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Kinetic Model of Coal Combustion

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Publications and Conferences

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Abstract

The larger availability and lower cost of coal, in respect to other fossil fuels, make it a leading energy resource for the power generation in the world, especially during economic crises as the actual one. Unfortunately, coal is a source of environmental concern not only because of its strong greenhouse impact but also because of the emission of nitrogen and sulfur oxides and the formation of aerosol particles. For these reasons "clean coal" technologies are of intense technological interest nowadays. Among these different technologies, the oxy-fuel combustion is the most interesting: air is substituted with an O_2/CO_2 mixture and thus numerous gas properties such as density, heat capacity, diffusivity and gas emissivity change with consequences on the coal reactivity.

Coal combustion is a multi-phase and multi-scale complex process which involves several species (gas, tar and char), different kinetics mechanisms (devolatilization, heterogeneous reactions, secondary gas phase reactions) as well as transport phenomena at both the particle and the reactor scale.

Several features of the coal combustion process have been analyzed in this work, with particular attention to the kinetic mechanism of pyrolysis and oxidations.

The most important source of the SO_x and NO_x during the solid fuel combustion is the "fuel" mechanism. Opportune mechanisms of pyrolysis have been developed in order to predict the main precursors of the NO_x and SO_x .

Generally the char fraction varies between 30 and 70% by weight (depending on the nature of the coal and operating conditions), with a heating value in the range 6000-8000 kcal/kg. Since the char oxidation and gasification reactions are the rate determining steps of the coal combustion, an improved knowledge of the mechanisms involved in such processes can lead to an increase in the efficiency of the combustion plants. A careful analysis of the elemental composition of the char residue has allowed the development of a kinetic mechanism of char heterogeneous reactions.

The mechanism of pyrolysis and oxidations has been applied in the study of single coal particle combustion in different mixture (O_2/N_2 and O_2/CO_2). At high temperature conditions, the heat and mass resistance can become the rate determining step of the solid combustion. An opportune mathematical model has been developed to analyze the effect of the transport phenomena within the particle.

The CFD instruments offers the possibility to approach complex combustion systems and to improve the efficiencies and to control the pollutant emissions. The direct coupling of detailed chemistry and CFD simulations is still prohibitive, especially in the multi-phase reactive system. For this reason, it is important to develop simple but reliable kinetic mechanisms. Two different simplified kinetic mechanisms have been developed, one for the pyrolysis of coal and one for the secondary gas phase reactions of the volatile matter. The models were valuated through the comparison with experimental data and with the respective detailed kinetic models.

Finally, these models have been employed in a CFD study of oxy-coal pulverized furnace through the use of commercial fluid-dynamics codes.

1 Introduction

1.1 The Coal Energy Scenario

The continuous growth of the worldwide energetic requirements is one of the main topics of interest. The energetic forecasts show that the global energetic trade will grow about 53% from 2008 to 2035 and that this increasing will be satisfied from all fuel sources through 2035, as shown Figure 1 [1].



Figure 1: World energy consumption by fuel between 1990 and 2035 [1].

Fossil fuels are expected to continue supplying much of the energy used worldwide. Petroleum remains the largest source of energy but its share of world marketed energy consumption will fall from 34% in 2008 to 29% in 2035. Among the fossil fuels, coal is the energy source that shows the most important growth. There are many reasons for which the coal is becoming a very desirable energy source, in particular:



1. a wide worldwide distribution, as shown in Figure 2

Figure 2: Worldwide distribution of Oil and Coal

The Oil reserves are not uniformly distributed in the World but they are placed most of all in the Middle East region. On the contrary, the coal reserve have a distribution more uniform. 2. lower price than Oil, as shown in Figure 3. The price of the Oil is about 10-5 times higher than the price of the Coal (depending on the reference). The peak in correspondence of 2008 represent the beginning of the First World Crises.



Figure 3: Comparison between price of Oil and Coal

3. the availability of the worldwide reserve. It seems that at the current energetic consumption rate the availability of the coal reserve are estimated to be about 130 years (or more) against an availability of the Oil reserve only 60 years [2].

The world coal consumption is expected to increase by 50%, from 139 quadrillion Btu in 2008 to 209 quadrillion Btu in 2035. Although world coal consumption will increase at an average rate of 1.5% per year from 2008 to 2035, its growth rates will be due mostly to the increase of the consumption in non-OECD countries. Currently the coal consumption rate is about 300 t/s.

Coal is an energetic source with a strong environmental impact. Indeed, coal is the most carbon-intensive energy source [1]. World energy-related carbon dioxide emissions will rise from 30.2 billion metric tons in 2008 to 35.2 billion metric tons in 2020 and 43.2 billion metric tons in 2035.



Figure 4: Percentage of CO₂ worldwide emission by fuels

Coal continues to account for the largest share of the carbon dioxide emissions throughout the projection (Figure 4). Moreover, under current policies, the developing non-OECD country will be the main responsible of the projected increase in carbon dioxide emissions. In 2008 non-OECD emissions exceeded OECD emissions by 24%, in 2035 they are projected to exceed OECD emissions by more than 100%.

Coal is employed in several energetic sectors but especially in power generation. Figure 5 shows the world net electricity supply between 2008 and 2035 for the main energy sources. In 2008, coal-fired generation has accounted for ~ 42% of world electricity supply while in 2035, its share will decrease to ~37%. This decreasing is due moistly at the higher use of other fuels, above all renewables source.



Figure 5: World net electricity supply by fuel, 2008-2035.

The power generation sector offers some of the most cost-effective opportunities for reducing carbon dioxide emissions in many countries. The emission of the gas to greenhouse effect can be reduced in several way, for example improving the efficiency of the power plant, with the introduction of a combined cycle, using mixture of fuel and biomass or through the Carbon Capture and Sequestration (CCS).

The CCS is the process of the capture of CO_2 directly from the power plants and its next stored in particular geologic deposit. The main steps of the CCS process are the capture of CO_2 , its transport from power plant to deposits (Oil fields, gas fields, saline formations), the succesive injection and finally the monitoring.

The CO₂ capture can be realized through four different system:

1. Pre-Combustion: the first step is the coal gasification or partial oxidation with formation of one gaseous current rich in CO and H₂. The second step is the conversion of CO in CO₂ through the water gas shift reaction with a further enrichment of H₂. The H₂ can be used as a fuel or directly stored. Generally this system is applied at IGGC plant (acronym of Integrated Gasification Combined Cycles).

- 2. Oxy-Combustion: the oxidizing current is not more a mixture of O_2/N_2 but a mixture of O_2 /flue gas. The pure O_2 current, obtained from an air separation plant, is mixed with a recycle flow coming from the combustor chamber and sent to the combustor. The flue gas from the combustor is particularly rich in CO_2 with the advantage of an easiest separation of the CO_2 and a reducing of the pollutants emission, as NO_x and soot.
- 3. Post-Combustion: CO_2 is separated from the flue gas through an adsorption process with chemical solvent, but others methods can apply as cryogenic separation or membrane filtration.
- 4. Chemical looping: this method uses two different fluid bed reactors. The first is employed for the exothermic process of the metal oxidation, the second for the endothermic process of the metal reduction and fuel oxidation. The reduced metal is so reintroduced in the first fluid bed rector. The advantage is the possibility to work without N_2 inert. Moreover the final flow, rich in CO_2 and H_2O , is adapted at the separation process .

The first three technologies have been widely studied in terms of power generation efficiency, capital costs and electricity costs [3-5]. One of the conclusions of these works points out that the most competitive technology option for retrofitting existing coal-fired power plants is the oxy-fuel combustion.

1.2 The Coal Combustion

Coal combustion is a multi-phase and multi-scale complex process which involves several species, different kinetic steps (devolatilization reactions, char heterogeneous reactions, secondary gas phase reactions) as well as transport phenomena at both the particle and the reactor scale. Figure 6 shows a sketch of the kinetic mechanism involved in the coal combustion process.

Coal pyrolysis or devolatilization is the first step in coal combustion and influences ensuing phenomena. During the pyrolysis a wide range of compounds are released, such as:

- ✓ Light gaseous species: CH₄, C₂H₆, H₂O, H₂, H₂S, CO₂, CO, HCN, C₆H₆, etc
- ✓ Heavy species, called TAR: these species are volatile compounds at the pyrolysis temperature but they can be liquid or solid at room temperature;
- ✓ Solid phase called CHAR.

Once formed, these products can react homogeneously with oxygen, if volatile species, or heterogeneously, if solid species. Depending on the operating conditions or the coal rank, the gas

phase reactions can occur before the heterogeneous reactions or simultaneously [6-8]. This different behaviour will be highlighted in the afterwards.



Figure 6: Sketch of the coal combustion process

1.3 Main goals of this work

The goal of this thesis is the development and the validation of a general kinetic model of coal combustion with a wide range of reliability both for coal rank and for operating conditions. The following topics have been approached:

- \checkmark the release of sulphur components
- \checkmark the release of nitrogen components
- \checkmark the elemental composition of char residue
- \checkmark the char heterogeneous reactions
- ✓ application examples of coal combustion processes

Both experimental data taken from literature and home-made experimental data have been used to validate the kinetic model.

2 Coal: genesis and classification

2.1 The coal genesis

Coal is a sedimentary rock of organic origin formed from the decomposition of organic materials that they have been subjected to geologic heat and pressure over a million of years. Coal is considered a nonrenewable resource because it cannot be replenished on a human time frame.

The formation process of coal is called carbonization. Figure 7 shows the coal formation process [9].



Figure 7: The coal formation process [9].

About 300 million years ago, the earth had dense forests in low-lying wetland areas. Due to natural processes such as flooding, these forests were buried under the soil. In these conditions the vegetable residue underwent bio-chemistry process by batteries. The product of these treatment was the formation of the peat. Afterwards as more and more soil deposited over them, they were compressed. The temperature also rose as they sank deeper and deeper. Under high pressure and high temperature, the dead vegetable underwent a second chemical and physical transformation that they led to loss of water and oxygenated compounds and an ever more graphitization of the hydrocarbon structure with coal formation.

The factors can influence the chemical and morphologic characteristic of the coal not only are the features of the original vegetable but most of all the operating conditions of the carbonization process [9,10]. As a consequence of this complicated and long process the coal is constituted both by an organic fraction both an inorganic fraction. The organic fraction is formed by atom of carbon, hydrogen, oxygen, nitrogen and sulphur. The inorganic fraction, called ash, consists in oxide of silicon, sodium, aluminum, calcium, potassium, magnesium, iron etc.

The coal structures is very complex and it consists in aromatic clusters linked by several bridges, side chains and functional groups on peripheral positions. Figure 8 shows an example of the coal structures, just give to reader the idea of the complexity of this solid fuels.



Figure 8: An example of a possible coal structure [15].

2.2 The coal maceral components

The coal structure is highly heterogeneous. The heterogeneity of the carbonaceous structures are due to present of the maceral components. The term "maceral coal" is analogous to the use of the term "mineral" in reference to igneous or metamorphic rocks [11], with the difference that the mineral have a crystalline structure and well-defined chemical composition, while the maceral can be classified only macroscopic point of view and they have properties much more variable. An more accurate definition qualifies a maceral as an organic component or a homogeneous optically aggregate of photogenic organic components that show a chemical and physical distinct properties [10]. A microscope observation in transmitted light of very thin coal section can allow a quick individuation of the maceral components, which colour can vary from red to yellow a second that come by spore, pollen, resin or cuticle.

The best approach to study of coal should start from the separation of the different maceral form: in fact, being the coal a composite material and maceral its base components, it would be logic to proceed at an analysis of the behavior of each maceral components. The difficulty to separate the different form in easy way and with revealing amount renders almost impossible to carry on this research forasmuch the all tentative applied so far have been insufficient and of difficult application.

The main maceral components are:

✓ liptinite macerals are derived from the waxy and resinous parts of plants such as spores, cuticles, and resins, which are resistant to weathering and diagenesis. Liptinite

macerals tend to retain their original plant form, i.e., they resemble plant fossils. These are rich in hydrogen and have the highest calorific values of all coal macerals [11,12].

- ✓ vitrinite macerals are derived from the cell wall material (woody tissue) of plants, which are chemically composed of the polymers, cellulose and lignin. Vitrinite macerals when observed under the microscope show a boxlike, cellular structure, often with oblong voids and cavities which are likely the remains of plant stems. This has a high calorific value (24 28 MJ/kg) and a large proportion of volatile matter (24 30%) [11,12].
- ✓ inertinite macerals are derived from plant material that has been strongly altered and degraded in the peat stage of coal formation. Inertinite is considered to be the equivalent of charcoal. The inertinite macerals have the highest reflectance of all the macerals and are distinguished by their relative reflectance and structures [11,12].

2.3 The coal rank ASTM classification

The different biological, chemical and physical conditions have influenced significantly the coal properties. In a coal global trade, the definition of index able to characterize the age, the quality and the average properties of generic coal is a necessary conditions. The most diffuse classification is the Coal Rank ASTM Classification.

The concept of the "coal rank" is defined on the basis of the volatile matter content determined through the approximate analysis and the calorific value estimated by the elemental analysis¹. This classification does not depend on directly by the structure or the elemental composition of the coal.

First of all, the coal is classified on the basis of the volatile matter (VM):

- ✓ VM <10% coal is called anthracite;
- ✓ 10% < VM < 13% coal is called semi-anthracite;
- ✓ 14% < VM < 20% coal is called low volatile bituminous;
- ✓ 20% < VM < 31% coal is called high volatile bituminous;

When the volatile matter is higher than 31%, the classification criterion used is the calorific value on ash free basis. The coal agglomeration characteristic are used to define the boundary line

¹ Approximate analysis and elemental analysis are two experimental measurement of the several properties of the coal. The approximate analysis estimates to moisture content, the volatile matter, the fixed carbon and the ash content. The elemental analysis allows to estimate the elemental composition of the organic fraction in terms of carbon, hydrogen, oxygen, nitrogen and sulphur content. Moreover with the elemental analysis is possible to determine the upper and lower calorific value.

among adjacent rank, as between sub-bituminous coal of type A and high volatile bituminous coal of type C. Figure 9 shows the ASTM classification.



Figure 9: Coal rank ASTM cassification

The main coal ranks are:

- ✓ Lignite coal: it is the youngest coal and so the less fine. Generally these coals have a high moisture content and of volatile matter. The calorific value is low enough. The chemical structure is highly aliphatic and poor in aromatic cluster. During the combustion process this coal tends to fragment.
- ✓ Sub-bituminous coal: in these coal the woody structures is not more evident. The coal has a black colour and they have the same tendency to soften as a lignite coals. These coal have a calorific value slightly higher than lignite coal and thus they can find more employment.
- ✓ Bituminous coal: they are the most employment coal. These coal have a high calorific value, similar to anthracite coal. They are of black colour. They are distinguishable in high, medium and low volatile matter.
- ✓ Anthracite coal: these coal are the maximum rank and they have at high calorific value. They content a small amount of volatile and moisture. It is possible to distinguishable in semi-anthracite, anthracite and meta-anthracite. Their structure is very similar to graphite and they are rich in aromatic cluster with few perimetral group and small aliphatic chain.

The coal structures change with the rank but this variation is only a simple progression from aliphatic structure to aromatic structure.



Figure 10: Van Kravelen 's diagram: the ageing process of the coal

Figure 10 highlights the ageing process of the coal, in which two different steps are visible:

- ✓ the first, from peat to bituminous coal, represents the loss oxygen atom in guise of water, because of the digestion process;
- ✓ the second, from bituminous coal to anthracite coal, represents the loss of hydrogenated components with consequent enrichment of the structure of carbon atoms.

3 Pyrolysis of Hydrocarbon Compounds

The kinetic model of coal pyrolysis, reported in Sommariva et al. [13], will be briefly illustrated in this chapter, both in terms of coal characterization and in terms of kinetic mechanism. Moreover, a few comparison between experimental data and numerical predictions will be shown.

3.1 Coal Characterization

The description of coal pyrolysis process first requires the characterization of the initial structure in terms of atoms, bonds and average or lumped chemical structures.

Coal consists of aromatic clusters with several bridges, side chains and functional groups on peripheral positions. As mentioned, coal composition and structure strongly differ from coal to coal; low rank coals contain large amounts of oxygen, longer side chains and smaller aromatic clusters. Increasing the coal rank, the oxygen content decreases, side chains become unlikely and shorter whilst the aromatic clusters gradually increase evolving towards graphite like structures.

The coal devolatilization model proposed simply refers to the elemental analysis of the coal, in the usual form C, H, O, S, N and ashes. S and N are usually present in a relatively small amount and they do not affect too much the overall devolatilization process (the pyrolysis of sulphur and nitrogen volatile species will be discussed in the next chapters). Ashes, whose composition and weight are strongly dependent on the coal grade and origin, do not affect coal devolatilization process. They are treated as inert and they remain in the solid residue. Catalytic effects of the different metals contained in the ashes are not considered.

As a first step of the coal characterization method, the elemental analysis of the coal is corrected and simply normalized to the C, H and O content, on dry, ash (and S, N) free basis. Figure 11 shows the composition of several coals of practical interest and investigated by several researchers [14-18]. Carbon content is always higher than 60-65% w, while hydrogen content is usually lower than 7% w. The rank of the coal increases with the rising carbon content, moving from the low rank of lignite, to average values for bituminous coals, up to the high rank and high carbon content of anthracite.

Figure 11 shows that most of the coal can be included in a triangle whose vertexes are pure carbon CHAR_c, and two reference coals: a lignite with high oxygen content COAL₃ ($-C_{12}H_{12}O_{5}$ -) and a reference coal without oxygen and particularly rich in hydrogen COAL₁ ($-C_{12}H_{11}$ -). A third reference coal, COAL₂ ($-C_{14}H_{10}O_{-}$), has been selected in the middle of in this triangle, close to a great number of bituminous coals. These reference coals can be described by three lumped or equivalent monomer structures which stand for reference configurations, saving the elemental

C/H/O composition. The plot of Figure 11 is thus divided in three triangles, and each coal lies inside one of them. Any individual coal is then considered as a simple linear combination of the three closest reference coals, and its devolatilization is considered a straightforward weighted combination of the pyrolysis of the reference coals. As already observed by Ulloa et al. [19], blends constituted by similar coals do not show significant deviation from the expected weighted average of the single coals.

Zhao et al. [20] proposed a similar approach to define the properties of any coals on the basis of a database of reference coals. The unknown coals are characterized through an interpolation from the properties of the reference coals. This approach was applied to define the preliminary structural parameters of unknown coals [21] and also the functional group parameters used to estimate the release of light gas from an unknown coal [22].



Figure 11: Composition of some literature coals and reference coal component.

3.2 Lumped kinetic model of coal pyrolysis

On the basis of the previous characterization, any coal of possible interest is simply considered as a linear combination of the reference coals and the same linear combination applies to devolatilization process and released products. A multistep devolatilization mechanism is assumed for the reference coals, with different product distributions and different kinetic parameters. Figure 12 very schematically shows the main devolatilization steps.



Figure 12: Coal decomposition and devolatilization mechanism

The multi-step devolatilization mechanism contains three sub-models, one for each reference coals with a total of 30 species involved in 33 reactions. The main reactions families involved in each sub-model are:

- ✓ low temperature decomposition of reference coals
- ✓ high temperature decomposition of reference coals
- \checkmark cross-linking and reticulation reactions
- ✓ annealing reactions

The mechanism considers that initially the coal forms a metaplastic phase, then, with different mechanisms at low and high temperatures, gas and tar species are released. At low temperatures (or low heating rates), the reference coals initially form char and volatile species, which still are in the metaplast phase. The apparent activation energy of this thermal decomposition is of about 33-40 kcal/mol. The chemical-adsorbed species in metaplastic phase are finally released in the gas phase with opportune kinetics which represents the volatilization step. The tar in the metaplast phase can be released with a proper kinetic rate or can interact with the solid residue in cross-linking and reticulation reactions. At high temperatures (or high heating rates) the reference coals more directly decompose to gas and tar, and always form more aromatic char structures. The activation energy of the high temperature decomposition reactions of different coals is in the range of 61-75 kcal/mol.

The transition temperature, where gradually high temperature decomposition prevails, is about 750 K COAL₃, 800 K for COAL₂ and becomes higher than 1200 K for COAL₁, because of its aromatic structure.

Finally, in order to account for a possible annealing effect, the solid carbon structure is described by using two different equivalent or reference species. The reference coals can either form a partially hydrogenated char (CHAR_H, brute formula C_2H , which stands for a coronene-like structure) or the more graphitic and completely carbonaceous structure (CHAR_C, brute formula C).

The description of gas species products is simplified. Light hydrocarbon gases are H_2 , CH_4 and a lumped pseudo-component with the equivalent formula (- CH_2 -), which represents the C_2 - C_5 hydrocarbons. Main oxygenated products are CO, CO_2 and H_2O . The proposed model only limits the primary production of minor oxygenated species to an equimolar formaldehyde and methanol mixture. Tar species from the different coals are grouped in pseudo-components, whose elemental composition reflects that of the corresponding reference coal. BTX fraction (benzene, toluene and xylene) is also accounted in terms of a single lumped component. Stoichiometric coefficients of the released products are of course evaluated saving the atomic (C/H/O) balances of the initial

reference coal. In according with the reference coal structure and composition, $COAL_3$ is the most reactive, followed by $COAL_2$ and finally by $COAL_1$.

3.3 Results and discussion

The kinetic model of coal pyrolysis has been developed and compared using several sets of experimental data, obtained in different experimental devices.

- 3.3.1 Thermogravimetric analysis: experiments of Solomon et al. [18]
- 3.3.2 Curie point pyrolyzer: experiments of Xu and Tomita [15,16]
- 3.3.3 Drop Tube Reactor: experiments of Fletcher et al.[14]
- 3.3.4 Drop Tube Reactor: IFRF Database [17]
- 3.3.5 Pressurized Drop Tube Reactor: experiments of Matuoska et al. [23]

These experiments were carried out in a wide range of experimental conditions with heating rates spanning from 0.5 to 10^5 K/s, final temperatures from 700 to 1700 K and coal rank variable from lignite to anthracite coal. The complete comparison between experimental data and numerical predictions are reported in Sommariva et al. [13].

3.3.1 Thermogravimetric analysis: experiments of Solomon et al. [18]

The first set of experiments was performed using a TGA, coupled with an in-line FTIR analyzer. This technique allows a good detail of permanent gases and tar species released during the pyrolysis experiments and gives good indications of the kinetic rates of the involved reactions. Seven different coals were analysed with a fixed temperature history. Coal was dried by holding the sample at 423 K for 5 min, then the temperature was increased up to the final temperature of 1173 K, with a limited heating rate of 30 K/min.

Figure 13 shows the good agreement between model predictions and experimental measurements of Pittsburgh coal. The volatile are properly predicted, as well as the different gases, see CO and CH_4 in Figure 13b and Figure 13c. Tar components agree with experimental measurement and they are properly predicted also in terms of the release rate. Different peaks indicate first the release of tar equivalent components from $COAL_3$, then the more significant formation of tar from the bituminous $COAL_2$ and finally tar from the bituminous $COAL_1$.


Figure 13: Devolatilization of coal Pittsburgh. Comparisons between model predictions (solid line) and experimental measurements (dashed lines).

3.3.2 Curie point pyrolyzer: experiments of Xu and Tomita [15,16]

Fifteen different coals with a carbon content varying from 65 % up to 94 % were analysed by Xu and Tomita [14, 15] in a Curie point pyrolyzer, with heating rate of ~ 3000 K/s, final temperatures up to 1193 K and end-times of 4 s. Data are reported in terms of total amount of released volatile species (gas and tar) and also in terms of H₂, CH₄, gaseous hydrocarbons (C₂ and C₃ species), Inorganic Oxygenated Gases (CO, CO₂ and H₂O) and benzene.

Figure 14 shows a more complete set of comparisons between model predictions and experimental data for all the 15 coals. These results, obtained at 1037 K, are in good agreement for all the ranks (C%) of investigated coals not only in terms of overall volatile components (tar and gases) but also in respect of minor individual species such as benzene, CH_4 and H_2 (this latter has not been reported here).

Figure 15 shows the scatter diagrams of total volatile and light gases and confirms the general agreement of model predictions and experiments in these conditions. Once again, the overall set of comparisons is reported as Supplemental material to this article.



Figure 14: Comparisons between model predictions (squares and lines) and experimental data of Xu and Tomita (circles) [15,16] at 1037 K.



Figure 15: Scatter between experimental data and numerical prediction in all conditions [15,16].

3.3.3 Drop Tube Reactor: experiments of Fletcher et al. [14]

Fletcher et al. [10] used a drop tube reactor with heating rates of $\sim 10^4$ K/s. Small coal particles (63-75 µm) of different rank were studied with end-time lower than 1 s in the temperature range 850÷1220 K. Volatile species in terms of gas and tars were measured.

Summarizing the overall set of comparisons it is possible to affirm that total volatiles are well reproduced by the model, even if tar is usually over-predicted. This effect could be at least partially explained on the basis of the secondary gas phase pyrolysis of tar components at high temperatures. Similar arguments will be better discussed at the point 3.3.5. Figure 16 shows a sample of these comparisons, for the coal Illinois#6.



Figure 16: Tar and total volatile species from coal Illinois#6. Symbol: circles are the experimental data [14], squares and lines are model predictions,

3.3.4 Drop tube Reactor: IFRF Database [17]

The IFRF database contains ~100 different coal devolatilization experiments. More than 50 coals were analyzed in three different drop-tube reactors, with experiments in the temperature range $1100 \div 1800$ K and contact times of $0.06 \div 0.4$ s. The total volatiles were measured for all the experiments.

The results are shown evident Figure 17, which represents a scatter diagram of experimental and predicted volatile matter. Predicted values range between 20 and 70%, while the experimental measurements move from 10% up to 90%. A wide dispersion of data is observed, but the average trends of experiments and model predictions do not show relevant or systematic deviations. Experimental data, at the same carbon content, are more scattered if compared with model predictions.



Figure 17: Scatter diagram of experimental and predicted volatile released. IFRF Database [17]

3.3.5 Pressurized Drop Tube Reactor: experiments of Matuoska et al. [23]

The elemental composition of tar and char residue is discussed in both these sets of data relating to the pressure effect on the devolatilization process. Accordingly to Wall et al [24], the pressure significantly affects the char structure and reactivity, because of changes in composition, porosity and internal surface area. These data are useful not only to verify model predictions of char and tar composition but also to discuss the role of secondary gas phase reactions. As a matter of facts, the high pressure and the significant residence times make noteworthy the importance of pyrolysis reactions of tar components. Fletcher and co-workers already observed the difficulty of steady operations in the pressurized drop tube reactor at 900-1100 K, because of relevant soot formation and coke deposit on the reactor wall. A stable operation was achieved only with three (Taiheiyo, Adaro, and Berau) of the twelve analysed coals. On the whole, these results showed similar trends as observed under atmospheric pressure. The effect of coal type on the ultimate analysis of coal char is not remarkable. Experimental measurements indicate an average oxygen content in tar components of ~5-13% and ~5-6% of hydrogen. Increases of the pyrolysis temperature led to the increase of carbon content in tar mainly accompanied by the decrease of oxygen content. Similar values of oxygen are also measured in coal chars, while hydrogen content is usually lower than 3% and it decreases with pyrolysis severity.

Table 1 reports a comparison between the experimental and the predicted yields of the devolatilization of Adaro coal at 1073 K. Elemental composition of the different fractions are reported on dry, ash, S and N free basis. The predicted large content of oxygen of the tar fraction comes from the relative importance of tar released by $COAL_3$: according to the kinetic model of coal devolatilization of Table 1, oxygen content in TAR₃ is higher than 18%. From this comparison it is possible to highlight an underestimation of the released gas, in favour of an overestimation of tar fraction. Species like H₂, CH4, C₂H₄, CO, CO₂ are slightly under-predicted. This deviation is also consistent with the over-prediction of hydrogen and oxygen in the tar fraction. As already mentioned, at least a part of this deviation can be attributed to the secondary gas phase pyrolysis reactions. As a matter of facts, volatile components, and mainly tars, may undergo successive decomposition and pyrolysis reactions in the surrounding gas phase.

In order to verify the contribution of secondary gas phase reactions, still a matter of large uncertainty [25], we analysed the reactivity of the released components from Adaro coal in a mixture with 90% mol He, in typical operating conditions of the pressurized drop tube reactor. To this aim it is necessary to characterize the released tar compounds:

- ✓ TAR₁: 52% w of acenaphthylene ($C_{12}H_8$) and 48% w of tetralin ($C_{10}H_{12}$);
- ✓ TAR₂: 100% of fenantren-4-olo ($C_{14}H_{10}O$)

• TAR₃: 28% w of coumaryl ($C_9H_{10}O_2$), al 43% w da fenantren-4-olo ($C_{14}H_{10}O$) e al 29% w da 1-(4-hydroxy-3,5-dimethoxyphenyl)prop-2-en-1-one ($C_{11}H_{12}O_4$)

Figure 18 shows some typical components useful in order to 'delump' the average and reference structure of the different tars in terms of equivalent mixtures with the same elemental composition and similar molecular weight.



Figure 18: Reference lumped structures of tar components.

The description of their gas-phase reactions is obtained by using a detailed kinetic scheme of pyrolysis and oxidation of hydrocarbon species [26]. Due to its modular and mechanistic nature, the inclusion of the new tar species was performed by adding the primary propagation reactions of these new compounds down to the formation of components already contained in the kinetic scheme. The whole kinetic scheme, constituted by more than 100 molecular and radical species involved in several thousand elementary and lumped gas-phase reactions.

Table 1 shows the predicted results after the secondary gas-phase reactions considered at 1 MPa, at two different temperatures 1073 and 1123 K, after 2 s. As expected, secondary reactions increase with increasing severity and the effect is to convert tar fraction into gases and heavy components, improving in this way the agreement between predictions and measurements.

		TAR		CH	AR
	as Released	after Secondary Reactions	Exp	Pred	Exp
С	83.4	86.6	89.5	89.9	90.5
Н	6.1	6	5.6	3.3	2.2
0	10.5	7.5	5.0*	6.8	7.2*

Table 1: Released products from Adaro coal pyrolysis and elemental composition of tar and coal char [16].

ADARO	as Released	after Seconda	ry Reactions	
P = 1. MPa	1073 K	at 1073 K	at 1123 K	EXP
H ₂	0.13	0.21	0.27	0.7
H ₂ O	6.48	6.58	6.67	10.5*
CO	11.1	13.14	13.59	9.9
CO_2	6.55	6.65	6.91	8
CH ₄	1.82	2.41	2.65	3.7
C_2H_2	0	0.28	0.55	
C_2H_4	0.42	0.94	1.04	2.9
C_2H_6	0	0.05	0.03	
C ₃ -C ₅	1.58	1.09	0.61	0.5
GAS Ox	1.4	0.54	0.21	
Total GAS	29.47	31.89	32.51	36.2
BTX	4.69	4.44	4.11	2.6
PAH	3.32	2.75	2.55	
ox TARs	17.42	12.3	10.46	9.5
Heavy PAH	0	3.14	5.81	4.4
Total liq/TAR	25.43	22.62	22.92	16.5
Coal_CHAR	45.47	45.47	44.5	47.3

* Authors indicate a poor accuracy of this analysis

3.4 Conclusion

A multistep kinetic model of coal devolatilization was developed and model predictions were compared with a very large set of experimental measurements relating to thermogravimetric experiments, as well as pyroprobe, Curie point and drop tube reactors. The general agreement is satisfactory and confirms the reliability of this model, able to predict a definite detail of the released gas and tar products during the devolatilization process. The novelty of this kinetic model lies in its predictive approach, without tuning activity of rate parameters and/or stoichiometries for the different coals. Finally the role of successive or secondary gas phase pyrolysis reactions is also discussed on the basis of a detailed kinetic scheme of gas-phase pyrolysis and oxidation reactions. The model is a reasonable compromise between accuracy and detail of the obtained results and computational efforts, in terms of number of reference species and lumped reactions. Of course, the detail of intermediate species, as well as the number of reference coals, can be modified according to the purpose of the devolatilization model.

4 Pyrolysis of Sulphur Compounds

4.1 Introduction

Coal is becoming an important energy resource in the modern world, but, as already mentioned, it is a cause of environmental concern not only because of the greenhouse effects resulting from the CO_2 it emits but also for the emission of SO_x and NO_x components [27-29].

With their negative impact on the environment and human health, sulfur oxides are significant pollutants created during coal combustion. Sulfur content in coals is generally in the 0.5-2% (wt) range, but can go up to and above 10% [30]. 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. 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. The rank and properties of the coal as well as the nature and amount of sulfur involved significantly influence heat and mass transfer as well as reaction rates. Therefore, reaction times, yields, and emissions all depend on the original source [31].

Coal pyrolysis releases sulfur as gas species (H_2S , COS, SO_2 , CS_2) and mercaptans in the tar phase, while the rest remains in the solid matrix of the residual char. Generally, H_2S is the most abundant gas component, and there is usually a significant amount of mercaptans too [28,32]. In other cases [33,34], large amounts of SO_2 are also revealed.

Typical kinetic models of sulfur release from coal pyrolysis refer to empirical models, which define kinetic parameters on the basis of *'ad hoc'* experimental data with specific coals and reaction conditions. The release of sulfur species with the one step model [32,34,35] is described simply as:

$$\frac{\mathrm{d}\mathbf{V}_{\mathrm{xs}}}{\mathrm{d}t} = \mathbf{k}_0 \exp\left(-\frac{\mathbf{E}}{\mathbf{RT}}\right) \left[\mathbf{V}_{\mathrm{xs}}^* - \mathbf{V}_{\mathrm{xs}}\right]$$
(4.1)

where V_{XS} is the sulfur fraction released and V_{XS}^* is its maximum value. The frequency factor, activation energy and released fraction are estimated on the basis of experimental measurements and are greatly dependent both on the original coal and the experimental conditions.

The distributed activation energy models [33] overcome some difficulties and are better able to characterize the devolatilization process across a wider range of conditions. The activation energy here is assumed with a density probability function, typically a Gaussian one:

$$\frac{V_{XS}^* - V_{XS}}{V_{XS}^*} = \int_0^\infty e^{\left[-\int_0^t k_0 \times e^{\left(\frac{E}{RT}\right)} dt\right]} \times \frac{1}{\sigma\sqrt{2\pi}} e^{\left[-\frac{(E-\bar{E})^2}{2\sigma^2}\right]} dE$$
(4.2)

where \overline{E} is the average activation energy and σ its standard deviation. Once again, the rate parameters (k₀, \overline{E} and σ) as well as the released fraction (V_{xs}^{*}) are fitted on the basis of the measurements and depend heavily on the original coal and the experimental conditions.

On the basis of the work of Sugawara et al. [36], Chen et al. [37] proposed a multi-step kinetic model made up of 7 reactions, which include the decomposition of organic sulfur and pyrite with formation of H_2S , sulfur tar, sulfur char, and pyrrhotite (FeS_x). This model and the related kinetic parameters were determined for a specific coal. Extending this model to different coals and different operating conditions would seem problematic.

This paper presents a similar multi-step kinetic model capable of predicting the release of main species, such as H_2S , SO_2 , gas lumped species like light mercaptans, sulfur tar, and the sulfur fraction which remains in the solid matrix. Its novelty lies in its predictive possibilities, without tuning activity for the rate parameters for the different coals. The resulting model is simple enough to be coupled with a previous coal devolatilization model [13], extending its overall validity and including the possibility of detailing sulfur volatile products too. Despite its conventional simplicity, the model compares quite well with a large set of experimental data.

4.2 Sulphur coal characterization

The kinetic model first requires the identification of the relative amounts of organic and inorganic sulfur species present in the coal. The general structure of coal consists of an aromatic cluster with several bridges, side chains and functional groups in peripheral position. The inorganic sulfur is not directly bound but is simply enclosed in the carbon matrix. It amounts to ~0.3-4 % wt on a dry basis and is made up mostly of pyrite, marcansite and sulfates of calcium, iron and barium. The mass fraction of sulfate is about a tenth of the whole inorganic fraction.

Figure 19 shows the experimentally-observed dispersion around a linear trend for the total inorganic sulfur and pyritic sulfur when plotted against the total sulfur content in the coal on a dry basis [30-33,38-45].

The following linear relations for the total inorganic sulfur (S_{IN}) as well as for pyritic (S_{PYR}) and sulfate sulfur (S_S) are:

$$S_{IN} = 0.54 \times S_{TOT} \tag{4.3}$$

$$S_{PYR} = 0.49 \times S_{TOT} \tag{4.4}$$

$$S_s = 0.05 \times S_{TOT} \tag{4.5}$$

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where S_{TOT} is the total sulfur in coal. Sulfates are indeed largely dispersed, but the very low amount of them makes this error acceptable.



Figure 19: Dispersion of experimental data relating to total inorganic sulfur and pyrite [30-33,38-45].

Padgett et al. [46] observed a similar linear trend for pyritic sulfur in Lower Block Coal. The presence of a wide scatter and outliers in Figure 19 can be partially explained by the lack of homogeneity in the seams. Several works show that sulfur content and distribution can vary significantly over short distances and/or depending on the depth of the coal deposit itself [47-49]. Organic sulfur consists of S-atoms inside the carbon structure.

It is possible to identify three main families of organic sulfur compounds with different reactivities [42,50-53]:

a) sulfur in the aliphatic chain: cyclic and aliphatic sulfides, thiols, disulfides, mercaptan

- b) sulfur in the aromatic structure: aril sulfides
- c) thiophenic sulfur.



Figure 20: Organic sulfur species.

Figure 20 reports several examples of organic sulfur species. George et al. [52] used X-ray absorption near edge spectroscopy (XANES) and X-ray photoelectron spectroscopy (XPS) to

characterize the organic sulfur in coals of different rank. In agreement with the data of Huffman et al. [53] and Attar [50], George et al. [52] identified a trend of increasing thiophenic and decreasing aliphatic sulfur with increasing coal rank.

On the basis of the previous considerations, the organic sulfur fraction is: $S_{ORG} = 0.46 \times S_{TOT}$, in line with several experimental measurements [33,38,42,52], Figure 21 clearly illustrates the distribution of aromatic, thiophenic and aliphatic sulfur within the organic fraction.



Figure 21: Cumulative distribution of organic sulfur compounds: the squares indicate the aromatic sulfur and the triangles indicate aromatic plus thiophenic sulfur [33,38,42,52].

It is evident that these distributions are heavily dependent on the coal's rank or carbon fraction content (ω_c). Despite the major uncertainties in these internal distributions [42], the following very simple linear relations for aliphatic sulfur fraction (S_{AL}), the aromatic fraction (S_{ARO}) and thiophenic fraction (S_{THIO}) were derived and proposed:

$$\mathbf{S}_{\mathrm{AL}} = \left[0.276 - 0.69 \times \left(\omega_{C} - 0.6\right)\right] \times S_{TOT}$$

$$\tag{4.6}$$

$$\mathbf{S}_{\text{ARO}} = \left[0.184 - 0.345 \times \left(\omega_C - 0.6 \right) \right] \times S_{TOT}$$

$$\tag{4.7}$$

$$\mathbf{S}_{\text{THIO}} = \left[1.035 \times \left(\omega_{C} - 0.6\right)\right] \times S_{TOT}$$
(4.8)

These relations clearly indicate an increase in thiophenic sulfur with coal rank and a corresponding decrease in aliphatic and aromatic sulfur in antracitic coals. Obviously, whenever detailed experimental information on the different sulfur species are available, it is used directly, while only unknown quantities are estimated with the aforementioned default relations.

The proposed approach is very simple and do not take into account different information like those referring to other inorganic element concentrations. It has to be noticed that the actual very large uncertainties both in the characterization of fuel and its homogeneity make less significant the use of more complex models. Anyway, further refinements are expected whenever a larger set of measurements will be available.

4.3 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 [13], we assume that two different mechanisms (low and the high temperature) compete during the release of the sulfur components. This multi–step kinetic mechanism is reported in Table 2.

	Reactions	А	E _{ATT}
R ₁	$S_{AL} \rightarrow 0.4 \; H_2 S^* \; + 0 \; .2 \; S_{GAS}^* + 0.4 \; S_{CHAR}$	5.5×10^{10}	33000
R_2	$S_{AL} \rightarrow 0.6 \ H_2S + .4 \ S_{GAS}$	$4.0 \mathrm{x} 10^{18}$	61500
R ₃	$S_{ARO} \rightarrow 0.2 \ H_2 S^* \ + 0.1 \ S_{GAS}^* + 0.7 \ S_{CHAR}$	8.0×10^{9}	36000
\mathbf{R}_4	$S_{ARO} \rightarrow ~0.3~H_2S + 0.3~S_{GAS} + .4~S_{CHAR}$	$8.5 x 10^{17}$	65000
R_5	$S_{THIO} \rightarrow 0.1 S_{GAS}{}^* + 0.9 S_{CHAR}$	5.0×10^9	38000
R ₆	$S_{THIO} \rightarrow 0.5 S_{GAS} + 0.5 \ S_{CHAR}$	$2.0 \mathrm{x} 10^{17}$	70000
\mathbf{R}_7	$S_{CHAR} + S_{TAR}^{} \bigstar \rightarrow 0.2 \ H_2 S^{\ast} + 0.1 \ S_{GAS}^{} \bigstar + 1.7 S_{CHAR}^{}$	3.7×10^5	24000
R_8	$S_{PYR} \rightarrow 0.25 \ H_2S \ + 0.3 \ S_{CHAR-ING} + 0.45 \ FeS$	1.6×10^7	36000
R ₉	$FeS \rightarrow H_2S + Fe$	1.3×10^{5}	75500
R ₁₀	$S_S \rightarrow 0.7 \; \mathrm{SO_3} + 0.3 \; S_{CHAR\text{-}ING}$	1.8×10^2	21000
R ₁₁	$S_{AL} \: S_{ARO} \: S_{THIO} \! \rightarrow S_{TAR}$	Equation	4.9
R ₁₂	$S_{AL} S_{ARO} S_{THIO} \rightarrow S_{TAR}^{*}$	Equation	4.10
R ₁₃	$\mathbf{S}_{\mathrm{TAR}}^{*} \rightarrow \mathbf{S}_{\mathrm{TAR}}$	Equation	4.11
R ₁₄	$\mathrm{H}_2\mathrm{S}^* \to \mathrm{H}_2\mathrm{S}$	5.0×10^3	20000
R ₁₅	$S_{GAS}^{}^{*} \rightarrow S_{GAS}$	2.0×10^3	22000

Table 2:Multi-step kinetic model of sulfur release.

 $k = A \exp(-E_{ATT}/RT)$ (units are cal, mol, l, K and s)

.At low temperatures or at low heating rates, the sulfur species are released first in the metaplast, as chemical-adsorbed species. These pseudo-species, which are precursors to volatile species, are indicated with the superscript ^{*}. (H_2S^* , S_{GAS}^* and S_{TAR}^*). Only when the temperature is high enough can these species be released in the gas phase as H_2S , S_{GAS} and S_{TAR} . The apparent activation energy for the low temperature mechanism is ~31-40 kcal/mol. At low temperatures, in line with the coal devolatilization model [13], tar components can react in the metaplast with cross-linking and reticulation reactions. A similar mechanism also involves S_{TAR}^* and char components. The result is a small release of S_{TAR} and an increase in sulfur content in the residual char at low temperatures. At high temperatures or high heating rates, the sulfur species directly decompose to sulfur gas and tar components, without remaining trapped in the metaplastic phase. The activation energy of these high temperature reactions varies between 61-70 kcal/mol. When the heating rate is increased, the direct release of S_{TAR} prevails on the reticulation and cross-linking reactions.

Rate parameters for the tar sulfur release are derived from the ones in the previous model [13]. This means that the sulfur tar is formed more from the cleavage of C-C or C-O bonds than from C-S bond breaking [24]. Rate parameters for the release of tar sulfur from coal are reported very simply in equations (3.9-3.11) as a function of the coal's rank or the carbon weight fraction in the coal (ω_c):

$$S_{AL} S_{ARO} S_{THIO} \rightarrow S_{TAR} * k = e^{-5.4 - 17.7 \times \omega_c + 24.2 \times \omega_c^2} T^{3.32} e^{-\frac{3.97 \times 10^4 \times \omega_c - 1.7 \times 10^4}{T}}$$
 (4.9)

$$\mathbf{S}_{\text{TAR}} * \to \mathbf{S}_{\text{TAR}} \qquad k = e^{-20.8 + 1.1 \times 10^2 \times \omega_c - 65.4 \times \omega_c^2} T^{0.12} e^{-\frac{1.68 \times 10^4 + 1.31 \times 10^3 \times \omega_c}{T}}$$
(4.10)

$$S_{AL} S_{ARO} S_{THIO} \rightarrow S_{TAR} \qquad k = e^{49.6 - 11.7 \times \omega_C} T^{8.16 \times 10^{-2}} e^{-\frac{2.62 \times 10^4 + 6.0 \times 10^3 \times \omega_C}{T}}$$
 (4.11)

A direct coupling of this sulfur release mechanism with the coal pyrolysis model [13] allows to remove these equations (4.9-4.11) and to adopt the usual form of the kinetic expression.

In general, it has to be underlined that most of the proposed kinetic constants come from the work of Sommariva et al. [13]. The modifications especially account for the different bond energy of C-S in comparison with C-C. Of course, a partial tuning was carried out to reduce larger deviations. Anyway, the modifications did not change significantly the initially adopted values and then the validation should not be considered a fitting activity.

In particular, the different organic sulfur component release rates are related to the weakness of the C-S bonds. Yan et al.[51] used the density function theory to estimate values of 50.3 kcal/mol for the C-S_{AL} bond and 79 kcal/mol in the case of C-S_{ARO} bond. These values show that C-S bonds are ~25-30 kcal/mole weaker than the corresponding C-C bonds. Due to the weaker bonds, aliphatic sulfur is released first, followed by S_{ARO} and S_{THIO} . S_{AL} mainly releases sulfur gas species, particularly H₂S, while the thiophenic sulfur, apart from a prevalent sulfur char, forms sulfur tar and light mercaptans (S_{GAS}).

The inorganic sulfur release is significantly slower than that of the organic fraction. Sulfates decompose to metal oxides and SO₃ with an activation energy of 21 kcal/mol. Two reactions describe pyrite decomposition and formation of pyrrhotite (FeS_{2-x}), a non-stoichiometric compound [54]. This process can be explained with the following reactions:

$$\operatorname{FeS}_2 \to \operatorname{FeS}_{2-x} + xS$$
 (4.12)

$$S + H_2 \rightarrow H_2 S \tag{4.13}$$

This reduction reaction is most likely due to the presence of hydrogen, which becomes available in the system due to dehydrogenations of aromatic clusters, aliphatic chains and peripheral groups. Niwa et al. [55], report an apparent activation energy of pyrite decomposition of ~29 kcal/mol, while several other authors [50,56] reported an apparent value of ~24 kcal/mol. We prefer a slightly higher value for this activation energy: 34.4 kcal/mol, estimated on the basis of the few

experimental data of pyrite pyrolysis. The FeS formed can undergo further reaction, with production of H_2S and of metal iron, trapped in the inorganic char structure (reaction 9).

In line with the above observations [57,58], sulfate release is a slower process than pyrite decomposition. Two different sulfur-char species are considered in the model. The first stands for structures derived from organic sulfur and the latter is derived from inorganic sulfur.

At present, the kinetic model does not include catalytic reactions, even though the expected catalytic outcomes could be included in the model in a simplified way.

4.4 **Results and discussion**

This kinetic model of the release of sulfur components was validated using several independent sets of experimental data available in the literature.

The first two sets of data mainly refer to the release of inorganic sulfur. Sulfate and pyrite decomposition are reported together with pyrrhotite formation.

4.4.1 Thermogravimetric analysis: experiments of Yani and Zhang [57,58]

4.4.2 Horizontal furnace: experiments of Gryglewich [31,59]

Two further sets of experimental data emphasize the role of sulphate and pyrite decomposition respectively:

4.4.3 Muffler furnace: experiments of Zhang and Tefler [60]

4.4.4 Fixed bed reactor: experiments of Zhou et al. [45]

Other experimental data mainly refer to the total initial sulfur with a detailed description of H_2S formation together with the release of sulfur gas and tar components. Thus, the following experimental data are also discussed:

4.4.5 Thermogravimetric analysis and Curie-point pyrolyzer: experiments of Miura et al. [33]

4.4.6 Mesh reactor: experiments of Garcia-Labiano et al. [32]

4.4.7 Fixed bed reactor: experiments of Sugawara et al. [36]

Furthermore, a set of experimental data refers to high pressure experiments:

4.4.8 Fixed bed reactor: experiments of Liu et al. [61] at high pressures

4.4.9 Thermogravimetric analysis: experiments of PoliMi

As mentioned we did not perform an optimization procedure in this work, but we started from the rate constants of coal volatilization [10] with some modifications for taking into account the differences induced by the sulfur bonds and some hand-made tuning to increase the agreement when evident systematic deviations occurred.

All these coal devolatilization data refer mainly to low heating rates, whilst only a limited set of information is available for higher heating rates. The experimental conditions span from

heating rates of 5 K/min to 3000 K/s, with final temperatures from 1173 to 1973 K. The carbon and sulfur content of analyzed coals of different ranks ranges from 61% to 87% (wt) and from 0.3% to 6% (wt), respectively. The respective amounts of pyrite, sulfates and organic sulfur are also often available. In the comparison between experimental data and numerical prediction, the release of sulphur components is related as the sulphur amount in each components over the initial total sulphur in coal.

4.4.1 Thermogravimetric analysis: experiments of Yani and Zhang [57,58]

In two separate papers, Yani and Zhang reported the decomposition of inorganic sulfur during the pyrolysis, in a nitrogen atmosphere, of sulfates [62] and pyrite [58] respectively. Yani and Zhang [58] performed the TGA at 10 K/min and 50 K/min and then carried out the thermal decomposition of pure iron sulphate and calcium sulfates at 10 K/min from room temperature to 1773 K [62]. The calcium sulfate data show very slow behavior, with weight loss starting at temperatures in the region of 1473 K, much higher than those typical of coal. For this reason, we only compare results referring to iron sulfates because their decomposition rate is closer to that observed in coal [60].



Figure 22: Residue of pyrite (a) at two different heating rates, sulfates (b) and comparison of model of pyrite and sulfates decomposition. Marks: experimental data [57,58]; lines: model predictions.

Figure 22 shows the comparison between experimental data and model predictions regarding inorganic sulfur, both pyrite (a) and iron sulphate (b). The agreement is fairly good and in the same order as other comparisons. It should, however, be noted that inorganic sulfur has little in the way of interaction with the other coal structure and this makes easier to define its volatilization kinetics. Lastly, Figure 22c shows the theoretical results of the volatilization of an equal weighted mixture of the two inorganic sulfur compounds under the same conditions. The pyrite decomposition is predicted to start first and is faster than the thermal decomposition of sulfates, in line with the observations in the literature [57,58].

4.4.2 Horizontal furnace: experiments of Gryglewich [31,59]

Table 3 reports the main characteristics of two different coals investigated in these experiments. The coals were heated in a horizontal furnace with a heating rate of 5 K/min to temperatures ranging from 600-1900 K. The final temperature was maintained for 60 min.

	Element	al Analys	is (w %	, daf)	w % dry	Sulfur [w % dry]					Thermal History			
Coal	С	Н	0	N	S _{TOT}	\mathbf{S}_{AL}^{*}	S _{ARO} *	S _{THIO} *	S _{PYR} **	S _S ^{**}	m [K/min]	T [K]	holding time [s]	
Polish	87.5	5.75	8.5	2.1	4.9	0.418	0.432	1.38	2.64	0.03	5	600-1900	3600	
Janina	77.1	4.8	-	-	1.23	0.131	0.103	0.146	0.81	0.04	5	600-1900	3600	

Table 3: Elemental and reference composition: Polish coal [31] and Janina coal [59].

* estimate on the basis correlation 6-8

** experimental information





Figure 23: Residue and main products from Polish and Janina coal. Marks: experimental data [31,59]; lines: model predictions.

The total and inorganic sulfur fractions are measured, predicted and plotted at the end of each experiment. Quite good results can be observed in the case of Polish coal in terms both of total sulfur and pyrite decomposition, and pyrrhotite formation.

In the case of Janina coal, on the other hand, even though the qualitative trends are correctly predicted, the agreement is not as good. It should be noted that this coal, which is of a lower rank than the aforementioned one, seems very reactive with a 30% of release even at 600 K, whilst moving from 700 to 800 K, the residue drops from 70% to just 65%. The model predicts a more significant temperature effect, with a lower sulfur release at low temperatures and an equivalent residue in the range of 800 K.

4.4.3 Muffler furnace: experiments of Zhang and Tefler [60]

A south Australian low-rank coal, Bowmans coal, is used in this study. Table 4 reports the elemental analyses as well as the amounts of total and pyritic sulfur. This coal has quite a different sulfur distribution than the others investigated. The total amount of sulfur is very high (about 5% wt, dry). The organic fraction is the largest we came across in this project (80% wt), while the pyrite content is the lowest (< 1%), with a significant presence of sulfates (~ 20% wt.).

Table 4: Elemental and reference composition Bowman	coal	[60]	Ĺ
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	Elemental Analysis (w %, daf)				w % dry	Sulfur [w % dry]					Thermal History		
Coal	С	Н	0	Ν	$\mathbf{S}_{\mathrm{TOT}}$	S_{AL}^{\ast}	$\mathbf{S}_{\mathrm{ARO}}^{*}$	$S_{\text{THIO}}{}^{*}$	$S_{PYR}^{ **}$	S ₅ **	m [k/min]	T [°C]	
Bowman	Bowman 69.4 4.6 25.2 0.8		4.82	1.77	1.271	0.816	0.045	0.919	17.7	300-1173			

* estimate on the basis correlation 6-8

** experimental information

Temperature-programmed pyrolysis experiments are carried out in a muffler furnace with a heating rate of 17.7 K/min from the starting ambient temperature to the final temperature of 1173 K C. The experimental data concern organic and inorganic sulfur as a function of different temperatures. Figure 24 shows the comparison between model predictions and experimental data.



Figure 24: Residue of total sulfur, organic sulfur and sulphate. Marks: experimental data [60]; lines: model predictions.

The sulphate release is correctly predicted. The organic sulfur fraction, however, reveals some discrepancies. Between 770 K and 970 °C, experiments indicate that organic sulfur release and total sulfur residue plateau, followed by a decrease of the weight loss. Lastly, after a maximum at about 1070 K, the degradation increases again. The model is not able to reproduce this residue shape. A possible recapture of gaseous sulfur species could explain this behavior. On the other side, it has to be considered that the flux of inert gas prevents most of the secondary reactions in the thermogravimetric analysis, including the sulfur recapture. On the contrary, the model correctly

predicts the temperature at which a reduction in the residue curve slope occurs, but it overestimates the sulfur release and does not account for the presence of a maximum.

4.4.4 Fixed bed reactor: experiments of Zhou et al. [45]

Four Chinese coals, with a different carbon and sulfur contents, were analyzed at ambientpressure, using a vertical quartz micro-fixed bed reactor, with a heating rate of 5 K/min and a final temperature about 1273 K, in different atmospheres (only the nitrogen atmosphere is of interest here, however). The sulfur distribution of products of pyrolysis (gas phase, tar phase and solid phase) was reported only for Datong coal, while for the other coals the evolution rate of hydrogen sulfide and methyl-mercaptan was measured. Table 5 shows the elemental and reference composition of these coals.

	Eleme	ntal Anal	lysis (w %,	daf)	w % dry		Sul	fur [w % di	[y]		Thermal	History
Coal	С	Н	0	Ν	S _{TOT}	\mathbf{S}_{AL}^{*}	S _{ARO} *	S _{THIO} *	S _{PYR} **	S _S ^{**}	m [K/min]	T [K]
Yanzhou	81.37	5.67	9.65	1.29	3.63	0.503	0.432	0.865	1.72	0.11	5	300-1273
Datong	76.94	4.08	18.08	0.54	1.6	0.107	0.085	0.118	1.2	0.09	5	300-1273
Yima	73.56	4.83	20.01	1.09	2.35	0.159	0.119	0.122	1.86	0.09	5	300-1273
Huolinhe	71.99	5.22	21.13	1.33	0.44	0.105	0.078	0.067	0.15	0.04	5	300-1273

Table 5: Elemental and reference composition of coals [45].

* estimated on the basis correlation 6-8

** experimental information

Figure 25 shows the agreement between model prediction and experimental data for Datang coal in function of temperature pyrolysis.



Figure 25: Sulfur residue and main products from Datong coal at low heating rates. Marks: experimental data [45]; lines: model predictions.

The sulfur distribution is influenced by the presence of a significant amount of pyrite, which limits the relative importance of organic sulfur. The agreement is generally quite good. The greatest discrepancy lies in the sulfur-tar release, where the model underestimates the measured values. This corresponds to an overestimation of sulfur char residue.

Figure 26 shows the comparison between model predictions and experimental data for H_2S evolution rate. In the cases of Huolinhe coal and Yanzhou coal, two peaks can be observed. The first is due to the release of organic sulfur, while the second comes from the inorganic sulfur release. The relative values of the peaks correspond to the different amounts of organic and inorganic sulfur in the coal. In other coals, the presence of two peaks is less evident because the inorganic fraction is much higher than the organic one.



Figure 26: Evolution rate of sulfur release from different coals at a low heating rate of 5 K/min. Marks: experimental data [45]; lines: model predictions.

The general agreement is quite good, even if the model overestimates the H_2S evolution rate. The same behavior pattern can be observed for the other total gas (not H_2S) evolution rate measured by Yima and Yanzhou coals. Sulfur gas mainly comes from the organic fraction and, consequently, its profile cannot produce two clear peaks. Figure 27 shows the sensitivity analysis of H_2S formation for two different coals, Datong and Yanzhou.



Figure 27:Sensitivity analysis for Datong coal (a) and Yanzhou coal (b).

Datong coal contains about 75% of S_{PYR} , thus the decomposition of this inorganic sulfur compound mainly controls the whole pyrolysis process. On the contrary, Yanzhou coal has a smaller amount of S_{PYR} (~33%) and a relatively large amount of S_{AL} (~20%). The aliphatic sulfur

degradation occurs fast and with a high H_2S^* formation. The release of H_2S^* from the melt to the gas phase is the then the most sensitive reaction with a lower contribution of the pyritic sulfur decomposition.

4.4.5 Thermogravimetric analysis and Curie-point pyrolyzer: experiments of Miura

et al. [31]

Six Japanese coals, three Argonne premium coals and one Chinese coal were used in this experiment. Table 6 reports the elemental analyses and the different sulfur distributions of the coals. Two different pyrolysis experiments were performed. A set of data were carried out as temperature-programmed pyrolysis in a helium stream with a heating rate of 20 K/min up to a final temperature of about 1173 K. Flash pyrolysis (at high heating rate) in an inert atmosphere using a Curie-point pyrolyzer was used in the case of the Illinois coal.

				_			-					
	Elemen	tal Ana	lysis (w %,	daf)	w % dry		Sulf	ùr [w % d	ry]		Thermal H	listory
Coal	С	Н	0	Ν	S _{TOT}	\mathbf{S}_{AL}^{*}	S _{ARO} *	S _{THIO} *	Spyr**	${S_{S}}^{**}$	m [K/min]	T [K]
SS001	85.9	4.9	7	1.7	0.65	0.098	0.104	0.297	0.14	0.01	20	300-1173
SS002	81.2	6.1	10.5	1.6	0.61	0.159	0.175	0.266	0.01	0	20	300-1173
SS003	82.9	4.7	10.3	1.8	0.33	0.072	0.078	0.15	0.03	0	20	300-1173
SS004	82.7	4.7	10.9	1.1	0.83	0.146	0.159	0.295	0.2	0.03	20	300-1173
SS005	78.7	6.2	13.8	1.2	0.32	0.03	0.034	0.036	0.2	0.02	20	300-1173
SS006	82.3	5.6	9.7	1.7	0.69	0.124	0.136	0.24	0.03	0.16	20	300-1173
Illinois	77.7	5	13.5	1.4	5.71	0.754	0.846	0.795	3.314	0	20-3000 [K/s]	300-1173
Enshuntohson	82.8	5.6	6.5	1.5	4.26	0.869	0.948	1.783	0.61	0.05	20	300-1173
Pittsburgh	83.2	5.3	9	1.6	2.41	0.212	0.231	0.457	1.51	0	20	300-1173
Upper Freeport	85.5	4.7	7.5	1.6	2.67	0.14	0.149	0.403	1.978	0	20	300-1173

Table 6: Elemental and reference composition of coals [33]

* estimated on the basis correlation 6-8

** experimental information

Figure 28 shows the comparison between experimental data and model predictions in terms of residue, tar and gas formation. The model predicts belated weight loss in the Illinois coal (figure 10a) and a small release at higher temperature. This corresponds to lower gas release, whilst the sulfur tar is in reasonable agreement. The initial estimated H₂S formation is in line with the experimental data, but in the temperature range between about 870 and 1070 K, the model indicates an intermediate plateau, which is the result of slower pyrite decomposition. Further investigation are required to clarify this behavior, both from a theoretical and, particularly, an experimental point of view, as very little information is available currently.

Figure 28b and Figure 28c shows the sulfur residue, gas and tar sulfur formation for Illinois and Enshuntohson coal under low heating rate conditions (20 K/min). The proposed mechanism describes sulfur tar formation well for both coals. H_2S formation is correctly predicted for the case of Enshuntohson coal, while there is underestimation for Illinois coal. Miura et al. [5], discussed the presence of secondary gas-phase reactions which influence sulfur distribution in the gas phase and which are not taken into account in this particular mechanism.



Figure 28: Sulfur residue and main products from different coals. Marks: experimental data [33]; lines: model predictions.

Figure 29 shows the sensitivity analysis of H_2S formation for Illinois coal in the two different pyrolysis conditions, low and high heating rate. In both cases S_{PYR} degradation reaction plays the most important role. At low temperatures the volatilization of H_2S^* from the melt is second most effective reaction. H_2S^* is mostly formed by S_{AL} . At higher temperatures, S_{AL} decomposition to H_2S^* inhibits the H_2S formation. As a matter of facts, this reaction forms a larger char amount in comparison with the reaction which directly releases H_2S in the gas phase always from S_{AL} .



Figure 29:Sensitivity analysis for Illinois coal in low heating rate (a) and heating rate (b) condition.

Figure 30 shows the comparison between the measurements and the predictions of the H_2S evolution rate. Some aspects and qualitative behaviors are reproduced, but some deviations are also clear. Two peaks (one from organic and one from inorganic sulfur release) are present in most cases. The model predicts the temperatures at which the maxima occur quite well. Quantitative values for the peaks are generally underestimated, especially those of inorganic origin.



Figure 30: Evolution rate of H_2S release from different coals. Marks: experimental data [33]; lines: model predictions.

Figure 31 shows the comparisons between experimental data and model predictions for each organic sulfur compound at both low and high heating rates. The aliphatic sulfur is the first compound to decompose, followed by the aromatic sulfur and, lastly, by the thiophenic sulfur compounds. The initial maximum observed both experimentally and theoretically comes from the partial transformation of aliphatic and aromatic sulfur char.



Figure 31:Residue of organic sulfur compounds from different coals. Marks: experimental data [33]; lines: model predictions.

4.4.6 Mesh reactor: experiments of Garcia-Labiano et al. [32]

In these experiments, 4 coals of different ranks were pyrolyzed. However, we discuss the results for only two coals, whose elemental analysis and experimental conditions are reported in Table 7.

	Elemen	ıtal An	alysis (w %	, daf)	w % dry		Sulf	ur [w % c	lry]		Thermal History			
Coal	С	Н	0	Ν	S _{TOT}	\mathbf{S}_{AL}^{*}	S _{ARO} *	${S_{\text{THIO}}}^{*}$	S _{PYR} **	S _s ^{**}	m [K/s]	T [K]	holding time [s]	
Anthracitic	86.2	3.7	7.56	1.2	1.34	0.205	0.201	0.584	0.3	0.05	1100	973-1473	0.5	
Bituminous	71.8	4.8	19.01	1.5	2.89	0.584	0.43	0.366	1.47	0.04	1100	973-1473	0.5	

Table 7: Elemental and reference composition of coals [32].

* estimated on the basis correlation 6-8

** experimental information

The carbon content of the other two coals is very low (less than 50 wt%, daf) and does not fall into the range of elemental composition of typical coals, for which the model was developed. The measurements were carried out in an Argon atmosphere, using mesh reactor, with a high heating rate of 1100 K /s and final temperatures between 973 and 1473 K followed by 0.5 s of holding time.



Figure 32: H_2S release from anthracite and bituminous coal. Marks: experimental data [4]; lines: model predictions.

The experimental data refer only to H_2S release. Figure 32 shows the comparison between model results and measurements. The agreement is quite good, particularly for bituminous coal. That said, the prediction overestimates H_2S release for the anthracitic coal. However, bituminous coal shows the higher tendency to form H_2S than anthracitic coal.

4.4.7 Fixed bed reactor: experimental of Sugawara et al. [36]

Sugawara et al. [9] pyrolyzed a bituminous coal (Ermelo) whose properties are reported in Table 8, at two different heating rates: 20 K/min and 100 K/min. The experiments were carried out in a fixed bed reactor provided with a thermogravimetric analyzer using a nitrogen stream at atmospheric pressure up to 1173 K.

	Eleme	ntal Anal	ysis (w %, c	laf)	w % dry	dry Sulfur [w % dry]						Thermal History		
Coal	С	Н	0	Ν	S _{TOT}	S _{AL} *	S _{AL} * S _{ARO} * S _{THIO} * S _{PYR} ** S _s **				m [K/min]	T [K]		
Ermelo	80.6	4.8	12.1	1.7	0.8	0.147	0.124	0.234	0.256	0.04	20-100	300-1173		

Table 8:Elemental and reference composition of Ermelo coal [36].

* estimated on the basis correlation 6-8

** experimental information

Figure 33 shows the comparison between model predictions and experimental data in terms of sulfur char residue, sulfur tar released, total sulfur gas released, pyrite decomposition and formation of pyrrhotite.



Figure 33: Sulfur residue and release of main organic sulfur species in two different heating rate condition (20K/min and 100K/min). Marks: experimental data [36]; lines: model predictions

The agreement is quite good at both the heating rates. Sulfur gas release is slightly overestimated. The inorganic sulfur evolution (pyrrothite formation and pyrite decomposition) is correctly described both in terms of release rate and asymptotic values. Measurements show a decrease in volatilization for organic sulfur, which is reflected in the total sulfur release. The corresponding decrease in sulfur tar observed indicates that cross-linking reactions have a significant effect in these conditions, which are not properly taken into account by the model.

4.4.8 Fixed bed reactor: experiments of Liu et al. [61] at high pressures

Liu et al. [34] pyrolyzed two different samples of Yima coal (one raw and one demineralized) in a vertical fixed bed reactor at temperatures in the range 620-920 K, under 2 MPa of pressure. The final temperature was always reached in 10 min, with a hold time of 30 min. Table 9 reports the elemental composition and sulfur distribution of Yima coal for raw and demineralized samples.

Table 9: Elemental and reference composition of Raw and Demineralized Yima coal [61].

	Elemental Analysis (w %, daf)					Sulfur [w % dry]					Thermal History			
Coal	С	Н	0	Ν	S _{TOT}	S_{AL}^{*}	$\mathbf{S}_{\text{ARO}}^{*}$	${S_{\text{THIO}}}^{*}$	S_{PYR}^{**}	S_{S}^{**}	m [K/min]	T [K]	holding time [s]	
Yima	61.6	4.9	31.1	1.2	2.58	0.622	0.419	0.039	1.22	0.28	32.4-62.4	620-920	1800	
Yima Dem	61.4	4.6	31.7	1.2	2.23	0.625	0.421	0.034	1.15	0	32.4-62.4	620-920	1800	

* estimated on the basis correlation 6-8

** experimental information

The effect of pressure on tar release from coal had already been already investigated [10]. The kinetic parameters of reaction R_{13} are modified accordingly to account for this effect:

$$k_{13}^* = k_{13} \times \left[\frac{p_{atm}}{p}\right]^{\alpha} \tag{4.14}$$

where $\alpha = 1$, P_{atm} is the atmospheric pressure and P is the experimental pressure.

Figure 34 shows the comparison between experimental data and model predictions. The agreement in quite good in the early stages, meanwhile at high temperatures the model underestimates the amount of sulfur released and also, partially, the inorganic decomposition of the sulfur. This discrepancy becomes even clearer in the case of demineralized coal. But the process to remove sulfates from coal must have a definite impact on overall coal structure. Moreover, the operating conditions, high pressure (2MPa) and relatively heavy samples (5-6 g), favor the importance of diffusion phenomena, which in turn affects kinetics.



Figure 34: Sulfur residue of raw and demineralized coal at 2 MPa. Marks: experimental data [61]; lines: model predictions.

Thermogravimetric analysis: experiments of PoliMi

The model was finally tested in comparison with a different set of experimental data, referring to a bituminous coal. This test was carried out without any tuning activity. Table 10 reports the elemental composition on daf basis and the estimated sulfur distribution, according to equations 4.3-4.8. Measurements were carried out using a high resolution simultaneous thermogravimetric and differential thermal analyzer (TGA-DTA, SDT Q600, TA Instruments). The TGA-DTA facilitated the acquisition of weight loss, heating rates and temperatures (or time). The sample was heated up at constant heating rates of 20 and 100 K/min to a desired temperature of 1073-1273 K using N₂ as carrier gas at a constant flow rate of 200 ml min⁻¹. Finally, the sample was kept in isothermal conditions for 5 to20 min. Coal and char samples were also characterized with a FISONS EA 1108 CHNS-O for ultimate analysis. Each experimental measurement was replicated three times and the average composition estimated on the basis of an external calibration.

Elementa	al Analy	sis (w %, c	laf)	w % dry	Sulfur [w % dry]					Thermal History			
С	Н	0	Ν	S _{TOT}	S _{AL} S _{ARO} S _{THIO} S _{PYR}				Ss	m [K/min]	T [K]	h. time [s]	
84.67	5.9	7.91	1.3	2.18	0.022	0.026	0.053	0.1	0.018	20-100	1073-1373	5-20	

Table 10:Elemental and reference composition of bituminous coal

Figure 35 shows the comparison between predicted and measured sulfur residue. The experimental data seem highlight a decreasing trend with the final temperature. The model does not capture this behavior, even though the estimated amount is always inside the experimental uncertainties. It has to be noticed that the experiment at 1173 K has a different heating rate (20 K/min, instead of 100 K/min) and a longer holding time. This explains the maximum of the residual amount predicted by the model.



Figure 35: Sulfur residue of different experimental conditions. Marks: experimental data; lines and mark: model predictions.

4.5 Conclusion

A predictive model of sulfur compound release 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. 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 15 species and 15 reactions, quite limited number, and easy to link to other coal volatilization models. Despite its simplicity, the model proved itself capable of identifying the main sulfur release trends in different conditions (from low to high heating rates) and for different coals.

5 Pyrolysis of Nitrogen Compounds

5.1 Introduction

Coal contains an important amount of nitrogen (0.5%-2%, wt daf) that during the coal combustion leads to formation of NO_x through a process called "Fuel-NOx". Pohl e Sarofim [63] have pyrolysed a lignite coal and a bituminous coal at high temperature (1500 K) with high heating rate of about 10^4 K/s. They found that the released nitrogen contributes to about 60-80% of the total amount of NO_x. Other works [64,65] have highlighted that more than 50% of initial nitrogen is converted in NO_x and that about 75% of total NO_x come from "Fuel-NOx" mechanism.

The reduction efficiency of NO_x depends on both of the amount and of the type of volatile nitrogen compounds released during devolatilization step [63-65]. Thus, in order to control the emissions of NO_x , it is necessary to understand the mechanisms at the base of their formation.

The coal nitrogen content is a property not tightly depending on rank showing a trend typically nonlinear. A more precisely correlation can be found respect to the maceral composition. The coal with a carbon content of about 85% show the highest nitrogen content [66].

Nitrogen has a nearly totally organic nature, even if inorganic nitrogen structures, as ammonium ion, are present in coals at a high rank [67,68], but in percentage definitely unimportant. Different types of organic nitrogen are incorporated inside macromolecule of coal in the shape of heterocyclic aromatic structures. Different techniques, as XPS (X-ray photoelectron spectroscopy) [69-72] and XANES (X-ray absorption near edge spectroscopy) [73-75] have been used to identify the different nitrogen structures:

- ✓ Pyrrolic structure
- ✓ Pyridinic structure
- ✓ Quaternary structure

Unlike the pyrrolic and pyridinic structure, the structure of quaternary nitrogen is not well known [75], but it could be a protonated nitrogen in a six atom ring, maybe chemically associated to oxygenate functional groups [76]. Glarborg et al. [27] reported that the pyrrolic, pyridinic and quaternary structures vary respectively between 50-80%, 20-40% and 0-20%. Several XANES studies indicate the present of another nitrogen structures, as ammines-aromatic structures, but in amounts of 5-10% [73,77].

Kelemen et al. [76] have used XPS analysis to determine distribution of nitrogen functional groups in tar and char formed both in high heating rate condition (about 10^4 K/s) and in low heating

rate conditions (about 0.5 K/s). In high heating rate condition, they found that the pyridinic nitrogen remains almost constant, and the pyrrolic nitrogen decreases during pyrolytic process. The increase of the quaternary structure is more important in the case of the high rank coals respect to the low rank ones. In condition of low heating rate, the dominant nitrogen form within the char residue were the quaternary and pyridinic nitrogen. In particular, these structures showed a specular trend, with quaternary nitrogen that increased with the pyrolysis temperature. Pyridinic nitrogen remained almost constant.

The nitrogen distribution in tar, obtained under low heating rate conditions, showed the presence of pyrrolic and pyrrydinic nitrogen form, while under conditions of high heating rate, it showed also the present of quaternary nitrogen (lower that coal parents) and amino-nitrogen groups (not present in coal parents).

Nelson et al. [78] have used a specific gas-chromatography techniques to the study of the nitrogen structures in tar components, obtained under high heating rate conditions. They have identified not only structures pyridinic and pyrrolic nitrogen, but also other structures, as indolo, quinoline, benzonitrile, even if their amounts are not comparable with the first two structures. The quaternary nitrogen in tar compounds resulted less compared to that present in coal parents. The distribution of nitrogen functionally groups in the tar compounds is enough independent from heating rate, as showed by a similar distribution between tar compounds obtained in both conditions.

Different works support that the distribution of different nitrogen functional groups depend on coal rank [79-81]. In Figure 36, sets of functional group distribution reported in literature [72,80,82-84] are plotted in the function of the carbon content in the coal parent.



Figure 36: Distribution of nitrogen compounds in function carbon content [72,80,82-84]

The experimental data show a high dispersion, without highlighting a possible empiric trend. Analogue behaviors can be found in terms of hydrogen, oxygen, nitrogen content or in terms of different ratio between carbon, hydrogen, oxygen and nitrogen. Moreover, it is not clear if these dispersions are an intrinsic characteristic or are imputable to the modality of the measurement.

Because of the strong variability of experimental data, it is not possible to predict accurately the nitrogen distribution.

The different nitrogen structures show different reactivity. The quaternary nitrogen evolves at relative low temperature, while the pyridinic and pyrrolic nitrogen forms result more stable and they evolve at higher temperature. Secondary pyrolysis of tar compounds, in an inert environment at high temperature, have highlighted a higher reactivity of pyridinc than pyrrolic to convert themselves in cyanonitril through reaction of ring opening [85]. On the basis of these observations, it is possible to identify the following order reactivity: quaternary, pyridinc and pyrrolic. It is important to underline that the conditions of the decomposition of pyridinic and pyrrolic carbonaceous structures are milder that the decomposition conditions of pure pyridine and pure pyrrolo [81,86].

Many attempts have been done in order to correlate the release of nitrogen components with the different nitrogen functional groups present in the coal [78,82] but there is not a close agreement among different literature works. Kambara et al. [82] have reported that the release of light-gas nitrogen is a characteristic of the nitrogen functionally groups, while other studies have not shown this evidence [83,87].

Blair et al. [88] have underlined how the increase of the pyrolysis temperature determines a proportional increase of volatile nitrogen released. Freihaut at al. [89-91] have analyzed the behavior of the coal particle pyrolyzed at moderate heating rate (500 K/s). They showed as the nitrogen distribution between volatile and residue is function of the coal rank: lignite coal released preferentially light-gas nitrogen, while bituminous coal released more nitrogen as tar-nitrogen species. Moreover, for a high volatile coal, the amount of nitrogen released as tar-nitrogen species was proportional to the amount of tar products and nitrogen content in coal parent.

Solomon and Fletcher [80] have reported that the nitrogen fraction released at high heating rate, about 10^5 K/s, is relatively constant for low and medium coal rank, whereas it falls drastically for anthracite coals. Solomon and Colket [92], in moderate heating rate conditions, have found that initial nitrogen evolution is proportional to tar species evolution. For low coal rank, only a little part is released as tar-nitrogen, with nitrogen content in tar species lower that coal parent [93].

Regearding the mechanism of the nitrogen compounds release, two different way can occur in [28,94]: as nitrogen content in tar compounds, due the breaking of C-C bonds of aromatic clusters and as light-gas nitrogen (NH₃ and HCN), because of the breaking of C-N bonds of ring. Generally, the tar-nitrogen release begins before than the release of light-gas nitrogen [95], but several workers [96,97] have measured important amounts of light-gas nitrogen in favorable condition during the first path. Perry [85] and Chen [97] have compared the release of tar nitrogen with the release of tar compounds founding that the nitrogen fraction is proportional to tar compounds released. The breaking of rings produces principally HCN, NH₃ and in less measure HNCO [91,95,98]. Li et al. [99] retain that the formation process of HNCO is not a direct consequence of primary pyrolysis, but is a result of the tar secondary reactions. Freihaut et al. [91], have showed that release of HCN takes place after tar-nitrogen release and at bigger temperatures (1050 K), in contrast with what reported by other workers [96,97] in line with the study of Blair et al. [88].

Depending on the type of coal, the selectivity to HCN or to NH_3 changes. low rank coals and biomasses produce principally NH_3 [93,100-102], while bituminous coals have as main product HCN [103]. Bassilakis et al. [28], have analyzed several coal at different heating rate conditions. In low heating rate conditions, they reported a comparable amount of NH_3 and HCN for bituminous coals, while in condition of high heating rate the amount of NH_3 was unimportant. At low heating rate, NH_3 is the principal product, both for coals and biomasses [93,104].Instead, Liu et al. [105] have found significant amount of NH_3 in high heating rate condition too.

In the case of the low rank coal, NH₃ should form before HCN, both at low and high heating rate [93,106]. The NH₃ spring is likely an amino or amide group and the release of NH₃ is linked to the presence of quaternary nitrogen, widely present in low rank coal [93]. Many evidences show that the formation of NH₃ can occur in different ways, both through a direct release from coal or through a hydrogenation reactions of HCN on the particle surface. The dependence of NH₃ formation on the heating rate, suggests that NH₃ can be produced starting from the reaction that involves HCN [106,107]. Large particles seem to favor the NH₃ formation, if compared to HCN formations [106]. Bassilakis et al. [28] reported that in all coals, HCN evolves before than NH₃ and consequently they have suggested three different mechanisms of NH₃ formation:

- hydrogenation reaction of HCN on the char particle surface. At low heating rate, the residence time is greater than under high heating rate conditions, favoring the conversion HCN to NH₃.
- hydrogenation reaction in gas phase that involves HCN and hydrogen released during pyrolysis.
- direct HCN and NH₃ formation from pyrolitic process without hydrogenation reactions.

Different models describe the nitrogen release from coal: FG-DVC [28], FLASHCHAIN [94] and CPD [108]. These models have a similar characteristic concerning the network structures of parent coal, which is defined on the basis of analytic information or empirical correlations. Different statistical methods are used to describe the evolution of lattice structures, as well as different chemical formulations. Regarding the nitrogen release, both models consider both the

release *via* tar and the release *via* breaking rings. In the case of FG-DVC and FLASHCHAIN, the kinetic mechanism are based on a first order kinetics at distributed activation energy whereas in the case of CPD, a three step kinetic mechanism has been implemented [109].

This chapter presents a multi-steps kinetic model able to predict the release of main species, such as NH₃, HCN, tar-nitrogen and nitrogen fraction reaming in the char residue. The characteristic of this model is its predictive possibilities, without tuning activity of rate parameters for the different coal or with kinetic at distributed activation energy. In particular, the relative simplicity of this model, constituted by series and parallel reactions, renders easy the coupling with the previous coal devolatilization model [13].

5.2 Kinetic Model

Many experimental data [85,96,98,110] show an analogue behavior between the released fraction of nitrogen and total fraction released of volatile matter. On this basis and to maintain a consistency in the model, we adopted for the nitrogen matrix the same criterion already used to characterize the effect of the solid phase composition on the formation of hydrocarbon species [13]. Four nitrogen solid references compounds are assumed COAL₁-N, COAL₂-N, COAL₃-N, CHAR-N, tightly tied to reference compounds COAL₁, COAL₂, COAL₃, CHAR of the C/H/O subsystem. According to the elemental composition (in terms of C, H and O), the nitrogen compounds of each coal are described as composed by the three reference coals vertex of the triangle in which are included (Figure 11).

The release of nitrogen components occur along with coal pyrolysis. Thus, in accordance with the previous multi-steps kinetic model of coal pyrolysis [13], we assume that two different mechanism, low and high temperature, compete during the release of the nitrogen components. The multi-step kinetic mechanism, reported in Table 11, contains 11 species involved in 17 reactions.

At low heating rates conditions, the products are not directly released to the gas phase but they are entrapped in the metaplastic phase as chemical-adsorbed species, which are precursors to volatile species (indicated with the superscript *, like NH₃*, HCN* and N_{TAR}*). Only when the temperature is high enough these species can be released in gas phase as NH₃, HCN (that constitute the light-gas nitrogen LGN) and N_{TAR}. The apparent activation energy of the low temperature mechanism is ~33-40 kcal/mol. At low temperatures, tar components can react with the solid residue through cross-linking and reticulation reactions. The result is a small release of N_{TAR} and an increase in nitrogen content in the residual char. At high temperatures or high heating rates, the nitrogen species directly decompose to nitrogen gas and tar components with activation energy of 61-75 kcal/mol. Increasing the heating rate, the direct release of N_{TAR} prevails on the reticulation and cross-linking reactions. The transition temperature between low and high temperature is \sim 750 K for COAL₃-N, \sim 850 K for COAL₂-N and \sim 1050 K for COAL₁-N.

The kinetic parameters regarding the N_{TAR}^* and N_{TAR} formation have been taken directly by multi-step kinetic model of hydrocarbon release work [13]. The kinetic model of nitrogen release, unlike of CPD, FLASHCHAIN and FG-DVC model, includes the NH₃ formation too, both in low temperature conditions and in high temperature conditions.

	Reactions	A^*	E_{ATT}^{*}
R ₁	$COAL_1$ -N $\rightarrow 0.07 \text{ NH}_3^* + 0.05 \text{ HCN}^* + 0.88 \text{ N}_{CHAR}$	2.0×10^{8}	40000
\mathbf{R}_2	$\text{COAL}_{1}\text{-}\text{N} \rightarrow \text{N}_{\text{TAR}}^{*}$	4.0×10^{7}	40000
R ₃	$COAL_1\text{-}N \rightarrow 0.05 \text{ NH}_3 + 0.3 \text{ HCN} + 0.65 \text{ N}_{CHAR}$	1.6×10^{15}	75000
\mathbf{R}_4	$COAL_1$ -N \rightarrow N _{TAR}	1.0×10^{14}	75000
R_5	$\text{COAL}_2\text{-N} \rightarrow 0.15 \text{ NH}_3^* + 0.03 \text{ HCN}^* + 0.82 \text{N}_{\text{CHAR}}$	7.6×10^{10}	36000
R_6	$\text{COAL}_2\text{-}\text{N} \rightarrow \text{N}_{\text{TAR}}^*$	5.0×10^{10}	36000
\mathbf{R}_7	$COAL_2\text{-}N \rightarrow 0.15 \text{ NH}_3 + 0.3 \text{ HCN} + 0.55 \text{ N}_{CHAR}$	3.0×10 ¹⁷	63000
R_8	$COAL_2$ -N \rightarrow N _{TAR}	4.0×10^{17}	63000
R ₉	$\text{COAL}_3\text{-}\text{N} \rightarrow 0.15 \text{ NH}_3{}^* + 0.15 \text{ HCN}{}^* + 0.70 \text{ N}_{\text{CHAR}}$	4.0×10^{10}	33000
R ₁₀	$\text{COAL}_3\text{-}\text{N} \rightarrow \text{N}_{\text{TAR}}^*$	1.6×10 ⁹	33000
R ₁₁	$\mathrm{COAL_{3}\text{-}N} \rightarrow 0.15 \ \mathrm{NH_{3}} + 0.1 \ \mathrm{HCN} + 0.75 \ \mathrm{N_{CHAR}}$	5.0×10 ¹⁸	61000
R ₁₂	$COAL_3$ -N \rightarrow N _{TAR}	2.0×10^{18}	61000
R ₁₄	$N_{CHAR} + N_{TAR} {\rightarrow} 0.1 \ NH_3 + 0.05 \ HCN* + 1.85 \ N_{CHAR}$	1.1×10^{6}	32500
R ₁₃	$N_{TAR}^{*} \rightarrow N_{TAR}$	3.8×10^{8}	33000
R ₁₅	$\rm NH_3^* \rightarrow \rm NH_3$	7.0×10^2	23000
R ₁₆	$HCN^* \rightarrow HCN$	4.0×10^{2}	23000
R ₁₇	$N_{CHAR} \rightarrow CHAR_{C} + HCN$	4×10 ⁹	80000

Table 11: Multi-steps kinetic model of nitrogen release

 $\overline{* k = A \exp(-E_{ATT}/RT)}$ (units are cal, mol, l, K and s)

5.3 **Results and discussion**

The kinetic model of nitrogen compounds release was validated using several independent sets of experimental data available in the literature. The first four sets of data were obtained in regime of low heating rate. The first two mainly refer to the release of gaseous nitrogen species such as NH₃ and HCN:

4.3.1 Thermogravimetric analysis: experiments of Bassilakis et al. [28]

4.3.2 Thermogravimetric analysis: experiments of de Jong et al. [111]

The third set of data refers the nitrogen content in the char residue

4.3.3 Thermogravimetric analysis: experiments of Pohl and Sarofim [63] and Perry [85]

The other sets of experimental data were obtained in regime of high heating rate using or a Drop Tube Reactor or a Flate Flame Burner Reactor. These sets moistly refer to the total nitrogen release:

- 4.3.4 Drop Tube Reactor: experiments of Fletcher and Hardesty [110]
- 4.3.5 Drop Tube Reactor: experiments of Hambly [96,112]
- 4.3.6 Drop Tube Reactor: experiments of Chen and Niksa [98]
- 4.3.7 Flate Flame Burner Reactor: experiments of Hambly [96,112] and Genetti et al. [108]

The experimental conditions span from heating rate of 0.5 K/s to 10^5 K/s, with final temperatures from 1173 to 2300 K. The carbon and nitrogen content of analyzed coals spans from 65% to 94 % and from 0.2% to 4.0%, respectively.

5.3.1 Thermogravimetric analysis: experiments of Bassilakis et al [28]

Eight coals, with different carbon and nitrogen content, were used in this experimentation. Table 12 reports the elemental composition of each coal and the distribution of the reference nitrogen compounds.

	Elen	nental Co	mposition	1 (% w, d	laf)	Nitrogen Distribution (%)				
Coal	С	Н	Ο	Ν	S	COAL ₁ -N	COAL ₂ -N	COAL ₃ -N	N _{CHAR}	
Beluah Zap	72.9	4.83	20.34	1.15	0.70	0.00	0.46	0.50	0.04	
Wyodak	75.0	5.35	18.02	1.12	0.47	0.16	0.39	0.44	0.00	
Illinois	77.7	5.00	13.51	1.37	2.38	0.03	0.73	0.24	0.00	
Blind Canyon	80.7	5.76	11.58	1.57	0.37	0.38	0.36	0.26	0.00	
Stockton	82.5	5.25	9.83	1.56	0.65	0.12	0.77	0.11	0.00	
Pittsburgh	83.2	5.32	8.83	1.64	0.89	0.16	0.75	0.08	0.00	
Upper Freeport	85.5	4.70	7.51	1.55	0.74	0.00	0.93	0.00	0.07	
Pocahontas	91.1	4.44	2.47	1.33	0.50	0.42	0.31	0.00	0.28	

Table 12:Elemental composition of Argonne Premiun coals [28] and distribution of reference nitrogen compounds.

The set of data were carried out in a temperature programmed pyrolysis in inert atmosphere with a heating rate of 0.5 K/s up to a final temperature of 1173 K, with hold time of 3 min. The experimental information refer only NH_3 and HCN released, while only for Blind Canyon coal have been reported the evolution rate both for NH_3 and for HCN, too.

Figure 37 shows the comparison between the experimental data and the model prediction in terms of NH_3 , HCN in function of the carbon content. The NH_3 released shows a constant decrease with the increasing of the carbon content in coals. The experimental data of HCN do not show a monotonous trend with the carbon content, but they show a little changeability with the rank. Moreover, it is interesting to observe as the amount of NH_3 is always bigger than HCN, not only for low coal rank but also for high coals rank. The numerical predictions show a good agreement with the experimental data both in the case of NH_3 and HCN.



Figure 37: Release NH_3 and HCN in function coal rank (%w C, daf). Symbols: experimental data [28]; line with symbols: model predictions

In Figure 38 are reported the experimental data and model predictions in terms of evolution rate of NH_3 and HCN for Blind Canyon coal.



Figure 38: Evolution rate of NH_3 and HCN for Blind Canyon coal. Symbols: experimental data [28]; line: model predictions.

The experimental evolution rate of NH_3 shows the presence of two peaks (Figure 38a). The model prediction underestimates the first peak and overestimates the second peaks. Regarding the numerical predictions, the first contribution is due to the release of NH_3 during the cross-linking and reticulation reactions, while the second peak is due to the NH_3 formation from metaplastic phase. The experimental data of evolution rate of HCN shows the presence of one peak. The model well catches this behavior, as highlighted in Figure 38b.

5.3.2 Thermogravimetric analysis: experiments of de Jong et al. [111]

Different type of solid fuels have been pyrolyzed in this experimentation, with particular attention to NH_3 and HCN formations. The only combustible of interest was a mixture of 50% South Africa coal and 50% Columbian coal. Table 13 reports the average elemental composition of this mixture and relative distribution in the reference nitrogen compounds.

Table 13:Elemental Composition of blend coal: 50 % South Africa coal and 50% Columbian coal and reference nitrogen compounds distribution.

	Eleme	ntal Comp	osition (%	6 w, c	laf)	N	itrogen Distril	oution (%)	
Coal	С	Н	0	Ν	S	COAL ₁ -N	COAL ₂ -N	COAL ₃ -N	N _{CHAR}
Blend Coal	80.19	5.27	11.8	2	0.74	0.14	0.66	0.2	0

The experimental condition were similar to those of Bassilakis et al. [28], with heating rates (30 K/min), from initial temperature of 423 K to final temperature of 1173 K, and a hold time of 3 min. In Figure 39 are shown the comparisons between the experimental data and the model predictions.



Figure 39: Release and evolution rate of NH_3 *and* HCN *of Blend Coal. Symbols: experimental data [111]; line: model predictions.*

The experimental data of de Jong et al. [111] are not perfectly in agreement with those of Bassilakis et al [30]: (i) the release of HCN is similar to the release of NH_3 ; (ii) for a coal with similar rank, the NH_3 /HCN suggested by Bassilakis et al [30] is about ~1.5 while the ratio obtained by Jong et al. [109] is only ~1. However, the evolution rate of NH_3 shows again the presence of two peaks while the release of HCN comes from one contribution. Moreover, the experimental data seem to shows an incomplete devolatilization.

The model describes quite well the NH_3 formation even if the model underestimates slightly the finale release. The model evolution rate anticipates slightly the experimental peaks. Unlike the previous comparison[30], the model shows a better agreement with the experimental data in terms of maximum peaks and a partial agreement in terms of HCN release.

5.3.3 Thermogravimetric analysis: experiments of Pohl and Sarofim [63], Perry [85]

These experimentations deepened the study of the evolution of nitrogen solid residue at different final temperatures. The experiments have been carried out in a thermogravimetric balance, with heating rate of 1 K/s, hold time of 20 min, from 900 to 2300 K. Table 14 displays the elemental composition of Pittsburgh coal, and the respective distribution of the reference nitrogen compounds.

Table 14:Elemental composition and reference nitrogen compounds distribution of Pittsburgh coal.

	Eleme	ntal Com	position	(% w, da	laf) Nitrogen Distribution				
Coal	С	Н	0	Ν	S	COAL ₁ -N	COAL ₂ -N	COAL ₃ -N	N _{CHAR}
Pittsburgh	82.77	5.61	8.90	1.74	0.98	0.32	0.54	0.14	0.00

Figure 40 shows the comparison between the model prediction and the experimental data. The model catches well the experimental trend. It is possible to observe as the main variations occur between 1300 and 1650 K and for temperatures higher than 1650 K, the nitrogen content in solid matrix is almost negligible.



Figure 40: Evolution nitrogen in solid matrix. Symbols: experimental data [63,85]; line and symbol: model predictions

5.3.4 Drop Tube reactors: experiments of Fletcher and Hardesty [110]

Fletcher and Hardesty [110] have pyrolyzed five coals, of different rank, in drop tube reactor, with heating rate of about 10^4 K/s. In Table 15 are reported the elemental composition of each coal and them nitrogen distribution. The testl were carried out at two different final temperatures, 1050 K and 1250 K, with residence time of 250 ms and 240 ms, respectively.

	Eleme	ental Cor	nposition ((% w, da	ıf)	Nitrogen Distribution (%)			
	С	Н	0	N	S	COAL ₁ -N	COAL ₂ -N	COAL ₃ -N	N _{CHAR}
Beluah Zap	65.00	4.78	28.32	0.94	1.81	0.00	0.14	0.82	0.04
Blue #1	74.23	5.48	18.35	1.30	0.65	0.24	0.27	0.49	0.00
Illinois #6	74.81	5.33	13.54	1.48	4.85	0.29	0.38	0.33	0.00
Pittsburgh #8	82.77	5.61	8.90	1.74	0.98	0.32	0.54	0.14	0.00
Pocahontas #3	90.92	4.51	2.41	1.34	0.82	0.43	0.30	0.00	0.27

Table 15: Elemental composition and reference nitrogen compounds distribution of coals [110].

The model predictions are compared with the experimental data in Figure 41 in terms of the total nitrogen fraction released. The model is able to describe with good carefulness the overall evolution of the nitrogen fraction, in particular for the bituminous coals. In the case of lignite Beluah Zap coal (Figure 41a), the model overestimates the initial evolution rate for both final temperature. At the highest temperature, the model estimates correctly the nitrogen fraction released while at 1050 K the model overestimates the final asymptotic value. Regarding the anthracitic coal Pocahontas #3 (Figure 41e), the model estimates correctly the initial evolution rate in both conditions, but it overestimate the fraction released.

In all cases, it is possible to observe the presence of a little plateau corresponding at the decomposition of most reactive reference nitrogen coals, N-COAL₃ and N-COAL₂.



Figure 41: Release nitrogen volatile a two different final temperature [110].Symbols: experimental data; line: model predictions.
5.3.5 Drop Tube reactors: experiments of Hambly et al. [96,112]

Five different coals were pyrolyzed by Hambly et al. [96,112] in a drop tube reactor, with heating rate of order 10^4 K/s, at three different final temperature (820, 1080 and 1220 K) with different residence time (170, 280, 410 ms, respectively). Table 16 reports the elemental composition of each coals and the distribution in the reference nitrogen compounds. The experimental information refers the total nitrogen fraction released.

	1 0			<u> </u>	1					
Elen	Elemental Composition (% w, daf)					Nitrogen Distribution				
С	Н	0	Ν	S	COAL ₁ -N	COAL ₂ -N	COAL ₃ -N	N _{CHAR}		
64.16	4.78	28.32	0.94	1.81	0.00	0.14	0.83	0.04		
74.23	5.48	18.35	1.30	0.65	0.24	0.27	0.49	0.00		
74.81	5.33	13.54	1.48	4.85	0.29	0.38	0.33	0.00		
82.77	5.61	8.90	1.74	0.98	0.32	0.54	0.14	0.00		
90.92	4.51	2.41	1.34	0.82	0.43	0.30	0.00	0.27		
	Elem C 64.16 74.23 74.81 82.77 90.92	Elemental Co C H 64.16 4.78 74.23 5.48 74.81 5.33 82.77 5.61 90.92 4.51	Elemental Composition C H O 64.16 4.78 28.32 74.23 5.48 18.35 74.81 5.33 13.54 82.77 5.61 8.90 90.92 4.51 2.41	C H O N 64.16 4.78 28.32 0.94 74.23 5.48 18.35 1.30 74.81 5.33 13.54 1.48 82.77 5.61 8.90 1.74 90.92 4.51 2.41 1.34	C H O N S 64.16 4.78 28.32 0.94 1.81 74.23 5.48 18.35 1.30 0.65 74.81 5.33 13.54 1.48 4.85 82.77 5.61 8.90 1.74 0.98 90.92 4.51 2.41 1.34 0.82	C H O N S COAL ₁ -N 64.16 4.78 28.32 0.94 1.81 0.00 74.23 5.48 18.35 1.30 0.65 0.24 74.81 5.33 13.54 1.48 4.85 0.29 82.77 5.61 8.90 1.74 0.98 0.32 90.92 4.51 2.41 1.34 0.82 0.43	Elemental Composition (% w, daf) Nitrogen Dist C H O N S COAL ₁ -N COAL ₂ -N 64.16 4.78 28.32 0.94 1.81 0.00 0.14 74.23 5.48 18.35 1.30 0.65 0.24 0.27 74.81 5.33 13.54 1.48 4.85 0.29 0.38 82.77 5.61 8.90 1.74 0.98 0.32 0.54 90.92 4.51 2.41 1.34 0.82 0.43 0.30	Elemental Composition (% w, daf) Nitrogen Distribution C H O N S COAL ₁ -N COAL ₂ -N COAL ₃ -N 64.16 4.78 28.32 0.94 1.81 0.00 0.14 0.83 74.23 5.48 18.35 1.30 0.65 0.24 0.27 0.49 74.81 5.33 13.54 1.48 4.85 0.29 0.38 0.33 82.77 5.61 8.90 1.74 0.98 0.32 0.54 0.14 90.92 4.51 2.41 1.34 0.82 0.43 0.30 0.00		

Table 16: Elemental composition and reference nitrogen compounds distributions of coals [96,112].

Figure 42 shows the comparison between model prediction and experimental data in function of the carbon content at the three different final temperature.



Figure 42: Total nitrogen release a three different temperature for different coals. Symbols: experimental data [96,112]; line and symbol: model predictions.

At the lowest temperature, the model is able to reproduce the quality trend even if the total nitrogen released is slightly overestimated. At 1050 K, the model shows a quite well agreement with the experimental data. Increasing the final temperature (Figure 42c), the total nitrogen released predicted by the model increase. On the contrary, the experimental data show a decreasing of the volatile release with the temperature in three case: Beluah Zap, Illinois #6 and Pocahontas #3 coal. For coal Pittsburgh #8 the total nitrogen fraction released remains almost constant. The agreement between experimental data and numerical predictions can be considered satisfactory enough according to the experimental variability.

5.3.6 Drop Tube reactors: experiments of Chen e Niksa [98]

Chen and Niksa [98] have analyzed the release of tar-nitrogen compounds and those of light gas nitrogen in a drop tube reactor employment four different coals. The experimental test were carried out with heating rate of order 10^4 K/s at different residence times: 56, 61, 66, 77, 83, 86, 89 ms. In Table 17 are reported the elemental composition and reference nitrogen compounds distributions for each coal.

Tueste Tre Elementati composition and reference introgen compounds distributions of cour [90]											
	Elem	ental Com	position (%	6 w, daf))	Nitrogen Distribution					
Coal	С	Н	0	Ν	S	COAL ₁ -N	COAL ₂ -N	COAL ₃ -N	N _{CHAR}		
Dietz	69.5	5.0	24.1	1.0	0.4	0.0	0.36	0.63	0.01		
Illinois	74.1	5.3	13.4	1.5	5.7	0.30	0.36	0.34	0.0		
Pittsburgh	82.5	5.6	8.5	1.8	1.6	0.34	0.54	0.13	0.0		
LowerK	88.7	5.0	2.1	1.7	2.5	0.54	0.27	0.0	0.19		

Table 17: Elemental composition and reference nitrogen compounds distributions of coal [98]

The model prediction and the experimental data are compared in Figure 43. It is important to underline that the experimental uncertainty in this experimentations are high enough, with an absolute error also of 20%.



Figure 43: Release of tar-nitrogen and LGN species. Symbols: experimental data [98]; line and symbol: model predictions.

The model describes quite well the behavior of bituminous coal (Illinois and Pittsburgh coal) both in terms of the tar-nitrogen compounds and in terms of the LGN release. In the case of Dietz coal (lignite), the model overestimates the initial release of tar-nitrogen compounds but it 52

predicts the final asymptotic amount almost correctly. In the case of LGN, the model underestimates the relating fraction released. Regarding the Lower Kittinning coal (anthracitic coal), the model underestimates both the initial release and the asymptotic value.

5.3.7 Flate Flame Burner Reactor of Hambly [96,112] and Genetti et al. [108]

The pyrolysis of six coals has been investigated by Hambly et al. [96,112] in a flat-flame burner reactor with a residence time of 18 ms. At the maximum of temperature of 1641 K. In the same reactor, Genetti et al. [108] has pyrolyzed other six coals at same temperature, but with residence time of 78 ms. The magnitude heating rate was 10^5 K/s. In Table 18 is reported the elemental composition of the coals employed in these experimentations.

Table 18: Elemental	l com	position an	d referen	nce nitro	ogen con	npounds	distributions	of coal [96,108,112	2]
	- 1	10	• •	(0)	1.0		A.T.	Di citat	

_	Eleme	Elemental Composition (% w, daf)				Nitrogen Distribution				
Coal	С	Н	0	Ν	S	COAL ₁ -N	COAL ₂ -N	COAL ₃ -N	N _{CHAR}	Ref.
Smith Roland	67.4	5.4	24.4	1.0	1.8	0.22	0.05	0.73	0.00	
Beluah Zap	68.5	4.9	24.9	1.0	0.6	0.00	0.31	0.67	0.02	
Botton	70.7	5.8	20.8	1.4	1.2	0.14	0.66	0.20	0.00	106 1121
Adaville #1	72.5	5.2	20.1	1.2	1.0	0.11	0.37	0.52	0.00	[90,112]
Deadman	76.5	5.2	15.9	1.5	0.8	0.12	0.53	0.35	0.00	
Kentucky #9	79.4	5.6	8.6	1.7	4.7	0.44	0.38	0.18	0.00	
Elkhorn	82.7	5.7	8.8	1.8	1.0	0.39	0.46	0.15	0.00	
Sewell	85.5	4.9	7.1	1.7	0.8	0.07	0.89	0.00	0.05	
Lower Kittaning	86.2	4.9	4.6	1.8	2.5	0.29	0.59	0.00	0.12	[100]
Penna Semian. C.	88.4	4.0	5.5	1.2	0.9	0.09	0.68	0.00	0.24	[108]
Lower Hortshore	91.2	4.6	1.5	1.8	0.9	0.52	0.19	0.00	0.29	
Lykens Valley #2	93.8	2.7	2.0	0.9	0.6	0.21	0.24	0.00	0.54	

The comparison between experimental data end model prediction are pointed in Figure 44. The model shows a satisfactory agreement with the experimental data, moistly with those with a carbon content lower than 85%, daf. In the case of coals with a carbon content higher than 85% (experimental data of Genetti et al. [108]), the model prediction overestimates the total nitrogen releases with a maximum absolutely error about 20%, however the qualitative trend is well predicted.



Figure 44: Total nitrogen release. Symbols: experimental data [96,108,112], line and symbol: model predictions

5.4 Conclusion

A multi-step kinetic model of nitrogen compound release from coal has been developed. The characteristic of this model is its predictive capabilities, without the tuning activity of the rate parameters for the different coal or for different operating conditions.

The model is based on the four reference nitrogen compounds and for each reference has been proposed a multistep kinetic mechanism. The completed mechanism includes 11 lumped species and 17 reactions. Despite its simplicity, the is able to characterize the release of the main of nitrogen compounds, as NH_3 , HCN and N_{TAR} , in a wide range of operating conditions of heating rate, temperature and coal ranks. The overall agreement between the experimental data and the numerical prediction is good enough.

6 Char elemental composition and heterogeneous reactions

6.1 Introduction

The char oxidation and gasification reactions are the rate determining steps of the coal combustion processes and an improving of the knowledge of the mechanisms involved in such processes can lead to increase the efficiency of the combustion plants.

There is a general agreement that physical and chemical char properties do not depend only on the coal rank but also on the pyrolysis conditions (low or high heating rates, temperatures, time) [6-8]. Russell et al. [113] have pyrolyzed two coal of different rank in a wire mesh reactor under high heating condition. Different temperature and different residence time were set in order to analyze the effect of the elemental composition on the char reactivity. They found a positive effect of the hydrogen content on the char reactivity.

The aim of this work has been the developing of a kinetic mechanism of char oxidation and gasification reactions able to take into account the effect of the elemental composition on the reactivity, in agreement with the previous experimental observation.

In order to realize this, it has been necessary to conduct an analysis of the elemental composition of the char residue. Afterward, on the basis of the results obtained, the global model of char heterogeneous reactions has been developed.

6.2 Char elemental composition

In the study of the char elemental composition have been employment both PoliMi experimental data and several experimental data available in literature, obtained by different research groups. The effect of the coal rank and operating conditions has been taken into account.

6.2.1 Detailed kinetic model of coal pyrolysis

On the basis of the experimental sets of the char elemental composition proposed by Sommariva et al. [13], the multi-step kinetic model has been modified, in particular the sub-model concerning the reference coal COAL₁, as pointed out in Table 19.

Table 19. Multi-ster	h kinetic model o	of coal pyrolysis
1 auto 17. muni-sici	J KINCHE MOUEL O	1 COM DYIOIYSIS

1	Reactions Mechanism	A [s m kmol]	E.m.[kca]/kmol]
		77 [3,111, KHO1]	LATTRead Killor
R.	$COAL \rightarrow COAL^* + 1 C_{2*} + CHAR_{2} + 5 H_{2}$	5.0×10^9	35000
R	$COAL_{4} \rightarrow COAL_{4}^{*} + 1 C_{2,5} + CHAR_{6} + 5 H_{2}$	1.0×10^{15}	65000
R ₂	$COAL_1^* \rightarrow 4$ CHAR ₁₁ +1 25 CHAR ₂ +75 CH ₄ + 5 H ₂	2.0×10^8	40000
R,	$COAL_1^* \rightarrow TAR_1^*$	1.0×10^8	40000
R ₅	$COAL_{4}^{*} \rightarrow 4$ CHAR ₁₁ +1 CHAR ₂ +1 CH ₄	1.0×10^{14}	75000
Re	$COAL_1^* \rightarrow TAR_1$	1.0×10^{14}	75000
R ₇	$TAR_1^* \rightarrow TAR_1$	2.5×10^{12}	50000
R ₈	$TAR_1^* + CHAR_H \rightarrow 5.CHAR_H + 1. CHAR_C + 1. CH_4$	2.5×10^7	32500
R ₉	$\operatorname{TAR}_{1}^{*} + \operatorname{CHAR}_{C} \rightarrow 4. \operatorname{CHAR}_{H} + 2. \operatorname{CHAR}_{C} + 1. \operatorname{CH}_{4}$	2.5×10^7	32500
_	$\frac{\text{COAL}_2}{\text{COAL}_2} \xrightarrow{(-C_{14}\Pi_{10}O^{-})} COAL_4 \rightarrow 2 \text{ CHAR}_6 + 3.94 \text{ CHAR}_{11} + 25 \text{ COAL}_4 + .04 \text{ BTX}^* + .31 \text{ CH}_4^* +$	10	
R ₁₀	$.11 C_{2.5}^{-2.5} + .11 COH_2^{+} + .15 CO_{2.5}^{+} + .41 H_2O^{+} + .18 CO^{+} + .265 H_2$	6.0×10^{10}	36000
R ₁₁	$COAL_2 \rightarrow 0.61 CHAR_C + 4.33 CHAR_H + .21 COAL_1 + .16 BTX^* + .27 CH_4$ + .5 CO + .1 H ₂ O + .3 COH ₂ [*] + .28 H ₂ + 0.1 CO*	$4.0 \mathrm{x} 10^{18}$	63000
\mathbf{R}_{12}	$\text{COAL}_2 \rightarrow \text{TAR}_2^*$	5.0×10^{10}	36000
R_{13}	$\text{COAL}_2 \rightarrow \text{TAR}_2$	$4.0 \mathrm{x} 10^{17}$	63000
R_{14}	$\operatorname{TAR}_2^* \to \operatorname{TAR}_2$	$2.4 \text{ x} 10^9$	39000
R ₁₅	$\text{TAR}_{2}^{*} + \text{CHAR}_{\text{H}} \rightarrow 1.5 \text{ CHAR}_{\text{C}} + 7.\text{CHAR}_{\text{H}} + 1. \text{ H}_{2}\text{O}^{*} + .5 \text{ CH}_{4}$	$4.5 ext{ x10}^9$	30000
R ₁₆	$TAR_{2}^{*}+CO_{2}TS^{*}\rightarrow CO_{2}TS^{*}+.15 CO_{2}^{*}S^{*}+1.94 CHAR_{C}+4. CHAR_{H}++.335H_{2}$ +.25COAL ₁ +.04 BTX*+.3CH ₄ *+.05 C ₂₋₅ *+.1COH ₂ *+.4H ₂ O*+.2CO*	1.5 x10 ⁸	30000
	$\frac{\text{COAL3}}{\text{COAL3}} (-C_{12}\text{H}_{12}\text{O}_{5}\text{-})$ $\text{COAL}_{3} \rightarrow 2.73 \text{ CHAR}_{C} + 1.8 \text{ CHAR}_{H} + .22 \text{ COAL}_{1} + .08 \text{ BTX}^{*} + .2 \text{ Ox}_{C} +$		
R ₁₇	.1 CH_4^* + .11 C_{2-5}^* + .2 H_2 +.6 COH_2^* +2.2 H_2O^* +.1 CO_2 + .38 CO_2^* +0.02 CO_2TS^* + 1. CO^*	2.0×10^{10}	33000
R_{18}	$COAL_3 \rightarrow COAL_3^*$	$5.0 x 10^{18}$	61000
R ₁₉	$\begin{array}{l} \text{COAL}_3^* \rightarrow 1.5 \text{ CHAR}_{\text{H}} + .82 \text{ CHAR}_{\text{C}} + 2.08 \text{ CO} + .25 \text{ Ox-C} + .14 \text{ CH}_4 + .7 \text{ C}_{2-} \\ _{5^+} .5 \text{ CO}_2 + .47 \text{ COH}_2^* + .16 \text{ BTX}^* + .25 \text{ COAL}_1 + 1.2 \text{ H}_2\text{O} + .29 \text{ H}_2 \end{array}$	1.2×10^{8}	30000
R ₂₀	$\text{COAL}_3 \rightarrow \text{TAR}_3^* + \text{CO}_2^* + \text{H}_2\text{O}$	1.6×10^9	33000
R ₂₁	$COAL_3 \rightarrow TAR_3 + CO_2 + H_2O$	$2.0 x 10^{18}$	61000
R ₂₂	$TAR_3^* \rightarrow TAR_3$	5.0×10^9	32500
R ₂₃	$TAR_{3}^{*} + CHAR_{H} \rightarrow 4CHAR_{H} + 2.5CHAR_{C} + .2CH_{4}^{*} + 2COH_{2}^{*} + .8H_{2} + .3C_{2-5}$	$1.4 \mathrm{x} 10^8$	30000
	Metaplastic release reactions		
R ₂₄	$\mathrm{CO}_2^* \rightarrow \mathrm{CO}_2$	$1.0 \mathrm{x} 10^2$	18000
R ₂₅	$\operatorname{CO}_{2S}^* \rightarrow \operatorname{CO}_2$		
R ₂₆	$\operatorname{CO}_{2S}^* \rightarrow \operatorname{CO}_2$	$1.0 x 10^{11.7}$	65000
R ₂₇	$\mathrm{CO}^* \rightarrow \mathrm{CO}$	$3.0 x 10^2$	20000
R ₂₈	$\text{COH}_2^* \rightarrow \text{CO}^* + \text{H}_2$	1.5×10^{9}	57000
R ₂₉	$H_2O^* \rightarrow H_2O$	1.0×10^3	18000
R ₃₀	$H_2O^* \rightarrow H_2O$	$1.0 x 10^{13.7}$	60000
R ₃₁	$BTX^* \rightarrow BTX$	$1.0 x 10^{12.6}$	48000
R ₃₂	$CH_4^* \rightarrow CH_4$	$1.0 \mathrm{x} 10^3$	17000
R ₃₃	$C_{2.5}^* \rightarrow C_{2.5}$	$1.0 \mathrm{x} 10^3$	17000
	Annealing Reactions		
R ₃₄	$CHAR_{H} \rightarrow CHAR_{C}$	$1.0 x 10^{11}$	80000

Similarly to $COAL_3$, $COAL_1$ forms an activated component called $COAL_1^*$ with the release of light hydrocarbon compounds. This thermal decomposition can follow a mechanism of low temperature or high temperature depending on the operating conditions (low or high heating rate). The results of this new thermal decomposition is a lower hydrogen content in the metaplastic phase. The activated pseudo components $COAL_1^*$ can undergo few competitive reactions of thermal decomposition with formation of solid species ($CHAR_C$ and $CHAR_H$), release of light hydrocarbon compounds, formation of tar fragments, called TAR_1^* , or a direct release of TAR_1 compounds in gas phase. The composition of TAR_1 is different from that one proposed by Sommariva et al. [13] and only one compound (naphthalene, $C_{10}H_8$) is necessary for its characterization. Moreover, the decomposition reaction of the pseudo-species COH_2^* has been reduced in order to increase the oxygen content in the solid phase.

However, these modifications have an unimportant effect on the comparison reported in the work of Sommariva et al. [13], as shown in Figure 45.



Figure 45: Comparison between experimental data [15,16] and model predictions: blue circle is the model of Sommariva et al. [13] and the red triangle is the model presented in this work.

The differences with the previous model are modest and they refer mainly the release of the inorganic oxygenated compounds. Moreover these differences are more important when the release of IOG is higher.

6.2.2 Experimental data of PoliMi

In these experiments, three coals with different rank were studied whose compositions are given in Table 20. According to the American rank classification system, the first coal is a subbituminous, the America coal is a bituminous and the coal Pocahontas is an anthracite.

In order to obtain char with different elemental composition, the pyrolysis of the investigated coals was performed by two methods. One is the temperature-programmed pyrolysis in a stream of helium gas (200 Nml/min): about 5 mg of coal particles sieved at 60 mesh were treated under low heating rate conditions (2, 20, 100 K/min) using a thermogravimetric analyzer (TA Instruments, SDT-Q600). With this experimental setup, the effects of different final

temperatures (1073, 1173 and 1273 K) and isothermal final periods (5, 20 and 30 min) on the char properties and compositions were evaluated. The other technique is the flash pyrolysis in an inert atmosphere (N_2 , 30 Nml/min) using a Curie-point pyrolyzer (CDS, Pyroprobe 5000). About 5 mg of coal particles sieved at 60 mesh were placed in a small quartz pipe (3 mm i.d.) and they were heated rapidly (100 and 1000 K/s) to the final temperature by an induction heating coil. Also in this case, the effect of different final temperatures (1073, 1273 and 1573 K) was investigated, while the isothermal final period was kept costant (10 s). Char samples obtained from pyrolysis tests were characterized by means of a CHNS-O Element Analyzer (Fisons, EA-1108 CHNS-O). The quantification limits for the detected species were 0.2 % wt. for S and 0.1 % wt. for C, H, and N; the oxygen amount was evaluated indirectly from the mass balance on the analyzed samples.

	Ultimate analysis, %wt. daf								
Coal	С	Н	0	Ν	S				
Sub-Bituminous	84.66	5.9	7.91	1.3	0.22				
America	85.32	5.16	7.15	1.48	0.89				
Pocahontas	91.24	4.45	2.48	1.33	0.5				

Table 20:Ultimate analysis and reference coal repartition for each coals

6.2.2.1 Thermogravimetric experiments

Figure 46-Figure 48 show the comparison between the experimental data of thermogravimetric analysis obtained at different thermal treatments and the respective model predictions. The general agreement is satisfactory enough, above all in the experimentation conducted at 20 and 100 K/min. At 2 K/min the model shows a systematic overestimation of the devolatilization rate. Moreover, the model predicts quite well the final amount of char residue, with a maximum absolute error of 9% (Bituminous coal at 2 K/min, Figure 46a, and America coal at 100 K/s, Figure 47c).



Figure 46: Comparison between the thermogravimetric analysis of Sub-bituminous coal at three different thermal treatment



Figure 47: Comparison between the thermogravimetric analysis of America coal at three different thermal treatment.



Figure 48: Comparison between the thermogravimetric analysis of Pocahontas coal at three different thermal treatment

Table 21 reports the experimental of elemental composition and those predicted by the model for the char samples obtained under low heating rate conditions. The elemental composition refers only to C, H, O, normalized to 100, without taking into account the N and S content.

Figure 49 shows the comparison between experimental data and model predictions. The experimental trends highlight an increase of the carbon content in the char residue with the increase of the final temperature and a decrease of both hydrogen and oxygen contents. This behavior can be ascribed to a more marked release of the volatile components (in particular the pseudo-species entrapped within the metaplastic phase) with the temperature. Several observations can be done about Figure 49. First of all, the model overestimates the hydrogen content into char residues while the carbon content is slightly under-predicted; indeed, the maximum difference between measured and predicted values for the carbon amount is always below 3%. Except for few experimental tests, the oxygen content estimated from the experiments is about zero. The model shows a similar behavior even if underestimates the oxygen content at the lowest temperature.

				Experimental data, %wt daf			Model Predictions, %wt daf		
Coal	h [K/min]	T _{pyrolysis} [K]	t _{holding} [min]	С	Н	0	С	Н	0
	2	1273	5	98.94	1.06	0.0	99.73	0.22	0.05
	2	1073	30	99.02	0.98	0.0	96.82	3.13	0.05
	2	1273	30	99.48	0.52	0.0	99.94	0.01	0.05
	2	1073	5	99.61	0.39	0.0	96.79	3.16	0.05
sno	20	1173	20	99.38	0.38	0.24	97.26	2.69	0.05
nin	20	1173	5	99.38	0.46	0.17	96.94	3.01	0.05
itur	20	1273	20	100	0.0	0.0	99.67	0.28	0.05
-B	20	1073	30	98.76	0.74	0.51	96.82	3.13	0.05
Sub	20	1173	20	99.72	0.28	0.0	97.26	2.69	0.05
•1	100	1073	5	98.13	0.86	1.01	96.37	3.16	0.48
	100	1273	5	100	0.0	0.0	98.23	1.72	0.05
	100	1073	30	98.83	0.49	0.69	96.83	3.12	0.05
	100	1273	30	100	0.0	0.0	99.84	0.11	0.05
	2	1073	5	98.92	1.08	0.0	96.75	3.25	0.0
	2	1073	30	99.14	0.86	0.0	96.77	3.23	0.0
	2	1273	5	99.56	0.44	0.0	99.77	0.23	0.0
ica	2	1273	30	99.55	0.45	0.0	99.99	0.01	0.0
ner	20	1173	20	99.42	0.58	0.0	97.25	2.75	0.0
Ar	100	1073	5	97.4	1.22	1.38	96.51	3.23	0.26
	100	1073	30	96.98	0.97	2.05	96.81	3.19	0.0
	100	1273	5	99.52	0.48	0.0	98.23	1.77	0.0
	100	1273	30	99.6	0.4	0.0	99.89	0.11	0.0
	2	1073	5	98.97	1.03	0.0	97.92	2.08	0.0
	2	1073	30	99.12	0.88	0.0	97.94	2.06	0.0
s	2	1273	5	99.58	0.42	0.0	99.86	0.14	0.0
nta	2	1273	30	99.64	0.36	0.0	99.99	0.01	0.0
ahc	20	1173	20	97.7	0.56	1.74	98.26	1.74	0.0
200	100	1073	5	98.7	1.3	0.0	97.9	2.03	0.08
I	100	1073	30	98.73	0.89	0.38	97.99	2.01	0.0
	100	1273	5	99.51	0.49	0.0	98.92	1.08	0.0
	100	1273	30	99.24	0.34	0.43	99.93	0.07	0.0

Table 21: Comparison between experimental data and model predictions for the char samples obtained from different TG tests.

The proposed model correctly catches the experimental trends even if the predicted compositions changes more rapidly with the temperature respect to the experimental data. At the highest final temperature (1273 K) the model is able to reproduce very well the experimental data, for both the hydrogen and the carbon contents.



Figure 49: Experimental data and model predictions of the elemental composition

6.2.2.2 Curie Point Pyrolyzer experiments

The elemental experimental composition and the model predictions are shown in Table 22 for the char samples obtained under high heating rate conditions with the Curie Point pyrolyzer apparatus.

Model Predictions. %wt daf Experimental data, %wt daf Coal h [K/min] С 0 С 0 T pyrolysis [K] Η Η 1000 1073 95.33 4.67 0.0 92.53 3.84 3.64 Bituminous. Sub-1000 94.88 93.66 1273 5.12 0.0 3.83 2.52 1000 1573 98.28 1.72 0.0 96.52 1.84 1.64 1000 1073 95.77 4.23 0.0 91.8 3.79 4.4 America 1000 96.29 3.71 0.0 93.24 3.72 3.04 1273 1000 1573 98.49 1.51 96.28 2.06 0.0 1.66 95.75 100 1073 96.38 3.62 0.0 2.59 1.65 100 1273 97.6 2.4 0.0 96.28 2.54 1.18 Pocahontas 1000 1073 95.07 4.93 0.0 95.9 2.58 1.52 1000 97.22 0.0 96.34 1273 2.78 2.61 1.05 1000 1573 97.08 2.92 0.0 98.15 0.72 1.13

Table 22: Experimental data and model predictions for the char samples obtained from flash pyrolysis tests.

In Figure 50 the experimental results evidence an increase of the carbon content and a decrease of both hydrogen and oxygen contents in the char residue with the increasing of the final temperature; this confirms also the trends obtained from the TG experiments, at low heating rates. A good agreement between model predictions and experimental data can be found for carbon and hydrogen contents, especially at 1273 and 1573 K.



Figure 50: Experimental data and model predictions. Symbol: see Figure 49.

Regarding the oxygen content, its amount was always negligible in the flash pyrolysis experiments, whereas the model over-predicted the oxygen content showing a decreasing monotonic trend influenced by the increase of the final pyrolysis temperature.

6.2.3 Comparison between literature experimental data and model predictions

In order to fully evaluate the predictive capability of the proposed model, several literature experimental datasets containing information on the char composition were also used for comparison purposes. The main operating conditions of these experiments are summarized in Table 23.

	Reference	N° Coal	Rank (%C, daf)	H.R [K/min]	T _{pyrolysis} [K]	Equipment
	Ochoa et al.[114]	2	68.5-74.5	5	1273	TGA
*	Roberts and Harris [115]	2	82.9-90.6	10	1373	TGA
	Varhegy et al.[116]	3	66.2-82.7	10	1223	TGA
H.R	Zhang et al. [117]	6	89.7-94.4	30	1173	TGA
Ľ.	Shim et al. [118]	5	73.2-90.4	-	973	QTB
	Chan et al. [119]	1	80.8	10	900-1173	TGA
	Wu et al. [120]	1	80.5	6	1223-1773	TGA
	Wu et al. [120]	1	80.5	10^{3}	1223-1773	DTF
***	BYU database [14,85,96,121]	27	64.2-93.8	$10^4 - 10^5$	850-1650	DTF/FFBR
[.H.F	Park and Ahn [122]	5	73.5-89.1	10^{4}	1673	DTF
Η	Russell et al.[113]	2	81.0-90.5	10^{4}	1273-2073	WRM

Table 23: Summary of operating conditions of literature experiments.

*L.H.R. = Low heating rate: K/min

** H.H.R. =High heating rate: K/s

In the following paragraphs, the comparison between model predictions and literature experimental data for low heating rate and high heating rate conditions, respectively, is discussed.

6.2.3.1 Low heating rate conditions [101-106]

The comparison between model predictions and experimental data in Figure 51 highlights three different aspects:

- 1. well predictions in term of hydrogen content
- 2. underestimations of oxygen content
- 3. overestimation of carbon content.

Except for the experiments of Shim et al. [118] (isothermal condition, 973 K), the other pyrolysis experiments were carried out with final temperatures equal or higher than 1173 K and with a long isothermal period at the end (variable between 20 min and 3 h). MacPhee et al. [123] compared, through FTIR measurements, the total oxygen released as CO₂, H₂O and CO for seven coals, characterized by different rank (from Beluah Zap to Pocahontas), respect to the initial oxygen content of the parent coal. In this case, the experimental thermal treatments were slightly milder than the ones previously discussed: similar final temperature of pyrolysis (1173 K) and 62

heating rate (30 K/min) were used but the sample did not undergo to a final isothermal treatment, being immediately cooled down to room temperature conditions. In this work, it was found that all the oxygen of the coal samples is expelled during pyrolysis and it was detected by measuring the amounts of three gaseous species, as H_2O , CO and CO_2 . Similar results were reported by Van Krevelen [124], Solomon et al. [125] and Giroux et al. [126]. These trends, for several operating conditions, do not agree with those highlighted in Figure 51. It is important to underline that the oxygen content is obtained as complement to 100 and consequently the whole uncertainty is shifted onto it. Moreover, as shown in Sommariva et al. [13], the model has been validated with the experimental data of organic oxygenated compounds released too, showing a very well agreement with them.



Figure 51: Experimental data and model predictions for low heating rate conditions. Symbols: Marks represent the experimental data (grey circle is carbon, blue triangle is oxygen, red diamond is hydrogen); line with open marks represents model predictions (circle and line is carbon, triangle and line is oxygen, diamond and line is hydrogen).

The results of Chan et al. [119] confirm the same trends observed in the present work for temperatures higher than 1000 K (Figure 49); moreover, as shown in Figure 52, a good agreement between experimental data and model predictions was found over a wide range of temperatures, both for hydrogen and carbon. An overestimation of the release of oxygenated gaseous species determined an underestimation of the oxygen content in the solid residues in the range 750-900 K, while in the other conditions the model well reproduces the experimental findings.



Figure 52: Comparison between experimental data [14] and model predictions. Symbol: see Figure 51.

6.2.3.2 Low and High heating rate conditions [120]

Wu et al. [120] investigated the pyrolysis of a bituminous coal both at low heating rate and high heating rate experimental conditions, then the elemental composition of char samples was analyzed.

A thermogravimetric muffle was used for low heating rate tests (6 K/min) whereas a smallscale falling reactor was employed for flash pyrolysis (10^3 K/s). The model predicts quite well the experimental trends in both heating rate conditions, as pointed out in Figure 53. The model predicts quite well the experimental trends. At low heating rate conditions both carbon and hydrogen profiles are well predicted by detailed model. The models shows an underestimation of the oxygen content for the lowest temperatures. At high heating rate conditions the model reproduces with a satisfactory agreement the evolution of the hydrogen content, while the oxygen and carbon content trends are over-predicted and under-predicted, respectively; however, the model is able to correctly reproduce the qualitative trends obtained from the experiments.



Figure 53: Composition of char samples obtained from Shenfu coal under different pyrolysis conditions: (a) low heating rate conditions (6 K/min), (b) high heating rate conditions (10³ K/s). Symbols: see Figure 51.

6.2.3.3 High heating rate conditions

6.2.3.3.1. Database of Brigham Young University [14,85,96,121]

Many experimental data were obtained from the database of the Brigham Young University. This database contains measurements carried out in a Drop Tube Reactor (DTR) and a Flat Flame Burner Reactor (FFBR) with coal particle heating rate of 10^4 and 10^5 K/s, respectively. Different conditions of final temperature, time and rank of coal were analyzed.

6.2.3.3.1.1. Drop Tube Reactor

Three different experimental campaigns were carried out in a Drop Tube Reactor: Fletcher et al. [14], Hambly [96] and Perry et al. [85,121]. In particular, Fletcher et al. [14] and Hambly [96] pyrolyzed the same five different coals, from lignite (Beluah Zap) to anthracite (Pocahontas), in slightly different range of temperatures. The comparison between experimental data and model predictions are reported in Figure 54.



Figure 54: Comparison between experimental data of Fletcher et al. [14] and Hambly [96] and model predictions. Experimental symbol: empty marks are [14] and full marks are [96] (carbon is circle, diamond is hydrogen and triangle is oxygen). Modeling symbol: dashed line and empty mark are [14] and solid line and full marks are [96].

Differences between the two experimental datasets are not due only to the different thermal treatments but also, as reported in these works, because of the different elemental composition of the same coals. Consequently, the model predictions are also slightly different. It is possible to notice that the variability among the experimental data is more relevant than those of the model predictions. However, the model shows a good capability to catch the hydrogen experimental

content, for both experimental datasets. The main difference between the two experimental datasets concerns the oxygen content. In the case of Pittsburgh and Pocahontas coals, Fletcher et al. [14] highlights an increase of the oxygen content in the range 900-1050 K, that was not evidenced by Hambly [96]. Moreover, the experimental data of Fletcher et al. [14] show a general overestimation of the oxygen content with respect to the measurements of Hambly [96].

The model predictions of the oxygen and carbon contents show a good agreement with the results of Hambly [96]. A good agreement between the model and the experimental data of the data of Fletcher et al. [14] was found only at the extremes of the investigated temperature range, while in the intermediate temperature region the model under-estimate the experimental results. This behavior obviously reflects on the carbon content predictions, with an over-prediction of the experimental data obtained in the intermediate temperature range and a good prediction of the char carbon content results measured at low and high pyrolysis temperatures.



Figure 55: Comparison between experimental data of Perry et al. [85,121] and model predictions. Symbol: see Figure 51.

Coal and char results reported by Perry et al. [85,121] belongs to the same database previously discussed. They analyzed seven different coals, from lignite (Yallourn) to anthracite (Pocahontas) in a drop tube reactor at four different temperatures (900-1250 K). In Figure 54, a 66

good agreement between predicted and the experimental results can be noticed over the whole temperature range, especially for carbon and hydrogen; the model reproduces both qualitatively and quantitatively the experimental trends, apart from the hydrogen data of the Miike coal which are over-estimated. The oxygen content is still slightly underestimated for the intermediate temperature conditions (1050-1200 K).

6.2.3.3.1.2. Flate Flame Burner Reactor

Hambly [96] and Perry et al. [85,121] performed several experiments also with a Flat Flame Burner Reactor at a nominal temperature of 1650 K and very short residence time (~18 ms), using 10 and 7 coals, respectively, with a carbon content variable between about 65 and 92 % wt. Figure 56 shows the comparison between experimental data and model predictions. The two sets of experiments highlighted similar hydrogen contents in the char residues. Concerning the oxygen content (and thus the carbon relative amount) the two experimental datasets show somewhat different results. The oxygen content found by Perry et al. [85,121], independently of the coal rank, is always lower than the corresponding amount measured by Hambly [96]; consequently, an opposite behavior was observed for the carbon content. These differences cannot be found in the model predictions because its estimations are more influenced by the coal rank, thus resulting in similar trends for both the investigated datasets. For this reason, Hambly [96] data concerning the carbon and oxygen contents for lignite and anthracite coals were well predicted by the model, while they were over-estimated and under-estimated for the bituminous coals, respectively.



Figure 56: Comparison between experimental data of (a) Hambly [96] and (b) Perry et al. [85,121] and model predictions. Symbol: see Figure 51.

Regarding Perry et al. [69, 112] results, the model shows a fairly good agreement with the hydrogen content data, in particular for lignite, low volatile bituminous and anthracite coals. Oxygen results are well predicted both for bituminous and anthracite coals, whereas are slightly over-estimated for lignite coals. Thus the model shows a better predictive capability when the coal

rank increases. According to the wide experimental variability, model predictions can be considered satisfactory.

6.2.3.3.2. Experiments of Park and Ahn [122]

Five coals, from sub-bituminous to low volatile bituminous, were analyzed in a drop tube reactor under high heating rate conditions (10^4 K/s) and at a nominal temperature of 1673 K. The residence time into the reactor was estimated in 0.6 s. The experimental data as well as the model prediction are reported in Figure 57.



Figure 57: Experimental char composition and model predictions for five different coal treated at 1673 K. Symbols: see Figure 51.

It this case, it was found that the Drayton coal (78 %wt) shows a complete different behavior respect to the other coals, showing a high oxygen content in the solid residue and thus a low carbon content. The model well predicted the hydrogen content results. Concerning oxygen, the model shows a decrease of the oxygen content in the solid residue with the increase of the coal rank; apart from the low bituminous Drayton coal the model tends to over-predict the oxygen content of the char residues. The discrepancy between model and experimental data about the oxygen content obviously determines an under-estimation of the carbon relative amount (except for Dayton coal).

6.2.3.3.3. Experiments of Russell et al. [113]

Two different bituminous coals, Pittsburgh #8 and Pocahontas #3 were pyrolyzed in a wire-mesh reactor at different final temperatures and isothermal times. The numerical prediction and the experimental data are shown in Figure 58.

The model shows an over-estimation of the H/C molar ratio at 1273 K, in particular for Pittsburgh #3 coal, but in general the agreement with the experimental data is satisfactory.



Figure 58: Temporal evolution of the H/C % mole ratio at different final temperatures. Symbol: full circle is experimental data, line is model prediction.

6.3 Char heterogeneous reactions

In literature there are many studies about the char heterogeneous reactions of oxidation and gasification, but an overall consensus on the magnitude of the global orders or on the activation energy does not exist. The causes of these variability are due to experimental problems, difference between fuel origin and the limited size of individual data sets [127].

Over the years, several models have been developed for the char oxidation and gasification reactions [71,128-135]. These kinetic models address different aspects of the char oxidation and gasification, including detailed kinetic mechanism [128,136,137], annealing mechanism [130,131,133], char morphology and particle distribution [71,129,130], and ash inhibition or catalytic effects [130,132].

As mentioned, a global char heterogeneous kinetic mechanism is presented in this section. The model describes not only the main features of the heterogeneous reactions but also the annealing effect on the char reactivity. The model has been developed using both PoliMi experimental data and experimental data taken from literature.

6.3.1 The thermal annealing

The thermal treatment of char particles at high temperatures causes an ordering of the turbostratic structure of the residual char with an increase of the graphitic domains and a parallel decrease of the intrinsic reactivity [120,138]. This process is known as thermal annealing. Several pertinent mechanisms have been discussed in the literature [130,131,133].

Oberlin [138] suggested that, as the heat treatment temperature increased, the structure of the solid matrix evolved in four steps forward a structure more and more crystalline, as reported in Figure 59 [32]. At temperatures below 770 K, the basic structural components are present; between 1070 and 1770 K the basic structures rearrange themselves face-to-face in distorted columns; at temperatures between 1873 and 2270 K, the adjacent columns coalesce into crumpled layers and at the end, at temperatures above 2370, these layers harden, becoming flat and perfect [113].



Figure 59: Four stages of structural rearrangements leading to crystalline order[113].

The annealing mechanism in the coal pyrolysis model [13] has been modified to take into account the rearrangement of the graphitic layers. Three different charry pseudo-components are considered in the residual charcoal matrix. Together with a hydrogenated species CHAR_H (C₂H) with a C/H ratio equal to coronene ($C_{24}H_{12}$), a distinction is made between an amorphous and disordered structure (CHAR_C) and an ordered graphitic one (CHAR_G). In a very simplified way, the three reactions reported in Table 24 describe the thermal annealing mechanism.

Table 24: Simplified mechanism of the thermal annealing process

	Annealing Reactions	Kinetic Expression [*]	ΔH_{r}^{0}
\mathbf{R}_1	$CHAR_{H} \rightarrow 2CHAR_{C} + 0.5H_{2}$	$1.0x10^{11}exp(-3.35x10^{5}/RT)[CHAR_{H}]$	0.0
R_2	$CHAR_C \rightarrow CHAR_G$	3.0x10 ³ exp(-2.10x10 ⁵ /RT)[CHAR _C]	0.0
\mathbf{R}_3	$CHAR_C \rightarrow CHAR_G$	1.0 x10 ¹¹ exp(-4.6x10 ⁵ /RT)[CHAR _C]	0.0
* • •	3 1 7 1 1		

Units are m^3 , s, kJ, kmol.

The first reaction describes the dehydrogenation of $CHAR_H$ to form $CHAR_C$, while both reactions 2 and 3 describe the formation of $CHAR_G$ with the progressive ordering and inertization of the char structure at lower and higher temperatures, respectively. The transition temperature between reaction 2 and reaction 3 is ~1700 K.

The validation of the annealing model will be shown afterwards the kinetic model of heterogeneous reactions.

6.3.2 The heterogeneous kinetic mechanism

The analysis of the elemental composition of the char residue has allowed the developing of a global kinetic mechanism of char heterogeneous reactions. The overall mechanism is reported in Table 25.

	Reactions Mechanism	Kinetic Expression [*]	$\Delta {\rm H}^{0}_{\rm r}{}^{*}$						
	O ₂ 2	Mechanism							
\mathbf{R}_4	$CHAR_{\rm H} + 0.75O_2 \rightarrow 0.5H_2O + CO + CHAR_C$	$5.5 \times 10^7 \exp(-1.20 \times 10^5 / \text{RT}) [\text{CHAR}_{\text{H}}] [\text{O}_2]^{0.78}$	-231000						
R_5	$CHAR_C + O_2 \rightarrow CO_2$	$7.3x10^7 exp(-1.35x10^5/RT)$ [CHAR _C] [O ₂]	-393700						
R_6	$CHAR_{C} + 0.5O_{2} \rightarrow CO$	1.5x10 ⁹ exp(-1.60x10 ⁵ /RT) [CHAR _C] [O ₂] ^{0.78}	-110500						
R ₇	$CHAR_G + O_2 \rightarrow CO_2$	2.3x10 ⁷ exp(-1.55x10 ⁵ /RT) [CHAR _G] [O ₂]	-393700						
R_8	$CHAR_G + 0.5O_2 \rightarrow 2CO$	6.1x10 ⁷ exp(-1.80x10 ⁵ /RT) [CHAR _G] [O ₂] ^{0.78}	-110500						
	H ₂ O Gasification Mechanism								
R ₉	$CHAR_{H} + 0.5H_{2}O \rightarrow H_{2} + 0.5CO + 1.5CHAR_{C}$	8.0x10 ⁷ exp(-1.75x10 ⁵ /RT)[CHAR _H] [H ₂ O]	65600						
\mathbf{R}_{10}	$CHAR_{C} + H_{2}O \rightarrow H_{2} + CO$	2.6x10 ⁸ exp(-2.03x10 ⁵ /RT)[CHAR _C] [H ₂ O]	131300						
R ₁₁	$CHAR_{G} + H_{2}O \rightarrow H_{2} + CO$	$5.0x10^7 exp(-2.07x10^5/RT)[CHAR_G] [H_2O]$	131300						
	CO ₂ Gasifi	cation Mechanism							
R ₁₂	$CHAR_{H} + 0.5CO_{2} \rightarrow 0.5H_{2}O + 0.5CO + 2CHAR_{C}$	6.0x10 ⁷ exp(-1.87x10 ⁵ /RT)[CHAR _H] [CO ₂]	20500						
R ₁₃	$CHAR_{C} + CO_{2} \rightarrow 2CO$	8.1x10 ⁷ exp(-2.07x10 ⁵ /RT)[CHAR _C] [CO ₂]	173000						
R_{14}	$CHAR_G + CO_2 \rightarrow 2CO$	2.0x10 ⁷ exp(-2.13x10 ⁵ /RT)[CHAR _G] [CO ₂]	173000						

Table 25: Simplified mechanism of the oxidation process

^{*} Units are: m³, s, kJ, kmol.

The solid species $CHAR_H$ is the most reactive pseudo-component, followed by $CHAR_C$, and $CHAR_G$ is the less reactive. The relative reactivity of the three char components $CHAR_H:CHAR_C:CHAR_G$ is ~40:20:1 at 1173 K. The first reaction in Table 25 (R₄) is a partial oxidation of $CHAR_H$ with the formation of $CHAR_C$, H₂O and CO. In order to take into account the selectivity to CO/CO_2 , two competitive oxidation reactions are considered for both $CHAR_C$ and for $CHAR_G$. The kinetic parameters of the oxidation reactions agree with kinetic parameters reported in the literature [127,139,140] as well as in term of CO/CO_2 ratio [128,141-143].

The reactions R_9-R_{14} describe the char gasification reactions with H_2O and CO_2 . The relative reactivity of the three chary components are similar to the previous ones. Gasification reactions with H_2O are about thousand times slower than the corresponding oxidation reactions. Gasification reactions with CO_2 are about 4-5 times slower than the ones with H_2O at 1200 K.

An optimization technique has been applied to define the previous kinetic parameters. The technique minimizes an objective function which measures the distance between the kinetic mechanism and the experimental data:

$$S(\mathbf{b}) = \sum_{i=1}^{n_E} \sum_{k=1}^{n_Y} \left[\left(y_{i,k} - g_k \left(\mathbf{x}_i, \mathbf{b} \right) \right) \right]^2$$
(7.1)

where n_E is the number of experimental point, n_y the number of dependent variable y_i , while x_i are the independent variable. b is a vector of parameters and g_k are the kinetic equations. The BzzNonLinearRegression class was used to find the minimum of the objective function [144].

6.3.3 Results and discussion

The kinetic model was validated using several independent sets of experimental data both home-made and available in the literature. The main experimental data can be grouped into three different experimental sets:

6.2.3.1 Experimental data of char oxidation

- 6.2.3.2 Experimental data of char gasification (H₂O and CO₂)
- 6.2.3.3 Experimental data of annealing

The experimental conditions of pyrolysis span from heating rate of 0.2 K/s to 10^4 K/s, with final temperatures from 1173 to 2300 K. The carbon content of analyzed coals varies from 66% to 91 %, respectively. The oxidation and gasification conditions include both isothermal experiments and temperature programmed experiments. Moreover, the mole fraction of the gasifier species is included between 10% and 100%.

6.3.3.1 Experimental data of char oxidation

A several experimental data of char oxidation are available in literature. Table 26 summarize the main operating conditions and elemental composition of coal employment in these experimentation.

	0	perating cond	itions of pyrolys	is	Operating conditions of oxidation			
Reference	%C, daf	HR [K/s]	T _{pyrolysis} [K]	time [s]	$% yO_2$	HR [K/s]	T ⁰ _{oxidations} [K]	
PoliMi [145]	84 83-87	$0.33 \\ 10^4$	1273 1673	1800 2.0	10-40 9-21	0 0	720-870 643-713	
[116]	66-83	0.17	1223	1800	100	0.17	713-723	
[131,146,147]	74-85	$\begin{array}{c} 0.75\\ 10^4 \end{array}$	1173-1673 1473-1613	900 0.68	20 10	0 0.08-0.33	823 703-813	
[148]	79	10 ⁴	1673	0.6	5-50	0.4	300	

Table 26: Elemental composition, operating conditions of pyrolysis and oxidation of the main sets of experimental data

6.3.3.1.1. Experiments of PoliMi

Experimental tests were carried out using a high resolution simultaneous thermogravimetric and differential thermal analyzer (TGA-DTA, SDT Q600, TA Instruments). The TGA-DTA facilitated the acquisition of weight loss, heating rates and temperatures (or time). However, a brief summary of the setup is as follows: a small sample of the pre-dried starting material (5-6 mg), preliminarily sieved to obtain a size fraction lower than 250 µm is weighed and spread evenly in a alumina cup, located on the balance sample holder; the startup protocol is initiated equilibrating the oven temperature at 343 K, then the sample is heated up at a constant heating rate of 20 K/min to a desired temperature of 1273 K using N₂ as carrier gas at a constant flow rate of 200 ml min⁻¹. Finally, the sample is kept in isothermal conditions for the desired time 30 min. The resulting char undergoes oxidation at atmospheric pressure, at different constant temperatures (723, 773, 823 and 873 K) and with a gas composition of 10%, 21% and 40% of oxygen in nitrogen.

Figure 60 shows the comparison between experimental data and numerical prediction in terms of char conversion. The model shows a good variability with the oxidation temperature in the all range of investigation. Regarding the effect of the oxygen concentration, the model reproduces well the experimental data at 10 and 21% of O_2 , while at high O_2 concentration, the model underestimates the char reactivity.



Figure 60: Comparison between the experimental data of char conversion and the relative numerical prediction in several condition of oxygen concentration and temperature

6.3.3.1.2. Experiments of Borgonovo and Calvi [145]

Borgonovo and Calvi have studied the char reactivity in different conditions of heating rate and oxygen concentration. The coalchar have been prepared pyrolyzing three bituminous coal in a Curie Point Reactor with high heating rate ~ 10^4 k/s at about 1550 K with a residence time of 2 s.



Figure 61: Comparison between experimental data of char conversion and model prediction in different operating conditions of heating rate and oxygen concentration

The experimental data and the numerical prediction have been compared in Figure 61. Ashland char is the most reactive, followed by the South Africa and finally by Illawara char coal. The model shows a quite well agreement with the experimental data, moistly with the South Africa coal char. In the case of Ashland char, the model is able to estimate correctly the initial reactivity but it underestimates that final. In the case of Illawara coal, the model shows a systematic over prediction of the reactivity, above all at the highest oxygen concentration.

The experimental data of DSC (Differential scanning calorimetry) and the model predictions are reported in Figure 62. The DSC is a thermo-analytical technique that allows to measure the heat flux of a sample, when it subjected a chemical-physical transformations, respect a reference sample maintained at the same temperature. It is the CO/CO_2 ratio that controls the global heat flux during the char oxidation.

At the lower oxygen concentration, the model shows a good agreement with the experimental trends of South Africa char and the Illawara char, but it underestimates the experimental profiles of Ashland char. At 21% O_2 , the model well reproduces the behavior of South Africa, but it underestimates that of Ashland coal and slightly that of Illawara char.



Figure 62: Comparison between experimental data of DSC and the respective numerical predictions.

As mentioned, the heat flux depends on the CO/CO_2 ratio. The experimental variability of CO/CO_2 ratio is quite wide, as highlighted by the empirical correlations of CO/CO_2 ratio reported in literature [141,143,149-154]. Thus, it is possible to consider the overall agreement with these experimental data quite satisfactory.

6.3.3.1.3. Experiments of Varhegyi et al. [116]

The char reactivity of several char has been analyzed by Varhegyi et al. [116] under different oxidizing mixture. The chars have been prepared in low heating rate conditions (10 K/min) until 1223 K with holding time of 30 min.

The comparison shown in Figure 63 refer to a lignite coal char (Gardanne) and a bituminous coal char (Arkadia), obtained in pure oxygen environment. In the first case the model predicts well the initial reactivity even if it underestimates slightly that final. In the second case, the model shows a opposite trend, overestimating the initial reactivity but replicating correctly the final reactivity.



Figure 63: Comparison between the experimental data of char conversion and the numerical prediction. The experimental have been carried out in pure oxygen with heating rate of 10 K/min.

6.3.3.1.4. Experiments of Zolin and co-workers [131,146,147]

Zolin and co-workers [131,146,147] have analyzed the reactivity of different chars both as coal parents both as of operating conditions of pyrolysis.

The model results have been compared with the experimental data of char conversion, as shown in Figure 64. These chars have been prepared under low heating rate conditions (0.75 K/s) at final temperature of 1173 K and with a holding time of 15 min. The model well predicts the initial reactivity but it underestimates the final conversion.



Figure 64:Comparison between experimental data and numerical predictions [147]. The oxidation conditions are: T = 823 K and 20% O_2 .

Other experimental data refer to the effect of the pyrolysis operating conditions on the char reactivity. The comparison with these experimental data will be shows in the afterwards section, in order to highlight the reliability of the annealing mechanism.

6.3.3.1.5. Experiments of Rathman et al. [148]

Rathaman et al. [148] have analyzed the reactivity of four different coals in a drop tube reactor in high heating rate conditions a different oxygen concentration. Moreover, the reactivity of a high-volatile coal char has been analyzed in a thermogravimetric balance at different oxygen concentration with heating rate of 25 K/min.

Figure 65 shows the experiments and numerical results. At low oxygen concentration, the model is able to catch the initial char reactivity but it overestimates the final reactivity, above all at $2\% O_2$ concentration. At intermediate oxygen concentration the model reproduces well the experimental data. At higher O_2 concentration, the model under-predicts slightly the char reactivity even if the maximum of evolution rate is quite well estimated, mainly at 21%.



Figure 65: Comparison between experimental data of evolution rate and model predictions a different oxygen concentration for a high-bituminous coal

6.3.3.2 Experimental data of char gasification

Table 27 summarize the main operating conditions of pyrolysis and gasification for several experimentations.

Table 27: Carbon content of coal, operating conditions of pyrolysis and gasification of the main sets of experimental data

	Operating conditions of pyrolysis					Operating conditions of gasification				
Reference	%C, daf	HR [K/s]	T _{pyrolysis} [K]	time [s]	$% yH_2O$	%yCO ₂	HR [K/s]	T ⁰ gasification [K]		
PoliMi	84	0.33	1273	1800	13-33	0	0	1160-1215		
[155 156]	74	0.25	1373	1800	20	0	0	1173-1273		
[155,150]					30	0	0.08-0.25	1000		
[114]	00	05	1172	1900	0	20	0	1072		
[114]	00	0.5	1175	1800	20-100	0	0	1275		
[152]	70.0	0.22	072	2600 20		0	0	1172		
[133]	79.9	0.55	975	3000	0	60	0	11/5		
[112]	68-74	0.08	1273	3600	0	50-70	0	1250-1330		
[118]	80.5	0.1-1000	1223-1773	0.5- 1200	0	20-100	0	1223-273		

6.3.3.2.1. Experimental data of PoliMi

The reactivity of bituminous coal char has been also studied in gasification condition with H_2O at two different temperature. The model shows a good agreement with the experimental data

(Figure 66). The model underestimates slightly the final conversion where the initial reactivity is quite well catches.



Figure 66: Comparison between the experimental data of char conversion and the numerical prediction at different gasification conditions.

6.3.3.2.2. Experiments of Fermoso et al. [155,156]

The effect of the gasification temperature on the char reactivity has been analyzed in the works of Fermoso and co-workers [155,156]. The char has been prepared in the low heating conditions, as reported in Table 27, employing a high volatile bituminous coal (C \sim 74%). Figure 67 shows a satisfactory agreement between experimental data and model predictions, in the all range of temperature investigated.



Figure 67:Comparison between the experimental data of char conversion and the numerical prediction at different gasification temperature. The H_2O concentration was 20%

6.3.3.2.3. Experiments of Zhang et al. [114]

Zhang et al. [114] have carried out an experimentation on the char gasification both with H_2O and with CO_2 . The chars have been made under low heating rate conditions, as reported in Table 27. The results, shown in Figure 68, refer to Jincheng char coal.



Figure 68: Comparison between the experimental data of char conversion and the numerical prediction. Figure a and b refer to gasificatiom with H_2O ; Figure c and c refer to gasificatiom with CO_2 .

The agreement with experimental data is partially satisfactory. In the H_2O gasification, the kinetic model shows an overestimation of the initial reactivity. The final conversion is predicted well enough. Under CO_2 gasification, the initial reactivity is well estimated whereas the intermediate and final reactivity is overestimated.

6.3.3.2.4. Experiments of Everson et al [157]

In the experimentation of Everson et al. [157], a bituminous coal char has been gasified in different mixture of H_2O and CO_2 . The char has been prepared pyrolysizing a bituminous coal at low temperature (973 K) for a long time (1 h). In Figure 70 are shown two comparison, the first one carried out in H_2O and the second one in CO_2 .

The kinetic model well predicts the char reactivity in H_2O gasification whereas in CO_2 gasification, the agreement is less satisfactory even if the model well predicts the final conversion of the char.

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Figure 69: Comparison between the char conversion experimental data of char conversion and the numerical prediction. Figures a refers to gasification with H_2O ; Figure b refers to gasification with CO_2 .

6.3.3.2.5. Experiments of Ochoa et al. [114]

Ochoa et al. [114] have analyzed the reactivity of two different char coal in different gasification temperature and in different CO_2 concentration. The operating conditions of pyrolysis as well as the rank of coal parent are reported in Table 27.

The overall agreement is well enough, as shown in Figure 70. In the case of lignite char coal (SB coal), the model underestimates the reactivity at the lower CO_2 concentration. The agreement improves with the increasing of the CO_2 concentration. An opposite trend has been found for the high-volatile char coal. The model shows a better agreement at the lowest concentration than the highest concentration.



Figure 70: Comparison between the experimental data of char conversion and the numerical prediction. Figure a and b refer to gasificatiom of SB coal (C = 68%, daf); Figure c and c refer to HV coal (C = 74%, daf).

6.3.3.3 Experimental data of annealing effect

The annealing model reported in Table 24 has been compared with the several experimental data [113,131,158]. The elemental composition of coal and the operating conditions for each experimentation are reported in Table 28.

							0	17		, ,		
		Elemer	ntal co	mpositi	ion,%v	w daf	Pyrolysis conditions			Oxidation Conditions		
Ref	Coal	С	Н	0	N	S	H.R. [K/s]	T _{pyr} [K]	h. time [s]	H.R. [K/s]	T ⁰ _{ox} [K]	yO_2
[113]	Pocahontas	91.2	4.5	2.5	1.3	0.5	104	1673-2073	0.15-5	15.0	673	0.063
	Pittsburgh	82.8	5.6	8.9	1.7	1.0	10					
[131,146]	Cerrejon	80.6	5.1	11.8	1.8	0.7		1173-1673	900	5.0	815	0.1
	Illinois #6	74.1	5.0	13.2	1.5	6.3	0.75					
	Blair Athol	82.3	4.3	10.9	2.2	0.3						
[158]	South Africa	80.7	4.5	12.7	1.4	0.7	15-	1172 0072	1-18000	0.0	773	0.21
	Ruhr	81.0	5.0	10.5	2.2	1.3	$17 \text{x} 10^4$	11/3-22/3				
[120]	Shenfu*	80.5	4.8	13.4	0.9	0.4	0.1-1000	1173-1773	0.5-1200	0.0	1223-1273	1.0
*	1.01 1 1											

Table 28: Coal Elemental composition and operating conditions of pyrolysis of [113,131,158].

*gasification conditions

The model predictions are compared with the experimental data in Figure 71 in terms of reactive loss (R.L.). The reactive loss is defined as the ratio between $R_{0.5}$ of any char and $R_{0.5}$ of the char prepared at the lowest temperature in each data set. The parameter $R_{0.5}$ is evaluated as $R_{0.5} = 0.5/t_{0.5}$, where $t_{0.5}$ is the time necessary to obtain the char conversion of 50%. The experimental data have been carried out under oxidation and gasification condition



Figure 71: Scatter of the reactive loss due the thermal annealing effect between experiments [113,120,131,146,158] and model predictions.

The model shows a good agreement with the experimental data of Zolin et al. [131,146] Senneca and Salatino [158] and Wu et al. [120]. In the case of experimentation of Russell et al. [113] the model shows a systematic deviation, underestimating the reactive loss. Anyway, the comparison is quite satisfactory, with a correlation coefficient $R^2 = 0.84$, confirming the ability of the model to catch the effect of the thermal annealing on the char reactivity.

In few cases, the conversion profile of the char oxidation and gasification are available. Figure 72 shows the effect of the thermal treatment on the conversion of Cerrejon char coal [146,147]. The char has been prepared pyrolyzing the coal parent at different heating rate (0.75 K/s and 10^4 K/s) and at different temperature (from 1173 K to 1673).

In the case at 1473 K, agreement is partially satisfactory, but in the other conditions the model well catches the effect of the thermal treatment on the char reactivity. This behavior depend on the different charry composition, as reported in Table 29.

Table 29: Reference char distribution										
T _{pyrolysis} [K]	$\mathrm{HT}_{\mathrm{pyrolysis}}$	$CHAR_C$	$\mathrm{CHAR}_{\mathrm{H}}$	CHAR _G	CO*					
1173	45	0.29	0.71	0.00	0.00					
1273	45	0.86	0.14	0.00	0.00					
1473	45	0.87	0.00	0.13	0.00					
1673	45	0.25	0.00	0.75	0.00					
1473	$10^{4^{**}}$	0.26	0.67	0.00	0.07					
1613	$10^{4^{**}}$	0.62	0.32	0.00	0.06					
**K/s										

Table 29: Reference char distribution

Increasing the pyrolysis temperature, the annealing reaction become always more important inducing a transformation of the amorphous graphitic structures toward more ordinate graphitic structures with consequent reactivity loss.



Figure 72: Comparison between experimental data of Cerrejon coal and numerical predictions[146,147]. Pyrolysis conditions: (a)-(d): heating rate = 0.75 K/s; (d)-(e) heating rate 10^4 K/s. The oxygen concentration is 10%.

The effect of the pyrolysis thermal treatment on the char reactivity has been also analyzed by Wu et al. [120] under gasification reactivity.



Figure 73: Comparison between the char conversion experimental data of char conversion and the numerical prediction. Figures a to d refer low heating rate conditions, 0.1 K/s; Figure e and f refer to high heating rate condition, 10^3 K/s.

A bituminous coal have been pyrolyzed in different conditions of temperature (from 1223 to 1773 K) and heating rate (from 0.1 to 1000 K/s). The loss reactivity has been studied in gasification regime using pure CO_2 at two different temperature 1223 and 1273 K.

The model, as shows in Figure 73, is able to catch both the effects of the operating conditions of pyrolysis and the effect of gasification conditions on the char reactivity. As the previous case, the decreasing of the reactive is due the transformation of hydrogenated and amorphous structures (CHAR_H and CHAR_G) toward more ordinated graphitic structures (CHAR_G).

6.4 Conclusion

The heterogeneous char reactions play an important role in the coal pyrolysis and combustion processes. The elemental composition of the char, together with its morphologic features, controls the char reactivity.

In the first section of this chapter, the elemental composition of many char coal has been analyzed. This analysis has shown as many experimental information about the elemental composition of char residues are available, but these measurements are often affected by a wide variability that can be ascribed to the strong heterogeneity of the solid fuels. For this reason, the predictive capability of the presented model can be considered satisfactory. In the second part of this chapter, a kinetic model of annealing and char heterogeneous reactions has been developed and compared with several experimental data obtained in different operating conditions of heating rate, temperature and gasifiering species concentration.

The overall agreement is satisfactory enough. The model is able to reproduce the reactive loss due to the increasing of pyrolysis thermal treatment. Obviously, because of the global nature of the kinetic model, in few case the agreement with experimental data is not so satisfactory. The main important characteristic of this kinetic model is the possibility to be coupled easily with the multi-step kinetic mechanism of pyrolysis, as shows in the next chapter.

7 Single Coal Particle Combustion

7.1 Introduction

Coal is a source of environmental concern not only because of its strong greenhouse impact but also because of emission of nitrogen and sulfur oxides [27-29] and the formation of aerosol particles [159]. Different strategies can be used for reducing the CO_2 emission from coal-fired power plants, as the oxy-fuel. In the oxy-fuel combustion, air is substituted with an O_2/CO_2 mixture and thus numerous gas properties such as density, heat capacity, diffusivity and gas emissivity change with consequences on the coal reactivity.

The effect of the N_2 and CO_2 atmosphere is not well defined in the literature. From one side, several experimental studies suggest that coal devolatilization increases in CO_2 atmospheres [148,160], due to the effect of the heterogeneous reactions between char and CO_2 . Rathnam et al. [148] reported that the devolatilization rate of a bituminous coal, pyrolyzed in low heating rate conditions (25 K/min), was similar in either N_2 or CO_2 at temperatures lower than ~1000 K, whereas at temperatures higher than 1000 K, the coal devolatilization rate was higher in CO_2 than in N_2 . They also reported similar results in CO_2 and in N_2 in a drop tube furnace with four different coals at 1673 K [148]. These results were confirmed by Al-Makhadmeh et al. [160]. They observed the combustion of a lignite coal and of a bituminous coal in a drop tube reactor in N_2 and CO_2 atmosphere. The released volatiles were similar for both atmospheres at temperatures lower than 1173 K, while a larger amount was observed in CO_2 , at higher temperatures.

From the other side, different studies show a minor or even a negative effect of CO_2 atmosphere on coal reactivity [161,162]. Brix et al. [161] analyzed the pyrolysis of a bituminous coal in a drop tube furnace in N₂ and CO₂ atmospheres, and they found a similar morphology of the residual char and a similar volatile release, in both cases. Borrego and Alvarez [162] analysed the pyrolysis of a high and a low volatile bituminous coal in a drop tube furnace at 1573 K in N₂ and CO₂ environments and they found a negative effect of CO₂ on the coal volatilization.

Experimental measurements have been conducted to assess the effect of physical aspects of coal particles (rank, origin and particle size) and operating parameters (temperature, heating rate, and the surrounding gas composition) on particle ignition, burnout times, and char combustion temperatures [163-168].

Both homogeneous and heterogeneous ignitions of the coal have been observed [163,164,166]. Khatami et al.[166] analysed the effects of the coal rank and surrounding gas composition on the ignition delay. They observed more tendencies of homogeneous ignition for a bituminous coal and heterogeneous ignition for two lignites at O_2 concentrations lower than 40% in

either N_2 or CO_2 background gases. Moreover, they also observed longer ignition delay times in CO_2 atmosphere. This behavior was mostly attributed to the higher heat capacity of O_2/CO_2 mixtures comparing to the O_2/N_2 mixtures for homogeneous ignition and lower mass diffusivity of O_2 in CO_2 than in N_2 , in heterogeneous ignition. Additionally, the experimental results highlighted a linear correlation between the ignition delay time and the O_2 concentration, in either the CO_2 or the N_2 mixtures. Similar results have been obtained by Shaddix and Molina [167], who concluded that the higher heat capacity of CO_2 is the main reason for the longer ignition delays in CO_2 mixtures in homogeneous ignition.

Levendis and co-wokers [165,166,169-172]studied the single-particle combustion of different coals by varying the temperature conditions and the oxygen concentration. Bejarano and Levendis [165] and Khatami et al. [169] investigated char surface temperatures and burnout times for a lignite and a bituminous coal, at O_2 concentrations from 21% up to 100% in N_2 and CO_2 background gases. They reported maximum char temperatures of 2000K for a lignite and 1800K for a bituminous coal, in air at a drop tube furnace temperature of 1400K. Accordingly, the burnout times of the bituminous coal were longer than those of the lignite coal (~50 ms versus ~40 ms, respectively). Temperature and burnout differences decrease with increasing O_2 concentration. At furnace temperatures of 1400-1600 K, Murphy and Shaddix [173] measured a char surface temperature of 2200 K for a sub-bituminous coal and of 2000-2100 K for a bituminous coal at 24% O_2 . The combustion of single coal particles (90-110 µm) in air at a drop tube furnace wall temperature of 1700 K was studied by Timothy et al. [174,175]. They found an opposite trend respect to the previous works, with an average char surface temperatures of 2000 K for a lignite and 2300 K for a bituminous coal.

In this work, two different coals are analysed in a drop tube furnace in a wide range of oxygen concentration (from 21% O_2 to 100% O_2) both in O_2/N_2 atmosphere and O_2/CO_2 atmosphere. The drop tube furnace was operated in quiescent gas conditions, in order to minimize the differences in the axial profiles of gas temperatures caused by the different heat capacity of the two gas environments [165,166]. The combustion of the same two coals in active flow environments in the drop tube furnace has been reported previously [169]. The experimental measurements obtained herein are then compared with the predictions of a general model of solid fuel combustion. The novelty of the model mainly relies in the comprehensive description of inter and intra-phase resistances with a detailed chemistry of coal devolatilization and secondary homogeneous and heterogeneous reactions.
7.2 Experimental Method

7.2.1 Fuels

A bituminous coal (PSOC-1451) and a lignite coal (DECS-11), obtained from the Pittsburgh Coal Bank, are analyzed in this study. Their proximate and ultimate analyses are shown in Table 30. The two coals were dried, ground and sieved to the size cut of 75-90 μ m. This size cut was selected to be consistent with previous experiments [29,165,166].

	PSOC-1451	DECS-11
Rank and Fuel Source	Bituminous High Volatile A Pittsburgh #8 Pennsylvania, USA	Lignite A Beulah, North Dakota, USA
Proximate	Analysis as receive	d
Moisture (%)	2.5	33.4
Volatile matter (%)	33.6	37.4
Fixed Carbon (%)	50.6	22.9
Ash (%)	13.3	6.4
Ultima	te Analysis (on a dr	y basis)
Carbon (%)	71.9	66.2
Hydrogen (%)	4.7	4.0
Oxygen (%) (by diff.)	6.9	18.6
Nitrogen (%)	1.4	0.9
Sulfur (%)	1.4	0.7
Ash (%)	13.7	9.6
Heating Value Dry [MJ/kg]	31.5	25.7

Table 30: Proximate and Ultimate analysis of the Coals used in this study

7.2.2 Drop tube furnace (DTF)

The combustion of free-falling coal particles was carried out in an electrically heated, laminar flow drop tube furnace at a constant nominal wall temperature of 1400K. The radiation cavity of this furnace is 25 cm long and it is heated by hanging molybdenum disilicide elements. A sealed 7 cm I.D. transparent quartz tube was fitted in the furnace. Gas was introduced to the radiation cavity of the furnace through a water-cooled stainless-steel injector (1 cm I.D.) as well as coaxially through a flow straightener to the furnace injector (Figure 74).

Optical access to the radiation zone of the furnace for the pyrometer was achieved from the top of the furnace, through the particle injector. Additional observations were performed through observation ports located at the sides of the furnace using a high-speed cinematographic camera, as outlined by Levendis et al. [170].



Figure 74: Schematic of the drop-tube furnace (DTF) and gas temperature measurement setup. More detailed figures can be found in [29,165,176].

7.2.3 Gas compositions

Gas compositions tested in the furnace included different mixtures of either O_2/N_2 or O_2/CO_2 . The first conditions were air (~20%O₂ in N₂) and (20%O₂ in CO₂). Then, the oxygen concentration was increased in increments of 10% or 20% up to pure oxygen. Additionally, testing was performed in a 100% O₂ environment to determine how the particles burned in the absence of either supplemental gas. Oxygen partial pressures were controlled with pre-calibrated flowmeters, and were verified by an oxygen analyzer (*Horiba, Model MPA-510*).

7.2.4 Gas temperature

Coal particle combustion experiments were conducted under a quiescent gas condition (inactive flow, i.e., no flow). Quiescent gas condition was created by turning off the gas flows a few seconds prior to the particle injection. Therefore when the particles were introduced in the furnace, the centerline temperature should have been already heated up to a temperature close to that of the wall, uniformly (axially and radially) throughout the radiation cavity of the furnace. The current method was deemed to be necessary given the absence of flow in the quiescent condition [166]. It also allowed temperature sampling closer to the injector tip. A slender bare thermocouple (*OMEGA* type K model *KMQXL-020*, 250 µm bead diameter, 50 µm wire diameter, 500 µm sheath diameter, 1 m long) was used to measure the centerline gas temperature. The measured

temperatures with this method were corrected for radiation effects as explained in References [177-179]. The results are illustrated in Figure 75.



Figure 75: Centerline gas temperature inside the drop-tube furnace for pure N2 and pure CO2 in quiescent gas condition. This plot also shows the furnace wall set-point temperature (1400 K).

As shown in Figure 75, the neat N₂ and CO₂ gases under quiescent condition behave in the same way and the gas temperature profiles are similar. At the furnace wall set-point temperature (T_w) of 1400 K, as monitored by type-*S* thermocouples embedded in the wall, both axial gas temperature profiles along the centerline of the furnace are stabilized at about 1340 K.

7.2.5 Three-color optical pyrometer measurements and cinematography measurements

Pyrometric observations of single particles were conducted from the top of the furnace injector, viewing downwards along the central axis of the furnace (see Figure 74), which ideally was the particle's path-line. Accordingly, the luminous burnout histories of single particles - from ignition to extinction - could be monitored. An optical fiber transmitted light from the furnace to the pyrometer assembly. Figure 76 shows a sketch of the Three-color optical pyrometer.



Figure 76: Sketch of the three optical pyrometer.

The pyrometer used two dichroic edge filters as spectrum splitters to direct the light to three interference filters. These filters had effective wavelengths of 0.640, 0.810 and 0.998 μ m with bandwidths (FWHM) of 70 nm. Details of the pyrometer can be found in Levendis et al.[180]. The voltage signals generated by the three detectors were amplified and then processed by a microcomputer using the LabView 8.6 software.

Temperature was deduced from the three output voltage signals of the pyrometer using a ratio method, based on Planck's law and gray-body assumption [176,180]:

$$\frac{S_i}{S_j} = \frac{C_i \int\limits_{\Delta\lambda_i} \varepsilon_{\lambda_i} I_{\lambda b} g_i(\lambda) d\lambda}{C_j \int\limits_{\Delta\lambda_i} \varepsilon_{\lambda_j} I_{\lambda b} g_j(\lambda) d\lambda} \quad i = 1, 2, \ j = 1, 2 \ i \neq j$$
(7.1)

where C_i and C_j are the calibration constant, S_i, S_j are measured voltage signals by the pyrometer at different channels, $\varepsilon_{\lambda i}$, and $\varepsilon_{\lambda j}$ the particle emissivity (constant), $I_{\lambda g}$ is the spectral radiation intensity for a blackbody surface, g_i and g_j are the wavelength function of the combined transmittance of the associated dichroic filter and $\Delta\lambda$ is the range of wavelength for different channel. Figure 77 shows the output voltage signals and respective temperature profiles for bituminous and lignite coal in air.



Figure 77:Signal and temperature profile for PSOC-1451 coal and DECS-11 coal burning at $21\%O_2$ -79%N₂.

The bituminous and the lignite coal particles have different burning behaviors. The bituminous coal shows both a homogeneous combustion with an envelope flame of the volatile matter and a heterogeneous combustion of the solid residue (Figure 77a and Figure 77b). The lignite coal mostly burns with the simultaneous combustion of the volatiles and the char residue (Figure 77c and Figure 77d), often with a significant fragmentation process. These behaviors depend on the devolatilization phase: bituminous coal releases a large amount of tar components while a larger amount of light hydrocarbon gases, CO and inorganic oxygenated compounds are released by lignite. Moreover, the combustion characteristics largely depend also on the O_2 concentration in the N_2 or CO_2 mixtures [166].

(a) Bituminous coal particle (PSOC-1451), 75-90 μ m, burning in 21%O₂-79%N₂



(b) Bituminous coal particle (PSOC-1451), 75-90 μ m, burning in 21%O₂-79%CO₂



(c) Bituminous coal particle (PSOC-1451), 75-90 μ m, burning in 40%O₂-60%CO₂



Figure 78: Typical photographs of bituminous coal particle (PSOC-1451) burning at (a) $21\%O_2$ -79%N₂,(b) $21\%O_2$ -79%CO₂ and (c) $40\%O_2$ -60%CO₂, along the life time of the coal particle. The diameter of the wire appeared in some frames is 80 µm.

Cinematographic measurements have been carried out in order to compare the particle life times obtained with the optical pyrometer. At low O_2 concentrations, there is a discrepancy between the two methods. This fact is due to the very low luminosity of the coal particle as it

approaches its extinction point. The radiation intensity emitted from the particle falls below the detection limit of the optical pyrometer, whereas it is still visible in the cinematographic records. Figure 78 shows several photographs of the burning of bituminous coal particles in different atmospheres.

The bituminous coal particle shows the formation of a flame envelope around the particle because of the combustion of the volatile matter released during the pyrolysis. As oxygen concentration increases, the volatile flame becomes more intense, brief and bright, which is also the case for the ensuing char oxidation. The flame is brighter and the reactivity of the char is higher in the N₂ mixtures when compared with the corresponding flame and reactivity in the CO₂ mixtures. The higher heat capacity of CO₂ and the higher diffusivity of O₂ in N₂ mixtures explain these behaviors.

7.3 Comprehensive mathematical model of coal particle combustion

A comprehensive mathematical model, which attempts to tackle the complex, multi-scale, multi-phase problem of coal combustion in the drop tube reactor, needs to analyze the chemistry of the process coupled with the intra and inter-phase heat and mass resistances.

7.3.1 Kinetic Model

Following kinetics describe the chemistry of the whole process:

- ✓ Pyrolysis or volatilization reactions of the coal particles
- ✓ Secondary gas-phase reactions of the released gases
- \checkmark Heterogeneous reactions of the residual char

The predictive multistep kinetic mechanism of coal pyrolysis was already discussed the third and sixth chapter. Table 31shows the distribution of the reference coal of the two coals employment in this experimentation.

	Reference coals distribution, daf basis						
Coal	$COAL_1$	$COAL_2$	$COAL_3$	CHAR			
PSOC-1451	0.249	0.670	0.081	0.0			
DECS-11	0.0	0.346	0.534	0.12			

The secondary gas-phase reactions, recently revised by Ranzi et al. [26], are available online in CHEMKIN format [181]. The char heterogeneous kinetic model, presented in the sixth chapter, has been applied. The coupled model refers 36 reactions of coal devolatilization, 11 heterogeneous reactions, and more than 1000 secondary-gas phase reactions of pyrolysis and oxidation.

7.3.2 Mathematical Model

The comprehensive model solves energy and mass balance equations for gas and solid phases, together with empirical submodels used for the closure of the balance equations. Pyrolysis is a primary process by which the coal produces residual char, heavy volatile species (tar) and permanent gaseous products. The released volatiles mix with the surrounding gas in the drop tube reactor. The model considers gas and solid temperature and species profiles not only in the gas phase but also inside the coal particle. Thus, the mathematical model consists of two sub-models: the first one at the particle scale and the latter at the reactor scale. This approach is a further extension of previous models discussed, applied, and validated elsewhere [182].

7.3.3 The Particle Mass and Heat Balances

The particle model provides the internal description to account for intraparticle heat- and mass-transfer resistances, assuming isotropic particles. The accuracy depends on the number of discretization sectors N (see Figure 79).



Figure 79: Particle sketch: the particle is divided into N spherical sectors (j = 1 to N) of equal volume.

Assuming N sectors inside the particle, the model governing equations regarding the mass (solid and gas phase) and energy balances around each particle sectors are:

$$\frac{dm_{j,i}^s}{dt} = V_j R_{j,i} \tag{7.2}$$

$$\frac{dm_{j,i}^{G}}{dt} = \left[J_{j-1}S_{j-1} - J_{j}S_{j}\right] + V_{j}R_{j,i}$$
(7.3)

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$$\frac{d\sum_{i=1}^{NCP} m_{j,i}^{S} c_{p,j,i}^{S} T_{j}}{dt} = \left[Q_{j-1} S_{j-1} - Q_{j} S_{j} \right] + \left[S_{j-1} \sum_{i=1}^{NCP} J_{j-1} h_{j-1} - S_{j} \sum_{i=1}^{NCP} J_{j} h_{j} \right] V_{j} H R_{j}$$
(7.4)

where $m_{j,i}^s$ is the mass of the i-th component in the j-th particle sector of the solid phase, $m_{j,i}^G$ is the mass of the i-th volatile component in j-th particle sector, *t* is the time variable, V_j and S_j are the volume and the external surface of the j-th particle sector. J_{j-1} and J_j are the mass fluxes of j-1th sector and j-th sector, respectively. R_{j,i} is the net formation rate of the i-th component resulting from the multi-step devolatilization model and from the heterogeneous gas-solid reactions. The energy balance determines the particle temperature and accounts for the heat conduction (Q_j), the enthalpy flux relating to the mass diffusion (J_ih_i) and the heat of reactions (HR).

Mass and heat fluxes terms inside the particle follow the constitutive Fick, Darcy and Fourier laws:

$$J_{j,i} = -D_{j,i}^{eff} MW_i \frac{dC_{j,i}}{dr} - y_{j,i} \frac{Da_j}{\mu_j} \rho_j^G \varepsilon_j \frac{dP_j}{dr}$$
(7.5)

$$Q_j = -k_j \left. \frac{dT}{dr} \right|_{r_j} \tag{7.6}$$

where $D_{j,i}^{eff}$, Da_j and k_j are the effective diffusion, Darcy and conduction coefficients inside the j-th particle sector, respectively. *MW_i* is the molecular weight of i-th gas species, $y_{j,i}$ is the mass fraction of i-th gas species in j-th sector of particle, μ_j is the viscosity in j-th sector, ρ_j^G is the gas density in j-th sector, ε_j is the porosity of j-th particle sector and C_{j,i}, P_j and T_j are the concentration of i-th gas species, pressure and temperature of j-th sector, respectively.

Inside the drop tube furnace, the coal particle moves in a quiescent environment with a velocity v_r derived from the momentum equation:

$$m_{p}\frac{dv_{r}}{dt} = -(\rho_{p} - \rho_{g})gV_{p} - 0.5f\rho_{g}v_{r}|v_{r}|$$
(7.7)

where m_p is the mass of the particle, g is the gravity constant and f is the friction factor.

At the external particle surface, the flux contributions inside the particle are replaced by the flux exchanged with the bulk phase:

$$J_{N,i} = k_{ext} M W_i \left[C_{Ni} - C_i^{bulk} \right]$$
(7.8)

$$Q_{N} = h_{ext} \left[T_{N} - T_{bulk} \right] + \sigma \varepsilon_{rad} \left[T_{N}^{4} - T_{wall}^{4} \right]$$
(7.9)

where k_{ext} and h_{ext} are the mass and heat-transfer coefficients, respectively, which were evaluated from Ranz and Marshall correlations [183], σ is the Stefan-Boltzam constant, T_{wall} is the wall temperature and ε_{rad} is the emissivity of carbonaceous particle, here assumed as 0.85 [184].

7.3.4 Thermophysical and Effective Properties

As already discussed by Lautenberger and Fernandez-Pello [185] in the mathematical formulation of their Gpyro model for the simulation of combustion and gasification of solid fuels, it is necessary to give a proper emphasis to the property estimations as well as to their modifications during the combustion process. As the coal particle is heated and pyrolyzed, different gaseous and condensed species are formed with relevant morphological modifications. The model does not consider the initial swelling and size increase during devolatilization, but it accounts for diffusivity variations with conversion. Effective properties of the residual char particle are calculated by proper weighting of the local compositions. The size and porosity of the individual particles change, not only because of drying and devolatilization but mainly because of char gasification and combustion. The effective diffusion coefficient, $D_{j,i}^{eff}$, is evaluated on the basis of equation

 $D_{j,i}^{eff} = \left[\frac{1}{D_{j,i}^{m}} + \frac{1}{D_{j,i}^{K}}\right]^{-1} \frac{\varepsilon_{j}}{\tau_{j}^{2}}, \text{ where } D_{j,i}^{m}, D_{j,i}^{K} \text{ are the molecular and Knudsen diffusion of i-th species into}\right]$

j-th sector, respectively. τ_j is the tortuosity of j-th particle sector. According to literature information [129,140,186-189], an initial mean pore diameter of ~0.3 µm for the bituminous coal and ~0.6 µm for the lignite have been chosen in this work.

Porosity is a property of each condensed phase species and is again calculated as weighted porosity with the local composition. Char porosity significantly varies with the fuel conversion and is estimated on the basis of empirical correlations. These variations are considered and the model accounts for particle shrinkage during char conversion. According to Gil et al. [135], a linear relation between the porosity (ε_j) and particle sector conversion χ_j is applied to each particle sector:

$$\varepsilon_j = \varepsilon_j^0 + \chi_j \left(1 - \varepsilon_j^0 \right) \tag{7.10}$$

An initial porosity of ~25% has been chosen for both coals, following literature information [135,189,190]. While the porosity increases with the conversion, the tortuosity is assumed to decrease linearly from an initial value of $\sqrt{2}$ [191]:

$$\tau_j = \tau_j^0 - \chi_j \left(\tau_j^0 - 1\right) \tag{7.11}$$

7.3.5 The Gas Mass and Heat Balances

Species and energy balances of the gas phase can be expressed as:

$$\frac{dg_i}{dt} = J_{N,i} + R_{g,i} \tag{7.12}$$

$$\frac{d\sum_{i=1}^{NCP} g_i \cdot C_{P_i}^g T^g}{dt} = \sum_{i=1}^{NC} J_{N,i} h_{N,i} + Q_N + HR_g$$
(7.13)

where gi is the mass of component i in the gas phase, $J_{N,i}$ and Q_N are the total mass and heat exchanged between the gas phase and the particles, respectively. Rg,i is the formation/disappearance of i-th species due to gas phase reactions, HRg is the total heat of formation rate due to gas phase reactions. More detailed information about ancillary equations was reported in Pierucci and Ranzi [192].

The model is constituted by a system of (NCPp+1)N+ NCPg+2 ODE equations to describe the particle system, where NCPp are the species involved in the solid kinetic model, N the number of particle sectors and NCPg the gas species taken into account in the gas kinetic. The large ODE system has been solved by using BzzMath library, which is available in [193].

7.4 Results and discussion

Particle surface temperatures and burnout times were experimentally measured and at least 20 replicate tests were analyzed in each condition.



Figure 80: Recorded particle life times (a,c) and maximum deduced temperatures (b,d) for particles (75-90 μ m) from pulverized USA coals (Pittsburgh # 8 bituminous HVA (PSOC-1451) and Beulah lignite (DECS-11) burning in O_2/N_2 and O_2/CO_2 atmospheres at $T_{furnace}$ =1400K.

Figure 80 shows an overall view of the experimental results in terms of the particle life time and the surface temperature versus the oxygen concentration, for both coals and gas mixtures.

The life time of the coal particle was estimated as the sum of the ignition delay and the particle burnout time [166]. The bituminous coal shows the longer particle life times until 40%-50% O_2 in both the gas mixtures. At higher O_2 concentrations, and high surface temperatures, the particle life times of the two coals become very similar. In these conditions, the life time of about 25-30 ms is mostly related to the heating of the particle. The maximum temperature reached by the lignite is always 100-200 K higher than the one of the bituminous coal.

At high O_2 concentrations excellent agreement was observed between pyrometric and cinematographic measurements of the burnout times. On the contrary at low O_2 concentrations, only the cinematographic measurements are reliable, due to the mentioned low luminosity of the bituminous char particles during the near-extinction phase.

7.4.1 Combustion in the O₂/N₂ mixture

Figure 81 shows the comparisons between experimental and predicted life times of bituminous and lignite particles in the N_2 mixtures. Two different predicted life times are reported. In agreement with the work of Senior [194], the predicted profiles assume the life time as those corresponding to both 90% and 95% conversion of coal, on dry ash free (daf) basis. The overall agreement is satisfactory, even if the life time of the lignite coal is slightly underestimated.

In order to better analyse the difference between the two predicted life times, Figure 82 shows the time evolution of the coal conversion, at different O_2 concentrations.



Figure 81: Life time of coal particles ($80\mu m$) in the furnace versus O_2 mole fraction in N_2 mixture (a) bituminous (PSOC 1451) and (b) lignite coal (DECS-11). Experimental data (symbols) and model predictions at 95% conversion (solid line) and 90% (dashed line).

From Figure 82 it is possible to observe that the initial heating of the particle and the first devolatilization phase are independent of the O_2 concentration. Released volatiles from bituminous

and lignite coals account for $\sim 20\%$ and $\sim 40\%$ by mass, respectively. The assumption of 90% and 95% conversion as corresponding to the life time differently affect the results of the two coals. Bituminous coal, because of its lower reactivity, shows a larger sensitivity than lignite coal.

Figure 83 shows the core and surface temperature evolution at different O_2 concentration. Due to the small particle diameter, only five discretization shells are sufficient to describe the internal resistances with a good accuracy. The combustion in pure O_2 is obviously much faster, and homogeneous and heterogeneous combustion occur almost simultaneously. The peak temperature is thus high and very sharp. On the contrary, the combustion in air is slower with different times for the gas phase combustion and the char oxidation, well highlighted by the plateau of the temperature at ~60 ms.



Figure 82: Time evolution of coal particle conversion (80 μ m) at different O₂ mole fraction in N₂ mixtures (a) bituminous (PSOC 1451) and (b) lignite coal (DECS-11).

Figure 84 shows the comparison between the maximum measured and the predicted core and surface temperatures versus the O_2 mole fraction, for both coals.



Figure 83: Time evolution of the surface (solid line) and core (dashed line) temperature of a coal particle (80 μ m) at different O₂ concentrations in N₂; (a) bituminous (PSOC 1451) and (b) lignite coal (DECS-11).

The temperature difference between the surface and the core of the particle increases with increasing oxygen mole fractions, because of the increase of the transport resistances. The general 98

agreement is satisfactory. The slight over prediction of bituminous coal temperatures could be attributed to the stronger effect of heterogeneous reactions. On the contrary, the model underpredicts the temperatures of the lignite coal mainly at low O_2 mole fractions. Two main factors allow to explain this deviation. First, the model considers only a single and completely mixed gas phase surrounding the particle, without the proper gas phase discretization. The assumption of the complete mixing of released species in the gas phase reduces the possibility of ignition. Second, the model does not account for lignite particle fragmentations, emphasizing in this way the role of diffusion phenomena within the particle.



Figure 84: Particle temperature versus O_2 mole fraction in N_2 . Comparison between experimental data for maximum surface temperature (symbols) and predictions of surface and core temperatures (lines) in the cases of (a) bituminous (PSOC 1451) and (b) a lignite coal (DECS-11). The experimental particle sizes were in the range of 75-90 µm, the modelled size was 80µm.

In order to show the model performances, Figure 85 displays the profiles of major species inside the bituminous coal particle in $21\%O_2$ -79%N₂ atmosphere. In the first 10 ms, i.e. during the pyrolysis process with the fast release of gas and tar products, there is sharp reduction of O₂ with corresponding peaks of CO, CO₂, and H₂O. The next peaks, at about 20 ms, correspond to a further release of CO, CO₂ and H₂O, derived from the metaplastic phase. Once the devolatilization phase is almost completed, O₂ can penetrate inside the particle and reacts with the residual char. Figure 85a shows that the reaction time is partially controlled by O₂ diffusion from the bulk to the core of the particle. Due to the diffusion limitations, O₂ can reach the core of the particle only after ~65 ms after the complete conversion of the external sectors. CO is the main gaseous product from the heterogeneous reactions. The CO, CO₂ and H₂O peaks observed at ~45 ms are the products of the combustion reaction of CHAR_H. The successive peaks are mainly due to combustion reactions of the less reactive CHAR_C.



Figure 85: Molar fraction evolution of the major gaseous combustion products in different particle shells in the case of a bituminous coal (PSOC-1451) particle ($80\mu m$) burning in air.

A parametric sensitivity on the model shows that for these small particles the predicted life time depends on the particle diameter with a power 1.2-1.4. This fact confirms that the relative importance of the mass and heat transfer resistance increases with the O_2 concentration.

7.4.2 Combustion in the O₂/CO₂ mixture

In comparison with the combustion in the N_2 mixtures, longer particle burnout times and lower surface temperatures are obtained when burning coal particles in CO₂ mixtures, as already shown in Figure 5. These facts are mainly due to the higher heat capacity of CO₂ and to the lower oxygen diffusivity in CO₂ than in N₂ mixtures.

Figure 86 shows a satisfactory agreement between experimental data and model predictions and the observed deviations are consistent with the previous ones. It is worth to underline that the overestimation and/or underestimation of the particle life time is also affected by the assumption of the particle conversion level.

A sensitivity analysis confirms the negligible effect of the gasification reactions on the coal reactivity under the conditions applied in this work [195], i.e. high temperatures and high oxygen mole fractions.



Figure 86: Life times and temperatures of coal particles in the furnace burning in O_2/CO_2 atmospheres. Experimental maximum surface temperatures and times (symbols) were compared with predictions of surface and core temperatures (lines) in the cases of (a) bituminous (PSOC 1451) and (b) a lignite coal (DECS-11). Predictions for conversions of 90 and 95% are shown. The experimental particle sizes were in the range of 75-90 µm, the modelled size was 80µm.

7.5 Conclusion

Experimental measurements of coal particle life times and surface temperatures of a high-volatile bituminous coal (PSOC-1451) and a lignite coal (DECS-11) were performed in a drop tube furnace, under quiescent gas conditions. Different reactive gaseous mixtures, both O_2/N_2 and O_2/CO_2 with oxygen mole fractions ranging from 21 to100%, were considered. The furnace wall temperature was set at 1400 K.

The experimental results show longer particle life times and lower surface temperatures for the bituminous coal, when compared with the corresponding lignite data. Especially at moderate oxygen mole fractions, longer particle life times and lower temperatures are observed in the O_2/CO_2 mixtures. Increasing the oxygen concentration, the differences between the two coals (bituminous and lignite) and the two background gases (N₂ and CO₂) become less important.

These experimental data are then compared with the predictions of a comprehensive model of coal pyrolysis and combustion. The main characteristics of the model lie in a detailed description both of the kinetic mechanisms involved in coal combustion processes and of the heat and mass transport resistances. The model predictions show an overall good agreement with experiment data both in terms of particle life time and surface temperature. Moreover, the comparison with the experimental data shows the capability of the model to predict the effect of the background gas. The effect of the coal rank is also quite well predicted. The larger deviations are observed at the lowest oxygen concentrations ($21\%O_2$), where a better description of the gas phase could improve the agreement with experimental data by accounting for faster ignition of the lignite coal.

8 Simplified kinetic mechanisms for CFD applications

8.1 Introduction

The contributory effect of improving computer power and new advanced numerical techniques is increasing the use of Computational Fluidynamics (CFD). These new instruments offers the possibility to approach complex combustion system and to improve the efficiencies and to control the pollutant emissions. The optimization of the design and operation as well as the minimization of the pollutant formation are faced in a more effective way, thanks to the support of kinetics and fluidynamics studies.

Despite the above mentioned improvements in the computational capability, the direct coupling of detailed chemistry and CFD simulations is still prohibitive in the case of real combustors, characterized by large computational grids. For this reason, it is important to develop simple but reliable kinetic mechanism for coal volatilization to be used in CFD modeling.

In several recent CFD coal combustion works, the pyrolysis mechanism has been described using one step kinetic model [196-199]. Sometimes, a pre-processing activity with detailed models was also necessary both to estimate the kinetic parameters and to individuate the main gaseous species. Moreover, a simplified gas phase kinetic model has been applied in the same works.

In this chapter will be presented two simplified kinetic model of coal combustion, the first for pyrolytic process and the second for the secondary gas phase reactions of volatile products of coal devolatilization. Moreover, the comparison on the one hand with experimental data and on the other hand with relative detailed model will be shown.

8.2 One Step Model of Coal Pyrolysis

Semi-detailed multi-step models of coal volatilization were already developed and tested against a very large set of experiments and conditions. Three different subsets of release models are involved in coal volatilization:

- ✓ organic and inorganic C/H/O/ compounds;
- \checkmark sulfur compounds;
- \checkmark nitrogen compounds.

The details of the three model have been illustrated in the previous chapters. The complete model for coal devolatilization is constituted of \sim 60 species and \sim 70 reactions. This model is too large for

a direct use inside CFD code. Therefore, simplified models are required, like the "one step" scheme here presented.

8.2.1 Rate constant parameters of One Step Model

The three previously described sub-mechanisms show similar values of the rate constants of the volatilization processes: the three mechanism have several analogies. At high temperatures, it is possible to derive a one-step model able to describe the coal pyrolysis:

$$COAL \to Products \qquad \qquad k = A \times e^{-\frac{E}{RT}}$$
(8.1)

This approximation of just adopting high temperature mechanism is quite reasonable, being the main interest of this model the simulation of industrial combustors and furnaces, where high temperatures and high heating rates occur.

An optimization technique minimizes an objective function which measures the distance between the simple one step kinetic mechanism and the results of the detailed model of coal volatilization:

$$S(\mathbf{b}) = \sum_{i=1}^{n_E} \sum_{k=1}^{n_Y} \left[\left(y_{i,k} - g_k(\mathbf{x}_i, \mathbf{b}) \right) \right]^2$$
(8.2)

where n_E is the number of experimental point, n_y the number of dependent variable y_i , while x_i are the independent variable. b is a vector of parameters and g_k are the kinetic equations.

The BzzNonLinearRegression class was used to find the minimum of the objective function [144]. The whole detailed model is used as a generator of dummy 'experimental data', in selected simulation conditions, typically those occurring in a coal furnace (high heating rates and temperatures higher than 1300 K).

Table 32: Elemental composition (daf) and corresponding coal reference distribution of the set of coals

Coal	С	Н	0	Ν	S	COAL ₁	COAL ₂	COAL ₃	CHAR _C
Yallourn	65.40	4.90	28.80	0.60	0.30	0.00	0.15	0.82	0.03
Morwell	67.40	5.00	26.80	0.50	0.30	0.00	0.25	0.74	0.01
Velva	69.10	4.80	23.90	1.40	0.60	0.00	0.32	0.64	0.04
Soyakoishi	70.20	5.20	22.40	1.80	0.20	0.11	0.29	0.61	0.00
South Beluah	71.80	4.70	19.20	1.40	2.90	0.00	0.49	0.47	0.04
Colowyo	74.00	5.00	18.60	1.90	0.40	0.00	0.58	0.42	0.00
Hunter Valley	80.30	5.00	12.20	2.00	0.40	0.00	0.83	0.17	0.00
Liddel	83.50	5.40	8.40	2.10	0.60	0.21	0.71	0.08	0.00
Newvale	84.20	5.00	8.90	1.40	0.50	0.00	0.95	0.04	0.01
Yubari Shinko	86.90	5.60	5.20	1.90	0.30	0.34	0.65	0.00	0.02
Vicary Creek	87.80	4.70	5.00	2.10	0.40	0.23	0.62	0.00	0.15
Keyston	89.40	4.40	3.10	2.20	0.80	0.36	0.39	0.00	0.25
Hongay	93.70	3.30	1.30	1.20	0.80	0.36	0.16	0.00	0.48

The coal database for 'experimental data' creation includes 13 coals of different elemental compositions, from lignite to anthracite (Table 32).

Figure 87 shows the results of the non-linear regression process in terms of the logarithm of pre-exponential factor and activation energy as a function of coal carbon content.



Figure 87:*Frequency factor (a) and activation energy (b) as a function carbon content [%] in coal. Units are s, cal, mol.*

It is evident a linear correlation between logarithm of pre-exponential factor and carbon content, and an exponential correlation between the activation energy and the same independent variable. Simple regressions allow to estimate the parameters of these relationships:

$$A = 10^{(22.1-0.067 \times C_{\%})} \left[s^{-1}\right] \qquad E = 5.67 \times 10^{-3} e^{\frac{C_{\%}}{6.35}} + 55653 \left[\frac{cal}{mol}\right]$$
(8.3)

On the basis of the only information of the coal carbon content is then possible to estimate the rate constant parameters of the one step model.

8.2.2 Products stoichiometric coefficients of One Step Model

Once defined the rate constants, it is necessary to identify the stoichiometry of the reactions, according to the following expression:

$$COAL \rightarrow \alpha_{char}CHAR + \alpha_{tar}TAR + \alpha_{CO}CO + \alpha_{CO_2}CO_2 + \alpha_{H_2O}H_2O + \alpha_{H_2}H_2 + \alpha_{C_2H_4}C_2H_4 + \alpha_{HCN}HCN + \alpha_{H_2S}H_2S$$
(8.4)

Main products are then char, tar and gases. Char is characterized in terms of an elemental composition considering only C, N and S atoms (no oxygen or hydrogen is included). Tar is assumed with the same elemental composition of tar predicted by the 'detailed' model. It contains C, H, O, N and S hetero-atoms.

Gases are described in terms of inorganic gases and small hydrocarbons. CO, CO₂, H₂O. They account also for the oxygenated part of the small amount of light oxygenated hydrocarbons. All the hydrocarbon gases are grouped in a single equivalent species (C_2H_4), which is representative of many compound moving from methane to benzene/toluene/xylene aromatic fraction. It is possible to de-lump this component and obtain an internal distribution, if of interest, with the same proposed approach. HCN e H_2S are the only gas products coming from the heteroatoms. Finally, C_2H_4 and H_2 amount allows to properly close the atomic balances.

Product distribution is derived from the composition of the released compounds from the reference coals. As mentioned, C_2H_4 component groups together the amounts of aromatics, methane and other light hydrocarbons. These distributions only marginally depend on the temperature in high heating rate conditions, as can be observed form the proposed mechanism [13], thus they are assumed fixed.

Each coal of interest needs to be characterized in terms of reference components, following the previously described rules. Successively, it is quite simple to evaluate the product distribution according to the weighted sum of the products coming from each reference coal.

An example can be of help. Liddel coal has the elemental composition reported in Table 32. This composition lies in the triangle whose vertexes are $COAL_1$, $COAL_2$ and $COAL_3$. The simple atomic balance allows to describe Liddel as composed by 20.6%, 71.2% and 8.1% of $COAL_1$, $COAL_2$ and $COAL_3$, respectively.

The rate constants of the one step model, according to equations (8.3) and considering that the carbon content (C%) is 83.5 can be evaluated as: $A = 3.2 \times 10^{16} \text{ [s}^{-1}\text{]}$; E = 58500 [cal/mol]

About product distribution, CO stoichiometric coefficient can be obtained from:

$$\alpha_{CO} = (100 - N_{\%} - S_{\%}) \sum_{i=1}^{4} \frac{\omega_{coal_i}}{W_{coal_i}} \beta_{CO_i} = 0.35$$
(8.5)

Where N_% and S_% are the nitrogen and sulfur content of the Liddel coal (2.1% and 0.6%, respectively). ω_{coali} is the reference coal distribution ($\omega_{COAL1} = 0.206$; $\omega_{COAL2} = 0.712$; $\omega_{COAL3} = 0.081$; $\omega_{COAL4} = \omega_{CHARC} = 0$, see Table 32). W_{coali} is the reference coal molecular weight. β_{COi} is the CO released by each reference coal. The same can be done for other products (CO₂, H₂O, CHAR and TAR).

In the case of tar, the stoichiometric coefficient evaluation requires the evaluation of its molecular weight.

$$W_{TAR} = C_{\%TAR} \times 12 + H_{\%TAR} + O_{\%TAR} \times 16 = 165 \quad \left[\frac{\text{kg}}{\text{kmol}}\right]$$
(8.6)

The elemental TAR composition can be estimated from the tar split in the three tars coming from the reference coals (COAL₄, that is $CHAR_C$, does not release tar, of course):

$$C_{\%TAR} = \sum_{j=1}^{3} x_{TAR_j} \times C_{TAR_j} \qquad H_{\%TAR} = \sum_{j=1}^{3} x_{TAR_j} \times H_{TAR_j} \quad O_{\%TAR} = \sum_{j=1}^{3} x_{TAR_j} \times O_{TAR_j}$$
(8.7)

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Where C_{TARj} , H_{TARj} , O_{TARj} are the C/H/O content of each tar coming from the reference coals, whose composition is considered the same of the coal of origin. The tar mole fraction (x_{TARj}) can be computed from:

$$x_{TAR_{j}} = \frac{\sum_{i=1}^{4} \frac{\omega_{coal_{i}}}{W_{coal_{i}}} \beta_{TAR_{i,j}}}{\sum_{k=1}^{3} \sum_{i=1}^{4} \frac{\omega_{coal_{i}}}{W_{coal_{i}}} \beta_{TAR_{i,k}}} \qquad j = 1, 2, 3$$
(8.8)

Finally the TAR stoichiometric coefficient is

$$\alpha_{TAR} = \frac{\left(100 - N_{\%} - S_{\%}\right)}{W_{TAR}} \sum_{j=1}^{3} W_{TAR_j} \sum_{i=1}^{4} \frac{\omega_{coal_i}}{W_{coal_i}} \beta_{TAR_{i,j}} = 0.143$$
(8.9)

The distribution of the sulfur and nitrogen content in char (N_{CHAR} , S_{CHAR}), tar (N_{TAR} , S_{TAR}) and gas (N_{GAS} , S_{GAS}) depends on the rank of the coal. Figure 88 shows the distribution obtained from the nitrogen and sulfur detailed models in the case of the 13 coals used for the regression and related fitting correlations.



Figure 88:Predicted Nitrogen (a) and Sulfur (b) distribution in solid, tar and gas phase. Open symbols stand for detailed model (circle for char, square for tar and diamond for gas) and line are fitting correlations. Close symbols are the N_{GAS} prediction for panel a and S_{CHAR} prediction for panel b calculated as complement at 1 of the fitting correlations.

Once again it is possible to observe some general trends of the repartition in function of the carbon content (%wt) of the coal, which can be summarized as

$$N_{CHAR} = 7.3 - 0.175 \times C_{\%} + 1.12 \times 10^{-3} \times C_{\%}^{2} \qquad S_{GAS} = -1.20 + 3.48 \times 10^{-2} \times C_{\%} - 2.182 \times 10^{-4} \times C_{\%}^{2}$$

$$N_{TAR} = -6.56 + 0.177 \times C_{\%} - 1.13 \times 10^{-3} \times C_{\%}^{2} \qquad S_{TAR} = 2.48 - 5.49 \times 10^{-2} \times C_{\%} + 3.45 \times 10^{-4} \times C_{\%}^{2}$$

$$N_{GAS} = 1 - N_{CHAR} - N_{TAR} \qquad S_{CHAR} = 1 - S_{GAS} - S_{TAR} \qquad (8.10)$$

These values allow to derive the stoichiometric coefficients of H₂S and HCN:

$$\alpha_{HCN} = \frac{N_{\%}N_{GAS}}{14} = 1.7 \times 10^{-2} \qquad \alpha_{H_2S} = \frac{S_{\%}S_{GAS}}{32} = 7.3 \times 10^{-3}$$
(8.11)

They also allow to characterize the whole elemental composition of TAR and CHAR, whose composition in terms of C, H and O can be evaluated as previously shown in the case of tar.

8.2.3 Results and Discussion

The One Step model has been compared both with the detailed model and with the different sets of experimental data.

In Figure 89 are showed the comparison between detailed model and One Step model for three coal of different rank: a lignite coal (Yallourn), a bituminous coal (Liddel) and an anthracite coal (Hongay).



Figure 89: Comparison between detailed model and One Step model for three different coal at 1500 and 1800 K in term of hydrocarbon species (heating rate of 10^4 \text{ K/s}).

The One Step model picks main features of detailed model. The kinetic parameters are evaluated with good precision and the asymptotic value are predicted with satisfactory agreement. The different can be establish both from a direct release of species (in case of detailed model several species are not directly released but are entrapped in metaplastic phase and they will be released only second time) and that detailed model takes in account the low temperature mechanism too, in spite of simplified model.

Figure 90 shows the comparison between experimental data [15,16,96,108,110,112] and predictions of the detailed and one step models of the total release of volatiles for different coals.



Figure 90: Comparison between experimental data of volatiles released (solid square) and model predictions (line and open triangle stand for detailed model, dash line and open circle stand for one step model). Pyrolysis conditions: (a) $h=10^5$ K/s, $T_{pyrolysis}=1641$ K, $t_{pyrolysis}=18$ ms [96,112], 78 ms [108]; (b) $h=10^4$ K/s, $T_{pyrolysis}=1220$ K, $t_{pyrolysis}=410$ ms [96,112]; (c) $h=10^5$ K/s, $T_{pyrolysis}=1600$ K, $t_{pyrolysis}=47$ ms [110]; (d) h=3000 K/s, $T_{pyrolysis}=1193$ K, $t_{pyrolysis}=4$ s [15,16].

Both the models agree quite well with the measurements, catching the reduction of the volatile fraction when the carbon content increases. It has to be noted the close results between the two models, detailed and global, also for coals which do not belong to the database used during optimization.

Figure 91 shows some product distributions as a function of the coal rank in the case of Xu and Tomita [15,16] experiments.



Figure 91: Comparison between experimental data of different volatiles species (gray solid square) and model predictions (line and open triangle stand for detailed model, dash line and open circle stand for one step Model): (a) GAS = total gas released; (b) IOG = inorganic oxygenated gas; (c) HCG = hydrocarbon gas. Pyrolysis conditions: h=3000 K/s, $T_{pyrolysis}=1193 \text{ K}$, $t_{pyrolysis}=4 \text{ s} [15,16]$.

One step model performs quite well in respect of the detailed model and also of the experimental data. As observed, gas products decreases with rank and then also oxygenated

inorganic components and hydrocarbons shows a diminishing trend, even though this trend is less evident (hydrocarbons are represented by lumped C_2H_4 and H_2 in the case of one step model). Differently from the detailed model, the One Step Model does not account for the low temperature mechanism and thus volatile species are not trapped as pseudo-species in the metaplastic phase. For this reason, the One step model slightly over-predicts the release of volatile species, but these systematic deviations are within the experimental uncertainties.

Volatile nitrogen compounds of different coals are also quite well reproduced (Figure 92). Both the models reproduce the behavior of such compounds, which show a weak dependence on rank up to about 80-85% of carbon content, after which their formation significantly decreases.



Figure 92: Comparison between experimental data of nitrogen volatiles released (solid square) and model predictions (line and open triangle stand for detailed model, dash line and open circle stand for one step Model): (a) $h=10^4$ K/s, $T_{pyrolysis}=1220$ K, $t_{pyrolysis}=410$ ms [96,112]; (b) $h=10^5$ K/s, $T_{pyrolysis}=1641$ K, $t_{pyrolysis}=1600$, $t_{pyrolysis}=47$ ms [10].

Finally, Figure 93 shows the comparison between experimental data [33] and the model predictions of the sulfur compound distribution during the pyrolysis of Illinois coal.



Figure 93: Comparison between experimental data of sulfur compounds from Illinois coal and model prediction: (a) Sulfur residue (circle) and sulfur gas (triangle), detailed model (solid line) and one step model (dash line); (b) Sulfur Tar release. Pyrolysis Conditions: h = 3000 K/s, $T_{pyrolysis} = 1200 \text{ K}$ [33].

Despite the fact that measurements refer to relatively low temperatures outside the validity of the one step model, the results are encouraging. Main trends are properly reproduced not only from the qualitative, but also the quantitative point of view. Both gas and tar sulfur components increase with the temperature. The models are delayed in reproducing the initial reactivity. This is 110

especially true for the detailed kinetic scheme, whilst the simplifications introduced in the one step mechanism make it more in line with the experimental evidences. The asymptotic values of the gas fraction is underestimated, whilst that of residue is overestimated. Sulfur tar fraction is better caught.

8.3 Skeletal mechanism for secondary gas phase reactions

The volatile matter of coal pyrolysis consist a wide range of products, from gaseous species at low molecular weight to tar species at high molecular weight. As reported in the section 3.3.1, the volatile products undergo thousand gas phase secondary reactions of pyrolysis and oxidation. In literature are available many detailed mechanism of gas phase reactions [26,200-204] but they are too much prohibitive to be applied directly in the CFD study of a multi-phase reactive system as the solid fuel combustion.

In order to find a good compromise between the computational efforts and the chemicalphysical carefulness, it is necessary to develop a simplified kinetic mechanism able to maintain the main features of the detailed kinetic mechanism

In this section, a reduced gas phase kinetic mechanism of the volatile products has been developed. This kinetic mechanism is formed by 47 species, from C_0 to C_{14} , involved in 415 reactions. The reduced mechanism maintains the modular and mechanistic nature of the detailed kinetic mechanism.

8.3.1 The kinetic model

The model considers the main chemical reactions of pyrolysis and oxidation for each gaseous species: molecular and radical reactions as well as equilibrium reactions have been taken into account. The simplified kinetic model has been obtained through an analysis of the formation and consumption fluxes of each species belonging to the detailed kinetic mechanism, in different operating conditions of temperature and equivalence ratio .On the basis of the absolute value of the total fluxes of each species it has been possible to individuate the most important species and reactions. The kinetic parameter of each reactions maintain the consistency with the kinetic parameter of the detailed kinetic mechanism. Because of the higher number of reactions of the simplified kinetic mechanism, Table 33 shows the kinetic mechanism only for tar components.

	Kinetic mechanism*	А	β	$\mathbf{E}_{\mathrm{ATT}}$					
	TETRALIN ($C_{10}H_{12}$)								
R_1	$TETRALIN \rightarrow CH_2CHCH_2 + 0.5C_6H_6 + 2C_2H_2$	$5.0 \text{ x} 10^{14}$	0.0	76500					
\mathbf{R}_2	$OH+TETRALIN \rightarrow CO+H+C_6H_6+1.5C_2H_4$	$1.0 \text{ x} 10^{13}$	0.0	2000					
R_3	$H+TETRALIN \rightarrow C_6H_6+SC_4H_7$	$2.0 \text{ x} 10^{13}$	0.0	5000					
R_4	$O+TETRALIN \rightarrow OH+C_6H_6+C_2H_3+C_2H_2$	$2.0 \text{ x} 10^{13}$	0.0	5000					
	$C_{12}H_{8}$								
R_5	$OH+C_{12}H_8 \rightarrow CO+H+0.333C_6H_6+.75C_{12}H_8$	$1.0 \text{ x} 10^{13}$	0.0	2000					
R_6	$H + C_{12}H_8 \rightarrow 0.25C_2H_3 + 0.25C_2H + 0.333C_6H_6 + .75C_{12}H_8$	$2.0 \text{ x} 10^{13}$	0.0	5000					
R_7	$O+C_{12}H_8 {\longrightarrow} 0.5CO+0.5HCO+.167C_6H_6+.75C_{12}H_8+0.5C_2H$	$2.0 \text{ x} 10^{13}$	0.0	5000					
	$C_9H_{10}O_2$								
R_8	$OH + C_9H_{10}O_2 \rightarrow CO + 2CH_2O + 0.5C_6H_6 + C_2H_2 + .5C_2H_4$	$1.0 \text{ x} 10^{13}$	0.0	2000					
R ₉	$H+C_{9}H_{10}O_{2} \rightarrow HCO+CH2O+1.5C_{2}H_{2}+0.5C_{6}H_{6}+.5C_{2}H_{4}$	$2.0 \text{ x} 10^{13}$	0.0	5000					
\mathbf{R}_{10}	$O+C_9H_{10}O_2 \rightarrow OH+0.5HCO+0.5CO+CH_2O+0.5C_6H_6+$ 1.5C ₂ H ₂ +0.5C ₂ H	$2.0 \text{ x} 10^{13}$	0.0	5000					
	$\mathrm{C}_{14}\mathrm{H}_{10}\mathrm{O}$								
R ₁₁	$OH+C_{14}H_{10}O \rightarrow 2CO+C_6H_6+C_6H_5$	$3.0 \text{ x} 10^{12}$	0.0	2000					
R ₁₂	$H+C_{14}H_{10}O \rightarrow CO+CH_3+C_{12}H_8$	$6.0 ext{ x10}^{12}$	0.0	5000					
R ₁₃	$O+C_{14}H_{10}O \rightarrow 2CO+2C_6H_5$	$6.0 ext{ x10}^{12}$	0.0	5000					
$C_{11}H_{12}O_4$									
R ₁₄	$\begin{array}{l} OH+C_{11}H_{12}O_4 {\rightarrow} 2CO+2CH_2O+HCO+0.25CYC_5H_6+1.875C_2H_2+0.0\\ 83C_6H_6+0.25C_2H_4+.625H_2 \end{array}$	$3.0 ext{ x10}^{12}$	0.0	2000					
R ₁₅	$H+C_{11}H_{12}O_4 \rightarrow 2CO+CH_2O+HCO+0.25CYC_5H_6+2.375C_2H_2+0.083C_6H_6+0.25C_2H_4+1.125H_2$	$6.0 ext{ x10}^{12}$	0.0	2000					
R ₁₆	$\begin{array}{l} O+C_{11}H_{12}O_4 \rightarrow 2CO+CH_2O+2HCO+0.25CYC_5H_6+1.875C_2H_2+0.08\\ 3C_6H_6+0.25C_2H_4+.625H_2 \end{array}$	$6.0 ext{ x10}^{12}$	0.0	5000					

Table 33: Kinetic mechanism of Tar decompositions

* $k = A T^{\beta} exp(-E/RT)$; units: kmol, l, cal, s

8.3.2 Results and discussion

The simplified kinetic mechanism has been compared both with experimental data and both with detailed model predictions. The experimental data shown in Figure 94 refer to flame speed of several C_1 - C_6 hydrocarbon species. The details of the experimental data as well as a wide modeling analysis of them are reported in Ranzi et al. [26]. The overall agreement is satisfactory for many compounds, highlighting the suitability of the simplified kinetic model to be applied in fluid-dynamics simulations.



Figure 94: Comparison between experimental data of flame speed and reduced kinetic mechanism.

The Figure 95-Figure 99 show the comparison between the simplified kinetic mechanism and the detailed kinetic mechanism for tar components. The simulations have been carried out a two different temperature, 1400 and 1600 K, considering an equimolar mixture of tar species and C_3H_6 in stoichiometric conditions (as generator of radical species).



Figure 95: Comparison between detailed and lumped kinetic mechanism predictions of a equimolar mixture of TETRALIN and C_3H_6 at 1600 K, in stoichiometric conditions



Figure 96: Comparison between detailed and lumped kinetic mechanism predictions of a equimolar mixture of $C_{12}H_8$ and C_3H_6 at 1600 K, in stoichiometric conditions.



Figure 97: Comparison between detailed and lumped kinetic mechanism predictions of a equimolar mixture of $C_9H_{10}O_2$ and C_3H_6 at 1400 K, in stoichiometric conditions



Figure 98: Comparison between detailed and lumped kinetic mechanism predictions of a equimolar mixture of FENAOH and C_3H_6 at 1400 K, in stoichiometric conditions

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Figure 99: Comparison between detailed and lumped kinetic mechanism predictions of a equimolar mixture of $C_{11}H_{12}O_4$ and C_3H_6 at 1400 K, in stoichiometric conditions

The reduced model is able to catch the trend both the main molecular species, as CO, CO_2 , soot precursor and the main radical species, as H and OH. Obviously, the agreement between the two model depend on the species number in the reduced kinetic model. Unfortunately, the maximum number of species is limited by structural constraints set of the fluidynamics code employment in the analysis of coal pulverized furnace, as shown in the next chapter. Thus, at light of these constraints, it is possible to consider the general agreement more than satisfactory.

8.4 Conclusion

Two simplified model for coal devolatilization and for secondary gas phase reactions of volatile matter have been developed and proposed. These mechanisms are suitable for CFD simulations.

The one step model of coal pyrolysis was developed on the basis of detailed models of hydrocarbon, sulphur and nitrogen release. Moreover, a non linear regression technique to estimate the optimal kinetic parameters has been applied. Stoichiometric coefficients are derived from the detailed models of volatilization of reference fuels. The agreement with detailed model is satisfactory for both evolution rates and cumulative values. This one step model, despite its simplicity, retains the predictive capabilities of the original detailed model for the formation of solid, tar and gaseous species, including sulfur and nitrogen compounds. The elemental composition of the coal is the only information needed to identify the rate constants and to estimate the product distribution.

The skeletal kinetic mechanism of gas phase reactions consists in 47 species involved in more than 400 reactions. The model takes into account both molecular and radical reactions as well

as thermodynamic equilibrium reactions. The simplified kinetic model has been compared both with experimental data and with the detailed kinetic model obtaining a good agreement in both cases.

9 MILD combustion of pulverized coal

9.1 Introduction

MILD combustion, acronym of Moderate and Intensive Low Oxygen Dilution, is an important success of combustion technology [205]. As already mentioned, the air is replaced with a mixture of O_2 and in inert flue gases with important effect on the coal reactivity. The reactants are introduced in the combustion chamber at temperature higher than the mixture self-ignition and with high inlet velocity in order to increase the internal recirculation and to control the temperature in the furnace. Chemical reactions take a place in almost the entire volume of the combustion furnace, reducing the gradient of the temperature and of the species concentrations. In this way it is possible to reduce the pollutant emission such as NO_x and soot, strongly reliant on the temperature peaks [206].

There are many reasons for which the NO_x emissions are lower in oxy-coal combustion than in air-combustion: (i) the lower partial pressure of N_2 limits the thermal and prompt mechanism (ii) the higher CO_2 concentration changes the radical and gas composition modifying the NO formation; (iii) the NO recycled is reburned in the combustion chamber [195].

9.2 The IFRF experiments

The IFRF, acronym of International Flame Research Foundations, carried out several experiments of MILD combustion of gaseous, liquid and solid fuels [207,208].

The IFRF experiments on the MILD oxy-coal combustion technology have been simulated by many researcher using different approaches [205,206,209]. Table 34 summarized the main models applied to describe the different chemical and physical processes.

Ref.	Code	Turbulence	Radiation	Chemistry- Turbulence	Pyrolysis	Volatile	TAR	Homogeneous Reaction Mechanism	Char Combustion
[209]	AIOLOS	STD k-e	DO	EDC	FG-DVC	CH_4	$C_xH_yO_z$	Global Mechansm[210]	Oxidation [210]
[205]	FLUENT	k-e	DO	EBU	CPD	Lumped Volatile	-	2-step kinetic mechanism	Oxidation
[206]	FLUENT	Realizable k.e	P-1	EDC	CPD	mixture	C_xH_y	GRI 2.2	Oxidation/ Gasification [211,212]

Table 34: Numerical simulations of IFRF experiments on the MILD coal combustion

In this chapter, the experiment of pulverized coal in MILD combustion of Orsino et al. [207] have been investigated using the commercial CFD code, FLUENTTM version 14.0 [213]. The IFRF furnace consists of a central pipe of 125 mm for oxidizer supply and two coal injectors of 27.3 mm which were located 280 mm away from the burner center, as shown in Figure 100. The furnace has a section of 2x2 m and a length of 6.25 m. The temperature of vitiated air and the transport air inlet were 1623 K and 313 K, respectively. The inlet velocity of air and transport air streams were 65 m/s and 26 m/s, respectively. The mass flows rate were 66 kg/h for coal (corresponding at 0.58 MW), 130 kg/h for the coal transport air and 675 kg/h for the vitiated air.



Figure 100: Sketch of the IFRF furnace

The compositions of the transport air and the vitiated air are reported in Table 35.

Table 35: Composition of transport and vitiated air

wt%, wet	O ₂	N_2	CO_2	H ₂ O	NO [ppm]
Trasnport air	23	77	-	-	-
Vitiated air	22	56	12.5	9.5	89

The coal feed is a high volatile bituminous. The elemental composition of Guasare coal is reported in Table 36. The coal was milled to give a particle size distribution of 80% less than 90 μ m. The classification of the particle size is reported in Kim et al. [209]. The coal particle are injected with the transport air inlet.

Table 36: Elemental composition of Guasare coal, %w, daf

%w, daf	С	Н	0	Ν	S
Guasare	81.6	5.5	10.7	1.5	0.6

The measurements were taken at several traverses, in a horizontal plane through the burner centerline, from a minimum of 15 cm to a maximum of 497 cm from the inlet section. The radial measurements of each traverses included axial velocity, gas temperature and composition (CO, CO_2 , O_2 , NO_x), solid burnout, solid concentrations, total radiance and total radiative flux at the furnace wall.

9.3 The IFRF simulations

As mentioned, the simulations have been realized using a CFD commercial code, FLUENTTM version 14.0 [213]. In the next paragraphs, the main chemical and physical models applied in this simulations will be briefly discussed.

9.3.1 The coal pyrolysis

The one step model of coal pyrolysis, illustrated in the previous chapter, has been applied. On the basis of the coal elemental composition, the stoichiometric coefficient as well as the kinetic parameters have been determinate and reported in Table 37.

Table 37: Stoichiometric coefficient and kinetic parameter of the pyrolysis reactions

Coal	CHAR	TAR	СО	H ₂ O	CO ₂	C_2H_4	H_2	A[s ⁻¹]	E[kcal/kmol]
Guasare	3.914	0.1524	0.413	0.128	0.052	0.334	1.152	5.24x10 ¹⁶	57000

The TAR mixture has been split in five different components, as reported in Sommariva et al. [13]. Table 38 shows the mole fraction of each components into the tar mixture.

Table 38: Mole fraction of single tar components in TAR mixture

Tar Mixture	$C_{10}H_{12}$	$C_{12}H_8$	$C_{14}H_{10}O$	$C_9H_{10}O_2$	$C_{11}H_{12}O_4$
Mole Fraction	0.352	0.332	0.235	0.046	0.0351

The numerical predictions of the one step pyrolysis model were compared with experimental data reported in Schaffel et al. [205], and shown in Figure 101. The experimental data were obtained in IFRF Isothermal Plug Flow Reactor operated at 1473 K with particle heating rate of 10^{5} - 10^{6} K/s.



Figure 101: Devolatilization of Guasare coal at 1473 K. Comparison between experimental data and model predictions.

The one step model shows a better comparison with experimental data in terms of initial devolatilization and in terms of asymptotic value, while the detailed models shows a better agreement with experimental data in terms of intermediate reactivity. Anyway, the general agreement is satisfactory for both models.

The low calorific value of Guasare coal, obtained by approximate analysis, is about 31.74 MJ/kg on daf basis. On the basis of the stoichiometric coefficient reported in Table 37 and Table 38 it has been possible to define the heat reaction of pyrolysis, about 0.268 MJ/kg (less 1% of low the calorific value).

The single kinetic rate devolatilization implemented in FLUENT[™] [213] assumes that the rate of devolatilization is first-order reaction and it depends on the amount of volatile remaining in the particle:

$$\frac{dm_p}{dt} = -k \times \left[m_p - (1 - f_{v,0}) \times (1 - f_{w,0}) \times m_{p,0} \right]$$
(9.1)

where m_p is the particle mass, $m_{p,0}$ initial particle mass, $f_{v,0}$ is the volatile mass fraction, $f_{w,0}$ is the dry mass fraction, k is the kinetic rate.

9.3.2 The heterogeneous reactions

In MILD combustion, because of the high concentration of CO_2 and H_2O and of the low O_2 concentration, the char gasification reactions can become as important as the char oxidation reaction. In order to take into account both heterogeneous reactions, the multiple particle surface model has been applied. In this model the particle surface species constitutes the reactive char mass of the particle, hence, if a particle surface species is depleted, the reactive char content of the particle is consumed, and turn, when a surface species is produced, it is added to the particle char mass.

In agreement with the reaction r: particle species j + gaseous species $n \rightarrow products$, the particle reaction rate can be expressed as:

$$R_{j,r} = A_p \eta_r Y_j R_{j,r}$$

$$R_{j,r} = k_{kin,r} \left(p_n - \frac{R_{j,r}}{D_{0,r}} \right)^N$$
(9.2)

where $\overline{R_{j,r}}$ is the rate of the particle surface species depletion (kg/s), A_p is the external surface particle, Y_j is the mass fraction of surface species j in the particle, η_r is the effectiveness factor, $R_{j,r}$ is the rate of particle surface species reaction per unit area (kg/m²/s), $k_{kin,r}$ is the kinetic constant of reaction r (kg/m²/s), p_n is the bulk partial pressure of the gas phase species (Pa), $D_{0,r}$ is the bulk diffusion coefficient for reaction r (m/s), N_r is the apparent order of reaction r.

The kinetic mechanism of char heterogeneous reactions reported in previous chapter have been modified in agreement with the formulations of the multiple particle surface sub model. Table 39 shows the kinetic parameters of char heterogeneous reactions.

	Kinetic mechanism* [kg/m ² /s]	A [kg/m ² /s/Pa ^{α}]	β	α	E _{ATT} [kJ/kmol]
\mathbf{R}_1	$C+O_2 \rightarrow CO_2$	1.23×10^2	-1.0	1.0	135000
\mathbf{R}_2	C+0.5O ₂ →CO	$1.85 \text{ x} 10^4$	-0.78	0.78	160000
R_3	$C+CO_2 \rightarrow 2CO$	$1.36 \text{ x} 10^2$	-1.0	1.0	208000
\mathbf{R}_4	$C+H_2O\rightarrow CO+H_2$	$4.38 ext{ x10}^2$	-1.0	1.0	203000

Table 39: the kinetic parameters of char heterogeneous reactions

* $r = A T^{\beta} \exp(-E_{ATT}/RT) [CHAR] [GAS]^{\alpha}$

Figure 102 shows the comparison between the kinetic mechanism reported in Table 39 and several kinetic rate for heterogeneous reactions applied in CFD work of coal combustion [206,214,215].



Figure 102: Comparison between the kinetic parameters reported in Table 39 and several kinetic parameters applied in CFD work [206,214,215]

The main different refers to the activation energy of the oxidation heterogeneous reaction. The two models show the same reactivity about at 1400 K. Because of the different activation energy, the PoliMi model has a reactivity ~10 time lower than the Field model [211] at 1000 K, while at 2000 K the reactivity of PoliMi model is ~10 time higher. Regarding the gasification heterogeneous reactions, the PoliMi model and Smoot and Pratt model [212] show a similar reactivity.

9.3.3 The particle energy balance

The particle energy balance considers both the convection heat transfer and the adsorption/emission of radiation at the particle surface:
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$$m_p C_p \frac{dT_p}{dt} = hA_p \left(T_\infty - T_p\right) + A_p \varepsilon_p \sigma \left(\theta_R^4 - T_p^4\right) + \frac{dm_p}{dt} h_{fg}$$
(9.3)

where m_p is the mass particle (kg), C_p is the heat capacity of the particle (J/kg/K), A_p is the particle surface area (m²), T_p is the particle temperature (K), T_{∞} is the local temperature of the continuous phase (K), h is the convective heat transfer coefficient (W/m²/K), ϵ_p is the particle emissivity, σ is the Stefan-Boltzmann constant (W/m⁴/K) and θ_R is the radiation temperature, evaluated on the basis of the incident radiation. The latter term accounts for the heat reaction of pyrolysis and for heat reaction of the heterogeneous reactions.

The heat transfer coefficient is evaluated by Ranz-Marshall equation [183]:

$$Nu = \frac{hd_p}{k_{\infty}} = 2 + 0.6 \operatorname{Re}_d^{0.5} \operatorname{Pr}^{1/3}$$
(9.4)

where d_p is the particle diameter (m), k_{∞} is the thermal conductivity of the continuous phase (W/m/k), Re_d is the Reynolds number based on the particle diameter and the respective velocity and Pr is the Prandtl number of the continuous phase.

The particle is assumed at uniform temperature without to consider the internal resistances to heat transfer.

9.3.4 The discrete phase model

The Eulerian-Lagrange approach has been applied during the simulation of IFRF furnace. The fluid phase is treated as a continuum by solving the Navier-Stokes equations, while the dispersed phase is solved by tracking a large number of particles through the calculated flow field. The dispersed phase can exchange momentum, mass, and energy with the fluid phase. A fundamental assumption made in this model is that the dispersed second phase occupies a low volume fraction.

The trajectory of the coal particle are calculated by integrating the force balance on the particle:

$$\frac{du_p}{dt} = \frac{18\mu}{\rho_p d_p^2} \frac{C_D \operatorname{Re}}{24} \times \left(u - u_p\right) + \frac{g_x \left(\rho_p - \rho\right)}{\rho_p}$$
(9.5)

where u is the fluid phase velocity, u_p is the particle velocity, μ is the molecular viscosity of the fluid, ρ is the fluid density, ρ_p is the density of the particle, and d_p is the particle diameter, Re is the relative Reynolds number, g_x is the gravity constant.

9.3.5 The gas phase reactions of volatile products

The skeletal mechanism shown in the previous chapter has been applied to describe the gas phase pyrolysis and oxidation reactions.

9.3.6 The Eddy dissipation concept

The eddy-dissipation-concept is an evolution of the eddy-dissipation model to take into account detailed kinetic mechanism in turbulent flow [216]. In this model the reactions occur in small turbulent structures, called fine scales. The main parameters of the fine structures are:

✓ the length fraction:
$$\xi^* = 2.13 \left(\frac{\nu \varepsilon}{k^2}\right)^{0.25}$$
 (9.6)

✓ volume fraction:
$$\gamma_{\lambda} = \left(\xi^*\right)^3$$
 (9.7)

$$\checkmark \quad \text{the time scale: } \tau^* = 0.4082 \left(\frac{\nu}{\varepsilon}\right)^{0.5} \tag{9.8}$$

where k is the turbulence kinetic energy, ε is its dissipation rate and v is the kinematic viscosity.

The combustion at the fine scales is assumed to occur as a constant pressure reactor, with initial conditions taken as the current species and temperature in the cell. The source term for the mean species i is modeled as

$$R_{i} = \frac{\overline{\rho}(\xi^{*})^{2}}{\tau^{*}[1-\gamma_{\lambda}]} (y_{i}^{*}-y_{i})$$

$$(9.9)$$

where y_i^* is the fine-scales species mass fraction after reacting over the time τ^* .

9.3.7 The P-1 model radiations

In combustion processes, the radiative exchange is the most important mechanism for heat transfer. In a oxy-coal pulverized combustion chamber there are many radiative contribution due the coal and char particles, soot, walls and gaseous species as CO_2 and H_2O .

In the P-1 radiation model [213] the transport equation for the incident radiation G is

$$\nabla \cdot (\Gamma \nabla G) - aG + 4an^2 \sigma T^4 = 0$$

$$\Gamma = \frac{1}{3(a + \sigma_s) - C\sigma_s}$$
(9.10)

where a is the absorption coefficient, σ_s is the scattering coefficient, G is the incident radiation, σ is the Stefan-Boltzmann constant, n is the refractive index of the medium and C is the linear-anisotropic phase function coefficient.

When a gray, absorbing, emitting, and scattering medium contains an absorbing, emitting, and scattering particles, the transport equation for the incident radiation can be written as

$$\nabla \cdot \left(\Gamma \nabla G\right) + 4\pi \left(an^2 \frac{\sigma T^4}{\pi} + E_p\right) - \left(a - a_p\right)G = 0$$
(9.11)

where E_p is the equivalent emission of the particles, a_p is the equivalent absorption coefficient.

Moreover, on the basis of the incident radiation G, it is possible to evaluate the θ_R , the

radiation temperature in the particle energy balance as $\theta_R = \left(\frac{G}{4\sigma}\right)^{1/4}$

9.3.8 The turbulence model

The Realizable k- ε model has been applied to describe the turbulence flows within the IFRF combustion chamber. The Realizable k- ε model has a better consistent with the physic of the turbulent flow than the Standard k- ε model and thus it more accurately predicts the spreading rate of both planar and round jets [213].

9.4 Results and discussion

The numerical predictions have been compared with the experimental data of:

- ✓ Axial velocity
- ✓ Gas phase temperature
- ✓ Gas concentration (O_2 , CO_2 , CO, NO)

9.4.1 Experimental measurements of axial velocity

Figure 103 shows the axial velocity contour plot on the axial section and the comparison between experimental data and model predictions for the axial velocity along five radial traverse, respectively.

The central and the lateral peak correspond to the secondary air inlet and the primary air, respectively. The same experimental authors [207] have highlighted a possible underestimate of the experimental velocity of the primary air in the nearness to the first three traverses. In according with the free jet theory, the jet in corresponding the first three traverse should have a velocity very close to the initial velocity. The calculation of the entrained mass flow in the air jet have confirmed these observation.

The general agreement is satisfactory, above all for the secondary air jet. The predicted velocity of the primary air jet is overestimated, in agreement with the author's observation.



Figure 103: Experimental data and numerical predictions of the axial velocity at different distant from the burner.

9.4.2 Experimental measurements of Temperature

In Figure 104 are shown the contour plot on the axial section and the comparison with experimental data along the radial traverses. In proximity of the first traverse, the model shows an initial ignition at the boundary of the secondary air but this ignition is not strong enough to allow the complete ignition of the secondary jet, as shown by the experimental data. The cold zone of the secondary jet persists until the fourth traverse. In the last two traverse the agreement between experimental data and numerical prediction is satisfactory.



Figure 104 : Experimental data and numerical predictions of the temperature at different distant from the burner.

9.4.3 Experimental measurements of O₂ concentration

Figure 105 shows the profile of O_2 mole fraction on dry basis. The numerical prediction show an overestimation of the oxygen concentration in the secondary air jet, in correspondence of the first and second traverse. This is in agreement with the underestimation of the numerical temperature profile.



Figure 105: Experimental data and numerical predictions of the O_2 concentration at different distant from the burner.

9.4.4 Experimental measurements of CO₂ concentration

The experimental data and the numerical prediction of CO_2 concentration are shows in Figure 106. The experimental data of CO_2 shows an anomalous behavior if compared with those of temperature. The temperature experimental data show a maximum in correspondence to the minimum of CO_2 concentration.



Figure 106: Experimental data and numerical predictions of the CO_2 concentration at different distant from the burner.

On the contrary, the model predictions show a consistent behavior between temperature and CO_2 predictions: where there is the minimum of the CO_2 there is the minimum of the temperature.

9.4.5 Experimental measurements of CO concentration

Figure 107 shows the CO contour plot and the comparison with experimental data. The model overestimates systematically the CO experimental concentrations, but consistently with the experimental data, the model predicts an increasing of the CO concentration between the first and second traverse and the next decreasing in the following traverses.



Figure 107: Experimental data and numerical predictions of the CO concentration at different distant from the burner.

9.4.6 Experimental measurements of NO concentration

The main kinetic mechanism involved in the NO_x formation are:

- ✓ fuel NO_x
- ✓ thermal NOx
- ✓ prompt NOx
- ✓ N_2O mechanism
- ✓ NO reburning.

Figure 108 shows a sketch of the main path for each kinetic mechanism.



Figure 108: Sketch of the kinetic mechanism of NO_x formations

9.4.6.1 Fuel-NO_x mechanism

As mentioned in chapter 5, the Fuel-NOx mechanism is the most important contribution in the NO_x formations during the solid fuel combustion, as coal and biomass.

In this work, it is assumed that the fuel nitrogen coming from volatile is converted in HCN and, in agreement with the work of Lockwood and Romo-Millares [217], the nitrogen coming from the char is converted in NO. The HCN released can interact with the oxygen with formation of NO. Finally, NO can be involved in two reburning reactions, the first via HCN path and the second via char heterogeneous path.

The formation rate of HCN and NO are proportional to the rate of coal pyrolysis coal and char burnout, respectively, as reported in the next equations:

$$S_{volatiles,HCN} = \frac{S_{vol}Y_{N,vol}M_{w,HCN}}{M_{w,N}V}$$

$$S_{char,NO} = \frac{S_{char}Y_{N,Char}M_{w,NO}}{M_{w,N}V}$$
(9.12)

where S_{vol} is the pyrolysis rate of coal [kg/s], S_{char} is the char burnout [kg/s], $Y_{N, Vol}$, $Y_{N, Char}$, are the mass fraction of nitrogen in volatile and in char (calculated on the basis of the one step kinetic model of coal pyrolysis), $M_{w,N}$, $M_{w,HCN}$, $M_{w,NO}$, are the molecular weight of N, HCN and NO, V is the cell volume [m³].

The HCN oxidation (R_1) and reburning (R_2) rate [mol/m³/s] are given by De Soete equations [218]:

$$R_{1} = 1.0 \times 10^{10} X_{HCN} X_{O2}^{\alpha} e^{-\frac{280500}{8.314T}} \times \frac{P}{RT}$$

$$R_{2} = 3.0 \times 10^{12} X_{HCN} X_{NO} e^{-\frac{251200}{8.314T}} \times \frac{P}{RT}$$
(9.13)

where X_i are the mole fraction and α is the exponent of oxygen and can vary between 0 and 1, depending on the flame conditions.

Finally, the reburning rate of NO $(R_3, kg/m^3/s)$ via char heterogeneous mechanism is given by the following equations,

$$R_{3} = A_{g} \times 230 \times P_{NO} \times [CHAR] \times e^{\frac{142700}{8.314T}} M_{NO}$$
(9.14)

where A_g is the surface area of char particle assumed supposed to 180 m²/g, P_{NO} is the partial pressure of NO [atm], [Char] is the concentration of particle [kg/m³] and M_{NO} is the molecular weight of NO.

9.4.6.2 Thermal mechanism

The thermal mechanism refers the formation of NO_x via N_2 oxidation. This mechanism is important at high temperature and low equivalent ratio. The NO_x formation via N_2 oxidation can be describe by the Zeldovich mechanism:

$$N_{2} + O \cdot \underbrace{\stackrel{k_{+1}}{\longleftarrow} N \cdot + NO}_{2} + N \cdot \underbrace{\stackrel{k_{+2}}{\longleftarrow} O \cdot + NO}_{N \cdot + OH} \cdot \underbrace{\stackrel{k_{+3}}{\longleftarrow} H + NO}_{K}$$
(9.15)

Assuming the hypothesis of pseudo-stationary of the radical N and the partial equilibrium of the radical species H, O and OH, it is possible to obtain the next rate equation $[mol/m^3/s]$:

9.4.6.3 Prompt mechanism

Fenimore [219] proposed a mechanism of NO_x formation based on the interaction between hydrocarbon radical species and N_2 with formation of ammine and cyano-components (NO_x precursors):

$$\begin{array}{c} \mathrm{CH} + \mathrm{N}_{2} \rightleftharpoons \mathrm{HCN} + \mathrm{N} \\ \mathrm{CH}_{2} + \mathrm{N}_{2} \rightleftharpoons \mathrm{HCN} + \mathrm{NH} \end{array} \tag{9.17}$$

This mechanism can become important in some combustion environments, such as at low temperature, in fuel-rich conditions and with short residence time.

A simplified kinetic model has been proposed by De Soete [218]:

$$r_{NO,Prompt} = f \times 6.4 \times 10^{6} \times e^{-\left[\frac{RT}{P}\right]^{b+1}} \times [O_{2}]^{\alpha} \times [N_{2}] \times [FUEL] \times e^{-\frac{303500}{8.314T}} \times V$$
(9.18)

where f is the Prompt factor and it accounts for the type of the fuel, α is the exponent of oxygen and can vary between 0 and 1, depending on the flame conditions.

9.4.6.4 N₂O mechanism

The NO_x formation via N₂O intermediate can be important during the combustion of lean mixture of hydrocarbons in low temperature (< 1500 K) or at high pressure (> 1 atm) conditions [220]. The kinetic equation of NO_x formation via N₂O intermediate is $[mol/m^3/s]$:

$$r_{NO,N_{2}O} = 2 \left[k_{f,1} \frac{k_{f,1} [N2][O][M] + k_{r,2} [NO]^{2}}{k_{r,1} [M] + k_{f,2} [O]} [O] - k_{r,2} [NO]^{2} \right] \times V \qquad k_{f,1} = 4.44 \times 10^{38} \times T^{-8.358} e^{\frac{-28234}{T}} \qquad k_{f,1} = 4.0 \times 10^{11} \times e^{\frac{-28234}{T}} \\ [M] = 1.4 [O_{2}] + 3.0 [CO_{2}] + 1.7 [N_{2}] + 12 [H_{2}O] \qquad k_{f,1} = 2.90 \times 10^{10} \times e^{\frac{-11651}{T}} \qquad k_{f,1} = 1.45 \times 10^{-26} \times T^{9.259} \times e^{\frac{-11651}{T}} \\ (9.19)$$

9.4.6.5 Reburning in gaseous phase

Chen et al. [221,222] proposed the following reburning reactions:

$$NO + CH_{2} \xrightarrow{k_{1}} HCN + OH$$

$$NO + CH \xrightarrow{k_{2}} HCN + O$$

$$NO + C \xrightarrow{k_{3}} CN + O$$
(9.20)

In this work the CH species has been applied that the as reburning agent. The kinetic rate is given by equations $[mol/m^3/s]$:

$$r_{NO,\text{Reburning}} = 4.0 \times 10^{-4} \times (k_1 + k_2 + k_3) [CH] [NO] \times V$$
(9.21)

where $k_1 = 5.30 \times 10^{12} \times T^{-1.54} \times e^{\frac{-27977}{RT}}$, $k_2 = 3.31 \times 10^{16} \times T^{-3.33} \times e^{\frac{-15090}{RT}}$, $k_3 = 1.356 \times 10^{15} \times T^{-2.64} \times e^{\frac{-144090}{RT}}$

9.4.6.6 Results and discussion

The equations developed in section 8.8.2 have been applied in order to define the nitrogen repartition between the volatile matter and solid residue, respectively of 51.9 and 48.1%, wt.

Figure 109 shows the numerical prediction of NO formation and the comparison with the experimental data. The model predicts well the experimental data in correspondence of the first traverse and the last two traverses. In proximity of the intermediate traverses, the model catches well the profile in nearness of the center of the furnace and of the walls, but it underestimates systematically the experimental data in correspondence of the secondary air jet.

Among the several terms that contribute to the NO formations, only the fuel-NO, the homogeneous NO reburning and heterogeneous NO reburning are significant. In particular, the

order of fuel-NO source is 0.4×10^{-3} kmol/m³/s, while the order of homogeneous and heterogeneous NO reburning are 30% and 20% of the fuel-NO, respectively.



Figure 109: Experimental data and numerical predictions of the NO ppm at different distant from the burner.



Figure 110: Experimental data and numerical predictions of the HCN ppm dry at different distant from the burner.

The under-prediction of NO concentration in proximity to the intermediate traverses can be due to the low conversion of HCN to NO, as shown from the high HCN concentration in Figure 110.

9.4.7 Model predictions of SO_x

The SO_x emissions are produced from the oxidation of fuel-bound sulphur. They are responsible of several effects as the acid rain and the corrosion of combustion equipment.

In this set of experimental data there are not information about the SO_x formation. In order to show the capability of the one step model of coal pyrolysis, several model prediction of SO_x emission are shown in this section.

9.4.7.1 Fuel-SO_x mechanism

Figure 111 shows a sketch of the main step of SO_x formations. The coal sulphur fraction is distributed between the volatiles and the char. The equations reported in section 8.8.2 have been applied to define the sulphur repartition between the volatile and the solid phase, respectively of 48.8% and 51.2%, w.



Figure 111: Sketch of the kinetic mechanism of SO_x formations

The formation rate of H_2S from volatile and the formation rate of SO_2 from char are proportional to the rate of coal pyrolysis and char burnout, respectively:

$$S_{volatiles,H_2S} = \frac{S_{vol}Y_{S,vol}M_{w,H_2S}}{M_{w,S}V}$$

$$S_{char,SO_2} = \frac{S_{char}Y_{S,Char}M_{w,SO_2}}{M_{w,S}V}$$
(9.22)

where S_{vol} is the pyrolysis rate of coal [kg/s], S_{char} is the char burnout [kg/s], $Y_{S, Vol}$, $Y_{S, Char}$, are the mass fraction of sulphur in volatile and in char (calculated on the basis of the one step kinetic model of coal pyrolysis), $M_{w,S}$, $M_{w,H2S}$, $M_{w,SO2}$, are the molecular weight of S, SO₂ and H₂S, V is the cell volume [m³].

9.4.7.2 Fuel-SO_x mechanism

A simplified gas phase mechanism of SO_x formation is implemented in FluentTM. The reduced kinetic model includes sulphur containing species as SO_2 , SO_3 , H_2S , SO and SH. The completed kinetic mechanism is reported in Table 40.

Table 40: Reduced kinetic model of sulphur oxidation

Reactions*		А	В	E_{ATT}
$H_2S + H \longrightarrow SH + H_2$		1.82×10^{7}	0.0	$7.48 \text{ x} 10^3$
$SH + H_2 \longrightarrow H_2S + H$		$9.38 ext{ x10}^{6}$	0.0	$6.25 \text{ x} 10^4$
$OH + H_2S \rightarrow H_2O + SH$		$1.38 \text{ x} 10^2$	0.0	$3.74 \text{ x} 10^3$
$\rm H_2O + SH \rightarrow OH + H_2S$		$3.10 \text{ x} 10^7$	0.0	$1.22 \text{ x} 10^5$
$SO + OH \rightarrow H + SO_2$		$1.62 \text{ x} 10^8$	0.0	$2.57 \text{ x} 10^3$
$H + SO_2 \rightarrow SO + OH$		7.69 x10 ⁹	0.0	$1.19 \text{ x} 10^5$
$\rm SH + O \rightarrow SO + H$		$3.55 \text{ x}10^8$	0.0	$2.69 \text{ x} 10^3$
SO + H v SH + O		2.99 x10 ⁹	0.0	$1.69 \text{ x} 10^5$
$\mathrm{O} + \mathrm{H}_2\mathrm{S} \longrightarrow \mathrm{SH} + \mathrm{OH}$		$4.37 \text{ x} 10^3$	0.0	$1.38 \text{ x} 10^4$
$\rm SH + OH \rightarrow O + H_2S$		9.89 x10 ⁸	0.0	$6.04 \text{ x} 10^4$
$SO + O_2 \rightarrow SO_2 + O$		$4.47 \text{ x} 10^5$	0.0	$2.70 \text{ x} 10^4$
$SO_2 + O \rightarrow SO + O_2$		1.66 x10 ⁶	0.0	$7.61 \text{ x} 10^4$
$\mathrm{H} + \mathrm{SH} + \mathrm{M} \rightarrow \mathrm{H}_2\mathrm{S}{+}\mathrm{M}$		$1.10 \text{ x} 10^3$	0.0	0.0
$\mathrm{H_2S} + \mathrm{M} \rightarrow \mathrm{H} + \mathrm{SH} + \mathrm{M}$		8.67 x10 ¹⁴	0.0	$3.82 \text{ x}10^5$
$\mathrm{SO} + \mathrm{O} + \mathrm{M} \rightarrow \mathrm{SO}_2 + \mathrm{M}$		$8.71 \text{ x} 10^9$	-1.8	0.0
$SO_2 + M \rightarrow SO + O + M$		1.91 x10 ¹⁴	0.0	$5.21 \text{ x} 10^5$
$SO_2 + O + M \leftrightarrow SO_3 + M$	Formation rate	$3.63 ext{ x10}^2$	0.0	$-4.18 \text{ x} 10^3$
	Reverse rate	$7.41 \text{ x} 10^{14}$	0.0	$3.46 \text{ x} 10^5$
$SO_3 + O \leftrightarrow SO_2 + O_2$	Reverse rate by equilibrium	$1.20 \text{ x} 10^6$	0.0	$3.98 \text{ x} 10^4$

* $k = A T^{\beta} \exp(-E_{ATT}/RT)$, units: m, mol, J, K.

The skeletal mechanism of secondary gas phase reactions offers the possibility to evaluate directly the concentration of the main radical species, as OH, O and H.

9.4.7.3 Results and discussion

Figure 112 shows the contour plot of the H_2S , SO_2 and SO_3 formation. Unfortunately, because of the lack of the experimental data, it has been not possible to do any comparison.

The H_2S release from coal devolatilization begins to be significant in correspondence to the second and third traverse and quickly it is oxidized to SO₂, as shown in Figure 112b. Moreover, significant amount of SO₃ are produced by the SO₂ oxidation (Figure 112c). The correct prediction of SO₃ is also important because it is responsible of the corrosion of combustion equipment.



Figure 112: Numerical predictions (ppm dry) of the $H_2S(a)$, $SO_2(b)$ and $SO_3(c)$ at different distant from the burner.

9.4.8 Furnace outlet

Table 41 shows the comparison between the experimental data and the numerical predictions of the main parameters at the furnace exit. The agreement is satisfactory in every conditions.

Parameter	Experiment	Predicted
T [K]	1503	1545
O ₂ , % mol dry	3.1	3.1
CO ₂ , % mol dry	25.5	25.6
CO, ppm dry	<50	38
NO, ppm dry	320	295
SO ₂ , ppm dry	-	2450
SO ₃ , ppm dry	-	75
Char	99.4	100.0

Table 41: Experimental measurement and model prediction at the furnace exit

9.5 Conclusion

The simplified kinetic models of the coal pyrolysis and of the secondary gas phase reactions of volatile matter as well as that of char heterogeneous reactions have been applied in a CFD study of a oxy-coal pulverized furnace.

The model are able to catch the main features of the experimental data, even if in few conditions the agreement are partially satisfactory, as those in nearness of the second traverse. It is important to underline that these experimental data show a partial unsubstantiality, as in the case of the experimental data of CO_2 and of temperature or as in the case of experimental data of velocity.

Moreover, the emissions of NO_x and SO_x have been analyzed. The model has highlighted an agreement satisfactory enough with the experimental data of NO_x . Unfortunately, it has been not possible to compare the model prediction with experimental data of SO_x because of the lack the experimental information.

Conclusion

A predictive multi-step kinetic model of coal combustion has been developed during this PhD thesis. The kinetic model is constituted from two modular sub-models, one of pyrolysis and one of heterogeneous reactions.

The pyrolysis model takes into account many chemical kinetic problems as the release of hydrocarbon compounds and the formation of SO_x and NO_x precursors during the coal devolatilization. These kinetic models of pyrolysis characterize the coal matrix on the basis only of the coal elemental composition through specific reference compounds. Any coal is simply considered as a linear combination of the reference coals and the same linear combination is applied to devolatilization process and released products. A multistep devolatilization mechanism is assumed for each reference coals, with different product distributions and different kinetic parameters. The model has been compared with several set of experimental data obtained in different operating conditions (heating rate, temperature, time, coal rank). The overall agreement with experimental data is satisfactory, showing the capability of the model to catch the effect of the coal rank and the operating conditions.

The kinetic model of pyrolysis has been employed in the analysis of the char elemental composition in order to develop a global kinetic model of char heterogeneous reactions. The char elemental composition predictions have shown a good estimation of the experimental data, moistly under high heating rate conditions. The char heterogeneous mechanism is based on three different charry components with different composition and reactivity. This model considers not only the oxidation and gasification reaction but also the annealing reactions. The model reproduces well the main features of the char oxidation and gasification reactions, both in terms of reactivity and in terms of selectivity to CO/CO₂.

The complete mechanism of pyrolysis and oxidations has been applied in the study of single coal particle combustion in different mixture (O_2/N_2 and O_2/CO_2). In high temperature conditions the heat and mass resistance can become the rate determining step of the solid combustion. An opportune mathematical model has been developed to analyze the effect of the transport phenomena within the particle. Experimental measurements of coal particle life times and surface temperatures of a high-volatile bituminous coal and a lignite coal were performed in a drop tube furnace, under quiescent gas conditions. The model predictions show an overall good agreement with experiment data both in terms of particle life time and surface temperature. Moreover, the comparison with the experimental data shows the capability of the model to predict the effect of the background gas. The effect of the coal rank is also quite well predicted.

The CFD instruments offers the possibility to approach complex combustion system and to improve the efficiencies and to control the pollutant emissions. The direct coupling of detailed chemistry and CFD simulations is still prohibitive, moistly in the multi-phase reactive system. For this reason, two simplified kinetic models, one for the coal pyrolysis and one for the secondary gas phase reactions of volatile matter have been developed. These models, despite their simplicity, retain the predictive capabilities of the original detailed models as shown from the comparison both with experimental data and with the respective detailed model.

Finally, these models have been employed in a CFD study of an oxy-coal pulverized furnace through the use of commercial fluid-dynamics code. The models are able to catch the main behavior of the experimental data, even if in corresponding the first portion of the furnace the model underestimates the initial reactivity. It is important to underline that these experimental data show a partial unsubstantiality, as in the case of the experimental data of CO_2 and of temperature or as in the case of experimental data of velocity.

As highlighted in this activity, an important feature of the coal combustion is the correct coupling between solid and gas phase. Several simplifications have been introduced in this work and therefore, in a few cases, the agreement with the experimental data was not fully satisfactory. The development of a model based on an accurate description of the transport phenomena in both phases could overcome these approximations and consequently give better performances.

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Appendix A

A kinetic approach to the mathematical model of fixed bed gasifiers

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Abstract

This work presents a comprehensive mathematical model of a fixed bed gasifier, where heat and mass transport resistances and chemical kinetics are accounted for both at the reactor and the particle scale. A multistep kinetic model of devolatilization of solid fuels, such as coals, plastics, biomasses and wastes has been employed and validated. The kinetic model of refuse derived fuels (RDF) and wastes is simply based on a linear combination of the devolatilization models of its main constituents. Ligno-cellulosic and plastic materials, together with ash and moisture, allow to account for the high heterogeneity of RDF. Successive gas phase reactions of the released species are described with a detailed kinetic scheme. Furthermore, an accurate description of heat and mass transport between gas and solid phases allows the proper characterization of combustion and gasification of the solid fuel at the particle and reactor scale. The mathematical model of a counterflow fixed bed reactor is then applied first to discuss the importance of heat transfer resistances at the particle scale, then to describe coal and biomass gasification. This work summarizes several facets of this problem with validations and examples and it allows to evaluate feasibility and limitations of the proposed approach.

1. Introduction

The environmental apprehension towards the combustion of fossil fuels together with the growing concern on waste materials drive the interest in gasification processes of biomasses, coals, plastics, and refuse derived fuels (RDF). Pyrolysis and gasification of solid fuels are nowadays promising alternative to direct combustion, both electric and thermal energy are viable products, together with chemicals. Gasification is a robust proven technology that can be operated either as a simple, low technology system based on a fixed-bed gasifier, or as a more sophisticated system using fluidized-bed technology [McKendry, 2002]. The properties of the biomass feedstock and its preparation are key design parameters when selecting the gasifier system. Differences between fixed bed and fluidized bed gasifiers are discussed by Warnecke (2000). The mathematical description of such processes is rather difficult due to the complex phenomena involved, such as modelling solid devolatilization, gas-solid interactions and secondary gas phase reactions.

During last years, many efforts have been devoted to understand and describe gasification process. Gronli and Melaaen (2000) studied wood pyrolysis using a mono-dimensional model, devoting a particular attention both to kinetics and transport resistances inside the biomass particles. Thunman and Leckner (2005) explored the influence of particle size and fuel density during oxidation process in a fixed bed reactor. In particular they showed that inter- and intraparticle resistances, more important in bigger particles, lead to different temperatures inside the particles and between solid surface and gas phase. Also Yang et al. (2006) analyzed the importance of chemical and physical processes during gasification showing the influence of oxygen concentration, fuel ratio and process temperature. Di Blasi (2004) developed a comprehensive model able to describe wood gasification in a counter current flow reactor. Such a model is able to describe the dynamic behaviour of the system taking into account mass and thermal diffusion along the reactor. The density of the bed varies in the devolatilization region, while solid velocity is assumed constant. On the other side, during gasification and combustion solid velocity changes due to the reaction effect, while bed density remains constant. A one-dimensional model of countercurrent fixed-bed coal gasification has been developed and discussed by Hobbs et al. (1992). Solid velocity is there evaluated using continuity equation, bed density is kept constant and porosity varies with conversion. Finally, Corella et al. (2007) analyzed the economic feasibility of different biomass gasification processes.

It is then clear that this multiscale and multiphase problem does require a very careful attention in order to define and develop at least preliminary models. However, it is worth to emphasize the importance of these models, which could first improve the understanding of the whole process and then simplify the scale-up and the optimization of the gasifier. In this work, we proposed the methodology for solving such problems, showing the approach for the main facets

involved in solid fuels gasification. Finally, an application example of a fixed bed gasifier model is provided, emphasising the thermal features of the reactor as well as the role of feedstock characterization.

2. Devolatilization of Coals, Plastics, Biomasses and Refused Derived Fuels (RDF)

2.1. Solid fuel characterization

The different solid fuels are described with a limited number of reference compounds and for each of them a multistep kinetic scheme was developed. While plastics, such as poly-ethylene (PE), poly-propylene (PP) and poly-styrene (PS) have a very well-defined structure and composition, the available information about coals and biomasses is usually limited to the elemental composition in terms of C/H/O. Degradation of plastics was already discussed by [Marongiu et al., 2007]. On the contrary biomass and coal have less defined and regular structures and they require a more empirical approach or better they do require further simplifications and a more careful discussion.

Biomass composition, if biochemical analysis is available, is simply defined in terms of humidity, ash, cellulose, hemicelluloses and lignin. If only the elemental analysis is available, then a suitable combination in terms of reference species is derived by atomic balance [Ranzi et al., 2008]. Several applications, mainly concerning thermo-gravimetric analysis are there reported, while further validation examples relating bio-oil formation are reported in Calonaci et al. [2010]. Finally, syngas production from biomass gasification in an entrained flow reactor at high temperature is discussed in Dupont et al. [2009].



Figure 1: Lumped reference components of tar products from reference coals

Following a very similar approach, the composition and reactivity of the different coals are described by using three reference species (COAL₁, COAL₂ and COAL₃). COAL₁ ($C_{12}H_{11}$), together with pure carbon (CHARC), is useful to describe anthracitic coals with different degree of

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aromaticity. $COAL_2$ ($C_{14}H_{10}O$) lies in the middle of bituminous coals, while $COAL_3$ is highly oxygenated ($C_{12}H_{12}O_5$) and is representative of lignitic coals [Sommariva et al., 2010].

Thus, the novelty of this kinetic model, when compared with the majority of the available ones in the literature, is the effort to describe the devolatilization reactions with a lumped characterization of gas and tar released. Thus, Figure 1 shows the lumped reference components describing the primary tar species released by coal devolatilization. Operating conditions affect the devolatilization selectivity and yields; furthermore this multistep kinetic model allows also to describe the chemical and morphological evolution of the solid phase in terms of composition and reactivity.



Figure 2 Typical compositions of different RDF in terms of C and H (wt% ash free)

In a very similar way, waste material and Refused Derived Fuels (RDF), typically with heating values of 4500-5000 kcal/kg, are described in terms of a proper combination of plastic wastes (15-30%), lignocellulosic material (30-50%), ash, and humidity [Giugliano et al., 2008]. Figure 2 shows typical compositions of different RDF in terms of C and H (wt% ash free)

2.2 Solid fuel devolatilization

The RDF or the solid fuel particles are assumed as fixed mixtures of reference components. The overall kinetic model of devolatilization is simply the proper combination of the multistep devolatilization models of Biomass [Ranzi et al., 2008], plastic [Marongiu et al., 2007] and coal [Sommariva et al., 2010]. The peculiarity of this approach is that all these schemes consist of a limited number of devolatilization reactions, which are able to describe not only the solid residue, but also the detailed composition of released gas and tar species.

As already mentioned, approximate and elemental analysis allow to characterize RDF in terms of lingo-cellulosic species, plastics, ash and moisture. Buah et al. [2007] reported interesting TG data and they showed that the selection of particle size used needs a particular attention, due to
the variability of product yields depending on particle size. These differences could be attributed mainly at a different RDF composition, even if also intra-particle resistances, which strong depend on particle shape, could play a definite role.

Figure 3 shows the weight loss curves of RDF particles of two different sizes versus temperature during TG analysis at 10 K/min under nitrogen. Predicted curves are obtained by varying RDF composition for fine and coarse particles. Plastic content, responsible of the second devolatilization step at 400-500 °C, is higher in coarse particles, while ashes or inert materials are more abundant in fine particles.



Figure 3:Effect of RDF particle sizes on TGA at 10 K/min.[Buah et al., 2007].

This dependence of RDF composition on the particle size was also observed in terms of different heating value by Skodras et al. [2009]. They analyzed two RDF samples (RDF1 and RDF2) from different locations and processes with different elemental composition and heating values (Table 1).

dry basis	RDF1	RDF2
wt C	51.3	56.3
wt H	7.5	4.7
wt O	29.7	20.9
wt N	0.77	1.65
wt S	0.21	0.13
ASH	10.4	16.1
V (MJ/kg)	28.5	21.3

Table 1 Elemental analysis of RDFs [Skodras et al., 2009]

While Skodras expect about 30% of plastic materials, only 25% of plastic material in RDF1 allows explaining both the larger heating value of this sample and the second step in the TG curve of Figure 4a. RDF2 contains a larger amount of ligno-cellulosic material and less than 10% of plastics (Figure 4b).

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Figure 4: Experimental and predicted weight losses of RDF at 20K/min (Skodras et al.[8]).

3. Combustion and gasification reactions of residual char

The heterogeneous oxidation and gasification reactions of char are critical for the design of gasifier units [Di Blasi 2009]. The rate determining step in the gasifier is the conversion of the residual char, which influences both the dimensions and the dynamics of the reactor [Gobel 2007]. The gasification and combustion of char, i.e. the set of heterogeneous reactions of oxygen and steam with the solid residue coming either from coal, biomass or plastics, are responsible for the autothermic behaviour of the whole gasification process. These reactions and related kinetic parameters are summarized in Table 2 [Groeneveld and van Swaaij, 1980, Kashiwagi and Nambu, 1992].

Table 2: Char gasification and combustion reactions. Units are: kmol, m³, K, kcal, s.

Kinetic Reactions	Kinetic expression
$CHAR + O_2 \longrightarrow CO_2$	5.7×10 ⁹ exp (-38200/ RT) [O2] ^{0.78}
$CHAR + 0.5 O_2 \rightarrow CO$	5.7×10^{11} exp (-55000/ RT) [O2] ^{0.78}
$CHAR + H_2O \longrightarrow CO + H_2$	$7.9 \times 10^9 \text{ exp} (-52000/ \text{ RT}) [\text{H}_2\text{O}]^{0.7}$

4. Detailed kinetics of secondary gas phase reactions

The volatile components released during the pyrolysis undergo successive decomposition or combustion reactions in the surrounding gas phase. Different methods have been used to describe gas phase reactions; some authors (Gobel 2007, Chen et al 2010) use a thermodynamic or equilibrium approach, while others (Di Blasi 2004, Sharma 2010 in press) refer to global kinetics in the gas phase. As clearly stated by Li et al (2004), a pure thermodynamic or equilibrium approach is not able to properly predict the composition of the gas mixture in a gasifier. The equilibrium approach largely over predicts the heating value of flue gases; in particular, higher amount of hydrogen is predicted, while only trace amounts of methane and hydrocarbons are obtained. On this basis, it is clear the utility to develop a detailed or semi-detailed kinetic scheme for the gas phase. An existing kinetic scheme for pyrolysis and oxidation of hydrocarbon species, already validated in a wide range of operating conditions [Ranzi et al., 2001], has been extended to properly describe successive gas phase reactions of released species. Due to the modularity of the detailed kinetic scheme, it is only necessary to describe the primary initiation, decomposition and H abstraction reactions of the new species. The overall gas-phase kinetic model, together with thermodynamic properties, is available at the website http://creckmodeling.chem.polimi.it/.

The number of new species included in the gas phase is a compromise between accuracy and computational efforts, maintaining the ability of the model to describe the gas composition and reactivity in a wide range of operating condition: in particular tar species are grouped into pseudocomponents representative of a set of similar species with similar reactivity.

As already discussed in a previous paper [Sommariva et al., 2010], the secondary gas phase reactions can also explain relevant temperature and pressure effects during coal devolatilization, not only related to the solid phase reactions.

5. Mathematical model of fixed bed gasifier

The mathematical model of the fixed bed gasifier consists of two models. The first one at the particle scale and the latter at the reactor scale. This approach is discussed in details elsewhere [Pierucci and Ranzi, 2008; Dupont et al., 2009]. The particle model provides an internal description in order to account for intraparticle heat and mass resistances. The accuracy of this description depends on the number of discretization sectors (N). This feature becomes fundamental for the analysis of the gasification of thermally thick solid fuel particles. The equation 1 summarizes the main terms of material and energy balances for the particle:

$$\begin{cases} \frac{dm_{j,i}}{dt} = J_{j-1,i} - J_{j,i} + R_{j,i} \\ \frac{d\sum_{i=1}^{NCP} m_{j,i} Cp_{j,i} T_{j}}{dt} = JC_{j-1} + \sum_{i=1}^{NCP} J_{j-1,i} h_{j-1,i} - JC_{j} - \sum_{i=1}^{NCP} J_{j,i} h_{j,i} + HR_{j} \end{cases}$$
(1)

where *m* is the mass and *j* refers to the j^{th} particle sector and *i* to the i^{th} component. *t* is the time variable and *J* the mass flux (Fick and Darcy's laws contributions) and *R* the kinetic term. Analogously, the energy balance settle the particle temperature *T* and accounts for conduction contribution (*JC*) as well as the convective contribution (*Jh*). *HR* is the heat of reactions involved in the solid phase.

A critical feature is the proper definition of the transport properties, effective diffusivity and thermal conductivity inside the solid particle. Transport properties are, of course, also dependent on the solid composition and they can vary due to morphological changes during the conversion process. The model is flexible enough and it allows for the descriptions of these variations, together with the shrinking of the solid particles. This particle model together with the kinetic models previously described is embedded in the fixed bed reactor model (equation 2). The reactor is considered as a series of elemental units (Fig. 3) which exchange mass and heat to each others. The single unit accounts for gas-solid interactions with particular attention to the inter-phase resistances. The balance equations (2) refer to a perfectly stirred reactor in dynamic conditions, where $R_{g,i}$ are the gas phase reactions and $G_{0,i}$ and G_i are the inlet and outlet gas feeds [Pierucci and Ranzi, 2008; Dupont et al., 2009].

$$\begin{cases} \frac{dg_{i}}{dt} = G_{0,i} + J_{NR,i}\eta + R_{g,i} - G_{i} \\ \frac{d\sum_{i=1}^{NCP} g_{i}Cp_{i}Tg}{dt} = \sum_{i=1}^{NCP} G_{0,i}hg_{0,i} + \sum_{i=1}^{NCP} J_{NR,i}h_{NR,i}\eta + JC_{NR}\eta + HR_{g} - \sum_{i=1}^{NCP} G_{i}hg_{i} \end{cases}$$
(2)

The term $J_{NR,i}\eta$ refers to the gas-solid mass exchange $(J_{NR,i})$ multiplied by the number η of particles in the bed. Four terms contribute to gas phase temperature (Tg) evolution: the enthalpy convective terms (*Ghg*) between adjacent reactor layers, the gas-solid heat exchange $(J_{NR,i}\eta)$, the enthalpy diffusion term $(J_{NR,i}h_{NR,i}\eta)$, and finally the contribution due to gas phase reactions (*HR*_g). Proper boundary conditions at the particle surface, together with the evaluation of heat and mass transfer coefficients, allow estimating mass and heating fluxes between the solid particle and the surrounding gas phase. More than one thousand balance equations are obtained, when considering ~10-15 solid species, 100 gas-phase components, 10 reactor layers and 5 discretizations of the solid particle. The numerical problem is structured in tridiagonal blocks. The resulting ODE system is solved by using BzzMath Library (www.chem.polimi.it/homes/gbuzzi/).

6. Application examples

Two different application examples are discussed in this paper. The first highlights the role of heat transfer resistance at the particle scale, while the latter refers to a counterflow gasification unit fed with coal and with biomass.

6.1. Gas-solid interactions in biomass gasification

This first application example underlines the potential of the model of gas-solid interactions at the particle scale. A small gasifier volume (a single layer of 1 m² surface and 0.1 m height) is here analized. A solid fuel flow contacts a countercurrent air stream in this elemental volume, as shown in Figure 5. Solid fuel is simply constituted by cellulose particles containing 16 wt% of inert ashes.; a fuel equivalent ratio (Φ) equal 3, which is typical of gasifier units, is adopted.



Figure 5: Analysis of the gas-solid interaction: simplified reactor volume.

In this system it is possible to attain the ignited (hot) steady state condition or it is possible to maintain the cold (low) solution, depending on the starting policy. In order to analyze the stability of the hot solution when feeding solid fuel and air stream at 300 K, it is convenient to first heat up the system with a proper start-up policy. Thus, the air stream is initially fed to the system at high temperature (T_{ig}), until the solid particles and the reactor volume reach appropriate temperatures. When enough volatiles are released by the solid, then the gas temperature can become higher than Tig , because of gas-phase partial oxidation and combustion. At this time, the inlet air temperature is gradually reduced to 300 K and steady conditions are reached and observed. Initial air temperature and quenching rates are assumed as parameters in this starting policy. Fig. 6 shows an example of these start-up policies for biomass particles with an equivalent spherical diameter of 5 mm. Air stream is fed at 1400 K for ~3500 s: solid temperature rises according to heat transfer conditions. When bulk temperature clearly shows a gas ignition, the air feed temperature is cooled down to 300K in 300 s. Before this cooling, gas stream and fuel particles reach adequate temperatures to maintain the hot gasification conditions inside the reaction volume. Because of partial oxidation reactions of the released volatile products, bulk gas temperature reaches and maintains a steady state temperature of \sim 1400 K for more than 1000 s. The residue of solid fuel particles, constituted by char and ash, leaves the system at a very similar temperature. The product gases mostly contain CO, H₂, H₂O and CO₂ together with ~45% of N₂. Fig. 6b shows that these hot conditions are not reached when the cooling period is reduced to only 10 s. The system behavior is exactly the same until 3500 s, then the direct and sharp cooling of the air feed to 300 K does not allow to maintain the gasification conditions and the system stabilizes the cold solution. This preliminary example not only shows a policy to find the hot steady state, but it also shows that different solutions can be obtained modifying this start up policy.

The ignition and extinction conditions can be verified by gradually increasing both the solid and air flow rates, always maintaining $\Phi = 3$ and using the same start-up policy as in figure 6a. Depending on the dimension of the fuel particles, the hot gasification conditions can be reached and maintained only with flow rate lower than a critical value, i.e. low contact times are not compatible with a hot solution.



Figure 6: System evolution and steady-state conditions of gasification (a) hot solution; (b) cold solution.

Figure 7 shows this critical solid flow rate versus the particle diameter. The specific solid flow rate, expressed as a velocity [m/h], decreases with the increase of particle diameter. Thus, the critical flow rate of the 1 mm particles is ~0.4 m/h (with $T_{ig} = 1400$ K), corresponding to a nominal fuel contact time of 900 s.



Figure 7: Critical solid flow rate versus particle diameter.

While at low flow rate the particle temperature is practically uniform, significant internal temperature gradients appear for large particles at high flow rate, because of intra-phase thermal resistances. The typical thermal penetration time is related to the diameter (d_p) and the thermal diffusivity (α_p) of the solid particle: $\tau = d_p^2 / \alpha_p$. Thermal penetration times of several minutes are needed to heat up the core of fuel particles of a few centimeters.

Fig. 8 shows the steady gas and solid temperatures versus the specific solid flow rates for spherical 3 cm biomass particles. These steady-state results have been obtained with the previous start-up procedure, i.e. by feeding heated air at 1400 K until the gas temperature higher than 1450

K, due to ignition, then by decreasing the air temperature to 300 K in 300 s. Two different regimes are observed. At reduced flow rates, up to 0.5-1 m/h, corresponding to residence times of the fuel of several minutes, temperature gradients inside the particle are minor and a prevailing gasification regime is obtained. When flow rates increase, it is possible to observe a second regime of the system. Inter-phase and intra-phase thermal resistances clearly indicate that the partial devolatilization and gasification of the solid fuel progressively promotes a combustion regime with steady gas temperatures higher than 2000 K. Further flow rate increase results in a final extinction of the system. As already mentioned, the hot steady solution, if reached, is not depending on the start-up policy. On the contrary, different starting policies could produce different extinction limits always exhibiting the same gasification and the combustion regime.



Figure 8: Gasification and combustion regime of 3 cm particles. (Φ =3). Gas and fuel temperatures versus solid flow rate.

Both Table 3 and Fig. 8 are useful to clarify the different behavior of this system. At low flow rates (i.e. in the gasification regime), the whole particle is completely gasified at high temperature. Molar fractions of CO and H_2 in the effluents are significant, while only a minor amount of CO₂ is produced. A typical molar composition of the outlet gas stream is 10-12% H_2 , 10-12% H_2 O, 20-25% CO, 8-10% CO₂ in ~45% N₂.

The combustion regime progressively involves only a superficial and external heating of the fuel particle. As a consequence, the minor amount of the released gases with the same gasification air allows to complete the combustion process to form CO_2 and H_2O . In other terms, the equivalence fuel ratio in gas phase is lower than the nominal one. Fig. 9 shows this combustion regime (solid flow rate = 40 m/h): cellulose conversion and char formation is only observed in the external sectors of the particle. The core of the fuel particle remains at about 300 K. As a consequence, the gasification efficiency E_{Gas} (defined as the mass ratio between released gases and initial fuel) is very low and more than 50% of the fuel remains unconverted. Table 3 also reports

the Biot number $(Bi = h d_p/2 k_p)$ at different solid flow rate. As expected, Bi is higher in combustion regime, that is heat conduction inside the sold particle is the controlling phenomenon.

	Gasification	Combustion
	Regime	Regime
		\bigcirc
Biot Number	0.2	7
Gasification efficiency*	~99%	~40%
Gas products heating value [kcal/kg]	~1100	~ 0

Table 3: Summary and features of gasification and combustion regimes.

*Defined as the ratio between gasified mass and inlet solid flowrate

The temperature gradients (Figure 9) inside the fuel particle at high flow rates reduce the mass of volatile products and correspondingly reduce the apparent fuel/air ratio. Gas phase reactivity and exothermic reactions to form CO_2 are promoted with a progressive attainment of the combustion regime with gas bulk temperatures higher than 2000 K.



Figure 9: Intra-particle analysis in the combustion regime (particle diameter 3 cm).

The presence of gasification or combustion regimes demands for careful numerical simulations. These features are relevant not only for the proper modeling of the whole gasifier, but could also provide useful information for the complete analysis of the transient behavior of industrial units.

7. Countercurrent moving bed gasifier.

The simple application involving one single layer has been extended to a multi-layers problem. This feature allows to simulate the bed behavior both in transient conditions and steady state solution. It is noticeable that the simultaneous interactions between layers are accounted for conferring further nonlinearity to the problem. Figure 10 show the dynamic evolution of gas phase 166

temperatures in the reactor bed obtained with a ten-layers and counter-flow configuration. The complexity of such a system is evident when compared the interactions between the layers due to heat transfer. While a lower level is cooling (due to the ignition policy), the successive layer respond to the disturbance given by the convective flow. The steady-state solutions are then obtained and then discussed with two different case studies. It is important to notice the complexity of the system which involves more than 2000 differential and non linear equations depending on the number of gas phase and solid phase species, particle sectors, and layers. The numerical complexity of the simulation has been handled by exploiting the block tridiagonal structure of the Jacobian.



Figure 10: Time evolution of gas and solid temperatures in the gasifier.

In order to speed up transient simulation, the reactor initial conditions have been changed. In fact, hot initial conditions avoid all calculation of gas-solid heat transfer. In this manner, steadystate solution are more easily obtained. The solutions obtained with *hot* initial conditions are the same compared to those obtained with the procedure described in the previous paragraph. Furthermore, a restart procedure has been developed to avoid transient calculations.

Figures 11 and 12 show the predicted gas and solid temperature profiles of a countercurrent fixed bed gasifier fed with coal and biomass respectively. Solid particles of 3 cm are treated with air at equivalence ratio 0.25-0.4 and with steam/fuel ratio of about 0.30 wt/wt.

Typical contact times of gases are of a few seconds while several hours are necessary to treat solid particles. The model characterizes the solid and gaseous streams, giving a proper emphasis to secondary gas phase reactions of tar and gas components. Typical molar composition of flue gases is about 11-15% of H₂, 13-17% of CO, 10-12% of CO₂, 15-20 % of H₂O and ~1-3% of CH₄ and hydrocarbons.

Maximum gas phase temperature is higher when treating biomasses, due to the largest extent of volatilization and the highest oxygen availability. Large temperature gradients are predicted in the first top layers of the bed. Char combustion in the third layer from the top of the gasifier justifies the maximum internal temperature of coal particles (~1100 °C), while this effect is less evident when biomass is treated in the gasifier, due to the lower presence of residual char. Depending on the ash content in the solid fuel, the shrinking of the bed is usually rather larger than 50%.



Figure 11: Counter-current fixed bed coal gasifier. Predicted gas and solid temperature profiles.



Figure 12: Counter-current fixed bed biomass gasifier. Predicted gas and solid temperature profiles.

These simulations require several hours of CPU time, due both to the stiff nature of the gas phase kinetics and to the dynamic approach to the steady solution. For these reasons a more complete model validation strongly demands for further simplifications in the solid and gas phase description.

8. Comments and conclusions

A mathematical model of a fixed bed gasifier has been developed giving particular emphasis to the kinetics of devolatilization and gas phase reactions. The devolatilization models of solid fuels have been also validated on the basis of thermogravimetric experiments. This model constitutes a prototype towards the characterization of complex multiphase and multiscale problem, where solid fuel devolatilation together with a detailed gas phase kinetic scheme interact at the particle and the reactor scale. Some applications of the model have been extensively discussed both at the level of a single stage as well as at the scale of the gasifier unit. Future works require to validate the proposed model at the reactor scale and the main difficulty lies in the scarcity of reliable experimental data.

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Appendix B

A Chemical Approach to Biomass Gasification

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This paper describes GASDS, a comprehensive model of a biomass gasifier on a travelling grate. This general mathematical model deals with the complex multiphase gas-solid problem of biomass gasification both at the reactor and the particle scale. Mass and energy balances plus proper closure equations describe the behavior of both the phases. Key elements of the model are the detailed kinetic schemes describing the biomass volatilization, including the formation of TAR species and char, and the secondary gas phase as well as the heterogeneous reactions. The model has been already tested and validated on semiquantitative basis in comparisons with a 12 MW biomass combustor operating in Belgium. In this paper, the model is extended and compared to recent experimental data obtained in a biomass regenerative gasifier. The comparison with experimental data highlights the role of devolatilization, mass transfer phenomena, and mainly the kinetics of char gasification in controlling system's reactivity and syngas composition. An alternative configuration for biomass gasification is also presented and discussed. It is based on three different steps, including biomass pyrolysis through the convective heating of a syngas recycle stream, followed by the oxidation of volatile products (gas and tar compounds) with an air/steam mixture and a final char gasification. The advantage of the proposed configuration lies in the direct oxidation of the released tars to form the hot stream used for char gasification.

Keyword: detailed kinetics, biomass gasification, syngas production

1. Introduction

Biomass fuels are a very important energy resource and are gaining an increasingly important role worldwide as a widely diffused, available, and renewable energy source. Besides coal, oil, and natural gas, the fourth largest source of the global primary energy is constituted by biomass that is of key interest mainly in developing countries [1-3].

Different technologies can be applied to biomasses: some technologies are used to produce heat and power based on direct firing of biomasses and co-firing with coal. In other cases the interest is towards the biomass upgrading, to obtain liquid, solid and gaseous products. In fact, gasification allows to convert the raw biomass into gaseous products, which can be employed in many applications: fuel for firing or co-firing, gas for engines, turbines, fuel cells and for successive synthesis of liquid fuels or chemicals [4,5].

The main reactors employed in the thermal treatment of biomass are fixed bed, fluidized bed, entrained flow and moving bed or traveling grate-fired system. Fixed bed reactors can have counter-current or co-current configurations.

An important characteristic of grate-fired system is the fuel flexibility and the possibility to work with raw biomasses. In fact, grate-fired boilers are not as sensitive to bed agglomeration, which limits the performances of fluidized bed reactors. This is an important advantage in the case of biomass combustion and gasification, since biomass fuels often have low ash melting temperatures. Modern grate-firing systems cannot be considered a mature technology, since they can be further developed and optimized in order to increase the efficiency, the applicability and to reduce the pollutant emission [6].

Chemical kinetics as well as inter and intra-phase heat and mass transfer processes play an important role in biomass pyrolysis, gasification and combustion. The crucial issues in gasification process are first the heating of the biomass particles, then their pyrolysis and devolatilization with the release of gas and tar components, finally the gasification of the residual char. To fully characterize this multicomponent, multiphase and multiscale problem, a comprehensive mathematical model of biomass pyrolysis and gasification needs to include:

- a lumped kinetic model of biomass devolatilization
- a detailed kinetic model of secondary gas phase reactions of released, volatile products
- a mathematical model at the particle scale to account for intraphase heat and mass transfer resistances, as well as heterogeneous reactions,
- a mathematical model at the reactor scale to account both for the interphase resistances and for the contact time distribution of the solid and gas phases inside the reactor.

2. Comprehensive Modelling of a Grate Gasifier

Mathematical models of gasification and combustion of solid fuels are present at various sophistication levels. For given operating conditions, a simple mass and energy balance model, together with appropriate thermodynamic and constitutive equations easily predicts temperatures and fuel gas composition. Since several years [7], it is well recognized that a comprehensive and detailed kinetic model of the entire process is required both to correctly determine the biomass conversion and to characterize the location of the maximum temperature, or the transient behavior of the fuel bed. In fact, thermodynamic models (for assigned conditions) can simply predict the exit gas composition, but they cannot be used for reactor design [8]. For these reasons, the developing of a comprehensive model is necessary to take into account not only detailed kinetics mechanism of homogeneous and heterogeneous chemical reactions, but also the heat and mass transfer phenomena between solid and gas phase [9].

A comprehensive model of biomass conversion on the grate needs to approach this multiphase gas-solid problem both at the reactor and the particle scale. Under typical gasification or combustion conditions upon a grate, biomass fuel particles could exhibit relevant internal temperature and mass gradients which affect the whole decomposition and burning characteristics [10]. The Biot number ($Bi=h\cdot dp/k$, where h is the external heat transfer coefficient, k the thermal conductivity and dp the diameter of the solid particle) is a useful ratio to evaluate the extent of the temperature gradients. In combustion and gasification conditions, particles exhibits significant Biot number (Bi>1), and then important temperature gradients are present. Gradients of temperature, solid fuel composition and gas concentrations both inside and outside the particles need to be predicted by the model, provided that the proper balance equations and boundary conditions are assumed. External boundary conditions are non-uniform and 3-D gradients are present inside the particles. Assuming isotropic particles and using an equivalent spherical diameter, it is possible to describe the problem in 1-D spherical coordinate.

Figure 1 shows a schematic representation of the gasifier. This is a slightly modified arrangement of a previous biomass combustor [11]. At the reactor scale, the bed on the grate is assumed to be stationary and a vertical stack of several biomass particles, depending on the bed height, form a slice of the bed. The dynamic solution along both the bed height and the grate length can be converted into a 1D time-dependant solution, with reference to the travelling speed of the grate. This approximation is acceptable for biomass decomposition and gasification/combustion on a travelling grate, due to the relatively small horizontal gradients in temperatures and species concentration [12-14].



Figure 1: Schematic representation of a Gasifier Unit.

A recycle stream of hot syngas is fed under the grate and flows through the vertical stack of particles. Each stack of the moving bed is opportunely simulated through a cascade of well stirred ideal reactors where the gas phase and solid particles are assumed to be perfectly mixed in each layer, as shown in Fig. 2. Generally, the fuel bed is heated by radiation from the furnace walls until it devolatilizes and partial oxidation and combustion takes place in the freeboard region. The height of the bed shrinks during the devolatilization and gasification process. The progressive heating in the bed determines the releases of volatiles, and affect the heat output from the grate.

The model has to describe the temperatures profile, species concentration, and velocity at the top of the fuel bed. Moreover, this information is used as inlet and closure conditions for the modelling of the secondary gas phase decomposition and combustion in the freeboard zone.



Figure 2: Schematic representation of the single reactor layer with solid fuel particles (left) and the vertical stack of elementary reactors on the grate (right).

The comprehensive and detailed kinetic model discussed in this work takes into account heat-up, drying, pyrolysis and devolatilization of the fuel particles with char formation, heterogeneous combustion and gasification reactions, and homogeneous gas-phase pyrolysis and oxidation reactions of tar and gaseous species. The next section is dedicated to present the kinetic models used for the solid and gas phase reactions.

3. Kinetic Models

A comprehensive kinetic model, which attempts to tackle the complex, multiscale, multiphase problem of biomass conversion in the fuel bed on the grate, needs to analyze heat and mass resistances both at the particle and the reactor scale. Apart from the heating and drying of fuel particles it is necessary to include the following kinetic processes:

- 3.1- Biomass pyrolysis and devolatilization reactions
- 3.2- Char reactivity
- 3.3- Secondary gas-phase reactions and tar decomposition

The next three paragraphs give a brief summary of the main characteristics of these kinetic models.

3.1- Biomass Pyrolysis and Devolatilization Reactions

A simplified, though representative, description of biomass composition is usually given in terms of proximate analysis (moisture, ash, fixed carbon and volatile matters), elemental analysis (C/H/S/N/O) or biochemical analysis (cellulose, hemicellulose and lignin together with extractives, either in water and ethanol or toluene). Heating value of biomass fuels increases as increases lignin content. Biomass will be characterized here in terms of the three major components: cellulose, hemicellulose and lignin, together with inert ashes and moisture. Cellulose is a regular polymer, consisting of a linear chain of glucose units. Hemicellulose is a polysaccharide, derived mainly from glucose and xylose, consisting of shorter and branched chains. Lignin is a more complex polymer with branched and random structures, mainly derived from three monomers: p-coumaryl, coniferyl and sinapyl-alcohols [15]. When biochemical analysis is available, it is possible to directly derive biomass composition in terms of cellulose, hemicellulose, lignin, moisture, and ash content. Alternatively, if only elemental analysis in terms of C/H/O content is available, then a suitable combination of the reference species (cellulose, hemicellulose and lignin) is simply derived from the three atomic balances. Products from biomass pyrolysis are then obtained with a direct combination of the pyrolysis products from the three major components separately. Details on this approach were already reported in Ranzi et al. [16]. Hemicellulose breaks down first, at temperatures of 450-550 K. Cellulose follows in the temperature range 500-620 K, while lignin components pyrolyze in a wider temperature range: 500-770 K. Cellulose, hemicellulose, and lignin decompose, release gases, and/or form intermediate components that are released and/or involved in substitutive additions and cross-linking reactions with a progressive charification of the solid residue. Levoglucosan (LVG) and hydroxyl-acetaldehyde (HAA) are typical cellulose decomposition products. Xylan is formed by hemicellulose. Phenol and phenoxy species are typical products of lignin decomposition. Typical organic compounds constituting complex bio-oil mixtures are methanol, formic, acetic and propionic acids, acetone, alcohols, aldehydes, hydroxypropanone and -butanone, furfural, methoxy- and dimethoxy-phenols [17, 18].

Table 1 summarizes the full detail of the multi-step devolatilization model, including the reaction heat.

Reactions	Kinetic constant [s ⁻¹]	$\Delta H^0_{\ r}$	
Cellulose			
$CELL \rightarrow CELLA$	8×10 ¹³ exp (-46000/RT)	107	
$CELLA \rightarrow 0.95 \; HAA + 0.25 \; Glyoxal + \; 0.2 \; C_2H_4O + 0.25 \; HMFU + 0.2$	1×10^9 ave (20000/BT)	215	
$C_{3}H_{6}O \ + \ 0.16 \ CO_{2} + 0.23 \ CO + 0.9 \ H_{2}O + 0.1 \ CH_{4} + 0.61 \ CHAR$	$1 \times 10^{-50000/K1}$	213	
$CELLA \rightarrow LVG$	4×T exp (-10000/RT)	175	
$CELL \rightarrow 5 \text{ H}_2\text{O} + 6 \text{ CHAR}$	8×10 ⁷ exp (-32000/RT)	-260	
Hemicellulose			
HCE $\rightarrow 0.4$ HCE1 + 0.6 HCE2	$1 \times 10^{10} \exp(-31000/\text{RT})$	131	
$HCE1 \rightarrow 0.75 H_2^{*+} 0.8 CO_2 + 1.4 CO + 0.5 CH_2O + 0.25 CH_3OH +$			
0.125 H ₂ O + 0.125 C ₂ H ₅ OH + 0.625 CH ₄ + 0.25 C ₂ H ₄ + 0.675 CHAR	$3 \times 10^9 \exp(-32000/\text{RT})$	116	
$HCE1 \rightarrow .25 H_2^* + .25 H_2O + .8 CO_2 + .65 CO^* + 1.5 COH_2^* + 25CH4 +$			
+.375C2H4+.675 CHAR	0.15×T exp (-8000/RT)	135	
$HCE1 \rightarrow XYLAN$	3×T exp (-11000/RT)	169	
$\mathrm{HCE2} \rightarrow 0.2 \; \mathrm{CO_2} \; + \; 0.5 \; \mathrm{CH_4} + 0.25 \; \mathrm{C_2H_4} + 0.8 \; \mathrm{CO_2}^* + 0.8 \mathrm{COH_2}^* + 0.7$	$1 \times 10^{10} \exp(-22000/\text{PT})$	67	
$CH_{2}O+0.25\ CH_{3}OH\ +0.125\ C_{2}H_{5}OH+0.125\ H_{2}O+CHAR$	$1 \times 10^{-33000/R1}$	02	
Lignine			
$ \begin{array}{l} LIG\text{-}C \rightarrow 0.35 \ LIGCC \ + \ 0.1 \ COUMARYL + \ 0.08 \ FENOL + \ 0.41 \ C_2H_4 + \\ H_2O + \ 0.495 \ CH_4 + \ 0.32 \ CO + \ COH_2 * + 5.735 \ CHAR \end{array} $	4×10 ¹⁵ exp(-48500/RT)	144	
$LIG-H \rightarrow LIGOH + C_3H_6O$	2×10 ¹³ exp(-37500/RT)	125	
$LIG-O \rightarrow LIGOH + CO_2$	$1 \times 10^{9} \exp(-25500/\text{RT})$	122	
$\label{eq:ligcc} LIGCC \ \rightarrow 0.3 \ COUMARYL + 0.2 \ FENOL + 0.35 \ C_3H_4O_2 + 0.7 \ H_2O +$	-	60	
$0.65 \ CH_{4} + 0.6 \ C_{2}H_{4} + COH_{2} * + 0.8 \ CO * + 6.4 \ CHAR$	$5 \times 10^{\circ} \exp(-31500/\text{RT})$	09	
$LIGOH \rightarrow 2 \; H_2O + 1.45 CH_4 + .7 C_2 H_4 + 10.15 \; CHAR + .5 \; H_2* + 1.8 \; CO* + 1.015 \; CHAR + .5 \; H_2* + 1.015 \; H_2* \; H$	1 10 ² (15000/DT)	30	
4.2 COH ₂ *	$1 \times 10 \exp(-15000/RT)$	50	
$LIGOH \rightarrow LIG + H_2O + CH_3OH + 0.45 CH_4 + 0.2 C_2H_4 + 1.4 CO^* + 0.6$	$3 \times 10^8 \exp(-30000/\text{PT})$	24	
$COH_2^* + 0.1 H_2^* + 4.15 CHAR$	3×10 exp(-30000/R1)		
$LIG \rightarrow FE2MACR$	12×T exp(-12000/RT)	138	
$LIG \rightarrow H_2O + 0.5 \text{ CO} + 0.2 \text{ CH}_2O + 0.4 \text{ CH}_3OH + 0.2 \text{ C}_2H_4O + 0.2$	1×10^9 avp(20000/ PT)	-50	
$C_{3}H_{6}O + 0.6 CH_{4} + 0.65 C_{2}H_{4} + CO^{*} + 0.5 COH_{2} + 5.5 CHAR$	1×10 exp(-30000/ K1)		
Metaplast			
$\mathrm{CO}_2^* \to \mathrm{CO}_2$	$1 \times 10^{5} \exp(-24000/\text{RT})$	0	
$CO^* \rightarrow CO$	$1 \times 10^{13} \exp(-50000/\text{RT})$	0	
$CH_4 * \rightarrow CH_4$	$5 \times 10^{13} \exp(-50000/\text{RT})$	0	
$H_2 * \rightarrow H_2$	$5 \times 10^{11} \exp(-50000/\text{RT})$	0	
$\rm COH_2 \rightarrow \rm CO + \rm H_2$	$5 \times 10^{11} \exp(-71000/\text{RT})$	0	

Table 1: Kinetics of biomass devolatilization

The heavy volatile species involved in the kinetic model are lumped-species and they represent a mixture of similar or analogous species with the given average chemical formula. The major features of this devolatilization model, including detailed comparisons with experimental measurements, are reported elsewhere [4,16].

a. Char reactivity

The heterogeneous oxidation and gasification reactions of the residual char are critical for the design of combustion and gasifier units [19]. The gasification and combustion of char, i.e. the set of heterogeneous reactions of oxygen and steam with the solid residue are responsible for the thermal behaviour of the whole process. The residual char formed from biomass pyrolysis is highly reactive, mainly because of its high porosity. The physical and chemical properties of the original biomass, as well as the pyrolysis conditions influence the morphology and the reactivity of the char residue. Table 2 summarizes the reference kinetic parameters for the combustion and gasification of the biochar obtained from biomass [20-22]. The kinetic parameters of oxidation reactions agree with the ratio CO_2/CO suggested by Tognotti et al. [23].

Table 2: Char gasification and combustion reactions. Units are: kmol, m³, K, kcal, s.

Kinetic Reactions	Kinetic expression
$CHAR + O_2 \longrightarrow CO_2$	$1.2 \ge 10^{10} \exp (-32300/\text{RT}) \cdot [\text{Char}] \cdot [\text{O}_2]$
$CHAR + 0.5 O_2 \rightarrow CO$	$2.5 \text{ x } 10^{11} \text{ exp } (-38200/\text{RT}) \cdot [\text{Char}] \cdot [\text{O}_2]^{0.78}$
$CHAR + H_2O \longrightarrow CO + H_2$	2.5 x 10 ⁹ exp (-52000/RT)·[Char] ^{0.5} ·[H ₂ O] ^{0.70}

3.3 Secondary Gas-phase Reactions

Volatile components released by biomasses are subject to successive gas-phase pyrolysis [24] and/or oxidation reactions [25-27] in the freeboard zone.

The number of species included in this homogeneous kinetic scheme is a compromise between accuracy and computational efforts, maintaining the ability of the model to describe the gas composition and reactivity in a wide range of operating conditions: in particular tar and heavy species are grouped into pseudo-components representative of isomers or analogous species with similar reactivity. The complete kinetic model, in CHEMKIN format, together with thermodynamic properties of all involved species, is available on the website [28].

4. Particle And Reactor Models

The model solves energy and mass balance equations for gas and solid phases, together with empirical sub-models used for the closure of the balance equations. Devolatilization is a primary process by which the biomass produces residual char, tar and other heavy species and permanent gaseous products. Released volatiles from biomass particles first mix with the surrounding gas-phase in the packed particle bed, only then enter the freeboard zone over the travelling grate. Rate of volatiles release depends on the biomass size and temperature gradient within the particles. Solid fuel bed on the grate is assumed as a stack of several layers. The model presented here considers gas and solid temperature and species profiles not only in the bed but also inside the single particles. Thus, the mathematical model of the whole combustor or gasifier consists of two models: the first one at the particle scale and the latter at the reactor scale. This approach is a further extension of previous models discussed, applied and validated elsewhere [11, 20, 29, 30].

4.1 Particle models

4.1.1 Properties of the Solid Particles

Lautenberger and Fernandez-Pello [31] emphasized the importance of material property estimations. Temperature dependencies of thermophysical properties of initial and intermediate solid species are assumed, but combustion and gasification models are not on the whole very sensitive to these temperature dependencies [19, 32]. As the particle is heated and pyrolised, different gaseous and condensed species are formed. Thermophysical and effective properties of the residual solid particle vary with conversion and are calculated by properly weighting the local compositions.

During the thermal conversion of biomass, also the size and porosity of the individual particles change, not only due to drying and devolatilization but mainly due to char gasification and combustion. Porosity is a property of each condensed phase species and is again calculated as weighted porosity with the local composition. Char porosity significantly varies with the fuel conversion, and is estimated on the basis of empirical correlations. These variations are taken into account within the model of the single particles and also within the model of each layer of the entire bed. Therefore, the model accounts for particle and bed shrinkage during biomass conversion.

4.1.2 Mass and Heat Balances at the Particle Scale

The particle model provides the internal description in order to account for intraparticle heat and mass transfer resistances, assuming isotropic particles. The accuracy depends on the number (N) of discretization sectors. This feature becomes fundamental for the analysis of the gasification (and combustion) of thermally thick solid fuel particles. The heat conduction along the radius of the particle is calculated by solving the heat diffusion equation. Similarly, internal

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gradients of volatile species are calculated by solving the corresponding continuity equations. Assuming N sectors inside the particle, the model equations refer to the mass (solid and gas phase) and energy balances around each particle sector:

$$\left\{ \frac{dm_{j,i}^{S}}{dt} = V_{j} \cdot R_{j,i} \\
\frac{dm_{j,i}}{dt} = \left[J_{j-i,i} \cdot S_{j-1} - J_{j,i} \cdot S_{j} \right] + V_{j} \cdot R_{j,i} \\
\frac{d\sum_{i=1}^{NCP} m_{j,i}^{S} c_{p,i}^{S} T_{j}}{dt} = \left[JC_{j-1} \cdot S_{j-1} - JC_{j} \cdot S_{j} \right] + \left[S_{j-1} \cdot \sum_{i=1}^{NCP} J_{j-i,i} h_{j-i,i} - S_{j} \cdot \sum_{i=1}^{NCP} J_{j,i} h_{j,i} \right] + V_{j} \cdot HR_{j}$$
(1)

where $m_{j,i}^{s}$ is the mass of the ith solid-phase component and $m_{j,i}$ is the mass of the ith volatile component in the jth particle sector, *t* is the time variable, and Vj and Sj are the volume and external surface of the jth particle sector, respectively. *J* are the diffusion fluxes, possibly including also Darcy's contribution. Mass exchange between adjacent sectors are only allowed for volatile species. $R_{j,i}$ is the net formation rate of the ith component resulting from the multistep devolatilization model and from the heterogeneous gas-solid reactions. The energy balance settles the particle temperature T and accounts for the heat conduction (*JC*), the enthalpy flux relating to the mass diffusion (*J*·*h*), and the reaction heat (*HR*). The density profile along particle radius is calculated as the sum of all the densities of different species present in each particle sector. Similarly, the shrinking and porosity of each sector, and of the whole particle, is calculated. Mass and heat diffusion terms inside the particle follow the constitutive Fick and Fourier laws:

$$\begin{cases} J_{j,i} = -D_{j,i}^{eff} \cdot MW_i \frac{dC_i}{dr} \Big|_{r_j} \\ JC_j = -k_j^{eff} \cdot \frac{dT}{dr} \Big|_{r_i} \end{cases}$$
(2)

where $D_{j,i}^{\text{eff}}$ and k_j^{eff} are the effective diffusion and conduction coefficient inside the particle. At the external surface, these terms are replaced by the flux exchanged with the bulk phase:

4.2- Reactor Modeling

The reactor model is divided into two different parts. First there is the biomass pyrolysis in the fuel bed and then there are the secondary gas phase reactions in the freeboard where special attention has to be paid to the effective mixing in order to improve combustion and minimize pollutant emissions.

The particle model together with the kinetic models previously described are embedded in the stationary model of the travelling grate gasifier. As already mentioned and shown in Fig.1 and 2, the grate movement is converted into a one-dimensional time-dependant solution and the fuel bed on the travelling grate is described by a vertical slice of the bed constituted by a stack of 179 dynamic ideal reactors, where both gas phase and thick solid particles are assumed as perfectly stirred. Then, the reactor model requires to describe the freeboard zone, where gas phase reactions describe the decomposition of the released tar species and the combustion of flue gases.

The whole reactor is considered as a series of NR elemental reactors that can exchange mass and heat to each others (Fig.2). The single unit accounts for gas-solid interactions with particular attention to the inter-phase resistances, assuming complete mixing for both the gas and the solid phase. The height of each bed layer is of the same order of biomass particles, to properly account for vertical dispersion phenomena. It is recognized that the mixing of the main gas flow is further increased due to the energy provided by the volatile species released from the particles during the solid degradation, they increase the turbulence in the system, especially at low air flows through the bed [33]. Furthermore, the movement of the grate promote a partial vertical mixing of fuel particles [14, 34]. The gas phase mass and energy balance equations refer to the cascade of perfectly stirred reactors in dynamic conditions. As a matter of simplicity, the reactor index (from 1 to NR) is not reported in these balance equations:

$$\begin{bmatrix}
\frac{dg_i}{dt} = \left[G_{IN,i} - G_{OUT,i}\right] + J_{N,i} \cdot S_N \cdot \eta + V_R \cdot R_{g,i} \\
\frac{d\sum_{i=1}^{NCP} g_i C_{P_i} T_g}{dt} = \left[\sum_{i=1}^{NCP} G_{IN,i} \cdot h_{g_{N,i}} - \sum_{i=1}^{NCP} G_{OUT,i} \cdot h_{g_{OUT,i}}\right] + \\
+ \sum_{i=1}^{NCP} J_{N,i} \cdot h_{N,i} \cdot S_N \cdot \eta + JC_N \cdot S_N \cdot \eta + V_R \cdot HR_g
\end{cases}$$
(3)

 $G_{IN,i}$ and $G_{OUT,i}$ are the inlet and outlet gas streams, and η is the number of fuel particles in the reactor volume (V_R). $R_{g,i}$ stands for the net formation of *i* species from the whole secondary gas phase reactions. The terms $J_{N,i}$ refers to the gas-solid mass exchange and is multiplied by the number of particles in the reactor. Four terms contribute to the evolution of gas phase temperature (T_g): the enthalpy associated to inlet and outlet streams ($G \cdot h_g$), the gas-solid heat exchange (JC_N ,) and the enthalpy diffusion term ($J_{N,i}$ · $h_{N,i}$), both multiplied by the number of particles, and finally the overall heat contribution due to gas phase reactions (HR_g).

Volatile components released by the bed of solid fuel on the grate, together with primary and secondary air or gas streams entering the whole reactor, go through secondary gas phase decomposition and/or oxidation reactions in the freeboard volume over the solid bed. A proper design and distribution of secondary jets of air and steam assure the proper mixing in this freeboard zone. Usually, the homogeneous reactions in the burnout zone are not sensitive to the bed pyrolysis and devolatilization process due to the high-speed flow from secondary jets [14, 35]. While the simplest model is constituted by an ideal perfectly stirred reactor, reactor network arrays constitute a simple and feasible option [11]. Depending on the complexity of this network, the simulation of the freeboard zone could directly moves towards fluid-dynamics computations. The biomass decomposition model describes the release and velocity of volatile species at the top of the fuel bed. These information are used as inlet and closure conditions for the modeling of the secondary gas phase decomposition of tar and combustion in the freeboard zone. Given the biomass, air and steam flowrates the model predicts the species concentration, temperature, and velocity of the flue gases entering the freeboard as well as the hot gases involved in the char gasification process. Finally the splitting of the syngas, its recycle to the solid bed, the preheating of the inlet air/steam close the mass and energy balances.

Simple radiation heat transfer is considered on the top of the biomass bed and temperature and composition of the syngas recycle are obtained in an iterative way. In fact, in order to close the whole energy balance on the gasifier unit, the gases (burned or oxidized) in the freeboard region need to supply the proper heat to the furnace walls in order to justify the assumed temperature distribution and the radiation terms in the balance equations.

4.3 Numerical models

GASDS program is used for the solution of the multi-phase problem of biomass devolatilization, gasification and combustion, while DSMOKE program is used for the secondary gas-phase ideal reactor calculations [36]. The numerical problem is structured in tridiagonal blocks. The resulting ODE/DAE system is solved by using BzzMath Library [37].

5. Comparison with experimental measurements

The biomass kinetic scheme, coupled with the reactor model, has been already used to simulate biomass thermal degradation, to analyze the gasification and combustion regimes of biomass particles, to study the fast pyrolysis to form bio-oil and the syngas production in an entrained flow reactor, and finally to simulate and control a travelling grate combustor [4, 11, 16, 20, 30].

In this work, the validation is further extended using recent experimental data relating to a regenerative gasifier of woody biomass (pine) [38]. This experimental device is equipped with ceramic honeycomb and four-way valves, which allow to preheat the air used for biomass gasification, thus promoting the gasification temperature and the reactivity of the system. Due to the vertical geometry and the transverse air/syngas flow, the system is certainly characterized by a complex non stationary fluid dynamics. Nevertheless, due to the cross-flow of air/syngas (horizontal flow) and biomass (vertical movement, from the feeding mouth to the ash outlet) we simulated this system using GASDS code. A relatively large syngas recycle ratio has been used in the numerical simulations. Of course, this structure differs from the real gasifier unit of Ran et al. [38] especially because the tar compounds, formed during the biomass devolatilization, are

completely oxidized in the freeboard region. The heat released in the freeboard oxidation zone is then used for the char gasification step which requires relatively high temperatures. In this way, tar species are not condensing or troubling the overall process. Figure 3 shows a schematic view of the process arrangement. The biomass pyrolysis and gasification is realized in different steps:

- 1. biomass heating and pyrolysis through the hot stream of syngas recycle.
- 2. oxidation of volatile products (tar and gas released compounds) with the air/steam mixture.
- 3. char gasification by the hot stream from the tar/volatile oxidation.
- 4. Splitting and partial recycle of hot syngas to step 1.



Figure 3: Process alternative for a biomass gasifier. The air/steam stream is pre-heated using the hot syngas stream.

Table 3 shows the elemental composition of the pine biomass and the assumed reference components. The biomass components (cellulose, hemicellulose and different lignins) are evaluated following the same approach already discussed in Ranzi et al. [16].

Elemental Composition (% w, ar)				
С	Н	0	MOIST.	ASH
44.84	5.56	39.63	1.80	8.17
	Bio	omass Refere	nces (%, daf)
CELL	HECELL	LIG	LIGH	LIGO
40.87	22.2	3.41	22.97	0.05

Table 3: Elemental composition of the pine biomass and reference biomass components.

Figure 4 shows a comparison amongst experimental data [38], model predictions and the thermodynamic equilibrium results.

The comparison highlights the ability of the model to predict the experimental trend, in particular for H_2 and CH_4 . The equilibrium model is not able to predict any CH_4 formation and significantly overestimates the formation of H_2 . A discrepancy between experimental data and model predictions is evident especially for the N_2 data. This deviation, being N_2 an inert species, is due to the incomplete conversion of the biomass and the significant presence of tar components in the gas phase. For this reason, in the experiments, the N_2 profile is almost independent on the equivalence ratio. The incomplete fuel conversion (tar and char) explains also the unexpected trend of CO and CO₂ profiles. In fact, CO decreases with decreasing of the ratio of Air and Stoichiometric Air, while CO₂ increases. It is also possible to observe a deviation between the equilibrium N_2 value and the prediction obtained using the GASDS code. The difference, which is significant especially at very rich conditions, is due to the incomplete char gasification. At rich conditions, the temperature of the freeboard oxidation zone decreases, thus limiting the char gasification process



Figure 4: Comparison amongst experimental data [38], model predictions (solid lines), and equilibrium calculations (dotted lines).

To describe the complex behavior of this system, it is necessary to take in account a detailed model, able not only to consider the kinetic in gas and solid phases but also to describe the effect of transport phenomena at the particle scale. The ability of the detailed model to better reproduce the reactivity of the system allows to improve the predictions especially at very rich conditions. Moreover, this model also allows to evaluate the effect of the operating conditions and residence time on the grate (incomplete char conversion). It is important to notice that a reliable model able to predict the biomass gasification rate is required to design and control the equipment.

6. Sensitivity analysis

The GASDS code allows to investigate the effect of the operating conditions as well as of biomass composition, solid phase geometry and properties. A sensitivity analysis to some of these parameters is discussed in the following, referring to this base and reference condition:

Biomass Elemental Analysis: C/H/O = 63/6/31

- Mass Air/ Biomass = 2.8
- Mass Syngas Recycle/ Air = 1.3

Figure 5 shows an example of the model output. The solid residue shows a first and relatively fast pyrolysis step, followed by a slow char gasification process.

The rate determining step is the char gasification process, as highlighted in figure 5a and 5b. In fact, the biomass devolatilization is completed after a few minutes, while the char gasification requires significantly more time (char conversion is still incomplete after 2500 s). The gas phase bulk temperature is shown in figure 5c. The bottom biomass layer is heated by the hot syngas recycle stream and therefore it is heated before the upper layers. The temperature peak observed in the figure 5c represents the adiabatic temperature of the partial oxidation in the freeboard zone. In this region, the volatile tar and gas species are oxidized with the preheated stream of air and steam.

As schematically shown in figure 3, the high temperature gases of the freeboard zone are used for the successive gasification of the residual char. Figure 5d shows the mole fraction of H_2 and CO in the top and bottom layer along the time. The initial and fast release of the species trapped in the metaplast is evident, at about 500-550 s, while more time is required to complete the char gasification.



Figure 5: Model prediction in the base conditions: (a) Solid Residue; (b) Char mass fraction into difference layers; (c) bulk temperature; (d) mole fraction in the bottom and top layers for H_2 (line) and CO (dotted line).

A sensitivity analysis has been done in order to evaluate the influence of relevant process parameters such as:

- 1. Syngas recycle
- 2. Steam/Air ratio

3 Air/ Biomass ratio

Figure 6 shows that, in comparison to the baseline condition, the steam addition has a positive effect. It increases not only the char gasification rate but also H_2 production. The syngas recycle has two competing effects: it favors the biomass devolatilization but, at the same time, reduces the freeboard temperature and thus decreases the char conversion and the formation of H_2 and CO. Decreasing the mass Air/Biomass ratio causes a lowering of the hot stream temperature and thus an increase of the solid residue. This negative effect on char gasification can be reduced increasing the Steam/air ratio, as highlighted in figure 6.



Figure 6: Effect of relevant process parameters on the mole fraction of several gaseous species.

7. Conclusion

A comprehensive mathematical model of biomass gasification and combustion on a travelling grate has been presented and validated on the basis of very recent experimental data. The experimental comparison highlights the necessity to take into account both transport phenomena and a detailed kinetic mechanism for a careful characterization of the gasification process, especially in terms of CH_4 and H_2 formation and incomplete conversion of thick particles of the solid fuel.

An alternative configuration of the gasifier, based on biomass devolatilization followed by the partial oxidation of tar and volatile components and residual char gasification is also proposed. The main advantage of this process alternative is the complete conversion of volatile pyrolysis products into gaseous compounds. The model showed that the char gasification is the rate determining step, because it requires high temperatures and relatively long contact times. Moreover, the increase of the syngas recycle reduces and controls the hot gas temperature, with negative effects on char gasification. On the other hand, steam injection favors both the gasification process and H₂ production.

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Nomenclature

C_i	$[\text{kmol/m}^3]$	gas concentration of component i	
$C_{pj,i}$	[kj/ kg K]	heat capacity of component i^{th} in the sector j	
d_p	[m]	particle diameter	
$D^{e\! f\! f}_{j,i}$	$[m^2/s]$	effective diffusivity of component i^{th} in the sector j	
g_i	[kg]	mass of component i^{th} in the gas phase	
$G_{IN,i}$ []	kg/s]	inlet gas streams of component i^{th}	
$G_{OUT,i}$	[kg/s]	outlet gas streams of component i^{th}	
HR	[kj/ m ³ s]	Reaction heat	
h _{ext}	[kj/ m ² s K]	gas-solid heat transfer coefficient	
$h_{j,i}$	[kj/ kg]	specific enthalpy of component i^{th} in the sector j	
$k_j^{e\!f\!f}$	[kj/m K s]	effective thermal conductivity of sector <i>j</i>	
k _{ext}	[kg/s]	as-solid mass transfer coefficient	
$J_{j,i}$	$[kg/m^2 s]$	mass flux of component i^{th} exiting the sector j	
JC_j	[kj/ m ² s]	conductive flux exiting the sector <i>j</i>	
JR_N	$[kj/m^2 s]$	radiative heat flux at the particle surface	
$m_{j,i}^S$	[kg]	mass of the i^{th} solid-phase component in the j^{th} particle	
$m_{j,i}$	[kg]	mass of the i^{th} volatile species in the j^{th} particle sector	
MW	[kg/kmol]	molecular weight	
Ν	[-]	number of sectors inside the particle	
N_R	[-]	number of reactors in the vertical stack	
r	[m]	particle radius	
$R_{g,i}$	$[kg/m^3 s]$	mass production of component i due to gas phase reactions	
<i>R_{j,i}</i> [k	$g/m^3 s$]	net formation rate of the i^{th} component from heterogeneous reactions	
S_j	[m ²]	external surface of the j^{th} particle sector	
t	[s]	time	
Т	[K]	temperature of the solid particle	
T_g	[K]	temperature of the gas phase	
V_{j}	[m ³]	volume of the j^{th} particle sector	
V_p	[m ³]	particle volume	
V_R	[m ³]	reactor volume	
η	[-]	number of particles in the reactor volume	
3	$[m^{3}/m^{3}]$	bed void fraction	

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