AIDIC *Conference Series*, Vol. 9, 2009
Editor Sauro Pierucci
DOI: 10.3303/ACOS0909006

ISBN 978-88-95608-10-5 ISSN 2036-5969

DEVELOPMENT OF GASIFIER MODELS FOR HYDROGEN PRODUCTION OPTIMIZATION

E. Biagini, L. Masoni, G. Pannocchia[a], L. Tognotti[a]

Consorzio Pisa Ricerche – Divisione Energia Ambiente, Pisa – ITALY
[a] Dipartimento di Ingegneria Chimica – Università di Pisa – ITALY

In this work different gasifiers (entrained flow reactors and dual beds) are modeled with AspenPlus® according to a procedure that 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 of the software or implementing structural models for coal devolatilization). All steps are connected to respect the material and heat balances according to the gasifier configuration. In this way, the gasification 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 of the entire reactor allows one to quantify the heat recovery, which could be crucial for the efficiency 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 a 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 process configurations and optimizing the operating conditions (Zheng 2005, Chiesa 2005, Mills 2006). The gasification reactor can be designed 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 optimization procedures. Some issues arise when introducing the equilibrium hypothesis in optimization studies, as detailed below:

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, oxygen and fuel can not be assumed independent of each other and the reactor temperature should arise from a global heat balance. Adiabatic equilibrium models may be a more realistic solution. Nevertheless, thermal profiles can not be introduced, though this opportunity could add value to the model approach and allow the optimization of the reactor. Heat recovery should be included, in case of steam or hot water production (for instance in the reactor jacket), as this contribution may be crucial for the global efficiency of the process.

Please cite this article as: Biagini E., Masoni L., Pannocchia G. and Tognotti L., (2009), Development of gasifier models for hydrogen production optimization, AIDIC Conference Series, 09, 45-52 DOI: 10.3303/ACOS0909006

2. By-products in the syngas (e.g. CH_4 and CO_2) 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 process efficiency and the quality of the syngas produced.
3. Gasification is a complex ensemble of chemical and physical phenomena. Each step can be operated under different conditions (of temperature and gaseous composition) and the optimal configuration of gasifiers (e.g. entrained flow reactors, fluidized beds, circulating beds, fixed beds) can be compared only by developing a detailed model. This is also the case of reactors that can be hardly represented with an equilibrium reactor (e.g., due to the low temperatures and residence times achieved).

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® to provide useful tools to be inserted in a comprehensive process model for hydrogen production via coal gasification. Particular attention is devoted to model 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 of the software or implementing structural models for coal devolatilization);
- connecting all steps to respect the material and heat balances according to the gasifier configuration.

2. DEVELOPMENT OF GASIFICATION SUB-MODELS

A general procedure is developed to represent different gasifiers in multizonal models. 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 sub-models described in the following sub-sections. Conventional blocks of AspenPlus® 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. Quench can be used to cool down the syngas and remove tar or solid residues.
The peak temperature is defined as the final devolatilization temperature and coincides with the combustion temperature (if included) and the initial temperature of gasification. It is obtained by the iterative solution of the heat balance. All feeding streams are heated to the peak temperature. The heat required, the heat lost (e.g., for the quench) and the heat of reaction of all steps are linked in the heat balance. Also some heat recovery can be included. A simplified scheme is reported in Figure 1, where a single reaction block is considered, though this approach can be applied to more complex schemes. All heat streams are algebraically summed in a *QMixer* that returns a global heat stream exiting the system. A *Design Specification* is imposed to vary the peak temperature and find the value of the global heat corresponding to the dispersion of the system (or in case to the heat recovery for steam production, for instance). The procedure is iterative (the peak temperature determines the extent of the reactions in all steps), so that the solution is obtained once all heat and mass balances are solved.

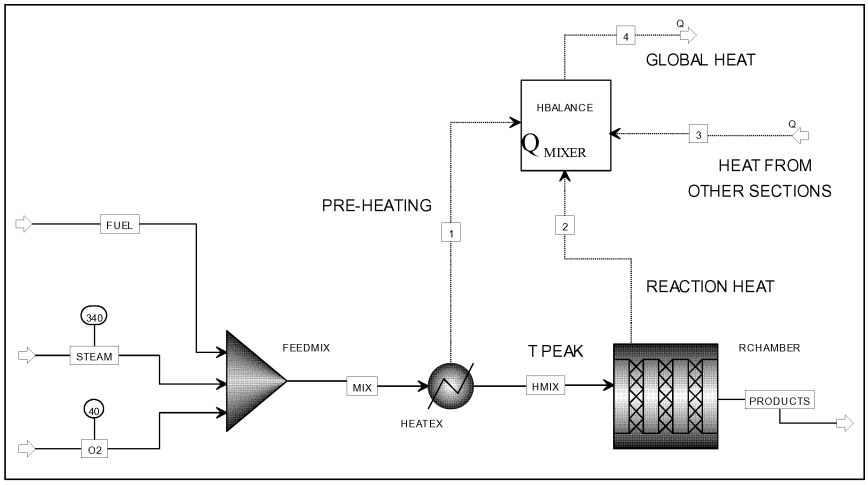

Figure 1. Scheme of a simplified heat balance solution with a Reaction Block.

2.1 Devolatilization sub-model

The coal flow rate is initially treated as a non-conventional solid and then divided into three streams according to the proximate analysis: water (considering the moisture content), ash and the organic matter. 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, CO_2, CH_4, H_2O, H_2, C_2H_2, N_2, NH_3, HCN, H_2S, COS). No conventional AspenPlus® 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 revised by our group (ABCD Advanced Biomass and Coal Devolatilization model, Falcitelli et al. 2009). This model gives the yield of macro-products and the speciation of gases once the coal composition and the operating conditions are known. It can be used also for biomass pyrolysis and this will allow to study the co-gasification of biomass/coal blends in future works. The ABCD code can be hardly implemented in AspenPlus® because of the expensive computational cost. Therefore, a *User Routine* for the devolatilization step (scheme of Figure 2) is developed. Basically, it consists of a database and a calculation function. The former is created with the results of off-line simulations of the ABCD model applied to the devolatilization of a coal in a wide range of pressures and temperatures. The calculation function dialogues with the main AspenPlus® model by receiving the actual values of temperature and pressure, interpolating the results of the database and returning the speciation of the devolatilization product stream. In all cases the material balance is verified.

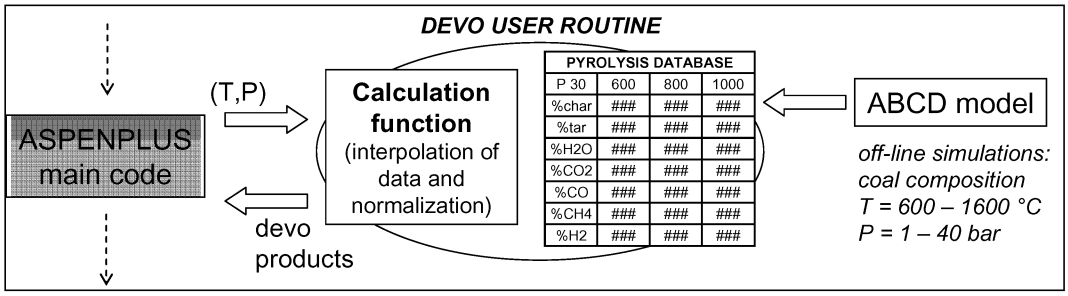

Figure 2. Scheme of the devolatilization block

Table 1. Reaction sets used in the sub-model development

Combustion reactions		Gasification reactions	
volatile combustion	$H_2 + ½ O_2 \rightarrow H_2O$ $CO + ½ O_2 \rightarrow CO$ $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ $C_2H_2 + 5/2 O_2 \rightarrow 2CO_2 + H_2O$	char gasification	$C (char) + H_2O \rightarrow CO + H_2$ $C (char) + CO_2 \rightarrow 2CO$ $C (char) + 2H_2 \rightarrow CH_4$
char oxidation	$C (char) + ½ O_2 \rightarrow CO$	methane reforming	$CH_4 + H_2O \rightarrow CO + 3H_2$
tar oxidation	$C_{14}H_{10} (tar) + 33/2 O_2 \rightarrow 14CO_2 + 5H_2O$	water gas shift	$CO + H_2O \rightarrow CO_2 + H_2$

2.2 Combustion sub-model

The combustion sub-model is represented as a *Kinetic Reactor* (*Plug Flow Reactor* or *Continuous Stirred Tank Reactor* depending on the reactor configuration). The list of reactions is given in Table 1. All combustion reactions are modeled assuming a first order kinetic model with parameters adapted from literature works. Different sets of kinetic parameters can be found in literature for combustion/gasification systems. Global and simplified kinetic models are desired for this approach and this requires a specific range of operating conditions where they are validated. Therefore, kinetics of combustion (as well as for gasification in the next sub-section) are divided in two ranges: for room pressure and relatively low temperatures (800-1200 °C) they are adapted from (Hobbs 1992, Bryden 1996), while for pressurized conditions (20-40 bar) and high temperatures (1200-1600 °C) they are adapted from (Wen 1979). Different thermal options (constant temperature, thermal profile, constant coolant temperature) can be set for the heat transfer according to the reactor configuration.

2.3 Gasification sub-model

The gasification sub-model consists of a *Kinetic Reactor* (*Plug Flow Reactor* or *Continuous Stirred Tank Reactor* depending on the reactor configuration). The reactions are listed in Table 1. Homogeneous reactions are modeled assuming a first order kinetic model with parameters from literature (Gordon 1946, Yoon 1978, Wen 1979). As for char gasification, the unreacted core-shrinking model was adapted from (Hobbs 1992) for low pressures and temperatures and from (Wen 1979) for high pressures and temperatures.

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 Italian project "Integrated Systems for Hydrogen Production and Use in Distributed Generation") formed by two circulating 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.
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 3. The top part of gasifiers 1 and 2 are actually modeled with the same scheme, because a reaction chamber (a burner with pure oxygen and steam) is common to both reactors. The high heating rate of these reactors allows one 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 total residence time is derived from the geometric configuration of the reactor.
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. In the bottom part of gasifier 1, the water quench is modeled along with the heat recovery to the cooling jacket (for the production of hot water) and the solid removal. The quench gas of gasifier 2 is modeled with a recirculation of the syngas, which is approximately a half of that produced. A second gasification sub-model is actually included after the gas quench, to simulate the simultaneous reactions and heat recovery.

The approach to the dual beds is substantially different with respect to the previous gasifier models. The functional scheme is reported in Figure 4. The coal is introduced in bed 1 with hot sand from bed 2 (thus providing the heat required by the pyrolysis/gasification reactions) and recirculation gas (for the fluidization of the bed). The mixture formed by the syngas, the char and the sand is then separated in cyclones. The syngas enters the heat recovery/gas cleanup sections. The solid is introduced in bed 2 with air for burning the char and heat the sand. Exhaust gases are then separated from the hot sand, which is recirculated to bed 1. The system operates at atmospheric pressure and the temperature of reactor 1 is in the range 800-900 °C.
The critical point is the management of the solid recirculation. The amount of residual char from bed 1 should be evaluated to provide the heat for the system in the combustion of bed 2. As for the sand, preliminary runs should be performed to initialize the sand temperature without recirculation. In the subsequent simulation run the sand recirculation can be reconnected.

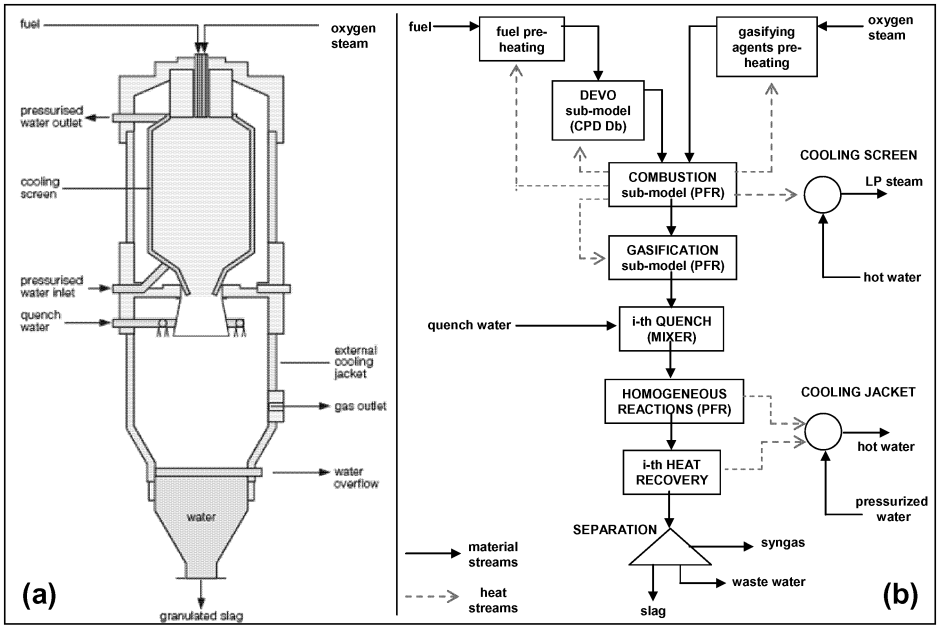

Figure 3. Sketch of gasifier 1 (a) and functional scheme for the model approach (b).

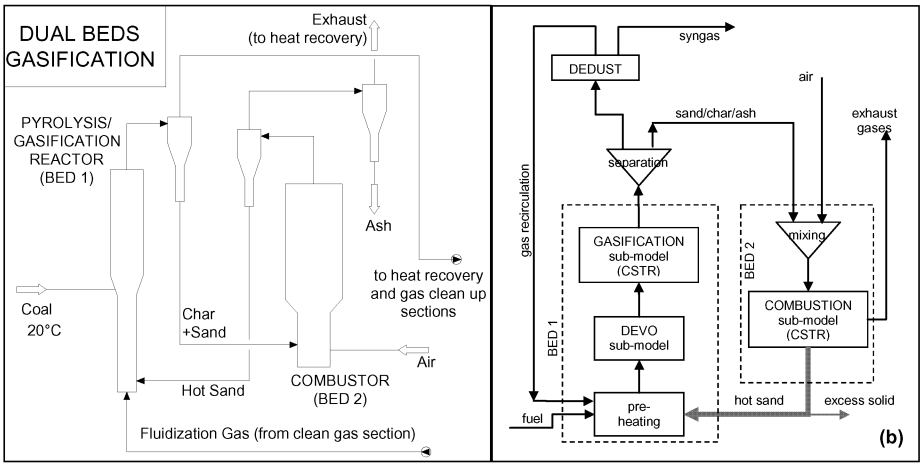

Figure 4. Sketch of gasifier 3 (a) and functional scheme for the model approach (b).

4. RESULTS

The simulation 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 general, the higher rO/C the higher the temperature in the reactor. This is due to the higher conversion of combustion reactions. As mentioned in the introduction, this is not the case for 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 used to substitute the scheme of gasifier 1 and 2 described above, the conditions being similar. The results of this approach are reported in Figure 5 for the hydrogen production (as molar ratio between H_2 production and C feed). Two values of temperatures and steam ratios (rSt/C) are considered. The effect of these two parameters is important but 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 6. The results of gasifier 1 and 2 models are compared in Figure 7, 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 different configuration and specifications adopted for the heat balance. The results are significantly different, while this difference can not be studied with an equilibrium approach, giving arbitrary results.

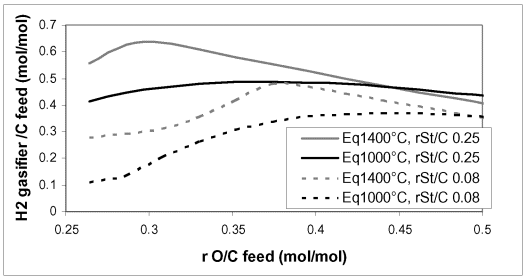

Figure 5. Hydrogen production at different steam ratios and temperatures (equilibrium model).

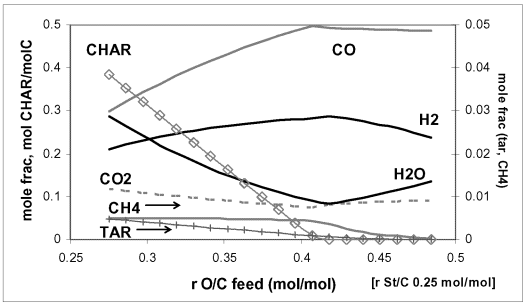

Figure 6. Syngas composition, char and temperature (gasifier 1 model).

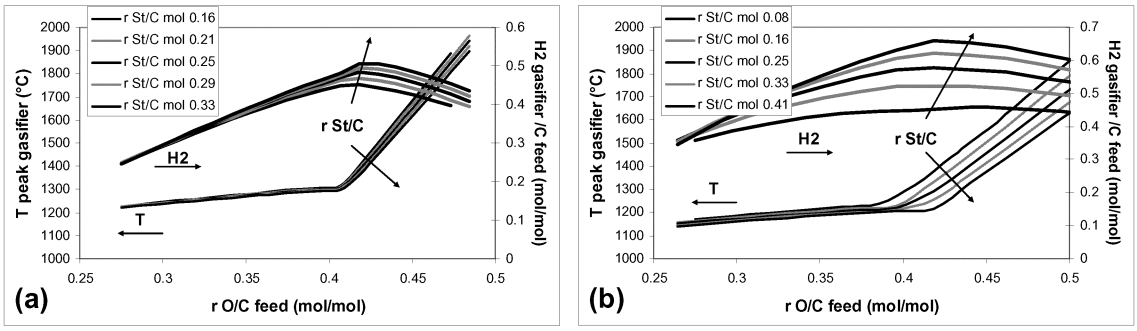

Figure 7. Hydrogen production and temperature: gasifier 1 (a) and gasifier 2 (b) models.

The simulation results of gasifier 3 model can not be directly compared with previous results because the configuration and the operating conditions are extremely different. In this case, the heat is provided by the hot sand recirculation between the two beds instead of the partial oxidation of the fuel. Therefore, the sensitivity analysis is carried out by varying the sand-to-coal ratio in the first bed (bed 1 gasifier). The thermal balance gives the exit temperature of the beds. The higher the sand-to-coal ratio, the higher the temperature at the exit of bed 1 and the lower the temperature at the exit of bed 2, as shown in Figure 8. Consistently, the lower temperature of bed 2 (at high sand-to-coal ratios) can be achieved with a lower amount of unconverted char from bed 1. This latter in fact decreases because the temperature of bed 2 increases, favoring the gasification reactions and thus the char conversion.
The syngas composition is also reported in Figure 8. The lower temperatures achieved in the dual bed configuration (800-900 °C) with respect to those achieved in entrained flow reactors give a higher amount of methane and tar, which can compromise the downstream units. A methane reformer and a tar removal section (cracking or separation) should be considered in case of production of pure hydrogen. In all cases, a loss in efficiency can be quantified and the optimization of the system can be obtained from a detailed process approach.

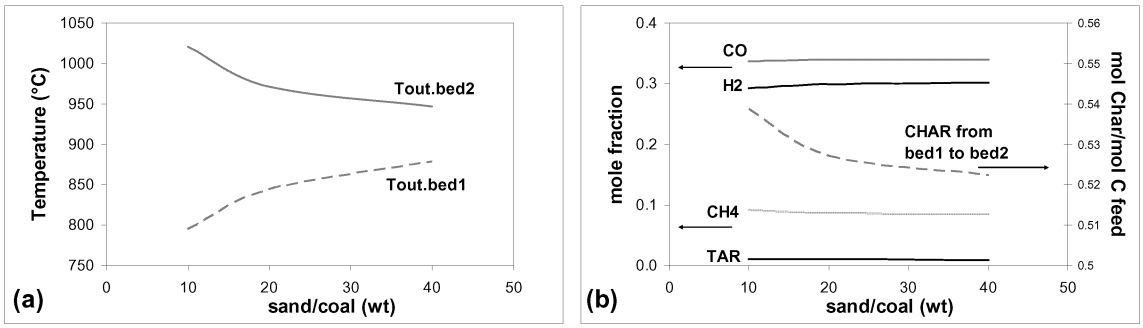

Figure 8. (a) Bed temperatures as functions of sand-to-coal ratio and (b) products from bed 1 (gasifier 3 model).

5. DISCUSSION AND CONCLUSIONS

Further analysis and comparisons can 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 one to optimize the entire process. 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 a constraint for the materials used in the reactor, so it should be taken into account when studying the optimization of the process. 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 6a and b. Also results of optimization would be different. The inclusion of the specific gasifier model described in this work in a comprehensive model represents an effective tool to optimize the gasification process, giving the syngas composition in terms of main gaseous species (H_2, CO, CO_2) as well as "by-products" (CH_4, tar) and pollutant precursors (HCN, NH_3,COS, H_2S). 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.

6. ACKNOWLEDGEMENT

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

7. REFERENCES

Bryden K. M., Ragland K. (1996) *Energy and Fuels*, 10, 296
Chiesa P., Consonni S., Kreutz T., Williams, R. (2005) *Int. J. Hydrogen Energy*, 30, 747.
Collot, A.G. (2002) Matching gasifiers to coal. IEA Clean Coal Centre, CCC/65.
Falcitelli M., Biagini E., Tognotti L. Development of the Advanced Biomass and Coal Devolatilization (ABCD) model. 10th Conference on Energy for a Clean Environment. Lisbon 7-10 July 2009
Fletcher T.H., Kerstein A.R., Pugmuire R.J., Solum M., Grant D.M. (1992) A Chemical Percolation Model for Devolatilization. Sandia Technical report, SAND92-8207.
Gordon A.S. (1946) *Ind. Eng. Chem.*, 38, 718.
Hobbs M. L., Radulovic P. T., Smoot L. D. (1992) *AIChE Journal*, 38, 681.
Mills S.J. (2006) Coal gasification IGCC in Europe. IEA Clean Coal Centre, CCC/113.
Ni Q., Williams A. (1995) *Fuel*, 74, 102
Wen C.Y., Chaung T.Z. (1979) *Ind. Eng. Chem. Process Des.*, 18, 684.
Xu X., Xiao Y., Qiao C. (2007) *Energy and Fuels*, 21, 1688.
Yoon H., Wei J., Denn M. M. (1978) *AIChE Journal* 24, 885.
Zheng L., Furinsky E. (2005) *Energy Conversion and Management*, 46, 1767.