Thermodynamic research on the effect of H$_2$O on transformation of organic sulphur during coal pyrolysis under CO$_2$ atmosphere

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Abstract. This study investigates the effect of H$_2$O on transformation of organic sulphur in coal during CO$_2$ atmospheres by thermodynamic equilibrium calculation by HSC Chemistry. The effect of water vapour on the release of sulphur containing compounds was studied. Detailed S distribution between 200-1400℃ was explored. The results show that CO$_2$ not only promotes the formation of inorganic compounds, but also moves the peak of released less complicated organic compounds such as Thiophene, Methylthiophene, Dimethylthiophene, etc. to a much lower temperature. The ranking of the sulphur release in CO$_2$ atmosphere by HSC is: SO$_2$ > Methyl thiophene > Dimethyl thiophene > Ethyl thiophene > dimethyl sulfone. Temperature affects the transformation of sulphur greatly during pyrolysis in CO$_2$ atmosphere. Below 700 ℃, COS and H$_2$S are two major sulphur containing compounds formed during pyrolysis in CO$_2$. Above 700 ℃, SO$_2$ plays the main role. H$_2$O at different temperature range during heating also reacts with organic sulphur compounds, leading to a further decomposition. Since more organic S stays in inert gas, water promotes the decomposition of organic S compounds more intense than that in CO$_2$ atmosphere. Besides, the effect of water vapour on S distribution depends on the amount of H$_2$O in the reaction.

Key words: Organic sulphur; Pyrolysis; CO$_2$; HSC Chemistry; Coal

1. Introduction
In oxy-fuel combustion, much higher concentration of CO$_2$ and water vapour in flue gas caused a few changes comparing to traditional coal combustion. Radiation is enhanced due to the increased radiative heat transfer from the flame by increased concentration of tri-atomic gas molecules[1, 2]. However, with wet flue gas recirculation, potential corrosion in piping became a problem, in case of water temperature below dew point, leading to the risk of low temperature acid corrosion. SO$_2$ is dissolved forming hydrogen sulphite, then it would be oxidated to sulphate in the atmosphere of high CO$_2$ concentration, which would highly likely cause corrosion during wet flue gas recirculation. Desulfurization is significant for oxy-fuel power plant with wet flue gas recirculation. In order to study the release of SO$_2$ during combustion, to understand the mechanism of sulphur containing compounds release during pyrolysis is the first step, especially in CO$_2$ atmosphere. Coal sulphur include organic and inorganic sulphur. The transformation and fate of sulphur during different reductive or inert pyrolysis atmosphere was studied by many researchers[3-7], while there are only a few researchers who work on sulphur transformation in CO$_2$ [3, 8, 9]. It was found out that aliphatic sulphide, thiophene, sulfoxide and sulphone became the dominant organic S after CO$_2$
gasification[3]. Atmospheric pressure-temperature programmed reduction (AP-TPR) “on-line” coupled with MS and AP-TPR “off-line” coupled with TD-GC/MS, were used for coal sulphur characterization[8, 9], the result shows that decomposition of organic sulphanic acids occurs before 500 °C and decomposition of sulphonics/sulphoxides is after 500 °C. However, the interactions of the inorganic sulphur and organic sulphur during pyrolysis with increasing temperature is hard to detect due to limits of experimental technology.

In oxy-fuel combustion with wet recycle, the concentration of water vapour in the flue gas can reach 30% vol, which is much higher than that in traditional coal combustion. The higher amount of H₂O and CO₂ have great effects on the transformation of sulphur containing compounds distribution[10-12]. However, the research on the effect of water vapour on the transformation of organic sulphur compounds was rare.

In this paper, HSC Chemistry was used for thermodynamic equilibrium calculation which is based on the principle of minimizing Gibbs free energy. The main focus is on the effect of H₂O on transformation and distribution of sulphur containing compounds during coal pyrolysis in CO₂ atmosphere.

2. Modelling procedure

In this paper, the thermodynamic equilibrium calculation software HSC Chemistry was used to study the organic sulphur decomposition and transformation during coal pyrolysis in CO₂ atmosphere. Based on the principle of minimizing Gibbs free energy, HSC Chemistry provides a powerful calculation method to study the effects of different variables on the thermal equilibrium of chemical systems.

Dibenzothiophene, is a typical organic sulphur in coal which is chosen for calculation. The released sulphur related compounds include SO₂, H₂S, COS, CS₂, SO₃, Thiophene, 2-Methylthiophene, 3-Methylthiophene, 2,3-Dimethylthiophene, 2,4-Dimethylthiophene, 2,5-Dimethylthiophene, Benzothiophene, 2-Methylbenzo[b]thiophene, Dimethyl sulfone, etc.. Besides, the effect of H₂O was also calculated during coal pyrolysis. For calculation 1kmol Dibenzothiophene was used, the atmosphere gas was 600 kmol to simulate the pyrolysis environment. With the certain given reaction temperature (200-1400 °C), the amount of chemical species can be determined in the program when all the specified sulphur containing compounds and pyrolysis gas in the reaction reach the equilibrium.

3. Results and discussion

3.1. The effect of pyrolysis atmosphere on sulphur distribution

Two atmospheres were used for thermodynamic equilibrium calculation, N₂ and CO₂ respectively. Figure 1 shows inorganic compounds distribution during pyrolysis in the atmosphere of N₂ and CO₂. It can be clearly seen in the right Figure 1(b) that more different sulphur containing compounds were released during pyrolysis in CO₂, including COS, H₂S, and SO₂, the amount was by three orders of magnitude larger than that in N₂. COS was released at the beginning from low temperature, with the first peak at 300 °C, the same as the peak of CH₄. Then COS increased slowly from 420 °C until 750 °C, where it reached a second peak. For H₂S, around 300 °C H₂S started to increase rapidly, with a peak at around 420 °C, which is also the start point that COS increased again. The release of SO₂ was from the temperature of 750 °C, which is at a considerably later stage, the increasing rate fell to almost zero at around 1100 °C. The result shows that the sulphur in part of H₂S converts to COS between the temperature range of 420 °C to 750 °C, while from 750 °C to 1100 °C sulphur in both COS and H₂S converts to sulphur in SO₂. The possible reactions were listed as below.

\[
\text{H}_2\text{S}+\text{CO}_2 \rightarrow \text{COS}+\text{H}_2\text{O} \\
\text{H}_2\text{S}+3\text{CO}_2 \rightarrow \text{H}_2\text{O}+\text{SO}_2+3\text{CO}
\]
In the left Figure 1(a) it shows that the pyrolysis gas N\textsubscript{2} has great effect on the release of inorganic sulphur related compounds. Comparing to all the different compounds in Figure 1(b), there were very few inorganic compounds released in N\textsubscript{2} atmosphere. COS was formed at low temperature before 400 °C, with a peak of 0.0012 kmol, while in CO\textsubscript{2} the first peak of COS almost reaching 1 kmol. Unlike that in CO\textsubscript{2}, H\textsubscript{2}S released in N\textsubscript{2} atmosphere was also very limited. The increasing of CS\textsubscript{2} also started at very low temperature, and it increased rapidly until at the temperature around 400 °C, afterwards, the release of CS\textsubscript{2} kept a very stable tendency even at high temperature. The results show that in N\textsubscript{2}, the sulphur in COS and H\textsubscript{2}S converts to sulphur in CS\textsubscript{2} with the increasing temperature. In addition, very small amount of SO\textsubscript{3} was found in CO\textsubscript{2} atmosphere, while that was not in N\textsubscript{2}.

Comparing to the organic sulphur containing compounds released in two different atmospheres which is shown in Figure 2, the obtained result shows that much more organic sulphur containing compounds were released in N\textsubscript{2} than that in CO\textsubscript{2}. In CO\textsubscript{2} atmosphere, most organic sulphur related compounds were released before 300 °C, with a peak temperature at around 240 °C. However, in the atmosphere of N\textsubscript{2}, the released compounds peak temperature differs a lot. Thiophene, Methylthiophene, Dimethylthiophene, Benzothiophene, Ethyl thiophene have its peak temperature at 1250 °C, 1125 °C, 1000 °C, 950 °C and 650 °C respectively. Generally speaking, more complicated compounds were released at considerably lower temperature, while at higher temperature during the pyrolysis, more complicated sulphur related compounds convert to less complicated compounds, which are more stable at higher temperature. For example, Thiophene, which has the smallest molecular weight of all the specified compounds, increased from 400 °C, reaching a peak at the temperature of 1250 °C in CO\textsubscript{2} atmosphere. Ethyl thiophene is an exception, having the same molecular weight with Dimethylthiophene, Ethyl thiophene’s peak temperature is only 650 °C. The possible reason might be that Ethyl thiophene is not stable and easy to convert to other compounds at higher temperature. Besides, the amount of Ethyl thiophene is very low, quantity class is at 10 of -18 power.
Figure 2 Organic sulphur containing compounds distribution during pyrolysis in N₂ and CO₂
For all the organic sulphur containing compounds, even the amount of each compounds in two different atmospheres are different, but the ranking for the released amount is similar: Thiophene > Benzothiophene > 2-Methylthiophene, 3-Methylthiophene > 2,3-Dimethylthiophene, 2,4-Dimethylthiophene, 2,5-Dimethylthiophene > Ethyl thiophene > Dimethyl sulfone. This ranking generally match to the previous AP-TPR experimental data[8] except Thiophene. The confirming shows the reliability of modelling method by comparison of experimental work and thermodynamic equilibrium calculation. But it also should be noticed that, in our previous work slow pyrolysis was performed while it is an ideal thermodynamic calculation for HSC Chemistry. There is still some difference between the two methods for studying sulphur transformation with increasing temperature. Another possible reason could be that, in AP-TPR experiments real coal was investigated, the organic sulphur structures in coal were complicated, inorganic sulphur compounds were also involved.
However, only one organic sulphur compound Dibenzothiophene was used for HSC calculation which also caused the different on S transformation comparing to real coal pyrolysis. For N$_2$ atmosphere, sulphur stays more in the form of organic compounds, while on the contrary in CO$_2$ atmosphere during pyrolysis. That’s because N$_2$ is an inert gas while CO$_2$ is more active, especially at higher temperature. CO$_2$ can reacts with many organic compounds to form COS, SO$_2$, etc. which leads to a much higher release of inorganic sulphur related compounds during coal pyrolysis. Overall, the ranking of the release of sulphur compounds in both inert gas or CO$_2$ by thermodynamic equilibrium calculation is: SO$_2$ > Methyl thiophene > Dimethyl thiophene > Ethyl thiophene > dimethyl sulfone.

3.2. The effect of H$_2$O on sulphur containing compounds distribution.

In order to investigate the effect of H$_2$O on sulphur containing compounds distribution during pyrolysis, 0, 5, 10 and 20 kmol water vapour were added into the reaction for comparison. With H$_2$O addition, organic sulphur containing compounds reacts with CO$_2$ and H$_2$O much quickly, leading to a much higher amount of inorganic sulphur containing compounds released during pyrolysis. Since the amount of organic sulphur related compounds is so low that we only focus on inorganic sulphur containing compounds distribution in this section, which includes SO$_2$, SO, COS, H$_2$S, and CS$_2$. As it was shown in Figure 3 (a) and (b), COS was first formed with a peak at around the temperature of 200-300 °C, afterwards, with the decreasing of COS, H$_2$S increased sharply until reaching the peak at around 420 °C. From the temperature of 420 °C, COS increased again with the decline of H$_2$S. From 700 °C, SO$_2$ was formed rapidly, at around 1000 °C, the increasing went smoothly, reaching a peak at around 1200 °C. Besides, CS$_2$ and SO were also formed with much smaller amount. CS$_2$ was formed at low temperature, with a peak at 200-300 °C, its increasing went along with the increase of COS at the temperature range of 420 °C to 750 °C. The formation trendy of SO is similar to SO$_2$ but with much less amount released. The increase of SO at the range of 1000 °C to 1300 °C is more rapidly than that of SO$_2$, but since the release amount of SO is too small, it doesn’t make much difference for sulphur distribution during pyrolysis.

![Graph showing the effect of H$_2$O on sulphur containing compounds distribution](image-url)
With 5 and 10 kmol water vapour addition, the small change can be seen in Figure 3 (a), (b) and (c).

The tendency of COS shows a curve with two peak points. The first peak of COS with zero, 5 and 10 kmol water vapour was at a temperature of 300 °C, 240 °C and less than 200 °C. It shows that H₂O promotes the release of COS to a lower temperature. The first peak values of COS with zero and 5 kmol water vapour addition have not too much difference at around 0.95 kmol, however, that with 10 kmol H₂O decreased to only 0.5 kmol, which means higher H₂O concentration affects the release of COS greatly. The dip at 420 °C was also different with and without water vapour. The value of COS at 420 °C is 0.42, 0.25, 0.18 kmol with H₂O of zero, 5 kmol and 10 kmol respectively. That’s partly
because at this temperature range H\textsubscript{2}S increased sharply with H\textsubscript{2}O addition. The peak point of H\textsubscript{2}S at 420 °C went up to 0.58, 0.75 and 0.84 kmol in Figure 3(a), (b), (c) respectively. The water vapour enhanced the formation of H\textsubscript{2}S significantly during pyrolysis in CO\textsubscript{2}. The value of the second peak of COS decreased greatly with increasing water vapour addition, which shows that the formation of COS was not favourable in CO\textsubscript{2} atmosphere with water vapour. When the temperature is above 700 °C, there is not too much effects on the formation of SO\textsubscript{2}. At higher temperature, the sulphur of both COS and H\textsubscript{2}S were mainly converted to the sulphur in SO\textsubscript{2}, which is more stable. Expect for the main compounds as COS, H\textsubscript{2}S or SO\textsubscript{2}, small amount release of SO and CS\textsubscript{2} also can be found. The release trend of CS\textsubscript{2} and SO match to that of COS and SO\textsubscript{2} respectively. Same as SO\textsubscript{2}, water vapour has very little effect on the formation of SO above 700 °C. For CS\textsubscript{2}, it has two peaks with the similar peak temperature to that of COS. H\textsubscript{2}O addition was not favourable for the formation of COS, while the release of CS\textsubscript{2} was restrained as well.

In Figure 3(d), when water vapour was increased to 20 kmol, the curve of COS release only showed one peak at around 820 °C. The first peak disappeared, while the release of H\textsubscript{2}S took the main role in sulphur containing compounds before 700 °C. The only peak value of COS was decreased as well with only 0.4 kmol. Similar as COS, the release of CS\textsubscript{2}’s first peak also disappeared, leaving only one peak around 800 °C with very small amount. However, it can be noticed that water vapour addition has little effect on the release of SO\textsubscript{2} and SO during pyrolysis in CO\textsubscript{2} atmosphere.

The results show that with different reaction temperature in CO\textsubscript{2}, sulphur containing compounds distribution during pyrolysis differs a lot. Below 700 °C, COS and H\textsubscript{2}S are two major sulphur containing compounds formed during pyrolysis in CO\textsubscript{2}. The distribution of COS and H\textsubscript{2}S depends on the amount of water vapour during pyrolysis. Without H\textsubscript{2}O, COS takes the significant role. But with the increasing water vapour amount, COS declines while the release of H\textsubscript{2}S increases rapidly, playing the main role during pyrolysis. When the temperature is above 700 °C, both COS and H\textsubscript{2}S decrease rapidly, while the release of SO\textsubscript{2} and SO increase. Since the amount of released SO is very small, SO\textsubscript{2} becomes the major sulphur containing compound in CO\textsubscript{2} atmosphere after 700 °C. The release curve of CS\textsubscript{2} is similar to that of COS, but with very small amount.

The possible reactions were listed as below.

\begin{align*}
\text{Below 700 °C:} & \quad \text{Above 700 °C:} \\
C_\text{x}_\text{H}_\text{y}_\text{S}_\text{i} + H\text{O} & \rightarrow C_\text{x}_\text{H}_\text{y}_\text{S}_\text{j} + H\text{S} \\
C_\text{x}_\text{H}_\text{y}_\text{S}_\text{i} + CO & \rightarrow C_\text{x}_\text{H}_\text{y}_\text{S}_\text{j} + COS \\
COS + H\text{O} & \rightarrow CO_2 + H\text{S} \\
COS + H\text{S} & \rightarrow CO_2 + C\text{S}_\text{2} \\
\end{align*}

Unlike reactions in CO\textsubscript{2}, the effect of H\textsubscript{2}O on sulphur containing compounds distribution in inert gas shows a different tendency in Figure 5. Since more organic sulphur containing compounds remain in inert gas, distribution of less complicated organic compounds was also shown in N\textsubscript{2}. Lacking of oxidative or more reactive gases, CS\textsubscript{2} was formed while SO\textsubscript{2} or SO went missing. With increasing water vapour from 0 to 5 kmol in the reaction, COS, H\textsubscript{2}S and CS\textsubscript{2} all rose rapidly with the releasing amount. Not only inorganic sulphur containing compounds increased, but also with the Thiophene, Methyl thiophene, Dimethyl thiophene and other organic compounds by two or three orders of magnitude larger. However, when water vapour increased to 10 or 20 kmol, all the organic intermediates disappeared. Only three inorganic sulphur containing compounds left in the whole reaction, COS, H\textsubscript{2}S and CS\textsubscript{2}. At the high water vapour environment, the release of COS and H\textsubscript{2}S shows not much difference with increasing H\textsubscript{2}O. CS\textsubscript{2} kept dropping because it might react with H\textsubscript{2}O to form H\textsubscript{2}S in inert environment. The possible reactions were listed as below.

With low amount of water vapour:
\[
C_\text{x}_\text{H}_\text{y}_\text{S}_\text{i} + H\text{O} \rightarrow \Sigma C\text{H}_\text{s}_\text{j} + H\text{S} + COS + CS_2
\]

With large amount of water vapour:
\[
\text{Below 500 °C: } \quad C_\text{x}_\text{H}_\text{y}_\text{S}_\text{i} + H\text{O} \rightarrow H\text{S} + COS + CS_2 \\
\text{Above 500 °C: } \quad C_\text{x}_\text{H}_\text{y}_\text{S}_\text{i} + H\text{O} \rightarrow H\text{S} + CS_2
\]
4. Conclusions

CO\textsubscript{2} not only promotes the formation of inorganic compounds, but also moves the peak of released less complicated organic compounds such as Thiophene, Methylthiophene, Dimethylthiophene, etc. to a much lower temperature. Temperature affects the transformation of sulphur greatly during pyrolysis in CO\textsubscript{2} atmosphere. Below 700 °C, COS and H\textsubscript{2}S are two major inorganic sulphur containing compounds formed during pyrolysis in CO\textsubscript{2}. Above 700 °C, SO\textsubscript{2} plays the main role. At higher temperature, organic sulphur containing compounds react with CO\textsubscript{2} to form less complicated organic or inorganic compounds.

The ranking of the release of sulphur compounds in both inert gas or CO\textsubscript{2} by thermodynamic equilibrium calculation is: SO\textsubscript{2} > Methyl thiophene > Dimethyl thiophene > Ethyl thiophene > dimethyl sulfone, which confirmed our previous AP-TPR data of DT coal, presenting the reliability of modelling method by comparison of experimental work and thermodynamic equilibrium calculation. With increasing H\textsubscript{2}O addition, the release of COS falls while H\textsubscript{2}S rises rapidly correspondingly.

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References

[1] S. Rehfeldt, C. Kuhr, M. Ehmann, C. Bergins, Modeling of radiative properties of an Oxyfuel atmosphere with a weighted sum of gray gases for variable carbon dioxide and water vapor concentrations, Energy Procedia, 4 (2011) 980-987.
[2] C.A. Hoerlle, F.H.R. França, P.R. Pagot, F.M. Pereira, Effects of radiation modeling on non-premixed sooting flames simulations under oxyfuel conditions, Combustion and Flame, 217 (2020) 294-305.
[3] J. Zhang, M. Zhu, I. Jones, C.O. Okoye, Z. Zhang, D. Zhang, The transformation and fate of sulphur during CO2 gasification of a spent tyre pyrolysis char, Proceedings of the Combustion Institute, 38 (2021) 3891-3898.
[4] G. Gryglewicz, S. Jasieńko, The behaviour of sulphur forms during pyrolysis of low-rank coal, Fuel, 71 (1992) 1225-1229.
[5] Q. Liu, J.F. Lu, J.S. Zhang, G.X. Yue, J.L. Lu, Sulphur removal during coal pyrolysis in a fluidized bed of reducing condition, Journal of China University of Mining & Technology, 32 (2003) 367-370.
[6] B. Zhao, J. Jin, S. Li, D. Liu, H. Yang, Co-pyrolysis characteristics of sludge mixed with Zhundong coal and sulphur contaminant release regularity, Journal of Thermal Analysis and Calorimetry, 138 (2019) 1623-1632.
[7] H. Zhao, L.I. Lei, Z.H. Liu, G. University, Experimental Study on Sulphur Escape from Coal at Different Temperatures under Nitrogen Atmosphere, Coal Technology, (2017).
[8] Y. Gu, J. Yperman, G. Reggers, R. Carleer, J. Vandewijngaarden, Characterisation of volatile organic sulphur compounds release during coal pyrolysis in inert, hydrogen and CO2 atmosphere, Fuel, 184 (2016) 304-313.
[9] Y. Gu, J. Yperman, J. Vandewijngaarden, G. Reggers, R. Carleer, Organic and inorganic sulphur compounds releases from high-pyrite coal pyrolysis in H2, N2 and CO2: Test case Chinese LZ coal, Fuel, 202 (2017) 494-502.
[10] L. Frigge, G. Elserafi, J. Ströhle, B. Epplle, Sulfur and Chlorine Gas Species Formation during Coal Pyrolysis in Nitrogen and Carbon Dioxide Atmosphere, Energy & Fuels, 30 (2016) 7713-7720.
[11] N. Meng, D. Jiang, Y. Liu, Z. Gao, Y. Cao, J. Zhang, J. Gu, Y. Han, Sulfur transformation in coal during supercritical water gasification, Fuel, 186 (2016) 394-404.
[12] M. Wang, Q. Du, Y. Li, J. Xu, J. Gao, H. Wang, Effect of steam on the transformation of sulfur during demineralized coal pyrolysis, Journal of Analytical and Applied Pyrolysis, 140 (2019) 161-169.