CHEMICAL ENGINEERING TRANSACTIONS Volume 17, 2009
Editor Sauro Pierucci
 ISBN 978-88-95608-01-3 ISSN 1974-9791
DOI: 10.3303/CET0917204

Development of gasifier models for hydrogen production optimization

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In this work different gasifiers (entrained flow reactors and dual beds) are modeled with AspenPlus™ according to a procedure which aims at providing useful tools for optimization studies of comprehensive process models. The innovative feature consists in the separation of the steps of solid fuel gasification (devolatilization, oxidation, gasification of the char, homogeneous reactions and tar cracking) and the development of dedicated sub-models (by adapting conventional blocks or implementing structural models as CPD for coal devolatilization). Therefore all steps are connected to respect the material and heat balances according to the gasifier configuration. In this way, the temperature can be related to the operating conditions, i.e. fuel, oxygen and steam flow rates. This aspect is valuable in itself because removes the hypothesis of equilibrium reactors, generally assumed in literature works. Furthermore, the heat balance on the entire reactor allows to quantify the heat recovery, which could be crucial for efficiency calculations of the hydrogen production plant. Also, "by-products" and residual char can be quantified and consequently minimized depending on the operating conditions. Finally, the development of a "gasifier model" instead of a "gasification model" allows different reactor configurations to be compared and optimized.

1. Introduction

Coal gasification is an attractive process to convert an "unpopular" solid fuel into a valuable and environmentally acceptable energy carrier, that is hydrogen. 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. Process studies should be performed for defining the best plant configurations and optimizing the operating conditions (e.g. Zheng 2005). The reactor of gasification can be realized under very different solutions (Collot 2002). The heat needed can be provided by partial oxidation of coal with air or pure oxygen. Steam may be added to promote gasification. The coal can be fed dry or in a slurry. Temperatures, pressures and residence times vary in wide ranges depending on the technological configuration. In spite of all these differences, most process studies in the literature modeled the gasifier as an equilibrium reactor. This approach is indeed fundamental for a preliminary study but hardly suitable for process analysis and

Please cite this article as: Biagini E., Masoni L., Pannocchia G. and Tognotti L., (2009), Development of gasifier models for hydrogen production optimization, Chemical Engineering Transactions, 17, 1221-1226 DOI: 10.3303/CET0917204

optimization procedures. Some issues arise when introducing the equilibrium hypothesis in optimization studies:

1. The gasification temperature is generally considered independent of other operating conditions, therefore syngas compositions as functions of the oxygen-to-coal ratio can be found at fixed temperatures (Ni 1995, Xu 2007). This is hardly suitable for practical applications. In the real reactor, the oxygen and the fuel can not be assumed independent of each other and the reactor temperature should arise from a global heat balance. Heat recovery should be also included, in case steam or hot water production is realized. This contribution may be crucial for the global efficiency of the process, but can not be derived from equilibrium assumptions.
2. Sub-products in the syngas (e.g. CH4 and CO2) are generally underestimated (Ni 1995) even though their value is fundamental for the process efficiency. Residual char is not predicted in equilibrium calculations, while the conditions for complete conversion should be determined to assure high efficiencies and avoid problems in downstream units. Similarly, tar is not predicted in most studies: its quantification is actually fundamental to estimate the quality of the syngas produced.
3. Gasification is a complex ensemble of chemical and physical phenomena. Each step can be studied under different conditions (of temperature and gaseous composition) and the optimal configuration of gasifiers (e.g. entrained flow reactors, bubbling and circulating fluidized beds, fixed beds) can be compared only by developing a detailed model. This is also the case of reactors which can be hardly represented with equilibrium reactors (e.g., due to the low temperatures and residence times).

For all the above points 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. The main steps in the gasification are modeled separately in AspenPlus^{TM} to provide useful tools to be inserted in a comprehensive process model for the production of hydrogen via coal gasification. Particular attention is devoted to the heat transfer when heat has to be provided (via partial combustion or sand recirculation), recovered (for steam production) or removed (via water or gas quench). The main points in the procedure are summarized here and discussed in the next sections along with some examples of results for entrained flow reactors and dual beds:

- defining the functional scheme of the gasifier;
- separating the characteristic steps of solid fuel gasification (devolatilization, oxidation, gasification of the char, homogeneous reactions and tar cracking);
- developing sub-models of each step (by adapting conventional blocks or implementing structural models as CPD for coal devolatilization);
- connecting all steps to respect the material and heat balances according to the gasifier configuration.

2. Development of gasification sub-models

First of all, a general procedure is developed to model different gasifiers. Each reactor is analyzed to get a functional scheme, which is the basis of the process model. The scheme is composed by the main blocks, which can be represented by the general sub-models, described in the following sub-sections. Conventional blocks of AspenPlus^{TM}

or dedicated models, opportunely implemented in the main code of the gasifier model, are adopted. Each block is linked to the others (and in case, with other parts of the entire plant of hydrogen production) by material and heat streams. Heat is provided by partial oxidation of the fuel or the syngas produced (with air or oxygen), by recirculation of a heat carrier (e.g. sand) or flue gases. In all cases, a combustion unit is generally adopted. Also, the reactor walls can be used to recover heat for steam production. Even quench can be used to remove tar or solid residues. All heat streams are linked to find the reaction temperature by the iterative solution of the heat balance.

2.1 Devolatilization sub-model

After the pre-heating, the stream of the organic matter from the coal enters the devolatilization sub-model. A thermal decomposition is modeled giving a solid residue (char), a condensable organic product (tar, here modeled as anthracene, C14H10) and the main gaseous species (CO, CO2, CH4, H2O, H2, C2H2, N2, NH3, HCN, H2S, COS). No conventional AspenPlus^{TM} block can represent this step. Therefore, a structural model, i.e. the CPD (Coal Percolation Devolatilization), originally developed by Fletcher et al. (1992), is used for the coal devolatilization in the form adapted by our group in previous works (Vizzini et al. 2008). This model gives the yield of macro-products and the speciation of gases once the coal composition and the operating conditions are known. The CPD code can be hardly implemented in AspenPlus^{TM} because of the expensive computational cost. Therefore, a *User Routine*, consisting of a database and a calculation function for the devolatilization step, is developed. The former is created with the results of off-line simulations of the CPD model in a wide range of pressures and temperatures. The calculation function dialogues with the main AspenPlus^{TM} model by receiving the actual values of temperature and pressure, interpolating the results of the database and returning the balanced products.

2.2 Combustion sub-model

The combustion sub-model is represented as a *Plug-Flow Reactor.* Combustion reactions are modeled assuming a first order kinetic model with parameters adapted from literature (Westbrook 1981). Different options (e.g. constant temperature, thermal profile) can be set for the heat transfer according to the reactor configuration.

2.3 Gasification sub-model

The gasification sub-model consists of a *Plug-Flow Reactor*. Homogeneous reactions are modeled assuming a first order kinetic model, while the unreacted core-shrinking model of char gasification was actually adapted from Wen (1979).

3. Development of gasifier models

Three reactors are studied here: two entrained flow reactors (Future Energy GmbH and Shell, see Collot 2002), which generally operates between 20 and 40 bar, and a dual beds solution (studied for the FISR project “Integrated Systems for Hydrogen Production and Use in Distributed Generation”) formed by two circulating fluidized beds. A South African coal (moisture 7.0, VM 24.8, FC 54.5, ash 13.7%wt; C 81.6, H 4.84, N 1.75, S 1.27%wt dry and ash free basis) is considered in all cases. A flow rate of 5000 kg/h is studied. This is a relatively small plant size, which may represent an attractive solution for a realistic starting scenario based on hydrogen economy.

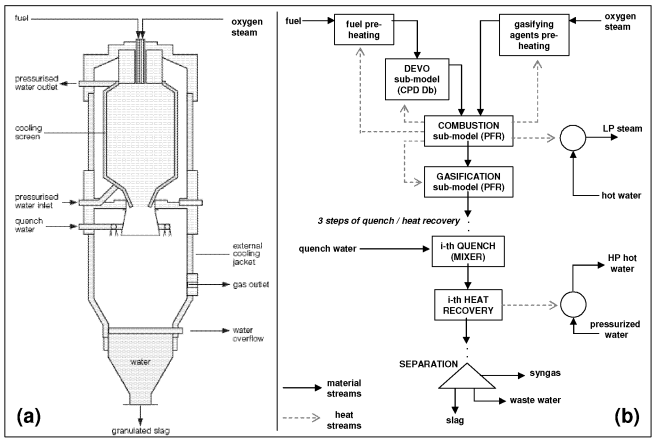

Figure 1. Sketch of gasifier 1 (a) and functional scheme for the model approach (b).

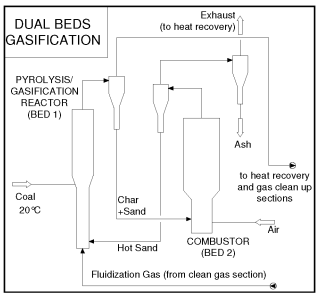

Figure 2. Sketch of gasifier 3.

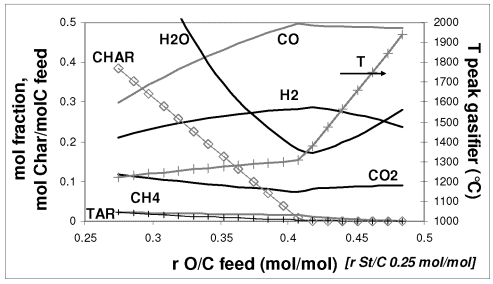

Figure 3. Syngas composition, char and temperature (results of model 1).

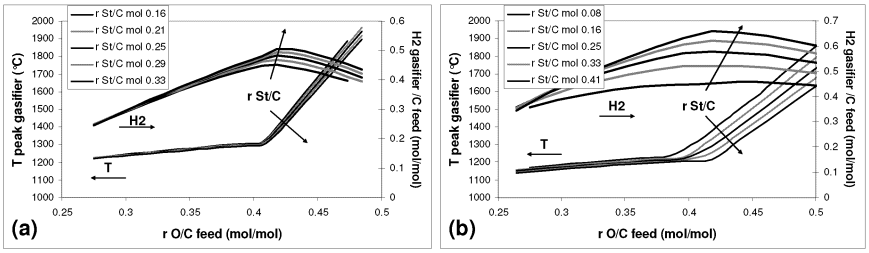

Figure 4. H2 production and temperature: results of model 1 (a) and 2 (b).

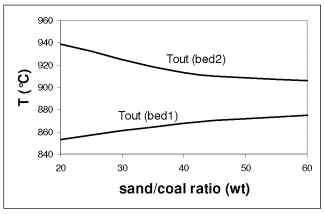

Figure 5. Bed temperatures as function of sand recirculation (results of model 3).

The models of all gasifiers are completely developed in AspenPlus™. The functional scheme of gasifier 1 is compared to the sketch of the reactor in Figure 1. The initial part of gasifiers 1 and 2 are actually modeled with the same scheme, because a burner with pure oxygen and steam is common to both reactors. The high heating rate of these reactors allows to separate the chemical steps (devolatilization, combustion and gasification) and assume them to evolve consecutively. The devolatilization is assumed instantaneous, while the combustion residence time is assumed to be 1/10 of that of gasification. The peak temperature is defined as the temperature of both devolatilization and combustion blocks, as well as the initial temperature of gasification.
The heat balance is common to all these blocks: only the combustion block generates heat, which is needed to the other blocks and the steam generation, too. Although the approach is similar for both gasifiers, some specifications in the heat recovery (and thus in the heat balance of the entire section) will give different results on the temperature dependence on the operating conditions. The water quench of gasifier 1 is modeled along with the heat recovery to the cooling jacket and the solid removal. The quench gas of gasifier 2 is modeled with a recirculation of the syngas.
The approach to the dual beds is substantially different. The functional scheme is reported in Figure 2. In this case, the critical point is the management of the solid recirculation. In the AspenPlus™ model, preliminary runs should be performed to initialize the sand temperature without recirculation. In the subsequent simulation run the sand recirculation is reconnected.

4. Results

The results of the models are useful for comparing different configurations and evaluating the effects of the operating conditions on the syngas conversion to optimize the gasifier performance. The fuel feed is maintained constant in all simulations, while the oxygen-to-carbon (rO/C mol/mol) and steam-to-carbon (rSt/C mol/mol) ratios are varied in wide ranges (0.25-0.50 and 0-0.35, respectively).
In the equilibrium model approach temperature and rO/C are independent and can be fixed *a priori*, so that the model loses in predictability. To compare the approaches, a *RGibbs Reactor* (an equilibrium reactor model, which minimizes the free energy in AspenPlus™) is also used. The results of this approach (not reported here) revealed that the effect of temperature and steam ratio is crucial. Nevertheless the effective temperature for the equilibrium is arbitrary, because the peak temperature is achieved for a short time in the gasifiers. The drawbacks of the equilibrium approach can be outperformed developing a detailed gasifier model as described in the previous section.
The syngas composition of gasifier 1 model is shown in Figure 3. The results of models 1 and 2 are compared in Figure 4, where the peak temperature and the hydrogen production are reported as functions of rO/C at different values of rSt/C. The results differ in the dependence of the temperature on the operating conditions (basically rO/C and rSt/C) and this is due to the reactor configuration and specifications adopted for the heat balance. The results are significantly different and could not be studied with an equilibrium approach. Specific analysis can be carried out on gasifier 3 model because the configuration and the operating conditions are extremely different with respect to the previous gasifier models. In the example shown in Figure 5, the sand-to-coal ratio is

varied and the thermal balance gives the exit temperature of the beds. It is worth noting that an equilibrium model in these conditions would give a complete conversion of the char, thus leading to an unrealistic configuration.

5. Discussion and conclusions

A lot of further analysis and comparisons could be drawn from the reported gasifier models to compare different configurations and evaluate the effects of the operating conditions. Equilibrium approaches can hardly offer this possibility. In general, the procedure and the model development described in this work allow to optimize the process. Actually, several parameters could be defined for optimizing the process. The hydrogen production or the heating value of the syngas can be maximized, depending on the goal of the process. The gasifier will be connected to other units that increase the hydrogen production via CO shift, so that the operating conditions can be chosen to maximize the final hydrogen production. Also, steam and oxygen consumption will affect the energetic and economic efficiency of the gasifier or the hydrogen production plant. Heat recovery and integration improve this efficiency. The maximum temperature arisen may be limited by the materials used in the reactor and thus represents a constraint for the model, reducing the range of operating variables in which the optimization procedure can be applied. Also, tar or pollutant removal should be evaluated as function of the operating conditions. These analysis can not be drawn from an equilibrium approach. Significant difference can be observed when comparing the results of figures 4a and 4b and significant results can be obtained as in Figure 5. Also results of optimization would be different. The implementation of the specific gasifier model described in this work in a comprehensive process model represents an effective tool to optimize the gasification process, giving the syngas composition in terms of main gaseous species (H2, CO, CO2) as well as "by-products" (CH4, tar). The separation of main steps allows the heat balance to be solved and give the gasification temperature as function of the operating conditions (rO/C and rSt/C). It also quantifies the heat recovery for the production of steam.

Acknowledgement

This work collects part of the results of the FISR Italian Project on "Integrated Systems for Hydrogen Production and Use in Distributed Generation".

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