

A predictive kinetic model of sulfur release from coal

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1. Introduction

Coal importance as energy resource in the world is continuously increasing. Its wide distribution, less subject to political constraints, and larger availability, which means lower costs, make its use the most attractive source for the electric production in the whole world and especially in developing countries. However, coal is a source of environmental concern, not only for its greenhouse impact in terms to CO₂. In order to make coal sustainable in comparison with other fossil fuels, it is necessary to develop new more effective and less pollutant technologies. This scenario opens to new fundamental studies and researches to understand the multiple phenomena occurring during coal combustion and gasification.

Important pollutants from coal combustion are the sulfur oxides (SO_x) which show negative effects on the environment and are very dangerous for the human health. Sulfur content in coals is generally between about 0.5 and 2 % (wt), but it can peak up to more than 10% [1]. The release of sulfur species in the gas phase during the volatilization process of coal gasification and combustion are responsible of the successive SO_x formation, its characterization is then a fundamental step in the control of this pollutant emission.

Sulfur compound release is the result of a complex process, which involves many interactions of chemical and physical phenomena. Coal rank and properties, as well as the sulfur amount and nature significantly influence heat and mass transfer as well as reaction rates. Therefore, times, yields, and emissions depend on the original source [2].

Coal pyrolysis releases sulfur as gas species (H₂S, COS, SO₂, CS₂), mercaptans in tar phase whilst the rest remains trapped in the solid char. Generally, among the sulfur gas species H₂S is the most abundant, and tar sulfur is another important amount [3,4]. In other cases [5,6] H₂S was not found as primary product, but SO₂ and mercaptans showed similar quantities.

Typical kinetic models of sulfur release from coal pyrolysis refers to empirical models, which necessitate experimental data to define the kinetic parameters, i.e., the rate parameters depend on the reaction conditions of the specific coal.

The simplest kinetic description refers to the single step decomposition reaction, i.e. the so called “one step model” [6,7]. The rate parameters, as well as the released fraction are fitted on the basis of measurements and, as mentioned, strongly depend on the original coal and the experimental conditions. The distributed activation energy models [5] overcome some difficulties and they are able to better distribute the volatilization process in a wider range of conditions. These models express the activation energy like a density probably function, typically a Gaussian function.

Chen et al. [8] proposed a multi-step kinetic model, on the basis of the previous work of Sugawara et al. [9]. This model is constituted by 7 reactions, which include the decomposition of organic sulfur and pyrite with formation of H₂S, sulfur tar, sulfur char, and pyrrotite (FeS). The kinetic parameters were determined for a specific coal and result of difficult applicability to different coals and different operating conditions. Further, this model needs experimental information, about released volatile fraction.

This work presents a multi-step kinetic mechanism, comparable to the last one and able to predict the release of main species, like H_2S , sulfur tar, SO_2 , gas lumped species like mercaptans and the sulfur fraction which remains in solid matrix. The novelty lies in its predictive approach, without tuning activity of rate parameters for the different coals. The resulting model is simple enough to be coupled to other coal pyrolysis models [10], retaining a general validity and a detailed description of the main volatile products. Despite its conventional simplicity, the model compares quite well with the experimental data.

2. Sulfur coal characterization

The key to understand the phenomena occurring inside the coal volatilization process lies first in the characterization of the initial sulfur contained in original coal. The general structure of coal consists of an aromatic cluster with several bridges, side chains and functional groups on peripheral position. In coal, sulfur is present as both inorganic and organic components. In the first group, the sulfur is not directly bound to the carbon matrix, but englobed in it. The inorganic sulfur, which generally is about 0.3% 4 % wt on dry basis, includes mainly pyrite, marcansite and calcium, iron or barium sulfates. Sulfates massive fraction is about a tenth of the whole inorganic fraction [2]. Organic sulfur consists of hetero-atoms inside the carbon structure. The different forms of organic sulfur show different reactivity. It is possible to identify three main families [11-14]: sulfur inside the aliphatic structure (cyclic and aliphatic sulfides, thiols, disulfides, mercaptan), sulfur inside the aromatic structure (aryl sulfides); thiophenic sulfur.

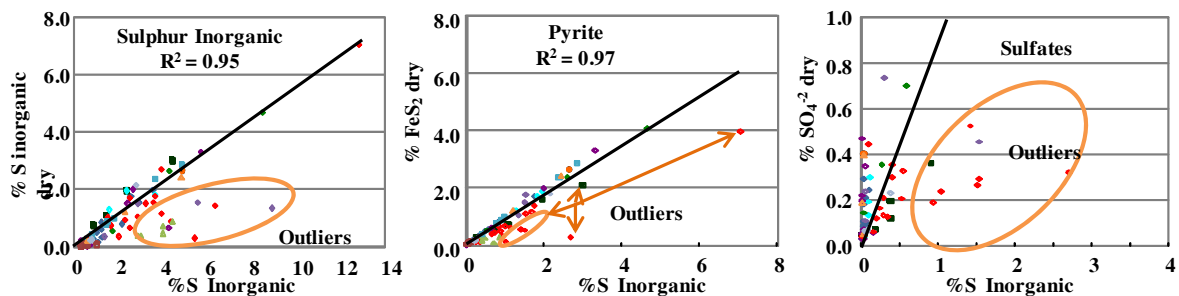


Fig. 1 Linear data fitting of inorganic sulfur compounds [1,2,4,5,14-19]

Different papers in the literature report measurements of the relative amount of the different sulfur components.

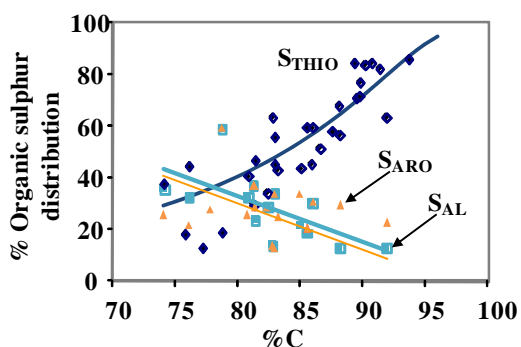


Fig. 2 Data fitting of organic sulfur compounds [2, 13]

Figure 1 shows the quite linear trend experimentally observed of the total inorganic sulfur (S_{ING}) when plotted against the total sulfur content in the coal on dry basis (S_{dry}). Moreover, the pyritic sulfur (S_P) can be linearly related to the inorganic sulfur. Sulfates (S_S) do not properly show a linear dependence, anyway they are estimated by the difference and the error acceptable, because of their general lower amount (one order of magnitude less, as mentioned). Padgett et al. [20] observed similar linear trends of pyritic sulfur in a Lower Block Coal.

Looking at figures 1, it possible to note that the scatter is quite high and some outliers are present. This can be related to unhomogeneity of the seams. Different works [21-23] show that the

difference of the sulfur content and distribution significantly varies over short distances and/or drawing depth.

Organic sulfur (S_{ORG}) is obviously the remaining part of the total sulfur. In order to differentiate the different types of organic sulfur, according to different experimental measurements, it is possible to correlate (fig. 2) their relative amount to the rank of coal, which is represented by the carbon content: anthracitic coal contains higher percentages of C than bituminous ones and the these last than the lignitic coals. The following simple expressions are proposed:

$$\omega_{S_{AL}} = 1.4 \times (100 - C\%_{daf})$$

$$\omega_{S_{THIO}} = C\%_{daf} \times \left[1 - 1.2 \times e^{\left(\frac{-18}{100 - C\%_{daf}} \right)} \right]$$

$$\omega_{S_{ARO}} = 100 - \omega_{S_{THIO}} - \omega_{S_{AL}}$$

$C\%_{daf}$ is the massive fraction of carbon on daf basis and ω is the fraction of the corresponding organic sulfur species respect of total organic sulfur. These relationships are quite scattered, indicating that coals of the same rank can partially have different sulfur group distributions. Anyway the uncertainties in the measurements of the different sulfur groups are also quite high [24].

Obviously, whenever experimental information about the different sulfur species are available, they are used in the modeling of the measurements, whilst eventual unknown are estimated by the previous relationships.

3. Kinetic model

A multi-step volatilization mechanism is proposed for the reference sulfur and reported in table 1. Rate parameters for reaction producing tar sulfur are directly taken from a previous work [10] about the kinetics of tar volatilization from coal. This implicitly means that the sulfur tar is formed mainly from the cleavage of C-C or C-O bonds, more than from C-S bond breaking.

Table 1: Multi-step kinetic model of sulfur release.

Aliphatic Sulfur (S_{AL})	Aromatic Sulfur (S_{ARO})
$S_{AL} \rightarrow 0.8 H_2S^* + 0.2 S_{GAS}^*$	$S_{ARO} \rightarrow 0.6 H_2S^* + 0.2 S_{CHAR} + 0.2 S_{GAS}^*$
$S_{AL} \rightarrow S_{TAR}^*$	$S_{ARO} \rightarrow S_{TAR}^*$
$S_{AL} \rightarrow 0.45 H_2S + 0.3 S_{GAS} + 0.25 S_{CHAR}$	$S_{ARO} \rightarrow 0.3 H_2S + 0.45 S_{CHAR} + 0.25 S_{GAS}$
$S_{AL} \rightarrow S_{TAR}$	$S_{ARO} \rightarrow S_{TAR}$
Thiophenic Sulfur (S_{THIO})	Inorganic Sulfur ($S_{PYR}; S_S$)
$S_{THIO} \rightarrow 0.8 S_{CHAR} + 0.2 S_{GAS}^*$	$S_{PYR} \rightarrow 0.25 H_2S + 0.7 S_{CHAR-ING}$
$S_{THIO} \rightarrow S_{TAR}^*$	$S_S \rightarrow 0.6 SO_3 + 0.4 S_{CHAR}$
$S_{THIO} \rightarrow 0.1 H_2S + 0.8 S_{CHAR} + 0.1 S_{GAS}$	Metaplast species (*)
$S_{THIO} \rightarrow S_{TAR}$	$H_2S^* \rightarrow H_2S$
$S_{TAR}^* \rightarrow S_{TAR}$	$S_{GAS}^* \rightarrow S_{GAS}$
$S_{TAR}^* + S_{CHAR} \rightarrow 1.65 S_{CHAR} + 0.2 H_2S^* + 0.15 S_{GAS}^*$	

Two different mechanisms, one for low temperature conditions and another for high temperature conditions, compete during volatilization process and are both accounted for. In a low temperature regime or at low heating rates, the reference sulfur species are assumed to be included in a metaplastic phase (similar to a condensate phase). Pseudo-species that are precursors of volatile species (indicated with the superscript *: S_{TAR}^* , H_2S^* , S_{GAS}^*) are trapped in this metaplastic phase, ready to be released in gas phase like gas or tar sulfur species. Only in a second moment, when the temperature is high enough, these can be released in gas phase as S_{TAR} , H_2S , S_{GAS} . The apparent activation energy of low temperature decomposition is about 31,000- 40,000 cal/mol. In

low temperature condition, in line with coal pyrolysis assumptions [lavoro coal] pseudo-species S_{TAR}^* can react in metaplastic phase with solid fragment S_{CHAR} in cross-linking and reticulation reactions. The result is a minor release of S_{TAR} and an increase of sulfur content in both the char and gas. At high temperatures or high heating rates, the sulfur species directly decompose to sulfur gas and tar, without passing through the metaplastic phase. The activation energy of these high temperature decomposition reactions varies between 61,000-75,000 cal/mol. Increasing the heating rate, the direct release of S_{TAR} prevails on reticulation and cross-linking reactions.

S_{AL} is the most reactive species, followed by S_{ARO} and S_{THIO} . Inorganic sulfur release is quite slower than organic fraction. S_{AL} releases mainly sulfur gas species, in particular H_2S , while the thiophenic structures prevalently form sulfur tar species and light mercaptans. Sulfates are assumed to decompose to metal oxide and SO_3 with quite high activation energy. Sulfate volatilization is generally slower than pyrite thermal decomposition and model accounts for it. Two different sulfur-char species are included. One accounts for structures coming from organic sulfur and the other from those coming from inorganic sulfur compounds.

The kinetic model does not include catalytic reaction, even though some catalytic outcomes are expected.

4. Results and discussion

Table 2: Elemental coal composition, sulfur species distribution and operating conditions.

Coal	Elemental Analysis (w %, daf)					Sulfur distribution %					Experimental conditions			Ref
	C	H	O	N	Stot	SAL	SARO	SP	STIO	SS	m [K/min]	T [°C]	h. time [s]	
Yanzhou	81.37	5.67	9.65	1.29	3.63	12.99	14.31	47.38	22.29	3.03	5.0	25-1000	-	15
Datong	76.94	4.08	18.08	0.54	1.6	6.31	6.45	75.00	6.61	5.63	5.0	25-1000	-	15
Yima	73.56	4.83	20.01	1.09	2.35	6.37	7.26	79.15	3.39	3.83	5.0	25-1000	-	15
Huolinhe	71.99	5.22	21.13	1.33	0.44	22.56	25.80	34.09	8.46	9.09	5.0	25-1000	-	15
Illinois	77.7	5	13.5	1.4	5.71	13.21	13.82	58.04	14.93	0.00	3000 K/s	25-900	-	5
Polish	87.5	5.75	8.5	2.1	4.9	7.90	9.36	53.88	28.24	0.61	5.0	330-1700	3600	2
Anthracite	86.2	3.7	7.56	1.2	1.34	14.22	17.14	22.39	42.52	3.73	1100.0	700-1200	0.5	4
Bituminous	71.8	4.8	19.0	1.5	2.89	19.1	16.32	50.87	12.34	1.38	1100.0	700-1200	0.5	4
Lignite	42.0	3.8	48.3	0.4	5.55	33.9	5.01	31.35	1.99	27.75	1100.0	700-1200	0.5	4

The model was tested in comparison with several experimental data. Figure 3 shows the model prediction of the weight loss for two different coals. Both the experiments are carried out at 5 K/min in a thermogravimetry apparatus. Polish coal starts releasing sulfur before and its residue is lower. Pyritic S degradation begins at temperature close to that of the other components. Model properly accounts for these results. Main products are also quite well reproduced. Gas products are about 25 % of initial S and tar about 20%.

Figure 2 shows the comparison between the model prediction and measurements of the sulfur evolution rate of several coals, carried out in TG conditions at 5 K/min. It is possible to observe the presence of two peaks. The former is due to the release of organic sulfur, while the second comes from the inorganic sulfur degradation. The relative value of the peaks correspond to the different amount of aliphatic, aromatic, thiophenic, pyritic sulfur, as well as of sulfates. Figure 5 shows the last validation test. Two different set at high heating values are compared with the model predictions. In the case of Illinois coal the weight loss and the gas and tar sulfur formation are investigated. Proposed mechanism is late of about 100 °C and underestimates gas formation (both H_2S and mercaptans). On the contrary the final amount of tar and residue are better

reproduced. H_2S formation from three coals of different rank is also investigated. Qualitative agreement of the total release moving from the anthracitic to the lignitic coal is observed. In the case lignitic and bituminous coal also the quantitative agreement is good, whilst an underestimation occurs in the the case of anthracitic coal.

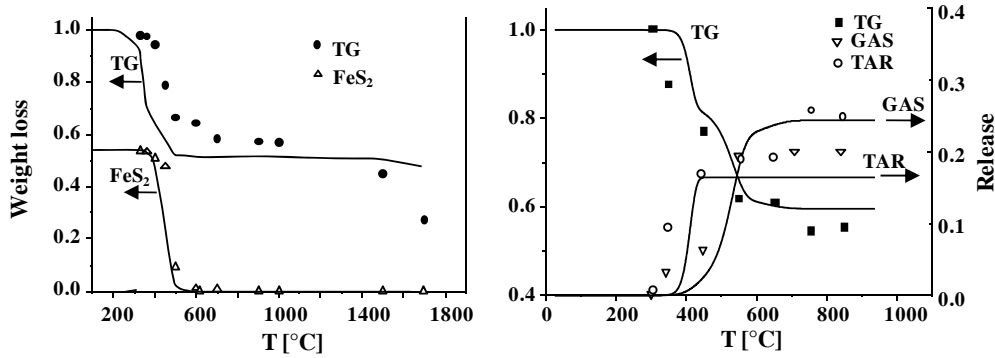


Fig. 3 Weight loss and main products from different coal at low heating rates
 a) Polish coal [2], 5 K/min b) Datong coal [15], 5 K/min

5. Conclusions

A predictive model of sulfur compound release from coal is proposed. It is based on the characterization of total sulfur content in terms of the main structure: organic sulfur is accounted in terms of aliphatic, aromatic and thiophenic sulfur, while inorganic sulfur is described as pyrite and sulfates. The distribution is proposed referring only to the elemental coal composition and in particular to the total sulfur and carbon content. A multistep model was also developed. It includes 12 species and 18 reactions, which are a quite limited number, easily to be linked to other coal volatilization models. Despite its simplicity, the model showed to be able to catch the main trends of sulfur release in different conditions (from low to high heating rates) and for different coals. Even taking into account both the lack of experimental information and the measurement uncertainties, deviations are still quite large in some cases, but this work intends to be a first step toward a better characterization of sulfur release from coal.

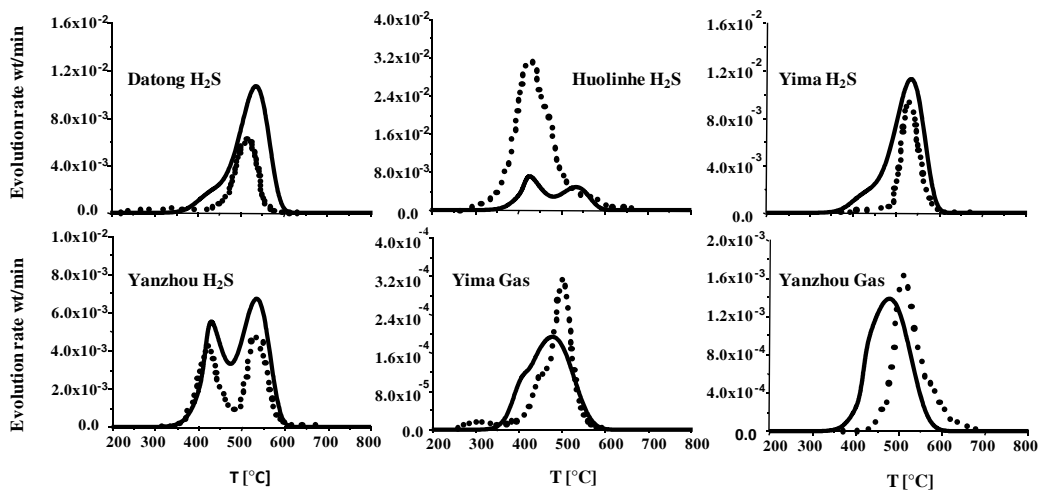


Fig. 4 Evolution rate of sulfur release from different coal [15] at low heating rates (5 K/min) as either H_2S or sulfur gas compounds different from H_2S .

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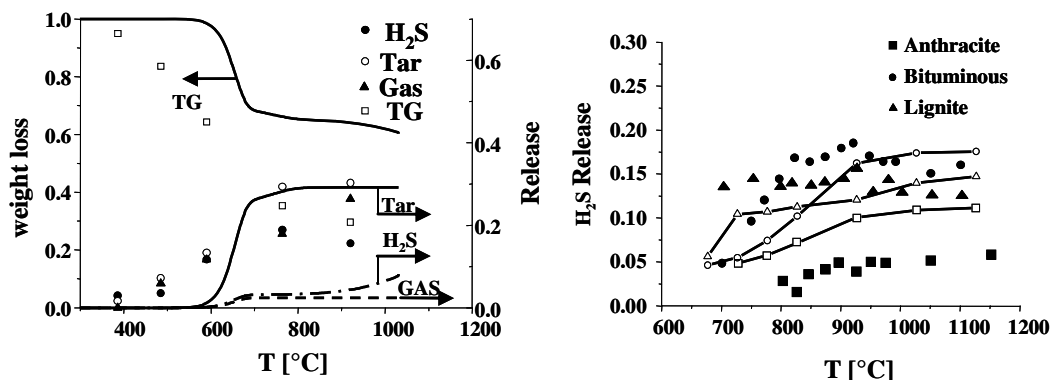


Fig. 5 Sulfur degradation and component release at high heating rates (HR):
 a) Illinois coal [5]; HR=3000 K/s b) Different coals [4]; HR = 1100 K/s

References

1. Uzun, D., Ozdogan S., Fuel, **76**:995 (1997).
2. Gryglewicz, G., Fuel **74**:356 (1995).
3. Bassilakis, R., Zhao Y., Solomon, P.R., Serio, M.A., Energy & Fuels **7**:710 (1993)
4. Garcia-Labiano, F., Hampartsoumian, E., Williams, A., Fuel **74**:1072 (1995)
5. Miura, K., Mae, K., Shimada, M., Minami, H., Energy & Fuels **15**:629 (2001).
6. Selsbo, P., Almen P., Ericsson, I., Energy & Fuels, **10**:751 (1996).
7. Lin, L., Khang, S.J., Keener, T.C., Fuel Processing Technology **53**:15 (1997).
8. Chen, C., Kojima, T., Fuel Processing Technology **53**:49 (1997).
9. Sugawara, T., Sugawara, K., Nishiyama, Y., Fuel Processing Technology, **37**:73 (1994).
10. Sommariva, S., Maffei, T., Migliavacca, G., Faravelli, T., Ranzi, E., Fuel **89**:318 (2010)
11. Attar, A., Fuel **57**:201 (1997).
12. Yan J., Yang J., Liu Z., Environ. Sci. Technol., **39**: 5043 (2005).
13. George, G.N., Gobarty, M.L., Kelemen, S.R., Sansone, M., Energy & Fuels, **5**:93 (1991)
14. Gryglewicz, G., Fuel Processing Technology **46**:217 (1996).
15. Zhou, Q., Hu, H., Liu, Q., Zhu, S., Zhao, R., Energy & Fuels **19**: 892 (2005).
16. Baruah, B.P., Khare P., Energy & Fuels **21**:3346 (2007)
17. Hu, H., Zhou, Q., Zhu, S., Meyer, B., Krzack, S., Chen, G., Fuel Proc. Techn. **85**:849 (2004)
18. Tsai, L.-Y., Chen, C.-F., Finkelman R. B., TAO **16**:641 (2005)
19. Rutkowski, P., Gryglewicz, G., Mullens, S., Yperman, J., Energy & Fuels **17**: 1416 (2003)
20. Padgett, P. L., Rimmer, S. M., Ferm, J. C., Hower, J. C., Eble, F.C., Mastalerz, M., Int. J. Coal Geology **39**: 97 (1999).
21. Mastalerz, M., Kvale, E.P., Stankiewicz, B.A., Portle, K., Organic Geochem. **30**:57 (1999)
22. Mastalerz, M., Padgett P.L., International Journal of Coal Geology **48**:217 (2002).
23. Mastalerz, M., Padgett, P.L., Eble, C.F., Int. J. Coal Geology **43**:211 (2000)
24. Maes I. I., Gryglewicz G., Machnikowska H., Yperman J., Franco D. V., Mullens J., Van Poucke L. C. Fuel **76**:391 (1997)