

Application of first-principles based techniques for compounds prediction in a gasification plant

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Abstract—In this work a first-principles based model for the prediction of the Syngas composition produced in a gasification plant is described. The model design is based on chemical-physical principles of the gasification process and is based on nonlinear static equations. For the formulation of the equations, Gibbs energy minimization of the compound used in the gasification process is taken into account together with computations of material balance.

The model has been validated on real data from a gasification plant. From the analysis of the results, it can be stated that good estimation performances have been achieved. This chemical-physical model overcomes the limitation introduced by the use of a linear model presented by the authors in a previous work. In fact, the new model provides a good estimation even when the range of the stoichiometric ratio is extended out of validity values of a linear model.

Given the results, the model can be used in a Model-Based Predictive Control (MPC) strategy for process optimization and/or for the development of a Fault Diagnosis system.

I. INTRODUCTION

THE gasification process basically consists in a clean transformation of low-value feedstocks into high-value products (like synthesis gas). The process is based on a clean energy technology that can provide an effective source of fuels to be used for electricity production.

Gasification is a reliable and flexible process that converts any material containing carbon into synthesis gas (called Syngas). The Syngas can be sent to a gas turbine where is burned to produce electricity or further processed to manufacture chemicals, fertilizers, liquid fuels, substitute natural gases (SNG), or hydrogen. Gasification has been largely used for more than fifty years in refinery plants and chemical industries, and for more than thirty-five years in the electric power industry. Nowadays there are more than 140 gasification plants operating worldwide. Nineteen of those plants are located in the United States. The projection of the worldwide gasification capacity is to grow 70 percent by 2015, with 80 percent of the growth occurring in Asia (see Figure 1): in China in 2010, about sixty new gasifiers have been built.

In general, gasification technologies are incorporated in modern Integrated Gasification Combined Cycle (IGCC) plant (see [1]) which utilizes the refinery residues for cleaner power production. The scope of a modern IGCC is to combine a coal gasifier and a set various equipments

based on a gas-steam combined cycle so to convert carbon into clean synthesized gas further achieving the target of power generation from the fuel produced by the gasification process. The electricity is produced in the gas turbine, where the mixture of fuel gas (Syngas) and nitrogen is forwarded, and in the steam turbine where the steam produced by the gas turbine is transformed into electric power. The capability of the entire combined cycle (gas & steam turbine) is about 300 MW.

Furthermore, the most important concept is that, compared with the capture of carbon dioxide from flue gas of traditional power plants, it will be more easily to capture carbon dioxide from synthetic gas using IGCC: this characteristic explains the great success of the gasification technology.

An IGCC unit of a refinery plant has been largely studied by the authors in previous works with the purpose of Fault Detection and Isolation (see [2], [3], [4] and [5]). In order to design complex control schemes that involve the solution of optimization problems or the application of model-based predictive control techniques [6], a model of the gasification process is required. For the prediction of the Syngas composition, several approaches have been proposed: Principal Component Analysis (PCA), Dynamic PCA [7], Robust Neural Estimator [8] or physical-chemical modeling [9]. Nevertheless, most of them, losing connections with the controllable process variables (like PCA, based on order reduction approach [10]) make the application of complex advanced control techniques not feasible.

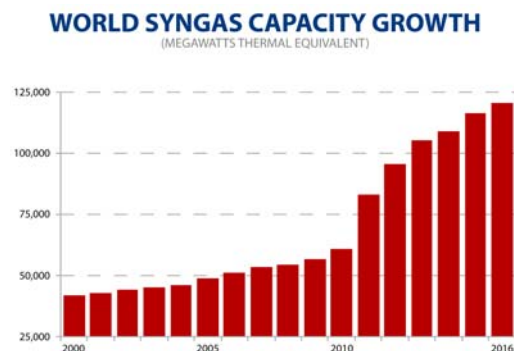


Fig. 1. Worldwide gasification capacity.
(source *Gasification Technologies Council*)

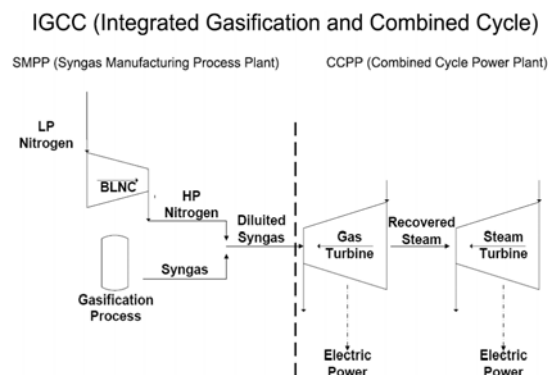


Fig. 2. Scheme of the Integrated Gasification and Combined Cycle

The main issue of this work concerns the development of a model for a gasification process, located in an IGCC plant, based on chemical-physical principles.

For the formulation of the model, chemical potentials of the chemical components involved in the reactions in terms of Gibbs energy and material balance conservation have been considered. The result is a nonlinear model that covers a wide range of the process variables variability. This physical model overcomes the limitations introduced by a previous linear model presented by the authors in a recent work [11]; here, typical maneuvers on the plant consisting on limited variations of the model independent variables (ratios O_2 /Charge Oil and Steam/Charge Oil) were considered and this justifies the adoption of a linear model. Nevertheless, there are cases when the range of the stoichiometric ratio is extended. For these cases, a linear model is not well fitted anymore and this has motivated the present work.

After having described the process at issue (section 2), in section 3 the thermodynamic of the gasification process and the Gibbs energy minimization approach are discussed. In section 4, the model structure for the gasification process is presented. Then in section 5, the results concerning the estimation of the Syngas composition and a comparison with the previous presented linear model will be shown. Finally, some important remarks are discussed in section 6.

I. DESCRIPTION OF THE GASIFICATION PROCESS

The focal point of this work is a gasification process placed in a Syngas Manufacturing Process Plant (SMPP) of a refinery plant, which is dedicated to the production of a particular synthetic gas, so called Syngas. This gas is forwarded together with the nitrogen gas to a gas turbine employed for the generation of the electric power. The SMPP plant together with the Combined Cycle Power Plant (CCPP), constitutes the Integrated Gasification and Combined Cycle (IGCC) (Figure 2).

The Syngas is produced in the gasification plant. The feedstock of the gasificator is the refinery residues; in particular, it is composed by the visbreaking residues and the crude oil refinery refuses, named TAR. In the following, the mixture of the visbreaking residues and the crude oil refinery refuses will be called Charge Oil (see Figure 3).

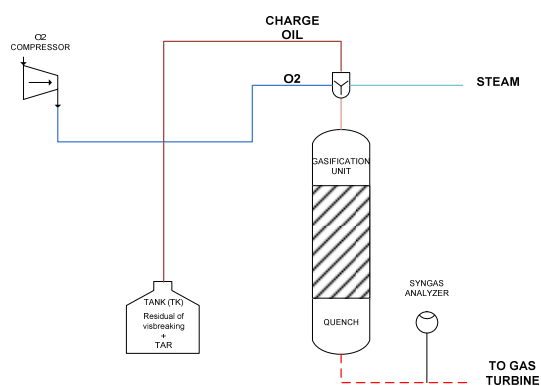


Fig. 3. Scheme of the gasification process.

In order to achieve high efficiency in the production of the Syngas, the Charge Oil at the inlet of the gasificator is mixed together with oxygen (used to feed the reaction) and steam (used for moderate the reaction). In particularly the efficiency of the gasification process depends on the mixture of the Charge Oil and the O_2 /Charge Oil and Steam/Charge Oil ratios. It is clear that from the Charge Oil composition and the previous stoichiometric ratios depends the composition of the Syngas produced. The main compounds of the Syngas at the end of the gasification process are H_2 (hydrogen), CO (carbon monoxide), CO_2 (carbon dioxide), CH_4 (methane) and smaller amount of COS (carbonyl sulphide). These compounds deeply influence the quality of the Syngas. A measurement of the Syngas quality is defined by the Lower Heating Value (LHV) which depends on the LHV of each compound present in the Syngas. The efficiency of a gasification process is maximized when the gasification reaction generates products with high LHV, such as H_2 and CO. Thus, for achieving high Syngas quality, high level supervisory controller should control the inlet feedstock composition (Charge Oil, ratio O_2 /Charge Oil, ratio Steam/Charge Oil) by maximizing the Syngas LHV.

From Figure 3 that depicts a schematic representation of the gasification process, it can be observed the presence of a syngas analyser. In fact, a gas chromatographer is employed so to measure the Syngas composition before the entry to the gas turbine. However, this type of measurement is not always available because of frequent periodic calibrations. For this reason and with Model-Based Predictive Control (MPC) and Fault Diagnosis in mind, the development of a model of the gasification process is considered. In order to achieve a good prediction in the various conditions of the plant, a physical model has been built.

II. THE THERMODYNAMICS OF THE GASIFICATION PROCESS

In the following, the theoretical background of the thermodynamics of gasification process will be summarized (see [12] for further details).

During the gasification process of any material containing carbon whether in the form of coal or coke, the principle chemical reactions are those involving carbon (C), carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2), water (or steam) (H_2O) and methane (CH_4) [12]. These reactions

can be grouped as in the following where, for every reaction, the *LHV* is indicated.

Combustion reactions



Boudouard reaction



Water-gas reaction

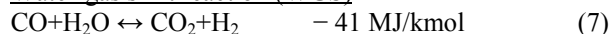


Methanation reaction

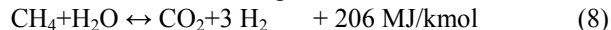


Under the gasification conditions, i.e. sub-stoichiometric conditions, the reactions (1), (2), and (3) with free oxygen are all complete reactions and consequently, in determining the equilibrium Syngas composition, they can be neglected. Thus, the only three reactions (4), (5), and (6) have been considered. In fact, the situations where the carbon conversion is almost complete are the ones of more interest. Under these circumstances, gas and solid phase equations (4), (5) and (6) can be reduced to the following two homogeneous gas reactions:

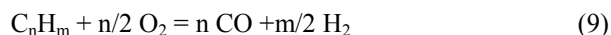
Water-gas shift reaction (WGS)



Steam methane reforming reaction



For real fuels the overall reaction can be written as:



where the stoichiometric coefficient for some feedstocks are summarized in the Table I.

Because gasification temperatures are very high, the presence of hydrocarbons, except methane, at the end of the gasification process, is very low. Reactions (4)-(8) are all reversible reactions and they can precede both from right to left and vice versa. For every direction, i.e. the forward and the reverse reactions, the so-called reaction rates can be considered. Once the temperature is fixed, these rates are proportional to reactants employed in each reaction and they take into account the considered direction.

In order to explain the physical connotation of the reaction rates, let consider for example the CO shift reaction (7): the forward reaction rate, r_f , is proportional to the molar concentrations of CO and H₂O:

$$r_f = k_f \cdot [CO] \cdot [H_2O] \quad (10)$$

where the constant of proportionality k_f is a function of the temperature. Similarly, for the reverse reaction the reaction rate can be defined as:

$$r_r = k_r \cdot [CO_2] \cdot [H_2] \quad (11)$$

been k_r dependent from the temperature.

TABLE I
STOICHIOMETRIC COEFFICIENT OF SOME FEEDSTOCKS

FEEDSTOCK	STOICHIOMETRIC COEFFICIENT		
	m	n	m/n
Methane	4	1	4
Oil	2	1	2
Coal	1	1	1

When the reaction is complete these rates tend to reach a common value and the gas compositions have reached a state of equilibrium. In these conditions, the forward and the reverse rates can be expressed as:

$$K_p = \frac{k_r}{k_f} \cdot \frac{[CO_2] \cdot [H_2O]}{[CO] \cdot [H_2O]} \quad (12)$$

where K_p is the equilibrium constant for the CO shift reaction which is function of temperature. The temperature dependency of the equilibrium constants are often expressed as in the following equation:

$$\ln(K_{p,T}) = \ln(K_{p,T_0}) + f(T) \quad (13)$$

where T is the absolute temperature in Kelvin and the function $f(T)$ can be derived experimentally from the process data.

Equations, (1)-(13), provide the solution for computing the Syngas composition on the assumption that all the reactions have reached an equilibrium point. In the considered problem for obtaining practical solution of (1)-(13) the fugacities have been neglected. Although many processes operate at pressures of 30–70 bar, this assumption is justified because of the very high temperature values in the processes, which lie very far from the critical temperature of each compound.

For systems of limited complexity, the use of the approach based on the equilibrium constant for the determination of the equilibrium compositions is very popular. The equilibrium constant approach is well documented in almost every thermodynamics text (see for example [13]). In the present case, the large size of the systems prevented a successful resolution of equilibrium compositions to be feasibly reached. Thus to solve the problem a different approach has been followed. The adopted methodology is based on the minimization of the Gibbs energy as it detailed in the next Section.

A. Complex Chemical-Reaction Equilibrium: Gibbs energy minimization

The approach based on equilibrium constants becomes very difficult when the composition of a particular gas, for example Syngas, is determined by a high number of simultaneous reactions (like gasification process). A more straight procedure (and suitable for large systems) is based on minimization of the overall Gibbs energy G^t of the chemical system (the generalized Gibbs approach can be found at [14] and [15]). The treatment is limited to gas-phase reactions for which the problem is to find the

equilibrium composition for given temperature T , pressure P and for a given initial feedstock.

The first step concerns the formulation of the constraining material-balance equations, based on conservation of the total number of atoms of each element in a system that contains w elements.

The material balance for each element k is defined as:

$$\sum_i^N n_i a_{ik} = A_k \quad (k=1,2,\dots,w) \quad (14)$$

where A_k is defined as the total number of atomic masses of the k th element in the feed and a_{ik} is the number of atoms of the k th element present in each molecule of chemical species (i) of a total N species of the system. By multiplying each balance element by λ_k and by summing over k , these equations give

$$\sum_k^w \lambda_k \left(\sum_i^N n_i a_{ik} - A_k \right) = 0 \quad (15)$$

Subsequently, by addition of G^t to this sum, a function F can be defined as follow:

$$F = G^t + \sum_k^w \lambda_k \left(\sum_i^N n_i a_{ik} - A_k \right) \quad (16)$$

From (15) it is clear that function F is identical with G^t ; nevertheless, their partial derivatives with respect to n_i are different, because function F combines the constraints of the material balances.

Finally, to find the minimum value of both F and G^t is sufficient to set equal to zero the partial derivatives of F with respect to n_i :

$$\left(\frac{\partial F}{\partial n_i} \right)_{T,P,n_j} = \left(\frac{\partial G^t}{\partial n_i} \right)_{T,P,n_j} + \sum_k^w \lambda_k a_{ik} = 0 \quad (17)$$

The first term on the right is the chemical potential (μ_i)

$$\mu_i = \left(\frac{\partial G^t}{\partial n_i} \right)_{T,P,n_j} \quad (18)$$

that for gas-phase reactions and standard states as the pure ideal gases at P^0 , is given by

$$\mu_i = G_i^0 + R \cdot T \cdot \ln \left(\frac{f_i}{P^0} \right) \quad (19)$$

where R is the gas constant and \hat{f}_i is the fugacity of a real gas, which is function of the pressure P of the system. Fugacity can be expressed in terms of the fugacity coefficient by [14],

$$\hat{f}_i = y_i \hat{\phi}_i P \quad (20)$$

where y_i is mole fraction of the specie i .

Conventionally, G_i^0 is set equal to zero for all elements in their standard states (like H_2 , O_2 and N_2), while for compounds, G_i^0 is the standard Gibbs-energy of formation for the specie i , that is

$$G_i^0 = \Delta G_{fi}^0 \quad (21)$$

Combining (20) and (21) with (19) gives

$$\mu_i = \Delta G_{fi}^0 + R \cdot T \cdot \ln \left(\frac{y_i \hat{\phi}_i P}{P^0} \right) \quad (22)$$

Finally, from equation (17) the following expression holds:

$$\Delta G_{fi}^0 + R \cdot T \cdot \ln \left(\frac{y_i \hat{\phi}_i P}{P^0} \right) + \sum_k^w \lambda_k a_{ik} = 0 \quad (i=1,2,\dots,N) \quad (23)$$

From equation (23) N equilibrium equations, one for each chemical species, and w material-balance equations, one for each element, can be derived. The result is a system of a total of $N + w$ equations.

Equation (22) is derived on the assumption that the $\hat{\phi}_i$ are known. If the phase is an ideal gas, then each $\hat{\phi}_i$ is unity. For low pressures or high temperatures, this result is usually adequate. Where it is not satisfactory, an equation of state is necessary to give a new and more nearly correct set of $\hat{\phi}_i$ for use in equation (22). Given that the following relation between the mole fraction y_i of the specie i and n_i holds:

$$y_i = \frac{n_i}{\sum_i n_i} \quad (24)$$

the unknowns of the $N+w$ equations of (14) and (23) are the N values of the n_i , and the w values of the λ_k , thus the determination of all unknowns is possible.

Now the focus is how to calculate the standard Gibbs energy for species i (ΔG_{fi}^0). The ΔG_{fi}^0 is the standard Gibbs energy of formation for species i from the elements that compose it [16]. Considering a system with a constant pressure, it is possible to define the standard Gibbs-energy of formation as:

$$\Delta G_i = a_i + b_i \cdot T + c_i \cdot T^2 \quad (25)$$

where it is clear the temperature dependence and where the constants a_i , b_i , c_i are different for every compound i .

III. CHEMICAL-PHYSICAL MODEL OF THE GASIFICATION PROCESS

By following the steps discussed in the previous section, the complete model of the gasification process can be presented. Considering the main reactions of the process, the chemical-physical model is based on $w = 6$ material-balance equation (14) (one for every element: C, H, O, S, N, Ar) and

TABLE II
NUMBER OF ATOMS OF ELEMENT IN CHEMICAL SPECIES

CHEMICAL SPECIES	C	H	O	S	N	Ar
CH ₄	1	4	0	0	0	0
H ₂ O	0	2	1	0	0	0
H ₂	0	2	0	0	0	0
CO	1	0	1	0	0	0
CO ₂	1	0	2	0	0	0
N ₂	0	0	0	0	2	0
H ₂ S	0	2	0	1	0	0
O ₂	0	0	2	0	0	0
Ar	0	0	0	0	0	1
COS	1	0	1	1	0	0

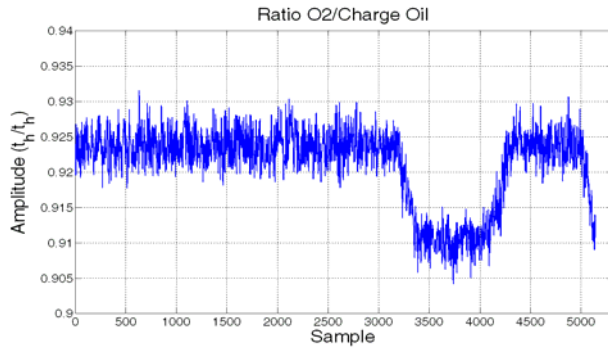


Fig. 4. Perturbation of the ratio O2/Charge Oil during the step test.

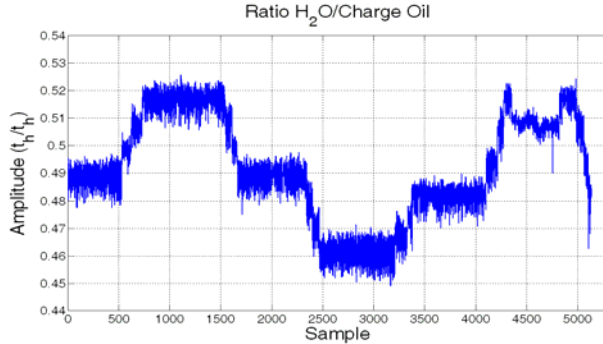


Fig. 5. Perturbation of the ratio Steam/Charge Oil during the step test.

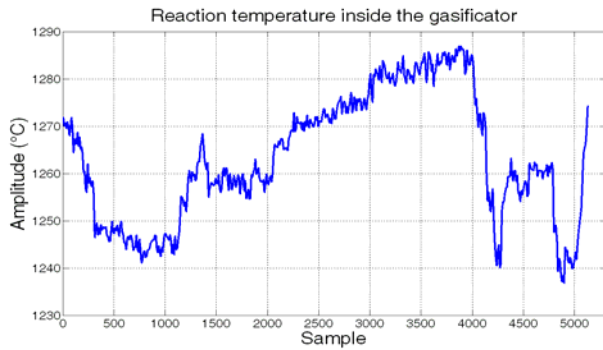


Fig. 6. Temperature behavior inside the gasificator.

$N = 10$ equilibrium equation (23) which taking into account the chemical species of the reactions.

The coefficient a_{ik} that represents the number of atoms of the k th element present in each molecule of chemical species i are depicted in the following table (Table II).

IV. RESULTS

In order to validate the performance of the model in estimating the Syngas composition, validation data have been gathered which refer to a step test performed on the plant under study. The test has consisted in perturbation of both O2/Charge Oil (Figure 4) and Steam/Charge Oil (Figure 5) stoichiometric ratios.

The dataset used for the model validation is composed of 5140 samples with a time interval of one minute. The dataset covers a time interval of about three and half operative days. The adoption of a chemical-physical model is justified by the wide range of the temperature (about 40 °C) reached inside the gasificator (see Figure 6). In fact, as it can be observed in the next figure the physical model performs a

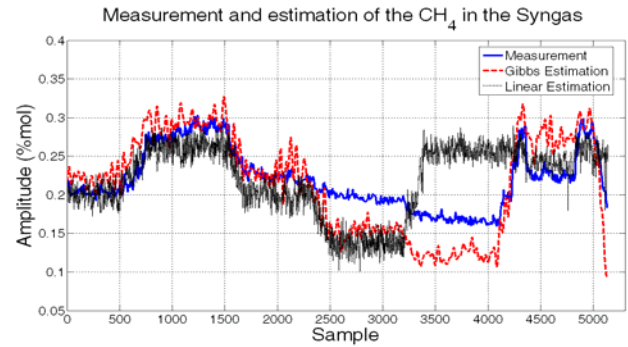


Fig. 7. Predictions of the CH₄ concentration in the Syngas.

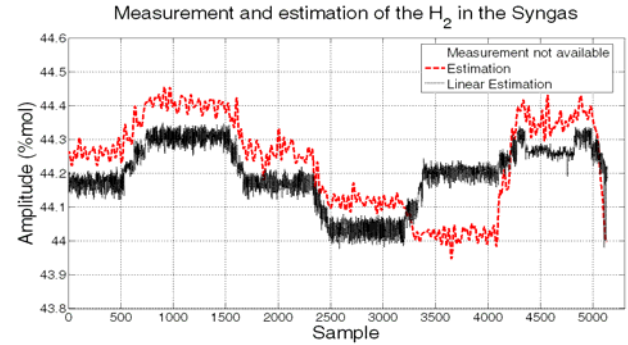


Fig. 8. Predictions of the H₂ concentration in the Syngas.

better estimation of the Syngas composition rather than the linear model previously presented.

In Figures 7, 8, 9 and 10 results relative to CH₄, H₂, CO and CO₂ estimations are shown and a comparison between the Gibbs based model and the linear model are depicted: from figures inspection it can be ascertained that the chemical-physic model of the gasification process performs better agreement with the real measurements; the only compound which is better estimated by the linear model is the carbon dioxide (CO₂) but the two estimations are very close to each other. The estimation of H₂ concentration cannot be compared with the real measurement owing to the unavailability of a gas chromatograph (Figure 8).

In Table III, the computed Root Mean Square Errors Prediction (RMSEP) relative to the Gibbs and linear estimation of every compound has been summarized. RMSEP index is given by the following expression:

$$\text{RMSEP} = \sqrt{\frac{\sum_{i=1}^N e_i^2}{N}} \quad (26)$$

where e_i is the difference between the estimation and the measurement and N is the number of samples.

TABLE III
FITTING COMPARISON

COMPOUND ESTIMATED	RMSEP	
	GIBBS MODEL	LINEAR MODEL
CH ₄	0.0352%	0.0469%
H ₂	Not available	
CO	1.7040%	2.0911%
CO ₂	0.1701%	0.1072%

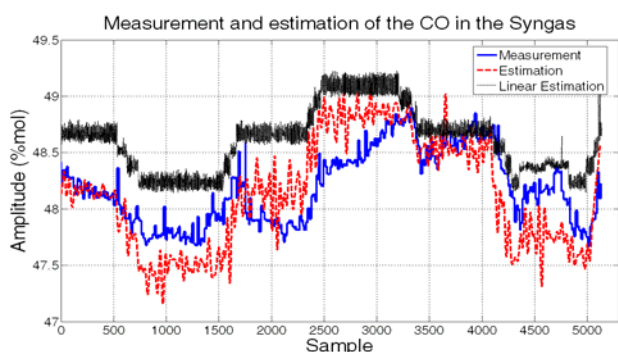


Fig. 9. Predictions of the CO concentration in the Syngas.

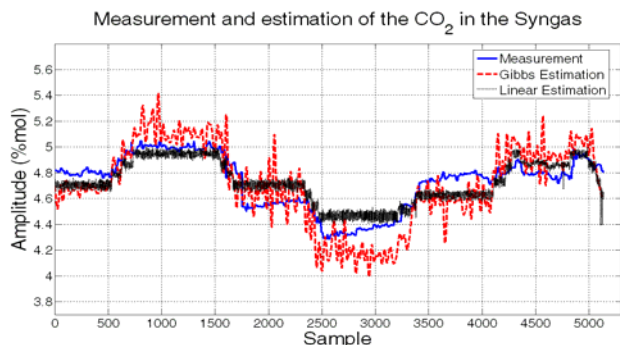


Fig. 10. Predictions of the CO₂ concentration in the Syngas.

V. CONCLUSION

In this work, a chemical-physical model of a gasification plant is presented. The model is able to predict the composition of a particular gas (called Syngas) produced by the plant and it can be used as internal model in a Model-Based Predictive Control (MPC) strategy and/or in a Fault Diagnosis system. Actually, the prediction provided by the model is used to support the online gascromathographic measurements of the Syngas composition which are often not available because of periodic calibration. Comparing the first-principles model proposed in this paper with the linear model obtained by the authors with a greybox approach presented in a previous work, it can be stated that better performances in the Syngas composition estimation are obtained with the new approach. This chemical-physical model overcomes the limitation introduced by the use of a linear model and provides good estimations even when the range of the stoichiometric ratio is extended outside the boundaries of validity of a linear model.

The proposed formulation takes into account the key reactions that occur during the process of gasification and the main compounds have been identified. The procedure is based on minimization of the total system Gibbs energy and the problem, that is limited to gas-phase reactions, is to find the equilibrium composition for given temperature and pressure and for a given initial feed. This procedure is particularly suited for complex systems and allows overcoming the difficulties introduced by the use of the classical approach based on the equilibrium constant to determine equilibrium concentrations of composition

compounds. In fact, in order to find the solution approaching the problem with classical methods it is necessary to hand write the equilibrium reactions and its application for large systems is very cumbersome. Conversely, the method based on Gibbs energy minimization does not require writing any chemical reaction and the only required information are the compounds of the equilibrium composition and the conditions (temperature and pressure) at which the reactions take place.

To test the model, a step test has been performed on the plant. In order to greatly excite the plant so to produce a significant step variation in the Syngas composition, the step test has been performed perturbing both the stoichiometric ratios (O₂/Charge Oil and Steam/Charge Oil). The validation phase has shown the goodness of the model to predict the real variation in the Syngas composition.

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