



Modeling of syngas composition obtained from fluidized bed gasifiers using Kuhn–Tucker multipliers

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ABSTRACT

This work aims to develop a modified chemical equilibrium model to accurately determine the syngas (synthesis gas) composition obtained from fluidized bed gasifiers. In order to do so, an optimization method was applied to determine the correction factors which modify the chemical equilibrium constants, the carbon conversion efficiency and the enthalpy of reaction. The gasification agents considered for this study were: air, steam, air–steam, and air–steam–oxygen. The optimization method used the Kuhn–Tucker multipliers to obtain small RMS errors.

A total of 76 experimental compositions of syngas were selected. Among these data 60 were used to obtain correlations for the correction factor, the carbon conversion efficiency and the enthalpy of reaction. Then, a modified chemical equilibrium model was formulated by a taking advantage of these correlations.

The modified chemical equilibrium model was validated showing very good accuracy for the determination of the syngas composition, the RMS error were found to be between 0.94 and 4.84.

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1. Introduction

Currently, gasification is one of the most widely used biomass applications [1–6]. Among the different gasifier types the fluidized bed gasifiers present several remarkable characteristics. Some of these characteristics are: good mixing between biomass and gasifying agents, low nitrogen content in syngas composition, high carbon conversion efficiency, moderate production of tars and elevated lower heating value of syngas [6]. There are two types of fluidized bed gasifiers, i.e. the bubbling and circulating fluidized bed gasifiers [4]. These gasifiers are schematically presented in Fig. 1. A detailed description of the characteristics and operation of fluidized bed gasifiers can be found in the literature [1–6].

The syngas (fuel gas obtained from gasification) composition can be basically obtained by two modelling approaches which are: chemical equilibrium modelling and kinetic modelling [4]. A chemical equilibrium model allows to calculate the concentrations of gaseous products of gasification at a given gasification temperature, these concentrations being invariable for a theoretically infinite reaction time [2]. Also, a chemical equilibrium model does not consider the geometrical characteristics of the gasifier and the

hydrodynamics of the mixing process between the biomass and the gasifying agents (air, steam or oxygen) [1]. On the other hand, a kinetic model is used to study the progress of chemical reactions that take place inside the gasifier, thus allowing to determine the concentrations of gaseous products at different positions along the gasifier evaluated in a given time. It takes into account the gasifier's geometry as well as its hydrodynamics [1].

In the works by Loha et al. [7] and by Karmakar et al. [8] a chemical equilibrium model (which does not consider char and tar as products) was developed. The chemical equilibrium model applied in both aforementioned works propose the solution of a system of equations. This system is constituted by the mass conservation equations of carbon, hydrogen and oxygen, and the chemical equilibrium equations of the methane formation reaction and the homogenous water–gas reaction. Subsequently, by solving this system of equations, the number of moles of the gases present in the reaction are calculated. Finally, the adjustment of the chemical equilibrium model consists of multiplying correction factors (calculated by trial and error) to the chemical equilibrium constants to evaluate the approximation of the theoretical composition of the syngas to the experimental composition, thus originating a decrease of the RMS error [9]. A chemical equilibrium model that incorporates correction factors for chemical equilibrium constants is referred to in the present research as a modified chemical equilibrium model. A modified chemical equilibrium

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Nomenclature			
\bar{c}_p^o	Specific heat capacity at constant pressure in molar basis, kJ/K-mol	WGHR	Water-gas homogeneous reaction
\bar{h}^o	Specific enthalpy in molar basis, kJ/mol	MRR	Methane reforming reaction
\bar{h}_{f-298}^o	Specific formation enthalpy at normal conditions in molar basis, kJ/mol	K_i	Equilibrium constant for the “ith” reaction
\bar{s}^o	Specific entropy in molar basis, kJ/K-mol	EP_i	Experimental percent amount of substance “ith”, %
\bar{g}^o	Gibbs free energy in molar basis, kJ/mol	RMS	Root mean square error
T_i	Inlet temperature of the “ith” gasifying agent into the gasifier, K	F_{Obj}	Objective function
$a_i (i = 1, \dots, 7)$	NASA-Glenn coefficients	f_{MFR}	Correction factor for the MFR
$b_i (i = 1, 2)$	NASA-Glenn integration constants	f_{WGHR}	Correction factor for the WGHR
\bar{R}	Universal gas constant, kJ/K-mol	f_{MRR}	Correction factor for the MRR
DBOA	Dry basis without biomass ash	<i>Chemical symbols</i>	
DBWA	Dry basis with biomass ash	C	Carbon
WBWA	Wet basis with biomass ash	H	Hydrogen
DBWN	Dry basis with nitrogen for the syngas composition	O	Oxygen
DBON	Dry basis without nitrogen for the syngas composition	N	Nitrogen
LHV _{Bio}	Lower heating value of biomass, MJ/kg	S	Sulfur
HHV _{Bio}	Higher heating value of biomass, MJ/kg	SiO ₂	Silicon dioxide
f_i	Number of moles for the “ith” substance per mole of carbon in the biomass, mol	H ₂ O	Water
PM _i	Molar mass for the “ith” substance, g/mol	O ₂	Oxygen gas
$(P_i)_{DBWA}$	Percentage of the “ith” substance in DBWA, %	N ₂	Nitrogen gas
$(P_{Ash})_{WBWA}$	Percentage of ash in WBWA, %	H ₂	Hydrogen gas
$(P_{Moist})_{WBWA}$	Percentage of moisture in WBWA, %	CO	Carbon monoxide
TM _{DBWA}	Total mass in DBWA	CO ₂	Carbon dioxide
H ^o	Total enthalpy, kJ	CH ₄	Methane
x_{Air}	Air coefficient as a gasifying agent	SO ₂	Sulfur dioxide
x_i	Number of moles for the “ith” substance, mol	<i>Greek symbols</i>	
x_T	Total number of moles for gases present in the global gasification reaction, mol	ρ_{atm}	Experimental percentage ratio between nitrogen and oxygen in the air
x_{Syn}	Number of moles of the syngas, mol	$\Delta \bar{h}_{React}^o$	Enthalpy of global gasification reaction, kJ/mol
n_{CC}	Carbon conversion efficiency, %	$\mu_i (i = 1, \dots, 6)$	Kuhn–Tucker multiplier
AF _{Exp}	Experimental air-fuel ratio, kg-air/kg-fuel	$\alpha_i (i = 1, 2, 3)$	Variable used for notation change of n_{CC} , x_{CO_2} and x_{CH_4}
AF _{Stq}	Stoichiometric air-fuel ratio, kg-air/kg-fuel	<i>Superscripts</i>	
ER	Equivalent ratio for gasification	o	Magnitude evaluated at normal pressure
S/B	Mass ratio of steam and biomass, kg-steam/kg-biomass	<i>Subscripts</i>	
O/B	Mass ratio of oxygen and biomass, kg-oxygen/kg-biomass	Ash	Ash
T_{Gas}	Gasification temperature, K	Moist	Moisture
P_{Gas}	Gasification pressure, atm	l	Liquid
P_o	Normal pressure, atm	s	Solid
MFR	Methane formation reaction	P	Products
		R	Reagents
		Steam	Steam
		Air	Air
		Oxy	Oxygen
		Bio	Biomass

model for modeling the syngas composition is also used in other studies [10–13].

In the work by Radmanesh et al. [14] a kinetic model was developed. This model uses the hydrodynamics of the solid and gaseous phases, as well as diverse heterogeneous and homogeneous reactions. The process of pyrolysis was considered very important and two kinetic models were used for this process. These models proved to be good to estimate the composition of the syngas and its LHV. In a similar way, in the work by Zheng and Morey [15], a biphasic kinetic model was developed, that model includes the kinetics of reaction and fluid dynamics for the gasification process of corn stover. The model predicts the compositions of syngas along the gasifier and the evolution of the particles over

time, under different gasification conditions. From the obtained results, it is observed that the homogenous water-gas reaction and the residence time are very influential factors in the composition of the syngas.

Thus, it was decided to use a modified chemical equilibrium model due to the simplicity of the model with respect to a kinetic model, in relation to the objective proposed in this research.

In view of the actuality of modified chemical equilibrium models, one of the main objectives of this study is to calculate in an analytical and simple way the correction factors for the chemical equilibrium constants. Another objective of this research is to calculate a theoretical syngas composition very close to the experimental one to obtain a very low value of the RMS error. In

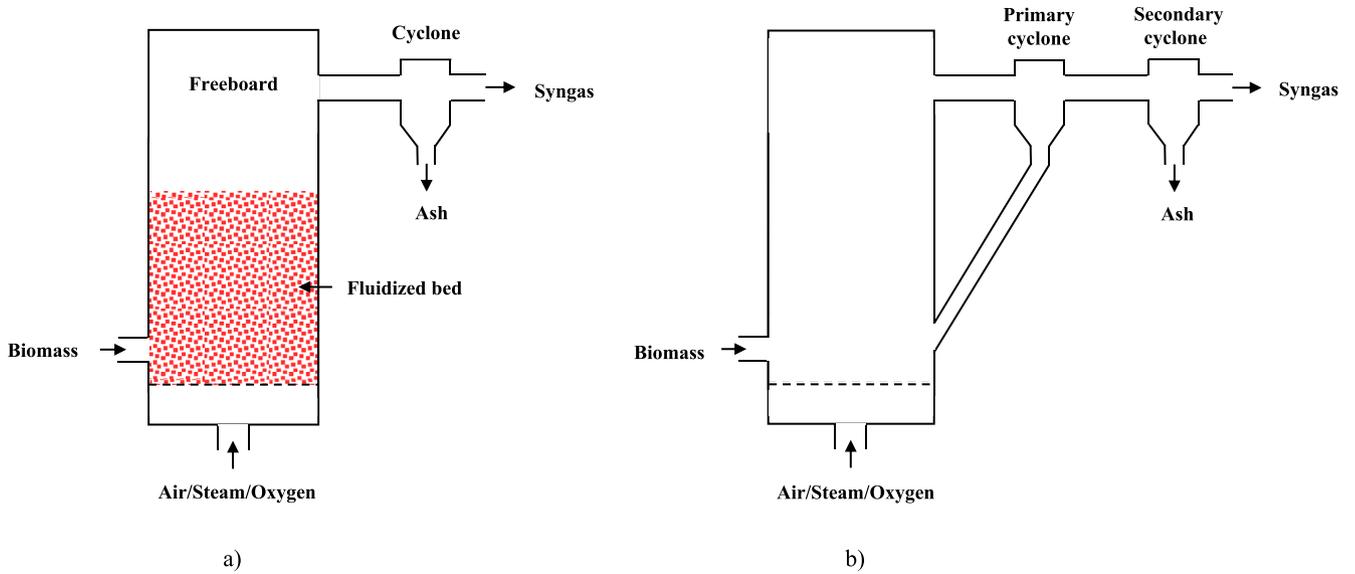


Fig. 1. Schematic representation of: a) bubbling fluidized bed gasifier and b) circulating fluidized bed gasifier.

addition, it is intended to consider the char, represented by $C_{(s)}$, as a product of the gasification process. Thus, establishing a more real modified chemical equilibrium model for the gasification. On the other hand, the present investigation is relevant for the following future studies:

- a) Study of the economic viability of the use of syngas in power generation systems (internal combustion engines, gas turbines or steam turbines).
- b) Thermodynamic study of syngas combustion in power generation systems.
- c) Study of the energy viability for the selection of a biomass based on the LHV of the syngas obtained from a fluidized bed gasifier.
- d) Study of optimal gasification conditions to obtain the highest concentration of syngas components obtained from a fluidized bed gasifier.

Each of the aforementioned future studies can be carried on by using the modified chemical equilibrium model proposed for: a) Gasification with air, b) Gasification with steam, c) Gasification with air and steam, and d) Gasification with air, steam and oxygen.

2. Determination of the correction factors

2.1. Biomass representation and properties

The concentration of carbon in the biomass is important for the production of CO , CO_2 and CH_4 , since carbon is one of the reactants of the exothermic reactions (fundamental in gasification) such as the carbon combustion reaction and the methane formation reaction [6]. In addition, these reactions provide the necessary heat for endothermic reactions such as the Boudouard reaction and the heterogeneous water-gas reaction, in which carbon is also one of the reactants [4]. The content of hydrogen in the biomass is very influential in the production of H_2 , CH_4 and H_2O present in the syngas (on a wet basis). This is because hydrogen helps the exothermic reactions of methane formation and methane reforming [6]. The oxygen content in the biomass promotes the combustion reactions thus helping the production of CO and CO_2 . A high concentration of oxygen in the biomass helps to reduce a little

the mass flow of the oxidizing agent [16].

There are different values of admissible upper limits of tar concentration for syngas applications [1]. The tars are constituted by diverse compounds among which H_2S , SO_2 , COS , NH_3 , HCN , nitriles (NO_x) are included [4]. Due to these upper limits, it is desirable that the biomasses have low concentration of sulfur and nitrogen in them.

The ash and the moisture contents of the biomass have a great influence on the production of H_2 and CO . This is because high concentrations of ash and moisture produce a great absorption of the energy supplied for gasification, as is the case of the gasification of rice husk [7,8,17–19] and of sugarcane bagasse [16] which present high concentration of ash and moisture, respectively. This energy absorption does not allow many endothermic reactions (such as the Boudouard reaction and the heterogeneous water-gas reaction) to occur inside the gasifier, thus causing the lack of H_2 and CO production, important syngas components for use in systems of power generation [6].

In this research, the thermodynamic properties were evaluated by using the NASA-Glenn coefficients provided by McBride et al. [20]. These properties were the specific molar heat capacity at constant pressure (\bar{c}_p^0), the specific molar enthalpy (\bar{h}^0) and the specific molar entropy (\bar{s}^0) of chemical substances. The aforementioned thermodynamic properties are calculating according to equations (1)–(3). On the other hand, the Gibbs free energy (\bar{g}^0) is obtained from the relation: $\bar{g}^0 = \bar{h}^0 - T\bar{s}^0$.

$$\bar{c}_p^0 = (a_1T^{-2} + a_2T^{-1} + a_3 + a_4T + a_5T^2 + a_6T^3 + a_7T^4)\bar{R} \quad (1)$$

$$\bar{h}^0 = (-a_1T^{-1} + a_2 \ln T + a_3T + \frac{a_4}{2}T^2 + \frac{a_5}{3}T^3 + \frac{a_6}{4}T^4 + \frac{a_7}{5}T^5 + b_1)\bar{R} \quad (2)$$

$$\bar{s}^0 = (-\frac{a_1}{2}T^{-2} - a_2T^{-1} + a_3 \ln T + a_4T + \frac{a_5}{2}T^2 + \frac{a_6}{3}T^3 + \frac{a_7}{4}T^4 + b_2)\bar{R} \quad (3)$$

The ultimate and proximate analysis of biomass are necessary in

order to represent the biomass as a chemical formula. The ultimate analysis provides the mass concentrations of C, H, O, N and S in the biomass, and it can be expressed in dry basis without ash (DBOA) or dry basis with ash (DBWA). The proximate analysis provides the mass concentrations of fixed carbon, volatiles, moisture and ash in the biomass, and it is generally expressed in wet basis with ash (WBWA).

There are several inorganic compounds contained in the biomass ash, because of this it is not possible to write a general chemical formula for the biomass ash. Therefore, in this work, biomass ash was assumed as being composed solely of silicon dioxide (SiO_2), as suggested by Souza-Santos [2] and applied in previous works [13,21].

In this work, the WBWA was used to express the number of moles of chemical elements in the biomass. Therefore, it was necessary to convert from DBOA or DBWA to WBWA. The expressions used to do so are presented in the [supplementary material](#). A chemical representation of the biomass is shown in equation (4).



When the higher heating value (HHV_{Bio}) and the lower heating value (LHV_{Bio}) of the biomass were not available, the correlation provided by Channiwala and Parikh [22] was used to determine the HHV_{Bio} . That correlation is presented in equation (5) and provides the HHV_{Bio} in MJ/kg. Notice that in order to use this correlation it is

$$\begin{aligned} & (\text{C H}_f \text{H}_f \text{O}_f \text{O}_f \text{N}_f \text{N}_f \text{S}_f \text{S}_f + f_{\text{Ash}} \text{SiO}_2 + f_{\text{Moist}} \text{H}_2\text{O}_{(l)}) + x_{\text{Steam}} \text{H}_2\text{O} + x_{\text{Air}} (\text{O}_2 + \rho_{\text{atm}} \text{N}_2) + x_{\text{Oxy}} \text{O}_2 \\ & \rightarrow (1 - n_{\text{CC}}) \text{C}_{(s)} + x_{\text{H}_2} \text{H}_2 + x_{\text{CO}} \text{CO} + x_{\text{CO}_2} \text{CO}_2 + x_{\text{CH}_4} \text{CH}_4 + \left(\frac{f_{\text{N}}}{2} + \rho_{\text{atm}} x_{\text{Air}} \right) \text{N}_2 \\ & + x_{\text{H}_2\text{O}} \text{H}_2\text{O} + f_{\text{S}} \text{SO}_2 + f_{\text{Ash}} \text{SiO}_2 \end{aligned} \quad (10)$$

necessary to express the biomass in DBWA.

$$\text{HHV}_{\text{Bio}} = 0.3491(P_{\text{C}})_{\text{DBWA}} + 1.1783(P_{\text{H}})_{\text{DBWA}} + 0.1005(P_{\text{S}})_{\text{DBWA}} - 0.1034(P_{\text{O}})_{\text{DBWA}} - 0.0151(P_{\text{N}})_{\text{DBWA}} - 0.0211(P_{\text{Ash}})_{\text{DBWA}} \quad (5)$$

for:

$$\begin{aligned} 0.00\% & \leq (P_{\text{C}})_{\text{DBWA}}\% \leq 92.25\%; \\ 0.43\% & \leq (P_{\text{H}})_{\text{DBWA}}\% \leq 25.15\%; \\ 0.00\% & \leq (P_{\text{O}})_{\text{DBWA}}\% \leq 50.00\%; \\ 0.00\% & \leq (P_{\text{N}})_{\text{DBWA}}\% \leq 5.60\%; \\ 0.00\% & \leq (P_{\text{S}})_{\text{DBWA}}\% \leq 94.08\%; \\ 0.00\% & \leq (P_{\text{Ash}})_{\text{DBWA}}\% \leq 71.40\%; \\ 4.745 \text{ MJ/kg} & \leq \text{HHV}_{\text{Bio}} \leq 55.345 \text{ MJ/kg} \end{aligned} \quad (6)$$

In order to apply the First Law of Thermodynamics, the enthalpy of formation of the biomass must be known, it can be determined by using equation (7).

$$\begin{aligned} (\bar{h}_{f-298}^{\circ})_{\text{Bio}} & = \text{HHV}_{\text{Bio}} \text{PM}_{\text{Bio}} + \left(\frac{1 \text{ mol CO}_2}{1 \text{ mol Bio}} \right) (\bar{h}_{f-298}^{\circ})_{\text{CO}_2} + \left(\frac{f_{\text{H}}}{2 \text{ mol Bio}} \right) (\bar{h}_{f-298}^{\circ})_{\text{H}_2\text{O}_{(l)}} \\ & + \left(\frac{f_{\text{S}}}{1 \text{ mol Bio}} \right) (\bar{h}_{f-298}^{\circ})_{\text{SO}_2} \end{aligned} \quad (7)$$

where the molecular mass of the biomass is given by equation (8).

$$\text{PM}_{\text{Bio}} = \text{PM}_{\text{C}} + f_{\text{H}} \text{PM}_{\text{H}} + f_{\text{O}} \text{PM}_{\text{O}} + f_{\text{N}} \text{PM}_{\text{N}} + f_{\text{S}} \text{PM}_{\text{S}} \quad (8)$$

This expression for the molecular mass of the biomass has also been adopted in other gasification studies [7,23]. The total enthalpy of biomass is presented in equation (9).

$$\text{H}_{\text{Bio}}^{\circ} = 1 \text{ mol}_{\text{Bio}} (\bar{h}_{f-298}^{\circ})_{\text{Bio}} + f_{\text{Ash}} (\bar{h}_{f-298}^{\circ})_{\text{SiO}_2} + f_{\text{Moist}} (\bar{h}_{f-298}^{\circ})_{\text{H}_2\text{O}_{(l)}} \quad (9)$$

2.2. Equilibrium modeling of the gasification process

The gasification agents generally employed in fluidized bed gasification are steam [7,24,25], air [8,26,27], oxygen and their mixtures [17,23,28,29]. Consequently, the global gasification reaction proposed herein has been determined with the aim of including all commonly used gasifying agents. In the adopted global reaction, unconverted carbon ($\text{C}_{(s)}$) can be found in the products. Thus, a carbon conversion efficiency was included and it is represented by n_{CC} [18,21]. The global gasification reaction adopted in this study is presented in equation (10).

The parameter ρ_{atm} represents the number of moles of nitrogen per mole of oxygen on the air. In this research, nitrogen and oxygen percentages were assumed to be 79% and 21%, respectively, this assumption implies that $\rho_{\text{atm}} = 3.76$.

When air is the gasification agent, the gasification equivalence ratio (ER) is used. The ER is defined as the ratio of the experimental air-fuel ratio to the stoichiometric air-fuel ratio, $\text{ER} = \text{AF}_{\text{Exp}} / \text{AF}_{\text{Stq}}$. Therefore, the coefficient of the air used in the gasification is defined in the equation (11).

$$x_{\text{Air}} = \text{ER} \left(1 + f_{\text{S}} + \frac{f_{\text{H}}}{4} - \frac{f_{\text{O}}}{2} \right) \quad (11)$$

When steam is the gasification agent, the steam to biomass ratio (S/B) is used. Therefore, the number of moles of steam can be obtained from equation (12).

$$\text{S/B} = \frac{x_{\text{Steam}} \text{PM}_{\text{H}_2\text{O}}}{\text{PM}_{\text{Bio}}} \quad (12)$$

When oxygen is the gasification agent, the ratio of oxygen mass flow rate to biomass mass flow rate (O/B) is used. This ratio is defined in equation (13).

$$O/B = \frac{PM_{O_2}(\dot{V}_{Oxy}/22.4)}{\dot{m}_{Bio}} \quad (13)$$

Where \dot{V}_{Oxy} is the volumetric flow rate of oxygen in Nm^3/h , \dot{m}_{Bio} is the mass flow rate of biomass in kg/h , and $22.4 m^3$ is the volume occupied by 1 kmol of an ideal gas at normal pressure and temperature conditions. Therefore, the number of moles of oxygen can be determined by equation (14).

$$x_{Oxy} = \frac{(O/B)PM_{Bio}}{PM_{O_2}} \quad (14)$$

Once the global gasification reaction has been adopted and the number of moles of the reactants have been determined, the Law of Mass Conservation was applied to each chemical element in the reaction. After some algebraic manipulations, the expressions shown in equations (15)–(18) were obtained. The total number of moles of the gaseous products (x_T) is given by equation (18).

$$x_{CO} = n_{CC} - x_{CO_2} - x_{CH_4} \quad (15)$$

$$x_{H_2} = C_{H_2} + n_{CC} + x_{CO_2} - 3x_{CH_4} \quad (16)$$

$$x_{H_2O} = C_{H_2O} - n_{CC} - x_{CO_2} + x_{CH_4} \quad (17)$$

$$x_T = C_T + n_{CC} - 2x_{CH_4} \quad (18)$$

where C_{H_2} , C_{H_2O} and C_T are input parameters that depend only on the reactants:

$$C_{H_2} = \frac{f_H}{2} - f_O - 2x_{Oxy} - 2x_{Air} + 2f_S \quad (19)$$

$$C_{H_2O} = f_O + f_{Moist} + 2x_{Oxy} + x_{Steam} + 2x_{Air} - 2f_S \quad (20)$$

$$C_T = \frac{f_H}{2} + f_{Moist} + x_{Steam} + \frac{f_N}{2} + \rho_{atm}x_{Air} + f_S \quad (21)$$

It should be noticed that equations (15)–(18) have been written in such a way that n_{CC} , x_{CO_2} and x_{CH_4} are independent variables, while, x_{CO} , x_{H_2} , x_{H_2O} and x_T are dependent variables.

The First Law of Thermodynamics was applied to the global gasification reaction, and the resulting expression is presented in equation (22). There is no work crossing the boundaries of the system, and changes in kinetic and potential energy are negligible.

$$1 \text{ mol}_{Bio} \Delta \bar{h}_{React} = H_P^0 - H_R^0 \quad (22)$$

where:

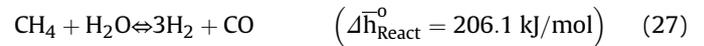
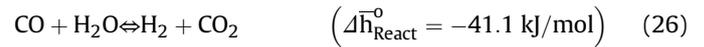
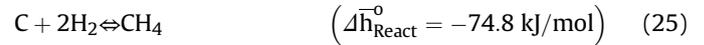
$$H_P^0 = (1 - n_{CC})\bar{h}_C^0 + x_{H_2}\bar{h}_{H_2}^0 + x_{CO}\bar{h}_{CO}^0 + x_{CO_2}\bar{h}_{CO_2}^0 + x_{CH_4}\bar{h}_{CH_4}^0 + x_{H_2O}\bar{h}_{H_2O}^0 + \left(\frac{f_N}{2} + \rho_{atm}x_{Air}\right)\bar{h}_{N_2}^0 + f_S\bar{h}_{SO_2}^0 + f_{Ash}\bar{h}_{SiO_2}^0 \quad (23)$$

$$H_R^0 = H_{Bio}^0 + x_{Steam}\bar{h}_{H_2O}^0 + x_{Air}\bar{h}_{O_2}^0 + x_{Air}\rho_{atm}\bar{h}_{N_2}^0 + x_{Oxy}\bar{h}_{O_2}^0 \quad (24)$$

T_{Steam} , T_{Air} and T_{Oxy} are the inlet temperatures of steam, air and

oxygen, respectively, which are used to evaluate their enthalpies. The gasification temperatures (T_{Gas}) are provided in the experimental works and they are used to determine the enthalpies of the products.

In order to complete the system of equation for determining the number of moles of the products at the gasification temperature T_{Gas} , the chemical equilibrium condition was applied. Three reactions have been commonly adopted to model the equilibrium composition of the gasification in fluidized bed gasifiers. These reactions are the methane formation reaction (MFR) [18,19,30–32], water–gas homogeneous reaction (WGHR) [7,8,19,33,34] and methane reforming reaction (MRR) [19,32,33], which are shown in equations (25)–(27), respectively.



The chemical equilibrium constants obtained from the reactions presented above are shown in equations (28)–(30), respectively [1,35,36].

$$K_{MFR} = \frac{x_{CH_4}x_T}{(x_{H_2})^2} \left(\frac{P_{Gas}}{P_o}\right)^{-1} \quad (28)$$

$$K_{WGHR} = \frac{x_{CO_2}x_{H_2}}{x_{CO}x_{H_2O}} \quad (29)$$

$$K_{MRR} = \frac{x_{CO}(x_{H_2})^3}{x_{CH_4}x_{H_2O}(x_T)^2} \left(\frac{P_{Gas}}{P_o}\right)^2 \quad (30)$$

Generally, the gasification pressure (P_{Gas}) in fluidized bed gasifiers is equal to the normal pressure (P_o), thus the ratio of gasification pressure to normal pressure might have no effect on equations (28) and (30).

2.3. Optimization method to obtain correction factors

There are different studies which present advances regarding the calculation of the correction factors. These studies are briefly described below.

In the work by Loha et al. [7] the adjustment of the chemical equilibrium model was made by multiplying the chemical equilibrium constants of the methane formation reaction and the homogeneous water–gas reaction by the correction factors of 0.93 and 0.71, respectively. In this way, average RMS error over six samples of syngas composition was decreased from an initial value of approximately 3.34 to a final value of 2.62.

In the work by Jarunghammachote and Dutta [10] correction factors with values 11.28 and 0.91 were multiplied to the chemical equilibrium constants of the methane formation and homogeneous water–gas reactions, respectively. This adjustment was made to approximate the modified chemical equilibrium model to the experimental data, being the factor 11.28 and 0.91 necessary to adjust the concentration of CH_4 and CO , respectively.

In the work by Barman et al. [12] the correction factor of the chemical equilibrium constant of the methane formation reaction was calculated by increasing in steps of 0.5 a correction factor that was initially 1. At the end of this process, the correction factor selected was 3.5. For the homogeneous water–gas reaction, a

correction factor was not included due to the high gasification temperature, instead it was considered that this reaction reaches chemical equilibrium.

In the work by Mendiburu et al. [13] the adjustment of the chemical equilibrium constants of the methane formation and homogenous water-gas reactions was performed. The correction factor of the methane formation reaction was obtained by adjusting the model to the experimental data of the selected works. A similar process determined the correction factor of the homogeneous water-gas reaction.

In the work by Lim and Lee [37], empirical relations (based on

the ER parameter) were used to calculate the correction factors for the methane formation and homogeneous water-gas formation reactions.

2.3.1. The objective functions

As aforementioned, the correction factors are used to better approximate the experimental syngas composition using chemical equilibrium models. In other works, these correction factors have been obtained by trial and error without relying in any analytical method for their calculation [7,10–13]. In the present work, the correction factors have been determined through an optimization

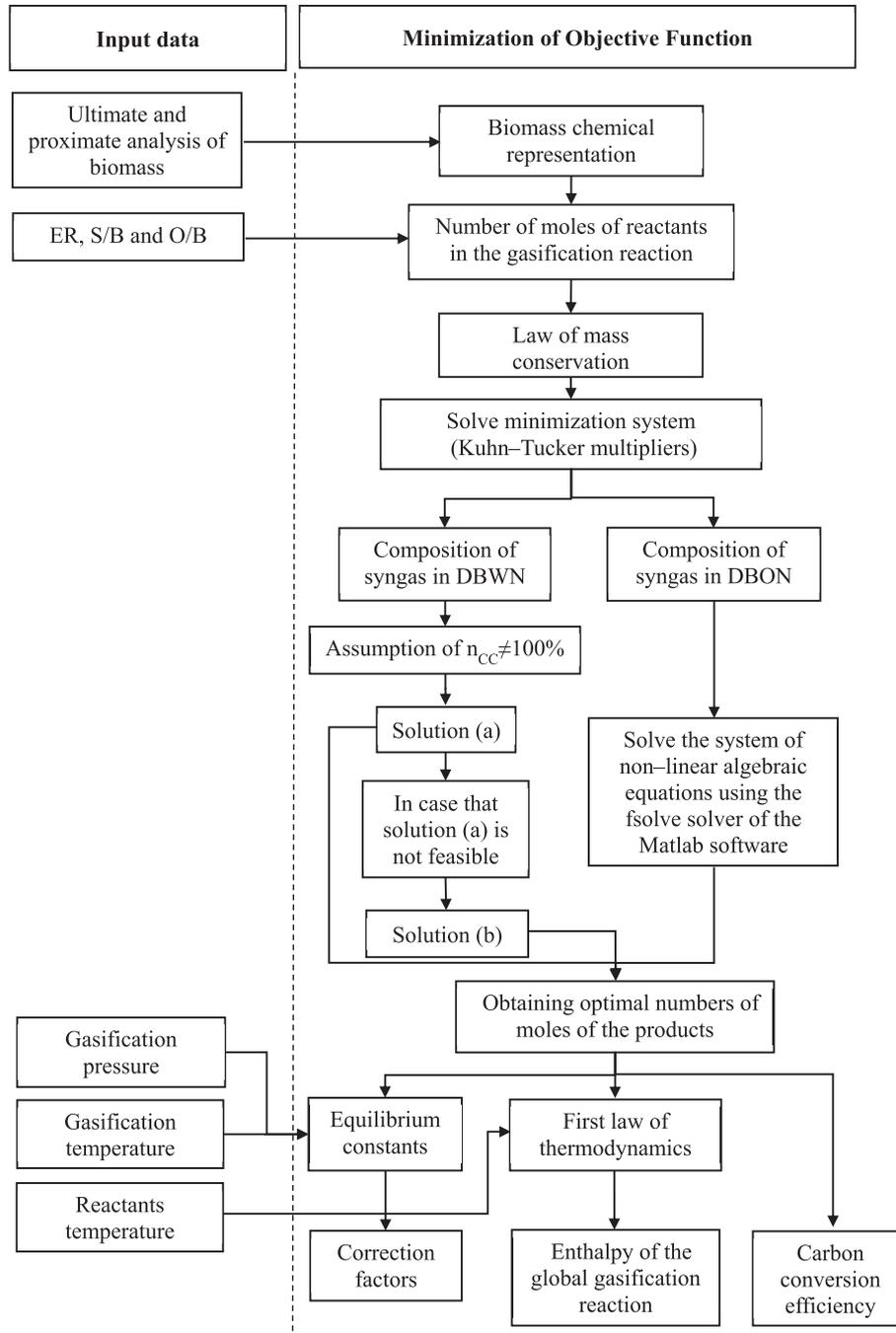


Fig. 2. Optimization method solution scheme.

method which uses the Kuhn–Tucker multipliers [38–42]. The procedure followed in this section is depicted in Fig. 2.

The proposed method consists in the minimization of an objective function that is derived from the definition of RMS error [9]. The objective function depends on the number of moles of syngas (x_{Syn}) derived from the experimental composition reported in scientific articles.

The syngas composition is generally given in dry basis with nitrogen (DBWN) or dry basis without nitrogen (DBON). DBWN is mostly used when air is the gasifying agent, while DBON is generally used when steam or oxygen are the gasifying agents. Therefore, the number of moles of syngas (x_{Syn}) is different from the total number of moles of gases (x_T), because the later considers the number of moles of steam (x_{H_2O}) and sulfur dioxide (f_s) present in the products while the former does not. The experimental concentration of the species “i” (H_2 , CO , CO_2 , CH_4 or N_2) is defined by equation (31).

$$EP_i\% = \frac{100x_i}{x_{Syn}}\% \quad (31)$$

The number of moles of syngas, x_{Syn} , in DBWN is given by equation (32). On the other hand, the value of x_{Syn} in DBON is given in equation (33).

$$x_{Syn} = \frac{100\left(\frac{f_s}{2} + \rho_{atm}x_{Air}\right)}{EP_{N_2}} \quad (32)$$

$$x_{Syn} = C_{H_2} + 2n_{CC} + x_{CO_2} - 3x_{CH_4} \quad (33)$$

The RMS error obtained is presented in equation (34) being “n” the number of species of the syngas. Hence, the objective functions obtained for DBWN and DBON are given by equations (35) and (36), respectively.

$$RMS = \sqrt{\frac{\sum_{i=1}^n (EP_i x_{Syn} - 100x_i)^2 x_{Syn}^{-2}}{n}} \quad (34)$$

Objective function for DBWN

$$F_{Obj}(n_{CC}, x_{CO_2}, x_{CH_4}) =: F_{Obj} = \sum_{i=H_2, CO, CO_2, CH_4, N_2} (EP_i x_{Syn} - 100x_i)^2 \quad (35)$$

Objective function for DBON

$$F_{Obj}(n_{CC}, x_{CO_2}, x_{CH_4}) =: F_{Obj} = \sum_{i=H_2, CO, CO_2, CH_4} (EP_i x_{Syn} - 100x_i)^2 x_{Syn}^{-2} \quad (36)$$

The independent variables of the objective functions have their domains defined in [0,1]. On the other hand, the co-domains of the objective functions are defined in R (set of real numbers). It is important to mention that the objective function for DBWN and DBON are a strictly convex and a convex function, respectively.

2.3.2. Optimization using Kuhn–Tucker multipliers

In the present section the variables n_{CC} , x_{CO_2} and x_{CH_4} have been substituted by α_1 , α_2 and α_3 , respectively. It is important to mention

that the optimization that uses the Kuhn–Tucker multipliers is the generalization of the Lagrange multipliers optimization method. Thus, in order to perform an optimization using the Kuhn–Tucker multipliers (μ) it is essential to define the Lagrangian expression (L) with inequality constraints obtained from the domains of independent variables (n_{CC} , x_{CO_2} and x_{CH_4}). The Lagrangian expression is shown in equation (37). While, the independent variables have to satisfy the inequality constraints, obtained from their domains, presented in equation (38).

$$L = F_{Obj} + \sum_{i=1}^3 \mu_i(\alpha_i - 1) - \sum_{i=1}^3 \mu_{i+3}\alpha_i \quad (37)$$

$$0 \leq \alpha_i, \alpha_i \leq 1 \text{ and } \mu_j \geq 0 \text{ for } i = 1 \text{ to } 3 \text{ and } j = 1 \text{ to } 6 \quad (38)$$

The Karush–Kuhn–Tucker conditions [38–42] were applied to equation (37) obtaining six equations (Complementarity constraints) which are the following: $\mu_i(\alpha_i - 1) = 0$ and $\mu_{i+3}\alpha_i = 0$ for $i = 1$ to 3. Notice that the conditions establish that $0 \leq \alpha_i$ and $\alpha_i \leq 1$. From the experimental results [7,8,14,16,17,19,23,25,28,29,43] it is known that the number of moles of CO , CO_2 and CH_4 must be greater than zero. Among the different possibilities that can satisfy the equations, some were discarded, for instance, it was discarded that:

- a) $\alpha_2 = 1$ or $\alpha_3 = 1$.
- b) $\alpha_2 = 0$ or $\alpha_3 = 0$.
- c) $\alpha_1 = 0$.

Therefore, some of the Kuhn–Tucker multipliers could be obtained which are shown in equation (39).

$$\mu_{i+1} = 0 \text{ for } i = 1 \text{ to } 5 \quad (39)$$

Substituting the values of the Kuhn–Tucker multipliers, shown in equation (39), into the system of equations obtained from the Lagrangian expression, the result is the system shown in equations (40) – (42).

$$\frac{\partial F_{Obj}}{\partial \alpha_1} + \mu_1 = 0 \quad (40)$$

$$\frac{\partial F_{Obj}}{\partial \alpha_{i+1}} = 0 \text{ for } i = 1 \text{ to } 2 \quad (41)$$

$$\mu_1(\alpha_1 - 1) = 0 \quad (42)$$

This system of equations is limited by the inequalities presented in equation (38), but knowing that equation (39) is also satisfied.

Now the objective functions for DBWN [equation (35)] and for DBON [equation (36)] are replaced in equations (40) and (41) to then solve the system of equations (40) – (42).

In the case of the objective function for DBWN there are two possible solutions: (a) for the case in which $\mu_1 = 0$ and $n_{CC} \neq 100\%$, and, (b) for the case in which $\mu_1 \neq 0$ and $n_{CC} = 100\%$. Then, for the solution (a) the values of n_{CC} , x_{CO_2} and x_{CH_4} are determined by the equations (43) – (45). On the other hand, for solution (b) the value of $n_{CC} = 100\%$ is replaced into equations (44) and (45). The number of moles of the other species can be obtained from the mass balance given in equations (15) – (18). The solution (a) is preferred over the solution (b) because the $n_{CC} \neq 100\%$.

$$n_{CC} = \frac{(EP_{H_2} + 9EP_{CO} + 8EP_{CO_2} + 12EP_{CH_4}) \left(\frac{f_N}{2} + \rho_{atm} x_{Air} \right) EP_{N_2}^{-1} - C_{H_2}}{10} \quad (43)$$

$$x_{CO_2} = \frac{8n_{CC} - 5C_{H_2} + (5EP_{H_2} + 11EP_{CO_2} + 2EP_{CH_4} - 13EP_{CO}) \left(\frac{f_N}{2} + \rho_{atm} x_{Air} \right) EP_{N_2}^{-1}}{29} \quad (44)$$

$$x_{CH_4} = \frac{12n_{CC} + 7C_{H_2} + (2EP_{CO_2} + 3EP_{CH_4} - 7EP_{H_2} - 5EP_{CO}) \left(\frac{f_N}{2} + \rho_{atm} x_{Air} \right) EP_{N_2}^{-1}}{29} \quad (45)$$

In the case of the objective function for DBON the solution was obtained by using the fsolve solver of the Matlab software [44–46]. The values obtained for n_{CC} , x_{CO_2} and x_{CH_4} were then replaced into equations (15) – (18) to determine the number of moles of the other species in the products.

The correction factors for the chemical equilibrium constants of the three chemical reactions [8,19,33] presented in equations (25) – (27) are denoted by f_{MFR} , f_{WGHR} and f_{MRR} , respectively. The expressions for determination of the correction factors are presented in equations (46) – (48). The number of moles of the species in equations (46) – (48) are those determined in the solutions for DBWN and DBON.

$$f_{MFR} = \frac{x_{CH_4} x_T \left(\frac{P_{Gas}}{P_0} \right)^{-1}}{K_{MFR} x_{H_2}^2} \quad (46)$$

$$f_{WGHR} = \frac{x_{CO_2} x_{H_2}}{K_{WGHR} x_{CO} x_{H_2O}} \quad (47)$$

$$f_{MRR} = \frac{x_{CO} (x_{H_2})^3 \left(\frac{P_{Gas}}{P_0} \right)^2}{K_{MRR} x_{CH_4} x_{H_2O} x_T^2} \quad (48)$$

The correction factors were determined using the data taken from several experimental articles [7,8,14,16,17,19,23,25,28,29,43]. The f_{MFR} was found to be on the interval [2.4044, 1236.3325], the f_{WGHR} on the interval [0.0990, 2.2639] and f_{MRR} on the interval [3.9033x10⁻⁰⁷, 0.6015]. As can be observed the interval of f_{WGHR} is not so small nor so large with respect to the intervals of f_{MFR} and f_{MRR} . Therefore, the f_{WGHR} was selected for the modeling process which is going to be presented in the next section.

It is also important to point out that it is not recommendable to simply use the experimental syngas composition and obtain the number of moles of the species in the products. That is because the value of n_{CC} and the composition of the solid residue are not reported in most experimental articles.

Finally, the enthalpy of reaction $\Delta \bar{h}_{React}^o$ is determined with equation (22) by considering in the products the number of moles of each component as determined by the optimization method.

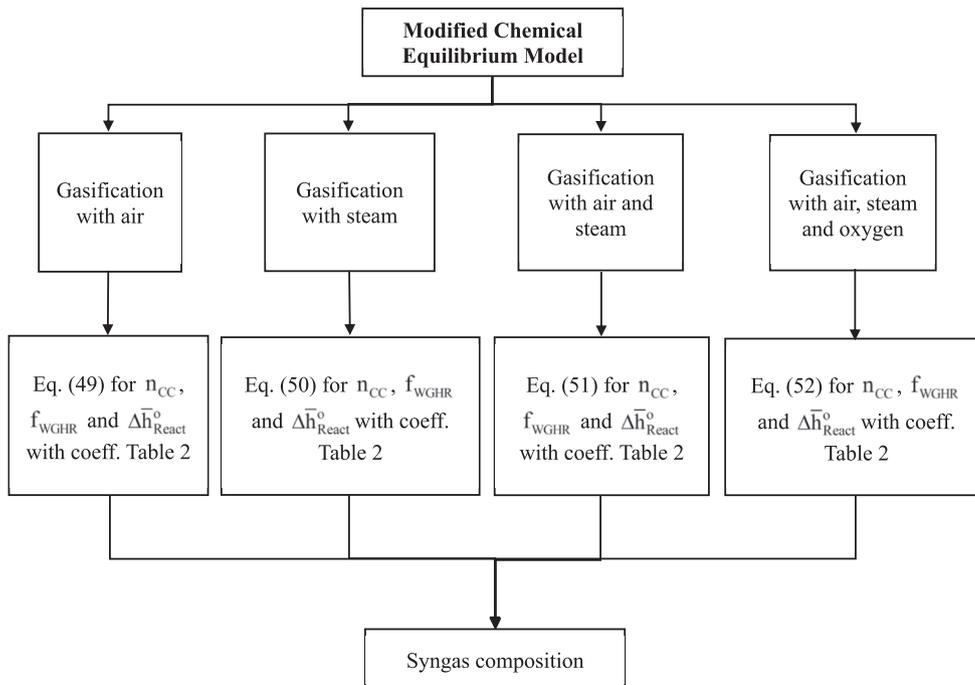


Fig. 3. Modified chemical equilibrium model solution scheme.

Table 1
Distribution of selected experimental compositions of syngas.

Gasifying agent	References	Number of data	Number of data for validation
Air	[8,14,16,43]	28	5
Steam	[7,19,25]	17	4
Air and steam	[17,23,28,29]	20	5
Air, steam and oxygen	[23]	11	2

3. Modified chemical equilibrium model

The proposed modified chemical equilibrium model consists of three correlations for the following parameters: carbon conversion efficiency (n_{CC}), correction factor (f_{WGHR}) and enthalpy of the global gasification reaction (Δh_{React}^o). These magnitudes were replaced in a system of two equations that is constituted by: The First Law of Thermodynamics and the modified chemical equilibrium equation for the homogeneous water-gas reaction [equation (53)]. The proposed correlations are related to the values obtained from the substitution of the optimal numbers of moles for the theoretical composition of the syngas. To calculate these optimal numbers of moles, the objective functions based on the definition of the RMS error were minimized. A disadvantage of the proposed modified chemical equilibrium model is the assumption that the tar is not present in the products of the proposed global gasification reaction. This assumption was made due to the small production of tar which is generally obtained from fluidized bed gasifiers.

These three correlations were obtained by applying linear regressions [47]. The solution scheme for the modified chemical equilibrium model is depicted in Fig. 3.

Seventy-six samples of syngas compositions from different experimental articles were selected [7,8,14,16,17,19,23,25,28,29,43]. The gasification agents were air, steam, air–steam, and air–steam–oxygen. The set of 76 samples was divided into a set containing 60 samples and another set with 16 samples. The first one was used to obtain the correlations for n_{CC} , f_{WGHR} and Δh_{React}^o while the second one was used to validate the modified chemical equilibrium model. The samples used for the validation were proportionally selected from each type of gasifying agent or agents. Table 1 presents the distribution of the number of samples adopted to develop each modified chemical equilibrium model. The modified chemical equilibrium model introduces three correlated values through one of the equations (49), (50), (51) or (52), which should be used together with the coefficients provided in Table 2. The

obtained correlations are shown below.

Gasification with air

$$Z = I + C_1 f_{Ash} + C_2 f_{Moist} + C_3 e^x + C_4 \left(\frac{f_{Moist}}{f_{Ash}} \right) + C_5 ER + C_6 ER^2 + C_7 T_{Gas} \tag{49}$$

Gasification with steam

It was assumed that carbon conversion efficiency (n_{CC}) is 100% because this value has always been obtained for all the optimization method's calculations.

$$Z = I + C_1 \left(\frac{f_{Moist}}{f_{Ash}} \right) + C_2 (S/B) + C_3 (S/B)^2 + C_4 (S/B)^3 + C_5 \left(\frac{T_{Steam}}{T_{Gas}} \right) + C_6 T_{Gas} \tag{50}$$

Gasification with air–steam

$$Z = I + C_1 f_{Ash} + C_2 f_{Moist} + C_3 ER + C_4 (S/B) + C_5 \left(\frac{T_{Air}}{T_{Gas}} \right) + C_6 \left(\frac{T_{Steam}}{T_{Gas}} \right) \tag{51}$$

Gasification with air–oxygen–steam

In this case the carbon conversion efficiency (n_{CC}) was also assumed to be 100% because this value has always been obtained for all the optimization method's calculations.

$$Z = I + C_1 ER + C_2 ER(S/B) + C_3 [ER(S/B)]^2 + C_4 (O/B) + C_5 (O/B)^2 + C_6 T_{Gas} \tag{52}$$

The value of 100% was adopted for carbon conversion efficiency when using the correlations for the carbon conversion efficiency presented in equations (49) and (51) exceeds 100%.

$$f_{WGHR} K_{WGHR} = \frac{X_{CO_2} X_{H_2}}{X_{CO} X_{H_2O}} \tag{53}$$

For the calculation of the composition of the syngas using the modified chemical equilibrium model, the values obtained by the model have to be substituted in the system of two equations conformed by the application of the First Law of Thermodynamics [equation (22)] and the modified chemical equilibrium equation for the homogenous water-gas reaction [equation (53)]. The solution of this system of equations are the number of moles of methane and

Table 2
Coefficients for correlations shown in equations (49) – (52).

Coefficients	Gasifying agent											
	Air			Steam			Air and steam			Air, steam and oxygen		
	Z = Eq. (49)			Z = Eq. (50)			Z = Eq. (51)			Z = Eq. (52)		
	n_{CC} (%)	f_{WGHR}	Δh_{React}^o (kJ/mol)	n_{CC} (%)	f_{WGHR}	Δh_{React}^o (kJ/mol)	n_{CC} (%)	f_{WGHR}	Δh_{React}^o (kJ/mol)	n_{CC} (%)	f_{WGHR}	Δh_{React}^o (kJ/mol)
x	f_{Moist}	f_{Ash}	f_{Moist}	–	–	–	–	–	–	–	–	–
I	–2979.4090	–522.3036	–2241.0450	100	7.3278	–143.3802	111.4569	–6.7994	124.7102	100	0.6108	117.0359
C ₁	402.3987	–550.5976	84.4509	0	0.0104	–0.7079	13.2464	–21.4213	–1038.5164	0	0.0000	–468.2000
C ₂	–3391.6953	0.5249	–1903.5383	0	–20.7697	39.8212	–537.7031	48.2313	765.7268	0	0.7189	0.0000
C ₃	3042.3198	519.8738	2139.1648	0	18.4715	–6.5110	157.4910	1.4444	–277.8947	0	0.0530	0.0000
C ₄	–10.8580	–0.0124	–11.5510	0	–5.1779	0.0000	24.1496	0.1007	49.2069	0	–15.5142	–229.5642
C ₅	76.2600	14.7958	–303.1547	0	2.4434	0.0000	–115.0108	8.5565	65.7674	0	37.9479	0.0000
C ₆	0.0000	–16.3996	0.0000	0	0.0000	0.3416	44.0283	–3.6423	–354.1102	0	0.0016	0.0205
C ₇	–0.0212	0.0004	0.1789	–	–	–	–	–	–	–	–	–
R ²	0.9662	0.9030	0.9877	1	0.9700	0.9862	0.9643	0.8843	0.9978	1	0.6676	0.9833

Table 3
Gasification conditions for the application of the optimization method.

Exp.	Reference	ER	S/B	O/B	T _{Gas} (°C)
1	Sarker et al. [43]	0.30	0.00	0.00	876
2	Arteaga-Pérez et al. [16]	0.34	0.00	0.00	803.5
3	Karmakar et al. [8]	0.45	0.00	0.00	600
4	Radmanesh et al. [14]	0.66	0.00	0.00	800
5	Karmakar and Datta [19]	0.00	1.70	0.00	750
6	Loha et al. [7]	0.00	1.32	0.00	690
7	Vecchione et al. [25]	0.00	1.00	0.00	830
8	Campoy et al. [28]	0.23	0.18	0.00	752
9	Loha et al. [17]	0.35	0.80	0.00	850
10	Sethupathy Subbaiah et al. [29]	0.18	0.30	0.00	650
11	Campoy et al. [23]	0.27	0.43	0.00	755
12	Campoy et al. [23]	0.36	0.32	0.1728 ^a	808

^a Value obtained by using the oxygen flow of 1.5 Nm³/h provided by the authors.

carbon dioxide. Finally, we will proceed to calculate the other chemical substances using the equations of conservation of the mass presented in equations (15) – (17).

4. Results and discussions

All the syngas experimental compositions selected for the application of the optimization method are presented in Tables S1 to S4 of the supplementary material. The number of moles obtained by applying the optimization method are presented in Tables S5 to S8. The correction factors, enthalpies of reaction and the Kuhn–Tucker multipliers (μ_1) are shown in Tables S9 to S12. Finally, the theoretical compositions of the syngas when the

optimization method is applied are presented in Tables S13 to S16.

For some experimental articles [28,29,43] considered in the present study it was assumed that the percentage of nitrogen was the difference between 100% and the concentrations of H₂, CO, CO₂ and CH₄ present in the products of the global gasification reaction [equation (10)].

The syngas composition was obtained by applying the input parameters shown in Table 3, which are the same input parameters reported in the experimental articles considered for the present study.

Table 4 shows the syngas composition obtained from the optimization method application. These compositions are very close to experimental ones, as expected. It can be observed from Table 4 that the calculated syngas compositions are closer to the experimental compositions when air is used as gasifying agent. Other information regarding the optimization method is presented in Table 5, where the enthalpies of reaction, correction factors and Kuhn–Tucker multipliers (μ_1) are reported.

In order to analyze the values of the enthalpies of reaction ($\Delta h_{\text{React}}^0$) with respect to each gasifying agent presented in Table 5, it is important to notice that a negative value of the enthalpy of reaction means that the process has liberated heat (exothermic).

In the case of gasification with air, it can be observed in Table 5 that the increase of ER produces a decrease on the value of $\Delta h_{\text{React}}^0$, which means that more exothermic reactions are taking place due to the increase of the available oxygen.

In the case of the gasification with steam, it can be observed in Table 5 that an increase of S/B produces an increase of $\Delta h_{\text{React}}^0$, which means that more endothermic reactions are taking place. In the case of gasification with steam there is more hydrogen available

Table 4
Results obtained from the optimization using different gasifying agents.

Exp.	Reference	H ₂ (%)	CO (%)	CO ₂ (%)	CH ₄ (%)	N ₂ (%)	RMS error from this work	RMS error from the reference
1	Sarker et al. [43]	3.82	13.15	13.23	3.14	66.66	0.88	–
2	Arteaga-Pérez et al. [16]	5.85	15.23	14.14	5.13	59.65	1.08	–
3	Karmakar et al. [8]	9.56	11.08	21.66	3.55	54.15	0.90	1.21
4	Radmanesh et al. [14]	4.60	11.25	14.47	0.50	69.19	0.33	–
5	Karmakar and Datta [19]	51.15	18.23	26.57	4.04	0.00	1.41	3.62
6	Loha et al. [7]	49.43	15.53	29.14	5.90	0.00	2.02	2.12
7	Vecchione et al. [25]	49.17	19.17	22.13	9.53	0.00	1.19	–
8	Campoy et al. [28]	14.60	13.80	16.90	5.20	49.50	0.00	–
9	Loha et al. [17]	13.00	14.30	20.50	2.80	49.40	0.09	–
10	Sethupathy Subbaiah et al. [29]	21.22	15.78	15.96	6.26	40.78	0.95	–
11	Campoy et al. [23]	31.20	22.90	35.80	10.20	0.00	0.00	–
12	Campoy et al. [23]	27.40	34.20	34.60	3.80	0.00	3.70	–

Table 5
Correction factors and enthalpy of reaction obtained from the optimization method.

Exp.	ER	S/B	O/B	$\Delta h_{\text{React}}^0$ (kJ/mol)	f _{MFR}	f _{WGHR}	f _{MRR}	μ_1
1	0.30	0.00	0.00	–2.17	1236.33	0.1257	3.90×10^{-07}	0.00
2	0.34	0.00	0.00	–3.87	507.15	0.0990	2.81×10^{-06}	0.00
3	0.45	0.00	0.00	–63.40	9.24	0.9887	0.0643	0.00
4	0.66	0.00	0.00	–153.00	59.18	0.3546	6.39×10^{-05}	0.00
5	0.00	1.70	0.00	159.90	3.81	0.6681	0.0042	22.07
6	0.00	1.32	0.00	134.01	2.71	0.8819	0.0206	32.93
7	0.00	1.00	0.00	124.12	16.64	1.2020	0.0007	7.18
8	0.23	0.18	0.00	–14.16	43.39	0.4464	3.04×10^{-04}	0.00
9	0.35	0.80	0.00	21.13	85.94	0.3690	1.65×10^{-05}	0.00
10	0.18	0.30	0.00	95.75	8.09	0.2923	1.31×10^{-02}	0.00
11	0.27	0.43	0.00	–17.41	37.83	0.5716	2.77×10^{-04}	0.00
12	0.36	0.32	0.1728 ^a	–75.96	30.59	0.4940	2.61×10^{-04}	339.93

^a Using the oxygen flow of 1.5 Nm³/h provided by the authors, this quantity is obtained.

Table 6
Validation of modified chemical equilibrium model applied to fluidized bed gasification.

Reference	ER	S/B	Oxygen flow rate (Nm ³ /h)	O/B ^a	T _{Gas} (°C)	n _{CC} (%)	H ₂ (%)	CO (%)	CO ₂ (%)	CH ₄ (%)	N ₂ (%)	RMS
Karmakar et al. [8]	0.35	0.00	0.00	0.00	700	82.68	14.63	22.47	16.67	1.32	44.91	
Predictive model	0.35	0.00	0.00	0.00	700	94.32	15.09	19.31	17.05	1.75	46.80	1.68
Radmanesh et al. [14]	0.32	0.00	0.00	0.00	805	—	9.20	16.20	12.70	2.50	59.60	
Predictive model	0.32	0.00	0.00	0.00	805	71.58	13.56	14.01	15.00	2.40	55.03	3.16
Arteaga-Pérez et al. [16]	0.34	0.00	0.00	0.00	801.5	—	5.40	16.18	13.67	3.54	60.49	
Predictive model	0.34	0.00	0.00	0.00	801.5	76.43	8.31	12.99	15.63	4.53	58.55	2.33
Sarker et al. [43]	0.35	0.00	0.00	0.00	874	—	3.84	14.31	14.98	2.67	64.20	
Predictive model	0.35	0.00	0.00	0.00	874	63.11	5.69	11.26	15.01	2.99	65.04	1.65
Karmakar and Datta [19]	0.00	1.32	0.00	0.00	650	84.10	47.25	11.25	31.90	9.60	0.00	
Predictive model	0.00	1.32	0.00	0.00	650	100.00	48.49	11.69	32.31	7.51	0.00	1.25
Loha et al. [7]	0.00	1.00	0.00	0.00	750	—	49.50	23.70	21.20	5.60	0.00	
Predictive model	0.00	1.00	0.00	0.00	750	100.00	46.71	27.87	20.73	4.69	0.00	2.56
Vecchione et al. [25]	0.00	0.70	0.00	0.00	830	—	47.93	21.11	22.81	8.15	0.00	
Predictive model	0.00	0.70	0.00	0.00	830	100.00	46.91	21.84	20.64	10.61	0.00	1.76
Campoy et al. [28]	0.19	0.28	0.00	0.00	727	89.00	16.20	11.50	18.60	5.90	47.80	
Predictive model	0.19	0.28	0.00	0.00	727	60.57	16.60	11.00	19.60	6.60	46.20	0.94
Loha et al. [17]	0.35	0.50	0.00	0.00	750	71.90	9.20	12.80	20.80	2.10	55.10	
Predictive model	0.35	0.50	0.00	0.00	750	79.61	10.90	14.30	20.40	1.70	52.70	1.50
Sethupathy Subbaiah et al. [29]	0.18	0.30	0.00	0.00	750	81.37	20.92	17.56	16.41	4.50	40.61	
Predictive model	0.18	0.30	0.00	0.00	750	67.43	21.93	17.20	14.83	5.52	40.51	0.97
Campoy et al. [23]	0.25	0.31	1.40	0.1235	781	96.00	31.60	32.90	24.90	10.60	0.00	
Predictive model	0.25	0.31	1.40	0.1235	781	100.00	34.70	36.30	24.60	4.50	0.00	3.82
Campoy et al. [23]	0.24	0.58	1.00	0.1190	765	96.00	34.30	23.50	31.30	10.90	0.00	
Predictive model	0.24	0.58	1.00	0.1190	765	100.00	38.40	28.80	28.30	4.60	0.00	4.84

^a This magnitude is calculated according to the theoretical development proposed in this work.

for the gasification reaction; however, it is necessary to provide more heat to the reaction by means of an electric furnace, for example.

The gasification with air–steam mixtures show a more complicated behavior in Table 5. We can analyze this behavior by considering experiments 8, 9 and 10 in Table 5. It is observed that for the experiment 8 the exothermic reactions dominate since $\Delta h_{\text{React}}^{\circ}$ is negative, then, for experiment 9 the values of ER and S/B are increased and the endothermic reactions dominate since $\Delta h_{\text{React}}^{\circ}$ is positive. An interesting comparison appear when we consider experiment 8 and 10, in which $ER_8 > ER_{10}$, $S/B_8 < S/B_{10}$ and the endothermic reactions dominate since $\Delta h_{\text{React}}^{\circ}$ positive ($\Delta h_{\text{React},8}^{\circ} < \Delta h_{\text{React},10}^{\circ}$). Therefore, there should be an optimum value of ER and S/B for which the exothermic reactions dominate (less external heat is needed) and at the same time the H₂ concentration in the syngas is adequate.

For the gasification with air–steam–oxygen, it is observed in Table 5 that the $\Delta h_{\text{React}}^{\circ}$ is negative; thus, we can conclude that the presence of oxygen enhances the combustion processes.

It can also be observed in Table 5, that the correction factors f_{MFR} and f_{MRR} present wider intervals than the correction factor f_{WGHR} which was selected for the modification of the chemical equilibrium model, this was also explained in section 2.

In Table 6 are shown the syngas compositions obtained from the modified chemical equilibrium model. For the gasification with air, steam and air–steam it is observed that the composition is accurately determined. However, the calculation of the carbon conversion efficiency is not as satisfactory, because in several cases the calculated value is higher than the experimental value. The reason for this might be that the modified chemical equilibrium model does not consider tars and, therefore, assumes a higher carbon conversion.

For the gasification with air–steam–oxygen the determination of the syngas concentration is not as accurate as in the other cases. On the other hand, the experimental carbon conversion efficiency presents a value of 96%, and the modified chemical equilibrium model assumes a value of 100% for these mixture of gasification

agents. The presence of oxygen in the gasification agents enhances the combustion reactions, thus, consuming more carbon.

Finally, with respect to the RMS error, it is considered that the modified chemical equilibrium model determines with very good accuracy the composition of the syngas. In the best cases the RMS is lower than 1 and it is always lower than 5.

5. Conclusion

The optimization method developed by using the Kuhn–Tucker multipliers was applied to analytically determine the values of the correction factors for the chemical equilibrium constants. While other authors have determined these correction factors empirically they were determined analytically in the present work. With the number of moles obtained from the application of the optimization method, very low RMS errors are obtained, in some cases equal to 0.

Three correlations were proposed for the modification of a chemical equilibrium model. These correlations were obtained for the correction factor, the enthalpy of reaction and the carbon conversion efficiency. A set of three correlations was obtained for each gasification agent considered, namely, air, steam, air–steam and air–steam–oxygen.

The modified chemical equilibrium model was applied to several biomasses and validated with experimental data, showing very good accuracy for the determination of the syngas composition.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.energy.2018.03.141>.

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