

# Generalized Simulation Tools for Coal, Biomass and Organic Waste Gasification Processes

Sauro Pierucci, Eliseo Ranzi, Flavio Manenti

Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta", Piazza Leonardo da Vinci 32, 20133 Milano, Italy  
[flavio.manenti@polimi.it](mailto:flavio.manenti@polimi.it)

This article describes modelling and simulation advances for the gasification systems. The generalized approach pursued in developing the models allows to characterize the main phenomena involved in the gasification process of coal, biomass and organic wastes. Actually, multi-scale, multi-phase, and multi-component systems are described by means of complex kinetic mechanisms for gas-solid phases and by first-principles dynamic modelling of non-ideal reactors of different types (e.g., downdraft, updraft, traveling grate). Catalytic effect of ashes is considered too in the case of coal gasification. The tools have been validated on literature data. The abovementioned tools have been used not only for design verification and operational optimization purposes, but also to assess and define radically new processes and technological solutions. The case of novel low-emission gasification process is broached in the paper.

## 1. Introduction

The gasification of coal, biomass and organic waste is an attractive way to efficiently exploit the energetic content of solid fuels in a greener fashion. Beyond direct applications in the power generation field (Tola et al., 2014), the syngas produced from this kind of processes could provide an interesting platform for the production of fuels and chemicals with a lower environmental footprint (Li et al., 2014). Actually, several Gas-to-Liquids technologies are available for the production of hydrocarbons, e.g. Fischer-Tropsch fuels (Pirola et al., 2014) and oxygenated chemicals, e.g. methanol (Manenti et al., 2013) and dimethylether (Ng et al., 1999). For these applications, it is crucial to focus the attention on the quality of the syngas produced, mostly in terms of  $H_2/CO$  ratio (Chen et al. 2012). In fact, the downstream catalytic processes typically need to be fed with a syngas with a proper composition, usually in the range of  $H_2/CO \approx 1-2$  (Manenti et al. 2011). For this reason, it is of the utmost importance to be able to predict the performance of a gasifier, not only in terms of the overall efficiency but also in relation to the chemical composition of the syngas produced.

Several papers propose mathematical models in order to better understand the complex phenomena occurring in gasifiers, with an interest towards the design, simulation, optimization and process analysis of the gasification processes. These papers mainly refer to mathematical models based on thermodynamic equilibrium and/or strongly simplified kinetics (Bassyouni et al., 2014). This approach has the advantage of being independent on reactor design, assuming a zero-dimensional perfectly mixed reactors at uniform temperatures. Gasification reaction rates are supposed to be fast enough to reach the equilibrium state, but they are not able to give information on reaction intermediates and formation of tar components (Soltani et al., 2015). The novelty of the proposed approach, consists in a greater chemical detail of the pyrolysis and devolatilisation process of coal and biomass, considering a large number of lumped tar and gas species. In fact, both for coal and biomass feedstocks a multi-step kinetic model for the pyrolysis of solid fuels was developed and embedded within the particle model, along with gas-solid reactions of char gasification and secondary gas-phase reactions of the released volatiles (Ranzi et al., 2014). The chemical evolution of the system is predicted with a mechanistic approach, and it is thus possible to infer the behaviour of gasification units also in case of scarce experimental data availability. An additional comparison is made between the responses of the two different kind of solid fuels keeping constant the

geometry of the gasifier and the energy flux associated with the solid feed stream. With respect to coal gasification, biomass gasification occurs at lower temperatures, due to the higher reactivity of the feedstock. On the other hand, biomass is more heterogeneous and difficult to characterize, leading to a demanding flexibility of reactors and processes. Authors also provide some comparisons of the model predictions with the experimental data on the available literature in order to validate the consistency of our approach for both biomass (Di Blasi et al., 2011) and coal (Grieco et al., 2011) gasification.

Finally, it's known that Hydrogen sulfide ( $H_2S$ ) and carbon dioxide ( $CO_2$ ) are two of the most critical chemical by-products discharged by gasification process (Maffei et al., 2012). Despite their massive production, they do not represent a major feedstock or commodity for subsequent industrial purposes. Then, they are pollutants and the venting to atmosphere, when admissible, leads to environmental issues; otherwise, expensive neutralization processes must be adopted (Manenti et al., 2012). Nonetheless, despite his bad reputation,  $H_2S$  is quite an interesting chemical since it contains a highly noble species, the hydrogen. Consequently,  $H_2S$  should deserve more attention than to be considered just a waste and then oxidized in Claus plants to obtain elemental sulfur and water. The new technology (Pierucci et al., 2014) presents three principle advantages: the recycle of acid gas (i.e low  $H_2S$  emissions), the reduction of  $CO_2$  that is vent into atmosphere and the production of  $H_2$  and  $CO$  that is economically appealing. Therefore, this technology can be used not only for coal gasification, as in this case, but also for all chemical process in which there are acid gases, such as hydrodesulfuration.

## 2. Description of the mathematical model

### 2.1 Characterization of the solid fuel

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 polyethylene, 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. Therefore, biomass and coal 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 (Ranzi et al. 2014). If only the elemental analysis is available, then a suitable combination in terms of reference species is derived by atomic balance (Ranzi et al. 2012). For this reason three mixtures of the reference components (cellulose, hemicellulose, and lignin) are proposed, and the biomass feedstock is characterized as a linear combination of these reference mixtures. The first is a molar mixture of 60 % cellulose and 40 % hemicellulose, while the remaining ones are mixtures of the kinds of lignin (80 % LIGO + 20 % LIGC, and 80 % LIGH + 20 % LIGC). Following a very similar approach, the composition and reactivity of the different coals are described by using three reference species (COAL1, COAL2 and COAL3) (Sommariva et al 2011). COAL1 ( $C_{12}H_{11}$ ), together with pure carbon (CHARC), is useful to describe anthracitic coals with a different content of aromatics. COAL2 ( $C_{14}H_{10}O$ ) lies in the middle of bituminous coals, while COAL3 is highly oxygenated ( $C_{12}H_{12}O_5$ ) and is representative of lignite coals. 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.

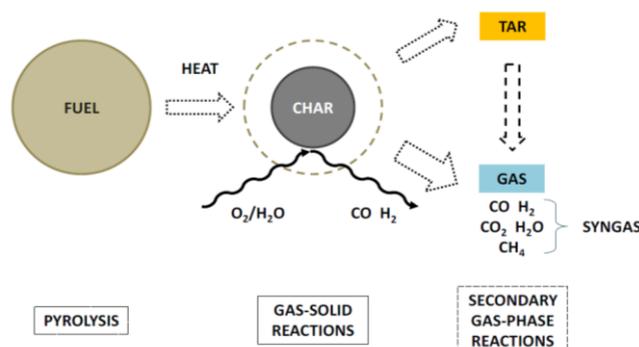


Figure 1: Solid fuel devolatilisation and gasification

## 2.2 Kinetic Model

During the gasification process, the chemical evolution of the system has been described by means of detailed kinetic schemes for solid fuel devolatilization and pyrolysis, residual solid (char) gasification with steam, CO<sub>2</sub> and oxygen, and finally, secondary gas phase reactions, as outlined in Figure 1. At first, the solid fuel, either biomass or coal, is heated up until devolatilization and pyrolysis occur. During this first stage the solid fuel is progressively converted to three main product groups: light gases, tar species and a residual solid, mainly composed by ashes and char, with a residual content of volatiles trapped within the porous matrix (i.e. metaplastic phase). In the model, this stage is described using the multi-step kinetics reported in (Ranzi et al., 2014) for biomass pyrolysis and in (Sommariva et al., 2011) for coal pyrolysis. After this first step, the carbonaceous residual solid is partially subject to gas-solid gasification reactions with steam and oxygen, with the preferential production of carbon monoxide and hydrogen. Moreover, volatiles, especially heavy tar species, as soon as are released in the gas phase, are cracked to lighter gaseous species through gas-phase secondary reactions (Ranzi et al., 2012).

## 2.3 Reactor Model

To model and simulate the gasification process, a suitable particle and reactor model is mandatory for the description of both kinetic and transport phenomena aspects. This leads to the solution of a multi-scale dynamic system, spanning from the description of kinetic and transport aspects at the particle scale, up to the description of mass and energy transfer as well as secondary reactions at the reactor scale (Ranzi et al., 2014). To further increase the complexity, the system is intrinsically multi-phase, due to the combined presence of gas, liquid and solid phases, which can exchange mass and energy. The structure of the system is outlined in Figure 2, where it is possible to highlight the presence of three main scales.

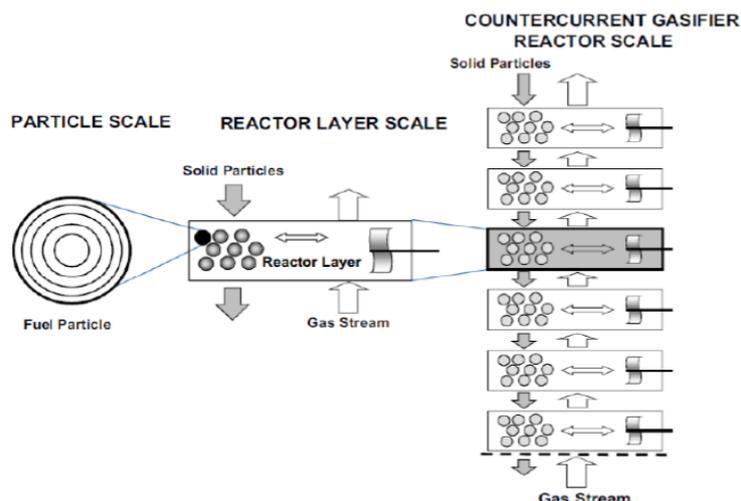


Figure 2: Multi-scale gasifier

At the particle scale, the system evolves along the radial coordinate, as well as through time. The intra-particle mass and heat transfer resistances are simply described by assuming an isotropic sphere. The particle is discretised into several sectors to characterize the temperature and concentration profiles, and the dynamic behaviour of the particle under pyrolysis, gasification and combustion regimes. The gradients of temperature and volatile species inside the particle are evaluated by means of the energy and continuity equations, respectively.

The successive scale (elementary reactor layer) accounts for the coupling between isotropic solid particles with an external gas phase, considered homogeneous and perfectly mixed. Finally, at the reactor scale, several elementary reactor layers are adopted and interconnected to reproduce different reactor configurations. For instance, the counter-current fixed bed gasifier (i.e. updraft) is reproduced through a cascade of elemental reactor layers. The height of each layer is of the same order of the size of the biomass particle, accounting for the vertical dispersion phenomena. The complete mixing inside the layer both for the gas and for solid phase is assumed. In fact, the mixing of the main gas flow is further increased because of the energy provided by the volatile species released from the particles during the biomass pyrolysis (Frigerio et al., 2008). In this configuration, which has been selected for the successive studies below in the paper, the solid fuel is fed from the top of the reactor where it encounters a rising gas stream, fed from the bottom of the tower. During the residence within the gasifier, particles are

progressively dried, pyrolyzed and gasified, leading to a residual solid stream withdrawn from the bottom and to a gas stream rich in hydrogen and carbon dioxide exiting from the top. The complete set of model equations is provided elsewhere (Ranzi et al., 2014).

### 2.4 Model sensitivity to the catalytic effect of ash

In order to improve the agreement of model results and experimental data, it is necessary to analyze and empirically include the ash catalytic effect. As already mentioned, several experimental data clearly confirm their catalytic activity on steam gasification of charcoal in these operating conditions (Kospel et al., 1990). This effect is considered by simply reducing the activation energies of the steam gasification reactions of the different pseudo-components characterizing the residual char. Due to the low temperatures, the annealing effects are negligible and only CHARH and CHAR are available for the following gasification reactions (Maffei et al., 2013):



## 3. Results and Model Validation

The mathematical model has been validated with some available experimental data from the scientific literature, mainly in terms of gas composition ( $\text{H}_2/\text{CO}$  ratio).

Following the partial validation of the model, a comparison has been performed between coal and biomass gasification, keeping constant in the two case studies both the gasifier geometry and the inlet solid energy flux (in terms of heating value multiplied by the mass flow rate). The complete summary of the simulation of coal gasification is reported in Figure 3 (Ravaghi et al., 2015). In the following Table 1 we summarize the main results and comparisons between the two different simulations for coal and biomass gasification.

Table 1: Comparison between coal (Grieco et al., 2011) and biomass (Di Blasi et al., 2011) gasification experimental data and model prediction

	Coal			Biomass		
	Exp	Model	Deviation	Exp	Model	Deviation
$\text{H}_2/\text{CO}$	0.58	0.70	-0.12	0.24	0.36	-0.12
$\text{CO}_2$	4.1 % dry	4.60	-0.54	7.0 % mol	8.2 % mol	-1.20
$\text{CH}_4$	1.4 % dry	0.00	1.30	1.8 % mol	2.0 % mol	-0.20

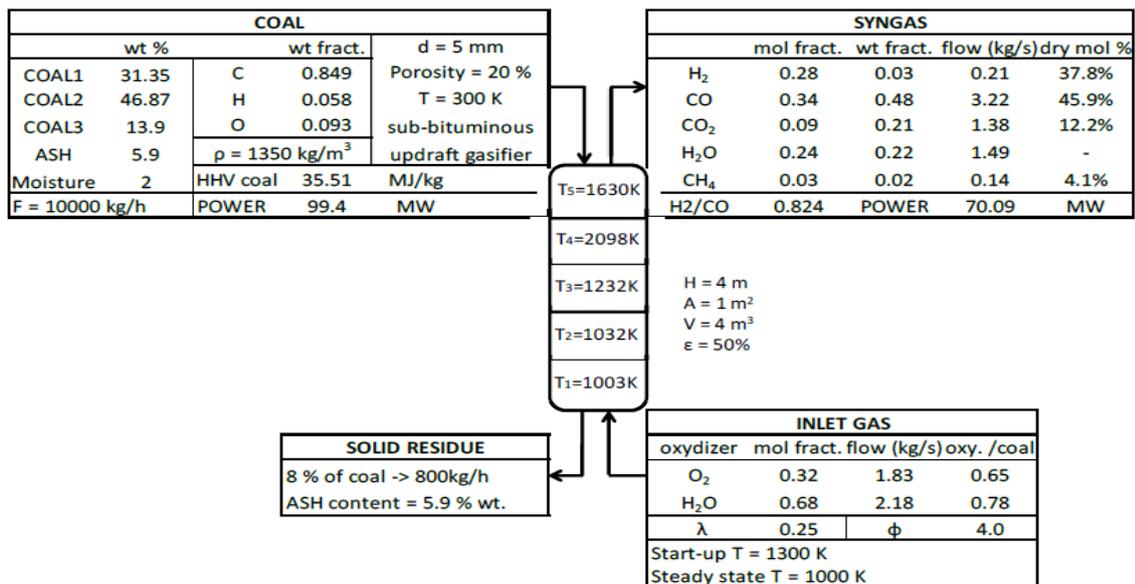


Figure 3: Summary of the coal simulation

#### 4. Innovative coal gasification process

In this section, the overall layout of the novel coal gasification process presented in the introduction is discussed. The process is simulated with the use of an industrial plant simulation software: Aspen HYSYS. A Peng-Robinson equation of state is used for the entire process except for the amine wash section where is used the amine package, included in Aspen HYSYS. Figure 4 shows a simplified BFD of the novel process.

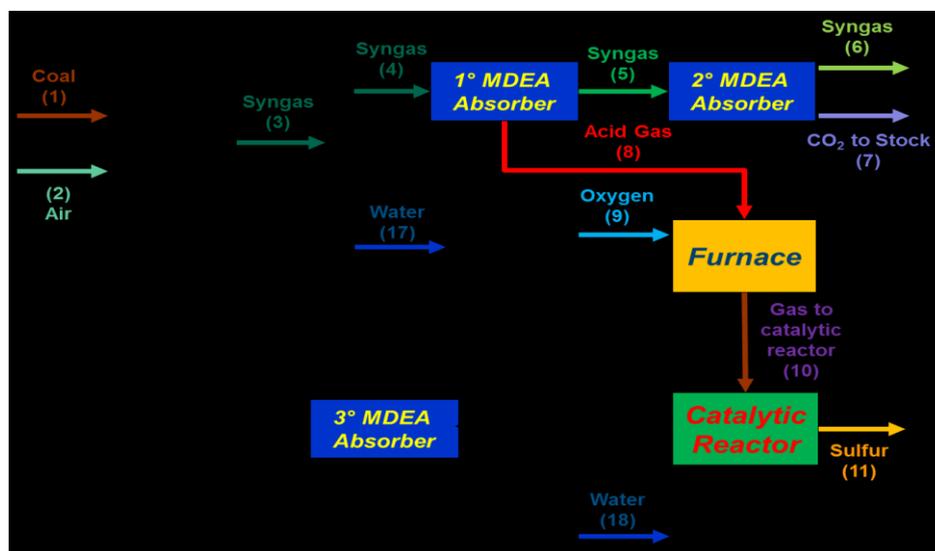


Figure 4: Process layout

The case study simulation, developed in this work, is built up starting from a syngas stream coming from the gasification section (Table 3). This is a typical composition of coal gasification products launching from Texaco basic layout with a high sulphur flow rate, e.g. 9.5 % mol/mol.

The surplus syngas produced deserves a special mention. In fact, the comparison between the input syngas with the output syngas should be made with the amount of syngas "clean" obtained from the same amount of initial syngas (Table 3), making one wash that allows to completely remove acid gases (traditional process).

Table: 3 Syngas stream composition coming from coal gasification section

	$X_{CO}$	$X_{H_2}$	$X_{CO_2}$	$X_{H_2O}$	$X_{CH_4}$	$X_{Ar}$	$X_{N_2}$	$X_{H_2S}$	$X_{COS}$	$X_{O_2}$	$n_{tot}$ [kmol/h]
Syngas from Coal Gasification (3) – vapour	0.19	0.13	0.09	0.55	0.00	0.00	0.00	0.03	0.00	0.00	3,375.68

Other relevant results are reported in Table 4. In particular, is important to highlight that in the outlet syngas stream is not present  $H_2S$ .

Table: 4 Simulation results of the main amine wash section ( $x_n$  is mole fraction,  $n$  = species)

	$X_{H_2}$	$X_{H_2O}$	$X_{CO}$	$X_{N_2}$	$X_{O_2}$	$X_{CO_2}$	$X_{H_2S}$	$X_{SO_2}$	$X_{COS}$	$X_{CS_2}$	$n_{tot}$ [kmol/h]
Syngas to 1 <sup>st</sup> amine wash (4) - vapour	0.28	0.00	0.40	0.00	0.00	0.25	0.06	0.00	0.00	0.00	1,635.40
Acid Gases from 1 <sup>st</sup> amine wash (8) - vapour	0.00	0.05	0.00	0.00	0.00	0.50	0.41	0.00	0.03	0.00	226.48
Syngas to 2 <sup>nd</sup> amine wash (5) - vapour	0.32	0.00	0.46	0.01	0.00	0.21	0.00	0.00	0.00	0.00	1,416.37
CO <sub>2</sub> to Stock (7) - vapour	0.00	0.05	0.00	0.00	0.00	0.94	0.00	0.00	0.00	0.00	269.58
Syngas Out (6) - vapour	0.39	0.00	0.56	0.01	0.00	0.04	0.00	0.00	0.00	0.00	1,156.01

## 5. Conclusions

We outlined a multiscale mathematical model for the simulation of solid fuels thermochemical conversion processes. The novelty of this approach relies on a kinetic modelling approach, which can characterize, with a reasonable detail, also the devolatilisation and pyrolysis steps, as well as the secondary gas phase reactions. A future development, related to kinetic scheme, is the possibility to improve the prediction of sulphur species formation, starting from the initial approach proposed by Maffei et al. (2012). This model has been here applied to the gasification process of biomass and coal, considering the updraft fixed-bed reactor. Comparisons with experimental data show the viability of the approach although some further comparisons should be done in order to improve the reliability of the model. Finally, is presented a novel process for conversion and treatment of acid gases (in particular H<sub>2</sub>S) coming from coal gasification.

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