

# Coal Combustion: Integrating Nitrogen and Sulfur Fraction in a Single Kinetic Mechanism

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Energy demand is facing worldwide demand growth. Besides the recent promotion of using clean and renewable energy, fossil fuels still represent the first answer to this increasing demand. In 2015, about 80% of the world energy production was fossil-fuel based, coal being used to generate one third of this fraction. The dependency of coal is mostly connected to developing countries, as it is widely available, cheap to extract and the energy production technology is well established.

However, coal combustion brings environmental concerns, not only for its greenhouse impact in terms of CO<sub>2</sub>, but also for the elevated pollutant emissions such as NO<sub>x</sub>, SO<sub>x</sub> and soot. For these reasons, clean coal technologies are necessary for bringing more efficiency, reduced pollutant emissions, and even CO<sub>2</sub> neutral processes. These improved processes demand the development of reliable models to support the design and optimization of industrial reactors.

During the past decades, many models were proposed to describe the chemistry and physics of thermochemical coal conversion during combustion and gasification, applying different levels of details and experimental data input in their development. Phenomenological models for pyrolysis such as the CPD, FLASHCHAIN and FG-DVC describe the solid fuel as a complex matrix and are able to describe many different coals, without using much experimental data in the development. Empirical models such as the SFOM's (Single First Order Reaction Model), C2SM's (Competing Two-Step Model) and DAEM's (Distributed Activation Energy Models) are developed on the basis of experiments and remain fuel- and operating conditions-dependent. These two categories widely differ in terms of computational cost and level of detail, being the empirical models applied in the majority of complex modeling activities such as CFD of single particle and reactors. In general, detailed light gases and tars description as well as nitrogen and sulfur compounds are not present in these models. The constant evolution of computational power opens the path for implementation of more accurate and detailed chemical kinetic models.

The POLIMI model provides an innovative approach for estimating the fate of nitrogen [1] and sulfur [2] in coal during pyrolysis. They are presented as dedicated sub-models, which account for the different reactivities of the functional groups and predicts various distribution of products depending on initial characterization. Gases such as NH<sub>3</sub>, HCN, SO<sub>3</sub> and tars are present in the model and the corresponding fractions of carbon, hydrogen and oxygen carried with these species must be depurated from the coal in a post-processing step. These sub-models are a complement to the coal pyrolysis model [3], which describe the thermochemical conversion of the hydrocarbon fraction. Nevertheless, the missing attribution of reference structures in the N and S sub-models makes difficult their directly coupling with the hydrocarbon fraction model, if the atomic mass balances are to be respected. The objective of the present work is to propose an updated version of the POLIMI coal mechanism, integrating both N and S sub-mechanisms, keeping the same results as the original version. To this aim, reference-structures containing a fixed amount of carbon, hydrogen and oxygen were attributed, so the nitrogen and sulfur fractions can be processed together with the hydrocarbon fraction.

In the POLIMI model a semi-empirical approach is used, which condenses the detailed structure of coal into a few reference structures that are able to comprehensively describe the overall coal conversion process of a wide range of fuel composition. The model accounts for several effects such as metaplastic phase formation and devolatilization, char degassing, char annealing, and

pollutant formation. The POLIMI model has the advantage of describing the volatile species in detail (several real and lumped light gases and tars), and its full compatibility with the secondary gas-phase and char oxidation kinetic models (developed by the same research group), dismissing a model shift to describe the whole combustion process.

The model starts with the fuel characterization in terms of the reference coals, through their simple linear combination, respecting the atomic mass balances [3]. For each reference coal, a series of reactions are attributed and describe the whole conversion, producing gas, tar and char species, represented by real and lumped species. The kinetic mechanism is presented in a CHEMKIN-like format, and the kinetic parameters in the Arrhenius format.

The reference structures attributed to nitrogen and sulfur were defined supported by the information provided in previous publications [1,2], and their composition are reported in Table 1.

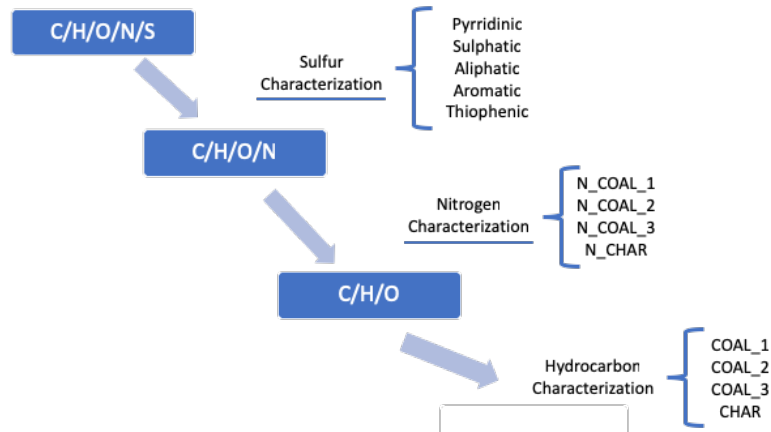
Species	Description	Composition
S_PYR	Pyridinic Sulfur (Inorganic)	H <sub>3</sub> S <sub>2</sub>
S_SUL	Sulphatic Sulfur (Inorganic)	SO <sub>2</sub>
S_AL	Aliphatic Sulfur (Organic)	C <sub>14</sub> H <sub>16</sub> S
S_ARO	Aromatic Sulfur (Organic)	C <sub>14</sub> H <sub>16</sub> S
S_THIO	Thiophenic Sulfur (Organic)	C <sub>12</sub> H <sub>8</sub> S
N_COAL_1	N associated to reference species COAL_1	C <sub>12</sub> H <sub>11</sub> N
N_COAL_2	N associated to reference species COAL_2	C <sub>14</sub> H <sub>10</sub> ON
N_COAL_3	N associated to reference species COAL_3	C <sub>12</sub> H <sub>12</sub> O <sub>5</sub> N
N_CHAR	N associated to reference species CHAR	C <sub>2</sub> HN

**Table 1 - List of reference species for Nitrogen and Sulfur in coal.**

Slight changes in the characterization procedure becomes necessary, as shown in Figure 1. First, sulfur is characterized following the correlation rules proposed by Maffei et al (2), splitting into the inorganic (pyridinic and sulphatic sulfur) and organic (aliphatic, aromatic and thiophenic). Whilst for the inorganic fraction a fixed ratio is attributed, the organic functionalities are a function of the coal rank (carbon content). The resulting elemental composition containing the sulfur is depurated from the initial coal, obtaining a sulfur free composition. Then, the sulfur-free composition is applied in the triangulation procedure to obtain a first guess to the characterization of the hydrocarbon fraction, in terms of the originally proposed reference species by Maffei et al. [3] (COAL\_1, COAL\_2, COAL\_3 and CHAR). This first estimate is used to characterize the nitrogen, attributing the obtained fractions to the analogous nitrogenated reference species. Again, the resulting composition containing nitrogen is depurated from the sulfur-free coal, obtaining a coal composition which contains only carbon, hydrogen and oxygen. This last composition is used in the triangulation procedure to obtain the final characterization. Following these steps, the content of nitrogen and sulfur is accounted for consistently.

The main changes in the kinetic mechanism refer to the reaction stoichiometries. While the previously proposed mechanism considered only the nitrogen and sulfur products released, the present mechanism must also release other compounds in order to respect the atomic mass balances of the reference species. The definition of the stoichiometric coefficients of these products was obtained from the analogous reactions in the original coal mechanism for the nitrogen fraction for the sulfur fraction, these values were defined in order to keep the previous distribution of volatile products as close as possible. The pyrolysis products present in the mechanism are reported in Table 2, together with their elemental composition and description. The species absent of sulfur and nitrogen are not reported, as they are identical to the species present in the previous mechanism.

Figure 1 - Scheme of the characterization procedure



Species	Phase	Description	Composition
S_PYR2	Solid (intermediate)	Intermediate pyridinic sulfur product	H <sub>2</sub> S
S_CHAR	Solid (char)	Sulfur chemically bonded to char	S
C <sub>2</sub> H <sub>3</sub> SH	Gas	Ethylene Sulfide	C <sub>2</sub> H <sub>4</sub> S
STAR	Gas	Lumped tar containing sulfur	C <sub>12</sub> H <sub>8</sub> S
H <sub>2</sub> S	Gas	Hydrogen Sulfide	H <sub>2</sub> S
SO <sub>3</sub>	Gas	Sulfur Trioxide	SO <sub>3</sub>
NTAR	Gas	Lumped tar containing nitrogen	C <sub>4</sub> H <sub>5</sub> N
NH <sub>3</sub>	Gas	Ammonia	NH <sub>3</sub>
HCN	Gas	Hydrogen Cyanide	HCN
G{species}	Metaplastic	All species in the form G{species} refers to their trapped state in the metaplastic phase	-

**Table 2 – List of Intermediate and final products containing Nitrogen and Sulfur in coal pyrolysis.**

The kinetic constants were kept exactly as the original mechanism for all the monomolecular reactions. The bimolecular reactions, which refer to the secondary char formation reactions (cross-linking, reticulation and repolymerization), were tuned in order to provide the same results as before. The previous mechanism considered the reaction between a trapped species (metaplastic) and the species N\_CHAR and S\_CHAR. It is more reasonable to consider the species CHAR (pure carbon) as the reactant in those reactions, but this was not possible before, as the mechanisms were separated.

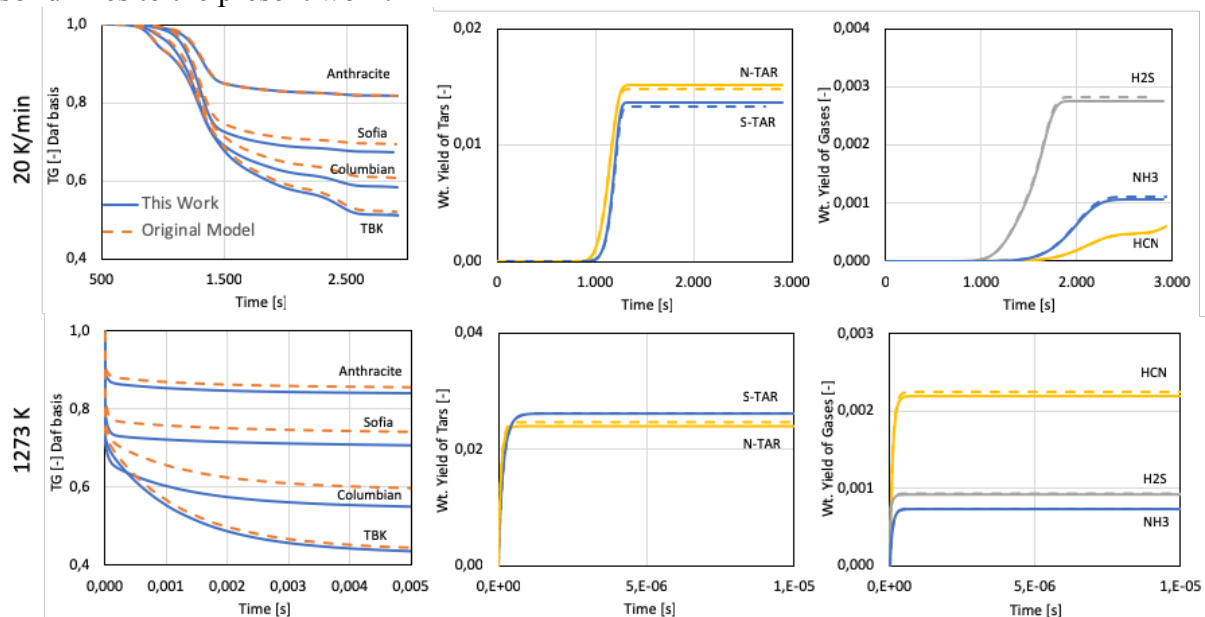
In order to validate the proposed changes, four different coals were characterized and their pyrolysis products were predicted using both the original and the present kinetic mechanisms. The composition of the coal samples, reported in Table 3, was obtained from the IRFR database and they refer to anthracite, Sofia coal, Columbian coal, and trockene Braunkohle (Dry brown coal). They widely differ in rank and content of sulfur and nitrogen. Two different operating conditions were considered, low heating rate (20 K/min) and high heating rate (isothermal at 1273 K). The parameters used for the validation were mass loss rate, final yield of char, yield of nitrogen and sulfur containing products, and yield of main hydrocarbon volatile products.

Sample	C	H	O	N	S	Ashes
Anthracite	91.7	2.0	4.4	1.1	0.8	14.6
Sofia coal	86.3	4.0	7.1	1.2	1.5	34.3
Columbian Coal	77.8	5.0	14.7	1.7	0.8	11.3
Trockene Braunkohle	69.0	5.0	25.0	0.7	0.3	4.3

**Table 3 - Composition of coal samples**

Figure 2 shows a set of comparisons between predictions of the original model and the present work, including mass loss, yield of tars and gas species. Many of the parameters evaluated result equal and only slightly different results are obtained for others. These differences are mostly caused by the tuning in the bimolecular reactions, which now depend on the coal rank, as the yield of CHAR species is directly connected to the carbon content of the initial coal. Other deviations are caused by the definition of the stoichiometry of the species that were not present in the original model, but can be easily fine tuned. However, these differences remain within the limit of experimental uncertainties and should be further tuned supported by more accurate experimental data.

Figure 2 - Comparisons of model predictions. Dashed lines refer to results from original model, solid lines to the present work.



The set of comparisons successfully validates the proposed changes, allowing the fully integration of the mechanisms. By using this updated version, it is possible to run the simulations considering all the mechanisms together, dismissing the dependency of post-processing the initial coal with the results from the separated simulations. It represents a great advantage in terms of computational cost and data processing, supporting the objectives of the project SFB/TRR 129 Oxyflame.

## References

1. Maffei, T., et al. "Predictive one step kinetic model of coal pyrolysis for CFD applications." *Proceedings of the Combustion Institute* 34.2 (2013): 2401-2410.
2. Maffei, Tiziano, et al. "A predictive kinetic model of sulfur release from coal." *Fuel* 91.1 (2012): 213-223.
3. Sommariva, Samuele, et al. "A predictive multi-step kinetic model of coal devolatilization." *Fuel* 89.2 (2010): 318-328.