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Devolatilization of Organo-Sulfur Compounds in Coal Gasification

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Coal gasification is a thermo-chemical process aiming at the production of high heating value syngas. The coal charges present, typically, a low quantity of sulfur compounds for prevent the formation of a large amount of sulfuric acid (H_2S), that is a pollutant and a poison for catalysts, in syngas stream. However, in the world there are a lot of coals that cannot be used for gasification because of their high sulfur content (e.g. Sulcis Italian coal or Inner Mongolia Chinese coal). The interest on these types of coal is increasing due to a novel technology that allows to convert H_2S and CO_2 into syngas (AG2S^{TM}). The aim of this work is to propose a predictive kinetic model of the release of sulfur compounds (e.g H_2S) from coal. This kinetic scheme is implement into GASDS, a package that includes a gasifier mathematical model, which accurately describes the inter-phase mass and heat transfer. The first complexity relies in the characterization of the coal, in particular the relative amount of the different forms of sulfur components (e.g. inorganic such as pyritic and sulfates, and organic sulfur such as aliphatic, aromatic and thiophenic) and their pyrolysis and devolatilization process. The kinetic model, with the related rate parameters, is validated through comparison with experimental data from the literature and obtained during several experimental campaigns at the Sotacarbo S.p.A. pilot platform. Finally, different operating conditions of gasification are analyzed in order to obtain the best yield in the downstream process, with special reference to the novel Acid Gas to Syngas (AG2S^{TM}) process.

1. Introduction

Coal is becoming an increasingly important energy resource, with solar one (Leonzio 2017), in the modern world. Its relatively low cost, widespread availability and distribution, the less vulnerability to political constraints than other fossil fuels, make it one of the most attractive fuel for the electricity production, particularly in developing countries (Fernando et al. 2016). Coal could be an interesting carbon sources in order to produced high value chemical (e.g. methanol) passing through the syngas production from coal gasification (Bozzano and Manenti 2016). That said, coal is a cause of environmental concern and not only because of the greenhouse effects resulting from the emitted CO_2. The release of sulfur species in the gas phase during coal devolatilization is responsible for successive SO_x formation, thus its characterization is the first crucial step in monitoring this pollutant emission. Hydrogen sulfide is another common byproduct in coal gasification process and the strict legislations that limits its release into the atmosphere have triggered renewed interest in the modeling of sulfur chemistry (Huang et al. 2016). For these reasons, the coal feedstocks that are industrially used present, typically, a low quantity of sulfur compounds in order to prevent the formation of a large amount of H_2S or SO_x. However, in the world there are a lot of coals that are not used in gasification processes due to their high sulfur content (Frau et al. 2015). Therefore, to make coal more attractive than other fossil fuels, new more effective and environmentally sustainable technologies need to be developed. Basing on recent advances (Bassani et al. 2015), it could be possible to convert H_2S and CO_2 into valuable products and specifically into syngas according to the oxi-reduction reaction:

$$2H_2S + CO_2 \rightarrow H_2 + CO + H_2O + S_2 \qquad (1)$$

This new technology, called AG2S^{TM} (Acid Gas to Syngas), increases the interest on coal charge with high sulfur content because a higher production of H_2S means a higher reduction of CO_2 emissions with the consequent environmental and economical benefits (Bassani et al. 2016). According with this new technology, fundamental new kinetic studies and research are required to improve our understanding of the multiscale and multiphase phenomena occurring during coal gasification and combustion. The aim of this work is to propose a predictive kinetic model of the release of sulfur compounds (with regards to H_2S) from coal. The release of sulfur compounds, parallel to coal devolatilization, is the result of a complex process, which involves many interactions between chemical and physical phenomena (Maffei et. al. 2011) This kinetic scheme is implement into GASDS, a package that include a gasifier mathematical model (Cabianca et al. 2016), which accurately describes the inter-phase mass and heat transfer. The first complexity relies in the characterization of the coal, in particular the relative amount of the different forms of sulfur components (e.g. Inorganic sulfur, such as pyritic and sulfates, and organic sulfur such as aliphatic, aromatic and thiophenic) and their pyrolysis and devolatilization processes. The kinetic model, with the related rate parameters, is validated through a comparison with experimental data taken from the literature and obtained during several experimental tests at the Sotacarbo pilot platform.

2. Materials and methods

In this work, as mentioned, coal gasifier is simulated using GASDS. This simulation package was introduced by Cabianca et al (2016) and already validated both on coal (Corbetta et al. 2015) and biomass feedstocks (Ranzi et al. 2014). It accounts for a detailed kinetic scheme and different scales. These are the particle, the reactor layer and the gasifier reactor scales. To set up a new simulation is mandatory to characterized the coal charge in terms of some reference compounds and to define the kinetic model.

2.1 Coal charge characterization

Typically, coal charge composition is expressed in terms of proximate and ultimate analyses, i.e. in terms of fixed carbon, moisture, volatiles, ash and C/H/N/S/O (Frau et al. 2015). For this reason, is necessary to characterize each charge with a limited number of reference compounds. Bassani et al. (2016) describe the composition and the reactivity of different coals by using three reference species (COAL1, COAL2 and COAL3). However, sulfur species are not included in this kind of analysis. This is due to the fact that the devolatilisation of organo-sulfur compound is usually neglected because in the traditional gasification process is used coal with low sulfur content. A previous work by Maffei et al. (2012) considers relative amounts of organic and inorganic sulfur species present in the coal. The inorganic sulfur is not directly bound but is simply enclosed in the carbon matrix. It amounts to 0.3–4.0 wt.% on a dry basis and is made up mostly of pyrite, marcansite and sulfates of calcium, iron and barium. Organic sulfur consists of S-atoms inside the carbon structure. It is possible to identify three main families of organic sulfur compounds (Figure 1) with different reactivities.

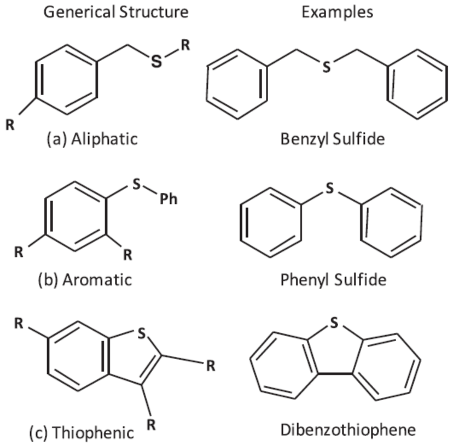


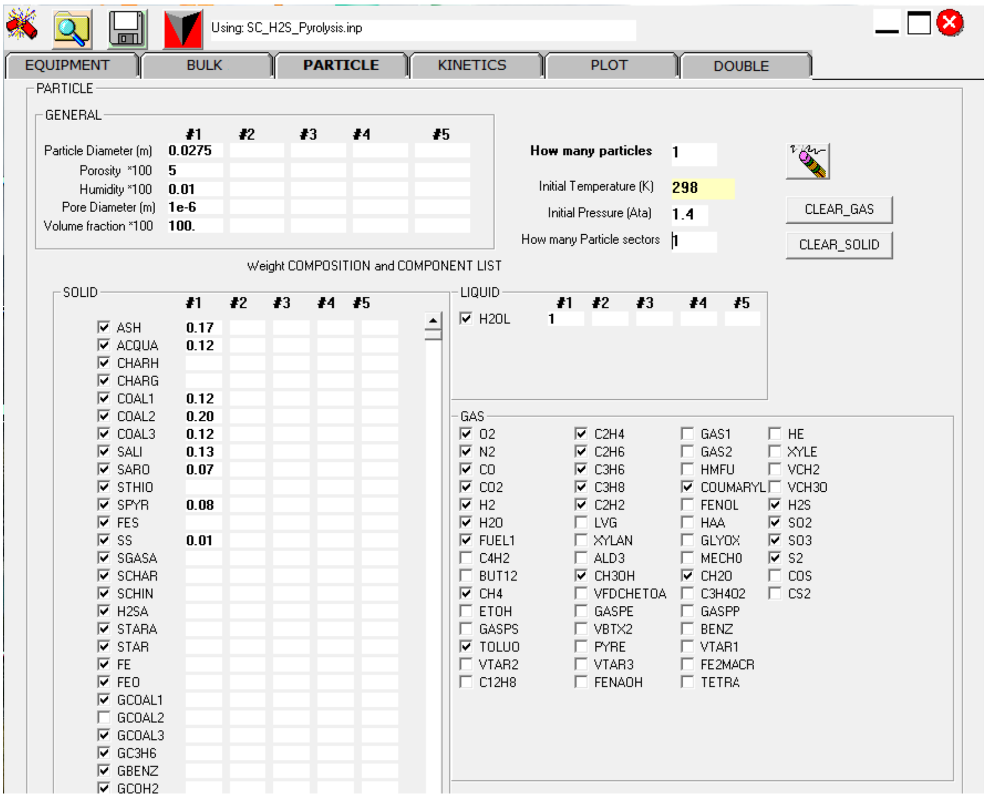
Figure 2: Organic sulfur species (Maffei et al. 2012)

Combining the coal characterization proposed by Bassani et al. (2016) and the one showed by Maffei et al. (2012), the composition in terms of reference compound of Sulcis coal (Pettinau et al. 2010) is reported in Table 1 with respect of the global atomic balance. Table 1 shows the ultimate analysis of the selected coal, carried out at Sotacarbo laboratories according to the international standards, together with the coal characterization in terms of the reference components.

Table 1 Ultimate analysis and coal characterization of Sulcis coal

Ultimate analysis							
	% C	% H	% N	% S	% O	Moisture	Ash
Composition (% wt)	53.17	3.89	1.29	5.98	6.75	11.51	17.31
Coal characterization in terms of reference species (Bassani et al. 2016) (Maffei et al. 2012)							
	%COAL1		%COAL2		%COAL3	Moisture	Ash
Composition (% wt)	12.00		20.00		12.00	12.00	17.00
	%SPYR	%SS	%STHIO	%SALI	%SARO		
Composition (% wt)	8.00	1.00	0.00	7.00	13.00		

Of course, GASDS database has to be modified in order to include the new sulfur species. Figure 2, shows the new Particle tab, where the users can input the coal characteristics. To any additional information on the graphic interface of GASDS the work of Cabianca et al (2016) is suggested.



Using: SC_H2S_Pyrolysis.inp

PARTICLE

GENERAL

	#1	#2	#3	#4	#5
Particle Diameter (m)	0.0275				
Porosity *100	5				
Humidity *100	0.01				
Pore Diameter (m)	1e-6				
Volume fraction *100	100.				

How many particles 1
Initial Temperature (K) 298
Initial Pressure (Ata) 1.4
How many Particle sectors 1

Weight COMPOSITION and COMPONENT LIST

SOLID

	#1	#2	#3	#4	#5
☑ ASH	0.17				
☑ ACQUA	0.12				
☑ CHARH					
☑ CHARG					
☑ COAL1	0.12				
☑ COAL2	0.20				
☑ COAL3	0.12				
☑ SALI	0.13				
☑ SARO	0.07				
☑ STHIO					
☑ SPYR	0.08				
☑ FES					
☑ SS	0.01				
☑ SGASA					
☑ SCHAR					
☑ SCHIN					
☑ H2SA					
☑ STARA					
☑ STAR					
☑ FE					
☑ FEO					
☑ GCOAL1					
☐ GCOAL2					
☑ GCOAL3					
☑ GC3H6					
☑ GBENZ					
☑ GCOH2					

LIQUID

	#1	#2	#3	#4	#5
☑ H2OL	1				

GAS

☑ O2
☑ N2
☑ CO
☑ CO2
☑ H2
☑ H2O
☑ FUEL1
☐ C4H2
☐ BUT12
☑ CH4
☐ ETOH
☐ GASPS
☑ TOLUO
☐ VTAR2
☐ C12H8
☑ C2H4
☑ C2H6
☑ C3H6
☑ C3H8
☑ C2H2
☐ LVG
☐ XYLAN
☐ ALD3
☑ CH3OH
☐ VFDCHETOA
☐ GASPE
☐ VBTX2
☐ PYRE
☐ VTAR3
☐ FENAOH
☐ GAS1
☐ GAS2
☐ HMFU
☑ COUMARYL
☐ FENOL
☐ HAA
☐ GLYOX
☐ MECHO
☑ CH2O
☐ C3H4O2
☐ GASPP
☐ BENZ
☐ VTAR1
☐ FE2MACR
☐ TETRA
☐ HE
☐ XYLE
☐ VCH2
☐ VCH3O
☑ H2S
☑ SO2
☑ SO3
☑ S2
☐ COS
☐ CS2

Figure 2: GASDS graphical interface, Particle tab with new sulfur reference compunds

2.2 Kinetic model

The release of sulfur components occurs along with the coal pyrolysis process. Thus, in accordance with a previously developed multistep kinetic model of coal devolatilization, two different mechanisms (low and high temperature) are assumed compete during the release of the sulfur components This multistep kinetic mechanism, reported by Maffei et. al (2012) with the kinetic parameters for each reaction, is used in this work. The only assumption is related to the the enthalpy of each reaction that is consider equal to zero. This could be a good assumption for these simulations because the previous simulations (Bassani et al. 2016) already very well predict the global temperature profile of the gasifier. Finally, the kinetic of the gas phase is combined with a gas sulfur kinetics, already validated elsewhere (Manenti et al. 2013), in order to take into account the sulfur species like H_2S.

3. Results and model validations

As mentioned before, Sulcis coal (Pettinau et al. 2010) was chosen as a possible feedstock for the plant, due to its relevant sulphur content and its possible impact in terms of the reduction of CO_2 by H_2S during the gasification process. In order to correctly validate the organo-sulfur devolatisation kinetic scheme, the simulation already provided in the previous work (Bassani at al., 2016), is selected without the assumption that 80-90% of inlet sulfur leads to the formation of H_2S. Table 2 summarizes the gasifier operating conditions. Model predictions are obtained by assuming 10 reactor layers without particle discretization. It is important to underline the fact that in this simulation only the reactions are considered, with their related kinetic parameters, reported by Maffei et al. (2012).

Table 2: Stream properties and composition

	Coal	Air	Steam	Syngas Composition	
Operating parameters				Experimental	Predicted
Mass Flow [kg/h]	7.0	8.87	4.20	18.5	17.6
Volume flow [Nm^3/h]	-	6.91	5.23	20.4	20.1
Temperature [°C]	25.0	75.0	120.0	270.0	227.0
Pressure [MPa]	0.14	0.14	0.14	0.107	0.11
LHV [MJ/kg]	20.8	-	-	7.27	6.23
Specific heat [kJ/kg K]	0.19	1.01	1.67	1.51	1.55
Stream composition (molar fractions)					
CO	-	0.000	0.000	0.169	0.188
CO_2	-	0.000	0.000	0.123	0.068
H_2	-	0.000	0.000	0.342	0.247
N_2	-	0.767	0.000	0.263	0.283
CH_4	-	0.000	0.000	0.020	0.017
H_2S	**-**	**0.000**	**0.000**	**0.012**	**0.004**
COS	-	0.000	0.000	0.001	0.000
O_2	-	0.206	0.000	0.000	0.000
Ar	-	0.009	0.000	0.003	0.000
H_2O	-	0.018	1.000	0.067	0.185
Other (C_2H6 and C_3H_8)	-	0.000	0.000	0.000	0.000

The results show that the prevision of H_2S formation is equal to about one third compared to the one provided by the experimental data. This could be due to the fact that only pyrolysis reactions of organo-sulfur compounds are taken into account. However, as reported by Bläsing (2010), some gasification reactions (e.g equation (2)) could occur between gas phase components (H_2O, H_2 etc) and the coal itself, with particular reference to organo-sulfur compounds. Some of these gasification reactions could be:

$$FES + H_2O \rightarrow FEO + H_2S \tag{2}$$

$$SCHAR + H_2 \rightarrow H_2S \tag{3}$$

This was also confirmed by the analysis of the compositions of ashes. As reported in Table 3, it is possible to observe the fact that a significat part of ash (≈ 15 %) consist in pyryte (FES) and sulfur-char. This two reference components are involved in the reactions (2) and (3).

Table 3: Ash composition with reference compound (Bassani et al. (2016) and Maffei et al. (2012))

	%ASH	%CHAR	%SCHAR	%FES	%OTHERS
Ash composition (%wt)	50.0	17.5	5.09	9.41l	18.0

For these reasons an additional simulation was done including the new reactions ((2) and (3)) using the kinetic parameters reported in Table 4. The results of this simulation are reported in Table 5.

Table 4: Kinetic parameters of the new reactions,k = A exp(-Ea/RT) (units are cal, mol, l, K and s).

	A	Ea	$\Delta H_{reaction}$
Reaction (2)	1.3E8	4.78E3	0.00
Reaction (3)	8.5E8	1.66eE4	0.00

Table 5: Stream properties and composition of the additional simulation

	Coal	Air	Steam	Syngas Composition	
Operating parameters				Experimental	Predicted
Mass flow [kg/h]	7.0	8.87	4.20	18.5	17.7
Volume flow [Nm^3/h]	-	6.91	5.23	20.4	20.1
Stream composition (molar fractions)					
CO	-	0.000	0.000	0.169	0.186
CO_2	-	0.000	0.000	0.123	0.070
H_2	-	0.000	0.000	0.342	0.246
N_2	-	0.767	0.000	0.263	0.283
CH_4	-	0.000	0.000	0.020	0.017
H_2S	**-**	**0.000**	**0.000**	**0.012**	**0.011**
COS	-	0.000	0.000	0.001	0.000
O_2	-	0.206	0.000	0.000	0.000
Ar	-	0.009	0.000	0.003	0.000
H_2O	-	0.018	1.000	0.067	0.180
Other (C_2H_6 and C_3H_8)	-	0.000	0.000	0.000	0.000

The results show that the prevision of H_2S formation is now very well predicted. Figure 3 briefly shows the comparisons between experimental data and simulated data. What is important to underline is the fact that this results are very similar to the results obtained in a previous work (Bassani et. al. 2016) without the hypothesis that 80-90% of the sulfur present in the coal charge is released as H_2S.

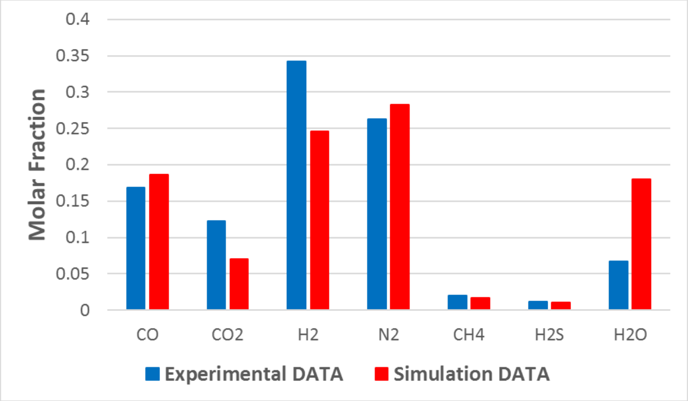


Figure 3: Gas outlet composition: experimental data versus model predictions

4. Conclusions

A predictive kinetic model of sulfur compound released from coal was proposed. It is based on the characterization of total sulfur content in terms of the main structure: organic sulfur is accounted for in terms of aliphatic, aromatic and thiophenic sulfur, while inorganic sulfur is described as pyrite and sulfates. A simulation using GASDS that includes the developed kinetic scheme is provided. The mechanism requires refinements and developments, as well as rate constants necessitate further investigations and improvements. This project is intended to be a first step towards a better characterization of both the environmental impact of coal gasification and of the capability of H_2S production in order to optimize the successive reduction of CO_2 emission in the AG2S™ process. In addition, raw sources currently unexploited for their high content in sulfur will be soon available for green uses thanks again to the AG2S™ technology.

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