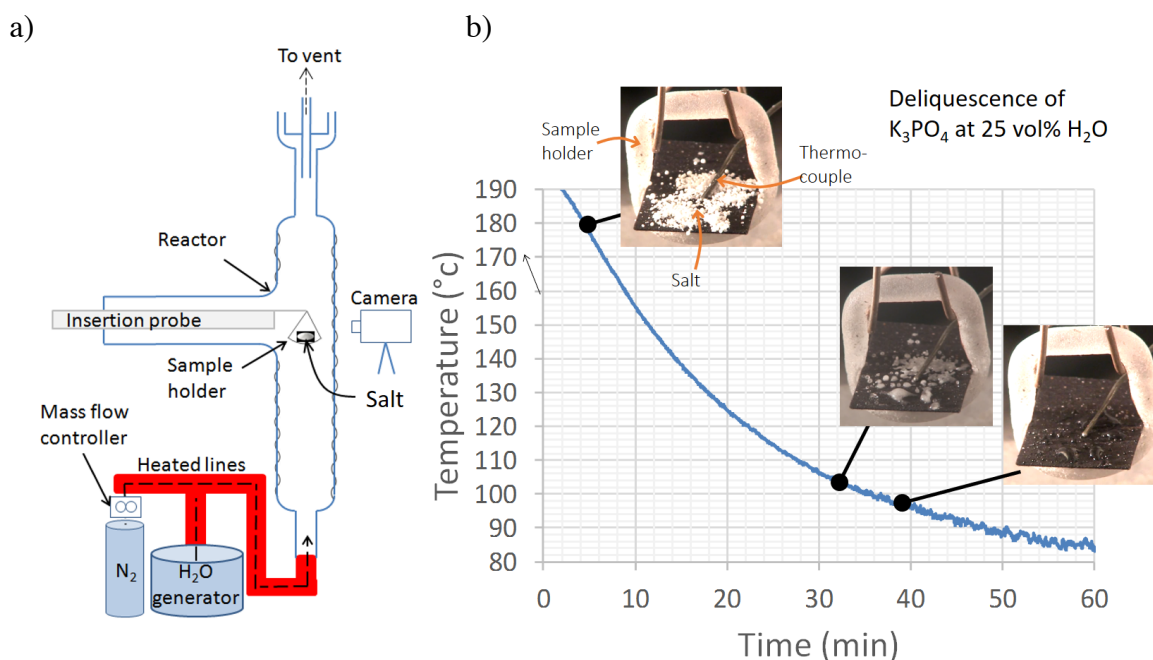


Fig. 1. a) Schematic of the reactor used to study the deliquescent behavior of K_3PO_4 . b) Typical temperature profile in the reactor and pictures of the sample holder from a test with 25 vol% H_2O .

The temperature of the furnace was slowly lowered and the uptake of water by the salt visually recorded with a video camera. The temperature of deliquescence was determined as the point at which the salt particles were completely dissolved by absorbed water. This was easier to observe using smaller salt grains than when using a larger salt pill. Fig. 1b shows a typical temperature profile in the reactor from a test with 25 vol% H₂O. The deliquescent point is at about 104°C.

RESULTS

The deliquescence temperature of K₃PO₄ at 15, 25, and 50 vol% H₂O are presented in Fig. 2. At 15 vol% water vapor in the gas, K₃PO₄ started to form a solution at 80°C. At 50 vol% H₂O deliquescence occurred at 102°C and at 50 vol% at 122°C. When heating up the salt at 25 vol% water vapor a hysteresis effect was observed; the salt started to recrystallize at a temperature about 20°C higher than the deliquescence temperature. These results illustrate that if a deposit contains K₃PO₄, it can absorb significant amounts of water well above 100°C. These deliquescent temperatures are the temperatures at which the salt absorbs enough water to fully dissolve. The salts will absorb some water at even higher temperatures. Near sootblowers wet deposits of hygroscopic K₃PO₄ can be formed at surprisingly high temperatures. However, KH₂PO₄ did not show deliquescence properties; with a water vapor concentration of 25 vol% deliquescence did not occur even when the temperature was dropped very close to the water dew point of 65°C.

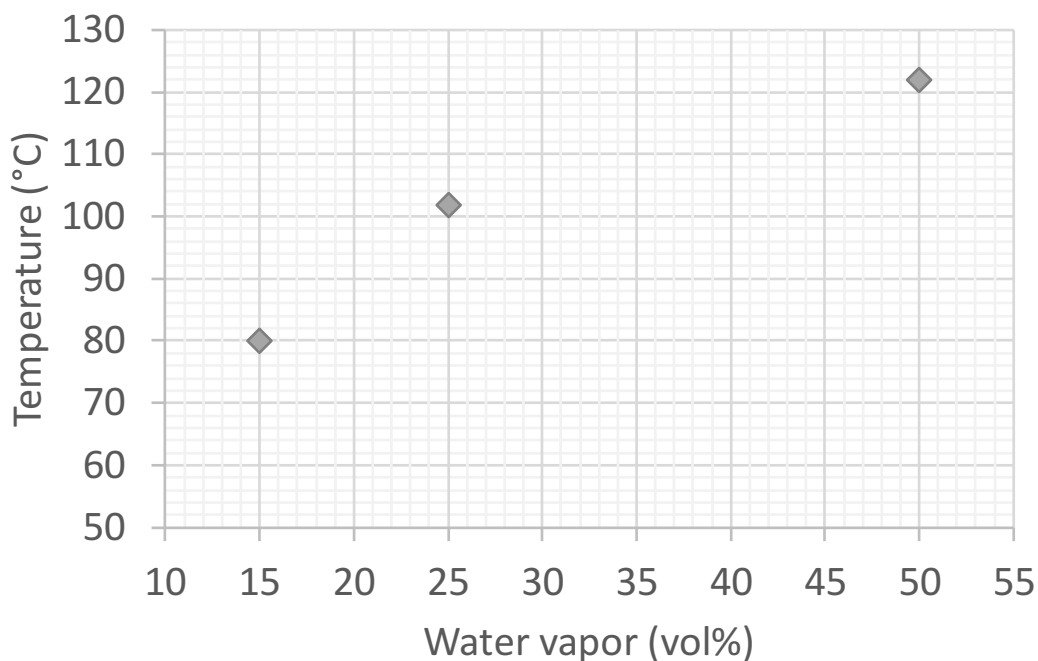


Fig. 2 Deliquescence temperature for K₃PO₄ at 15, 25, and 50 vol% H₂O in the gas. Deliquescence of KH₂PO₄ was not observed.

CONCLUSIONS

Particulate matter formed in biomass thermal conversion may cause severe corrosion of heat-exchangers and flue gas ducts by forming hygroscopic deposits. Hygroscopic deposits may absorb water and if the temperature is below the deliquescence temperature, i.e. the temperature at which the salts absorb enough water to totally dissolve, it will lead to wet corrosion. For K_3PO_4 and a water vapor concentration of 25 vol%, this will occur at temperatures above 100°C. The temperature of deliquescence at 15 vol% H_2O is about 80°C. The deliquescence temperature at 25 and 50 vol% H_2O were 102 and 122°C, respectively. Once K_3PO_4 absorbs water, the water is released at a much higher temperature than the deliquescence temperature. Near sootblowers the water content may locally be high and thus cause wet corrosion at relatively high temperatures. On-going work studying deposits and salt mixtures containing various other phosphates together with other salts (KCl , K_2CO_3 , K_2SO_4 , $CaCO_3$, $CaSO_4$ etc.) will provide more detailed information of the corrosiveness as well as deliquescent properties of other hygroscopic salts and mixtures.

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