Development of an integrated procedure for comprehensive gasification modelling

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1. Introduction

Biomass gasification is an attractive process to convert a solid fuel into a gaseous product. Although gasification is a relatively old process, the versatility of the process (with production of syngas, electricity, hydrogen or chemicals) and the multiplicity of technological solutions (fixed beds, moving beds, fluidized beds and entrained flow reactors) make it a current topic of investigation. In spite of all these differences, most process studies in the literature modeled the gasifier as an equilibrium reactor (see for instance [1]). This approach is indeed fundamental for a preliminary study but hardly suitable for process analysis and optimization procedures. A detailed approach allows the operating conditions to be related with a heat balance and introduce a thermal profile. Also by-products in the syngas (e.g., CH₄ and CO₂) and residual char and tar, that are generally underestimated in equilibrium models, can be quantified on the basis of the operating conditions. Finally, a detailed model can simulate each step of the gasification according to the gasifier configuration for the specific optimization. Therefore a “gasifier model” should be developed instead of a “gasification model”. So, the aim of this work is the development of a procedure for modeling different gasifiers and show some examples of gasifier models.

2. Development of the modelling procedure

A general procedure is developed to represent different gasifiers as multizonal models. The main points are summarized here and discussed in the next sections along with some examples for different reactors:

- definition of the functional scheme of the gasifier;
- separation of the characteristic steps of solid fuel gasification (devolatilization, oxidation, gasification of the char, homogeneous reactions and tar cracking);
- development of sub-models of each step (by adapting conventional blocks of the software or implementing specific models);
- connection of all steps to respect material and heat balances according to the gasifier configuration.

A pyramidal approach is developed dividing the phenomena occurring in the gasifier on different levels (Fig. 1). On the first one the evaluation of the heat and mass transfer phenomena at the molecular level is based on the operating conditions and allows the initial reactions to be described. The pyrolysis model is the basic step of all gasification models and is known to depend strongly on the operating conditions and fuel characteristics. The homogeneous reactions are fast and connected to the previous evaluations.
Heterogeneous reactions (involving the solid char particle) are the controlling step of the entire system and are studied on a second level as the consequent transformations involve the particle (size variation, fragmentation, ash distribution and porosity evolution phenomena). Diffusion of gasifying agents (O₂, H₂O, CO₂), kinetics of char reactions, diffusion of gaseous products should be represented in a realistic model (considering intra-particle phenomena) to take into account the variation of the conditions during the gasification. Gas-particle interactions, gas and solid fluid-dynamic, solid-solid interaction should be studied on a reactor level by considering the reactor configuration. Also the heat transfer on a macro-scale (e.g., presence of heat transfer surfaces) can be described only once the geometry of the gasifier is defined. Finally the gasifier model should be validated with experimental data. Lab-scale reactors can be used to validate decoupled sub-models on molecular and particle levels. Pilot-scale and large-scale gasifiers can be used to validate the entire models.

The main sub-models will be described in the following sections for the reacting steps. All models are developed using Aspen Plus® in view to be linked to other unit models for studying different processes in global models. The same procedure will be applied to other codes (gPROMS for a downdraft reactor and Aspen HYSYS® for an entrained flow gasifier).

3. Description of main sub-models

All reactive sub-models are represented as Kinetic Reactors (Plug Flow Reactor or Continuous Stirred Tank Reactor depending on the reactor configuration). Different thermal options (adiabatic, constant temperature, thermal profile) can be set for the heat transfer according to the reactor configuration. The list of all reactions is given in Table 1.

3.1. Devolatilization sub-model

The first reacting step of the biomass is the devolatilization. It is a thermal decomposition that produces a solid residue (char, that will be the reactant in the following gasification reactions), a condensable organic product (tar) and the main gaseous species. No conventional block can represent this step in any commercial codes. Here, a structural model (ABCD Advanced Biomass and Coal Devolatilization model [2]) is used for the biomass devolatilization. The ABCD model gives the yield of macro-products and the speciation of gases once the fuel composition and the operating conditions are given.

![Fig. 1 Pyramidal approach for gasifier modelling.](image)

<table>
<thead>
<tr>
<th>Devolatilization reactions</th>
<th>Combustion reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>fuel → char + tar + light gas</td>
<td>volatile combustion: H₂ + ½ O₂ → H₂O CO + ½ O₂ → CO</td>
</tr>
<tr>
<td></td>
<td>CH₄ + 2O₂ → CO₂ + 2H₂O C₂H₄ + 3O₂ → 2CO₂ + 2H₂O</td>
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<tr>
<td></td>
<td>char oxidation: C (char) + ½ O₂ → CO</td>
</tr>
<tr>
<td></td>
<td>tar oxidation: (tar) + 17/2 O₂ → 6CO₂ + 5H₂O</td>
</tr>
<tr>
<td>Gasification reactions</td>
<td></td>
</tr>
<tr>
<td>char gasification: C (char) + H₂O → CO + H₂ C (char) + CO₂ → 2CO C (char) + 2H₂ → CH₄</td>
<td></td>
</tr>
<tr>
<td>tar reforming: (tar) + H₂O → 6CO + 6H₂</td>
<td></td>
</tr>
<tr>
<td>methane reforming: CH₄ + H₂O → CO + 3H₂</td>
<td></td>
</tr>
<tr>
<td>water gas shift: CO + H₂O → CO₂ + H₂</td>
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</tr>
</tbody>
</table>
3.2. Tar reactions sub-model
The quantification of the tar is a fundamental issue in gasification models to define the quality of the produced syngas, the downstream cleaning units and the end-use of the process. Therefore it is important to develop a global model that allows one to study the optimal conditions to limit the tar formation or enhance the tar destruction. The tar is formed during the pyrolysis step and is destroyed in the subsequent steps: tar cracking, oxidation or reforming. The tar from biomass is here represented as levoglucosane (C$_6$H$_{10}$O$_5$) that is the monomer of cellulose, while anthracene (C$_{14}$H$_{10}$) represents the tar from coal. In all cases, a power law expression is used for the reaction rate (like the other homogeneous reactions).

3.3. Heterogeneous reactions sub-model
Heterogeneous reactions are modeled assuming the unreacted core-shrinking model. Both the diffusion and kinetic transfer coefficients are considered for all heterogeneous reactions:

$$r_j = \frac{c_j}{k_D + k_R} \cdot A_S$$

where $c$ is the concentration of the j-th species (O$_2$, H$_2$O, CO$_2$, H$_2$), $k_D$ is the diffusion coefficients that takes into account the mass transfer to the particle, $k_R$ is the reaction coefficient (that has the Arrhenius form) and $A_S$ is a surface factor that depends on the external surface area of the particle and varies during the reaction.

Different sets of kinetic parameters can be found in literature for combustion/gasification systems. Every set was validated and thus can be applied in a specific range of operating conditions. In this work, kinetics of combustion and gasification are divided in two ranges:
- range 1, for room pressure and relatively low temperatures (800-1200 °C) [3,4];
- range 2, for high pressure (20-40 bar) and high temperature (1200-1600°C) [5].

4. Development of gasifier models
The development of different gasifiers (Fig. 2) are discussed in this section.
The scheme of a downdraft gasifier is shown in Figure 2a. After the heating of the biomass, a Yield Reactor (DECOMP) represents the devolatilization step, that gives the pyrolysis macro-products (with the speciation of light gases) balancing the moisture and ash content of the biomass. The pyrolysis products are then mixed with the gasifying agents to feed the reactor block (H-REACT) in which all the above equations of combustion, gasification and tar-cracking are modelled in a PFR configuration. The temperature is calculated from the heat balance of the system (with a design specification on the MIXHEAT block).
The second gasifier is a circulating fluidized bed (Fig. 2b) that is fed with oxygen and steam in the riser. The high temperature and heating rate allow one to consider the devolatilization step completely separated from the combustion and gasification reactions. The hydrodynamics of the fluidized beds is modeled by following the considerations on a fluidized bed combustor model exposed in [6]. The reactor bed is divided in two regions:
- a dense lower region with a constant suspension density (turbulent fluidized bed);
- a more dilute upper region with an acceleration zone and a fully developed zone.

The lower region is represented by a single CSTR, while a series of CSTR with decreasing voidage is used to take into account the solid fraction variation in the upper region. Another important topic is to determine the conditions for the fast fluidization of the beds. An iterative
Fig. 2. Sketch of the gasifiers studied and relative scheme for modeling
procedure is implemented to assure the proper superficial velocity by varying the recirculation gas flowrate. Iterations are necessary because variations in the fluidization gas recirculated causes variations in the syngas produced.

The third gasifier is a dual bed gasifier that is formed of two fluidized beds (Fig. 2c):
- bed1 is fed with the fuel and the hot sand and works as a pyrolyzer/gasifier;
- bed2 is fed with air and the cold sand from bed1 (that contains also some residual char) and work as a combustor to heat the sand.

The main pro of this configuration is the use of air (instead of pure oxygen) to get a syngas with no nitrogen. The sand recirculation is used as a heat carrier and variations in the fuel-to-sand ratio can be studied only with a detailed approach. Both beds are modeled with the same approach described above for the circulating fluidized bed.

The last example is an entrained flow reactor with a water quench (Fig. 2d). The pressure is 30 bar. A burner in the top section feeds the fuel and sub-stoichiometric oxygen. Very high peak temperatures are achieved (1500-1600°C). A cooling screen shields this part of the gasifier and recovers heat for steam production. The high gasification temperatures limit the tar in the syngas and make the ash to melt, thus forming a slag on the reactor walls, that is cooled and removed by the quench water in the bottom part of the gasifier. As in the previous cases, the first sub-model is the devolatilization of the fuel, followed by a separated combustion chamber (modelled as a PFR reactor) that represents the burner. The high heating rate expected in this reactor justifies this hypothesis. The subsequent gasification step includes the other reactions of Tab. 1. The heat produced in the combustion step is used for the other endothermic reactions (pyrolysis and gasification), the pre-heating of the reactants and the heat recovery in the cooling screen with an iterative procedure.

Fig. 3. Results of (a) the downdraft gasifier model for the gasification of poplar wood with oxygen/steam mixtures and (b) the dual bed system model for the gasification of coal/poplar wood blends (bed1: gasifier, bed2: combustor).

5. Results

Some examples are commented here remarking the capability of each approach and the peculiar results with respect to equilibrium or simplified models.

In the first example, the downdraft model was used for the gasification of poplar wood with mixtures of oxygen and steam. In all cases the temperature achieved in the gasifier is limited to 1200°C. The results are shown in Fig. 3a as functions of the Equivalent Ratio (ER). The higher the value of ER, the lower the heating value of the syngas produced in the gasifier (due to the higher oxidation level). So, the conditions for the maximum LHV could be considered
for a direct combustion of the syngas (e.g., for power production). Other conditions should be considered in case of hydrogen production: the syngas from the gasifier shows a maximum in hydrogen production for a value of ER near 0.5. Above this value the excess oxygen oxidizes the gaseous products and thus a decrease in the production of hydrogen is observed. The high tar content in the syngas for values of ER between 0.35-0.40 makes prohibitive the direct utilization of the syngas in engines or turbines for power production. In this case onerous gas-cleaning units should be installed and a loss in efficiency should be expected. Values of ER slightly higher (0.45-0.50) can be programmed for obtaining a syngas with a lower heating value but with limited tar content. It is worth remarking that this consideration can not be done with an equilibrium model of the gasifier because tar can not be predicted.

In the second example, a biomass/coal blend is studied for the dual beds gasifier. In this case the co-gasification is dictated by the need of residual char that has to be passed from bed1 to bed2 to assure the autothermal feasibility of the system. Generally equilibrium models give unrealistic char conversion. The temperature of both beds are shown as function of the biomass-to-coal ratio in Figure 3b. The higher this ratio, the lower the temperature of both beds. Also the residual char from bed1 to bed2 decreases significantly as shown in the figure. Finally, the hydrogen production decreases.

Results for the entrained flow reactor can be found elsewhere [7].

6. Conclusion

To summarize, a modeling procedure has been developed to provide powerful tools for process analysis and optimization of solid fuel gasification. Different biomass and coals (even in blend) can be studied. The basic steps of pyrolysis, combustion, gasification are described in detailed sub-models that are combined to represent the reactor configuration. In particular, different sets of kinetics are adopted for the appropriate range of application. Also heat streams are connected to respect the heat balance of the system. This approach allows one to optimize the operating conditions and compare different configurations (fixed beds, fluidized beds and entrained flow reactors) for a subsequent integration in several processes of current interest (e.g., combined power production, chemical and hydrogen production).

7. References