

# Journal Pre-proof

Empirical and chemical equilibrium modelling for prediction of biomass gasification products in bubbling fluidized beds

D.T. Pio, L.A.C. Tarelho

PII: S0360-5442(20)30761-1

DOI: <https://doi.org/10.1016/j.energy.2020.117654>

Reference: EGY 117654

To appear in: *Energy*

Received Date: 29 July 2019

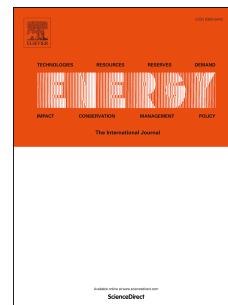
Revised Date: 9 April 2020

Accepted Date: 15 April 2020

Please cite this article as: Pio DT, Tarelho LAC, Empirical and chemical equilibrium modelling for prediction of biomass gasification products in bubbling fluidized beds, *Energy* (2020), doi: <https://doi.org/10.1016/j.energy.2020.117654>.

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Published by Elsevier Ltd.



**Daniel Torrão Pio (D.T. Pio):** Conceptualization, Methodology, Formal analysis, Visualization, Writing – Original Draft, Writing – Review & Editing

**Luís António da Cruz Tarelho (L.A.C. Tarelho):** Conceptualization, Writing – Review & Editing, Supervision, Project administration

Journal Pre-proof

**Empirical and chemical equilibrium modelling for prediction of biomass  
gasification products in bubbling fluidized beds**

D.T. Pio<sup>1,\*</sup>, L.A.C. Tarelho<sup>1</sup>

1 = Department of Environment and Planning & Centre for Environmental and Marine Studies (CESAM), University of Aveiro, Campus Universitário de Santiago, Aveiro, Portugal.

\*Corresponding author: danieltp@ua.pt (D.T. Pio)

**Abstract**

In this work, two approaches to predict the producer gas composition obtained by direct (air) biomass gasification in bubbling fluidized beds were developed and compared, namely empirical modelling based on reported experimental results in the literature and non-stoichiometric chemical equilibrium modelling. For this purpose, an extensive database containing a set of 19 published experimental results from the literature was compiled and a non-stoichiometric chemical equilibrium model developed.

The prediction capability of the empirical and chemical equilibrium model was evaluated by comparison with experimental data obtained in an 80kWth bubbling fluidized bed direct (air) biomass gasifier. The empirical model shows moderate accuracy in the determination of the producer gas composition (CO, H<sub>2</sub> and CH<sub>4</sub>), whereas the chemical equilibrium clearly overestimates the concentration of H<sub>2</sub> and CO, and underestimates the concentration of CH<sub>4</sub>, leading to subpar accuracy in the determination of typical gasification efficiency parameters. Thus, the empirical model is suited for preliminary estimates of gasification products, while black-box chemical equilibrium modelling, without experimental knowledge integration, is considered as unreliable for these gasification conditions.

Keywords: biomass; bubbling fluidized bed; gasification; producer gas; chemical equilibrium; empirical modelling.

**Abbreviations and nomenclature**

## Latin symbols

ANN	Artificial neural network [-]
BFB	Bubbling fluidized bed [-]
C	Carbon (monoatomic) [-]
C(s)	Char as unconverted solid carbon [-]
CCE	Carbon conversion efficiency [%]
CEM	Chemical equilibrium model [-]
CFD	Computational fluid dynamic [-]
CGE	Cold gas efficiency [%]
CH <sub>4</sub>	Methane [-]
C <sub>2</sub> H <sub>4</sub>	Ethylene [-]
C <sub>2</sub> H <sub>6</sub>	Ethane [-]
C <sub>3</sub> H <sub>8</sub>	Propane [-]
CO	Carbon monoxide [-]
CO <sub>2</sub>	Carbon dioxide [-]
daf	Dry ash free [-]
db	Dry basis [-]
ER	Equivalence ratio [-]
H	Hydrogen (monoatomic) [-]
H <sub>2</sub>	Hydrogen [-]
H <sub>2</sub> S	Hydrogen sulfide [-]
H <sub>2</sub> O	Water [-]
i	Gaseous compound CO <sub>2</sub> , CO, CH <sub>4</sub> and C <sub>2</sub> H <sub>4</sub> [-]
LHV	Lower heating value [MJ/Nm <sup>3</sup> ]
LHV <sub>F</sub>	Lower heating value of the biomass [MJ/kg db]
LHV <sub>G</sub>	Lower heating value of the dry gas produced [MJ/Nm <sup>3</sup> ]
M <sub>C</sub>	Molar mass of Carbon [kg/mol]
mF	Biomass (dry basis) mass flow rate [kg db/s]
N	Nitrogen (monoatomic) [-]
N <sub>2</sub>	Nitrogen [-]
Nm <sup>3</sup>	Refers to m <sup>3</sup> at normal pressure (1.013×10 <sup>5</sup> Pa) and temperature (273 K) [-]
O	Oxygen (monoatomic) [-]
PCC	Pearson-R correlation coefficient [-]
P <sub>G</sub>	Absolute pressure of the dry gas [Pa]
R	Ideal gas constant [J.mol <sup>-1</sup> .K <sup>-1</sup> ]
RFB	Residual forest biomass [-]
S	Sulfur [-]
SO <sub>2</sub>	Sulfur dioxide [-]
T <sub>G</sub>	Absolute temperature of the dry gas [T]

$V_G$	Dry gas volumetric flow rate [ $\text{Nm}^3/\text{s}$ ]
$W_{CF}$	Mass fraction of total Carbon in the biomass [ $\text{kg C/kg biomass db}$ ]
$Y_{\text{gas}}$	Dry gas specific production [ $\text{Nm}^3$ dry gas/kg dry biomass]
$y_i$	Molar fraction of $\text{CO}_2$ , $\text{CO}$ , $\text{CH}_4$ , $\text{C}_2\text{H}_4$ , in the dry gas produced [-]
%v	Volume percentage [%]
%wt	Weight percentage [%]

## Greek symbols

$\varepsilon_{C,i}$	Molar fraction of Carbon in i [ $\text{mol C/mol i}$ ]
---------------------	--

Journal Pre-proof

## 1. Introduction

Biomass gasification modelling is recognized as a promising approach for designing, up-scaling and operating gasification processes and technologies [1–3], serving as an useful complement to experimental research [1,4–6]. This technique allows the evaluation of the impact of operating parameters, such as equivalence ratio (ER), feedstock composition and temperature on the producer gas quality and overall process efficiency [7]. The desired composition of the producer gas is a major parameter that defines the configuration and design of the gasifier and the selection of the process operating parameters. Thus, numerical modelling is a relevant supporting tool for the configuration and design of gasification plants, including equipment size, startup and shutdown requirements, process control and the determination of the necessary infrastructures to handle the feedstock and the gasification agent [2]. During the gasification plant operation, modelling tools can also be important to predict the impact of unintended operating parameters modifications, such as the variation of feedstock characteristics, to interpret the causes behind gas composition changes [2], to assist in reducing problems related to tar and char formation [3] and to be able to continuously optimize the process.

In this respect, several mathematical modelling approaches have been under research and were proposed in the literature to characterize and predict this complex process [3,5,8–10]. Generally, these can be classified into the following main groups [3,11]:

- i) Kinetic models;
- ii) Computational fluid dynamic (CFD) models;
- iii) Artificial neural network (ANN) models;
- iv) Chemical equilibrium models (CEM).

Kinetic models study the progress of reactions in the reactor, giving the products composition in distinct locations along the gasifier [3]. It is argued that these models

provide accurate and reliable results, however, they are complex and computationally intensive and have limited application for distinct gasification plants with different design and characteristics [10,11]. CFD models can simulate physical phenomena, solving equations of balance of mass, momentum and energy over a discrete region of the gasifier, providing an accurate prediction of temperature and gas yield in the whole reactor [3,11]. However, these models require large amount of information (detailed reactor design, material properties, etc.) and high computational resources [11]. ANN models are relatively novel for modelling gasification processes [3]. These models do not require a mathematical description of the phenomena associated with the system [5] but require large amount of consistent experimental data to train the network to be able to predict the behavior of the gasifier with accuracy [3]. A more detailed explanation and in-depth review of these models is out of the scope of this work. Readers can refer to other published works [4,8,10,12].

CEMs are the most common modelling approach for biomass gasification [4,13]. These models can predict the products of gasification by assuming that the reactants are allowed to react in fully mixed conditions for an infinite period of time [14], reproducing ideal gasification performance and predicting the maximum yields attainable by the reagent system [3]. The main advantages are the possibility of running the model without knowing the gasifier design [1,10] and the simplicity and reduced computational time [3]. CEMs are promising to determine first estimates of the composition of the producer gas, taking in account the influence of the process operating parameters (e.g., ER, temperature and pressure) and the feedstock characteristics (e.g., the chemical composition) [14] and to perform concept studies, preliminary analysis and optimization procedures [1]. These models are commonly used as a first approach to predict the producer gas composition from biomass gasification and to determine the optimal biomass feedstock for specific applications [3,15–18].

There are two main types of CEMs: stoichiometric models, which are based on equilibrium constants and require knowledge regarding the reactions paths and reactions equations, and non-stoichiometric models, which are based on minimizing the Gibbs free energy in the system and do not require knowledge of the process reactions mechanisms [9,10,14]. Puig-Arnavat et al., [10] argues that the two approaches are equally suitable to model biomass gasification processes. Sikarwar et al., refer that stoichiometric models can present significant deviations from real life scenarios if important reactions are neglected, and that the non-stoichiometric approach is more suitable for biomass gasification processes due to the uncertainty of gasification reaction mechanisms [7]. These modelling techniques can also have different approaches, for example by integrating experimental knowledge [19,20] and kinetics [10] or considering that only part of the process attains equilibrium [1]. In this respect, modified CEMs [21–23] and restricted CEMs [13,24] are under research.

In practical gasifier plants, the chemical interactions inside the gasifier take place in a finite time, and the CEM predictions have mixed success depending on the reaction temperature and residence time [7]. Therefore, assumptions of infinite reaction speed and that all reactions will be complete can be far from realistic for several practical gasifiers [14]. In fact, it is argued that chemical equilibrium may not be achieved when the gasification temperature is lower than 900°C and only a finite time is available for the reactants to react in the gasifier [1,3,25]. Besides, it is also suggested that CEMs are not reliable when the ER of the gasification process is between 0.10 and 0.30 [26]. Unfortunately, the common operating conditions for biomass direct (air) gasification in bubbling fluidized beds (BFB) fall between these ranges (Bed temperature: 600-900°C and ER: 0.20-0.30 [27]). Accordingly, it has been argued [7,11] that CEMs typically present better results for entrained flow gasifiers and downdraft gasifiers than for fluidized beds. In fact, reasonable agreement has been reported by some authors regarding CEMs predictions and experimental biomass gasification data obtained in



these type of gasifiers [11,28–33]. Nonetheless, CEMs have also been intensively used for biomass gasification in fluidized beds [10,13,24,34–36].

Furthermore, several assumptions are also reported to lead to deviation between experimental observed values and predicted values [7]. For example, assuming ash as inert [7], neglecting tar production, even though tar is one of the major barriers of biomass gasification [14,27], and considering char as pure solid carbon [7]. Thus, CEMs determine ideal yields [3] that may not be attained in practical gasifiers (e.g., H<sub>2</sub> and CO overestimation [14] and hydrocarbon underestimation [25]), consequently leading to deviations in the prediction of the lower heating value (LHV) of the producer gas and the process efficiency parameters. These aspects need to be analyzed to determine the suitability of CEMs to support and model direct (air) gasification of biomass in BFBs.

In this work, two models to predict producer gas composition from direct (air) biomass gasification processes in BFBs were developed, compared and evaluated, namely a non-stoichiometric CEM and an empirical model. For this purpose, an extensive database regarding direct (air) gasification experiments of biomass in BFB reactors, including experimental data obtained in previous works performed by the authors [27,37], was compiled and organized. First, the CEM predictions were compared to the experimental database to identify deviations. Afterwards, correlations were derived from this experimental data and from the CEM predictions. The objective of both these correlations is to be used as tools for determining first estimates of gasification products from direct (air) gasification processes in BFBs. The empirical and CEM correlations prediction capability was addressed briefly by comparison with experimental data obtained in an 80 kWth BFB gasifier with different operating conditions.

The comparison and evaluation of these two types of modeling approaches can help in determining weaknesses and strengths, and consequently in guiding researchers to adopt and develop more suitable and integrated modelling approaches.

This may contribute for the successful development of these numerical prediction tools, which represents an important step for the up-scale, demonstration and commercial breakthrough of biomass gasification technologies, potentially diminishing the gap between existing theoretical and practical knowledge in the estimation of gasification products and process efficiency parameters.

Journal Pre-proof

## **2. Methods and literature data collection**

The database was compiled by collecting and organizing published experimental results from the literature (Tables 1 and 2), regarding direct (air) gasification processes in BFBs reactors with distinct biomass types and different operating conditions [16,27,38–53].

Journal Pre-proof

Table 1 – Experiment references and operating conditions of BFB direct (air) biomass gasification studies reported in the literature.

Experiment reference	Biomass type	BFB scale	T [°C]	ER	Ref	
AE	AE0.17	Woodchips	Pilot	718	0.17	[46]
	AE0.18	Woodchips	Pilot	722	0.18	[46]
	AE0.23	Woodchips	Pilot	733	0.23	[46]
BC	BC0.22	Rice husk	Pilot	784	0.22	[47]
	BC0.24 - 790	Rice husk	Pilot	790	0.24	[47]
	BC0.24 - 828	Rice husk	Pilot	828	0.24	[47]
	BC0.28 - 821	Rice husk	Pilot	821	0.28	[47]
	BC0.28 - 823	Rice husk	Pilot	823	0.28	[47]
	BC0.28 - 846	Rice husk	Pilot	846	0.28	[47]
	BC0.28 - 874	Rice husk	Pilot	874	0.28	[47]
	BC0.28 - 781	Rice husk	Pilot	781	0.28	[47]
	BC0.32 - 812	Rice husk	Pilot	812	0.32	[47]
	BC0.32 - 866	Rice husk	Pilot	866	0.32	[47]
	BC0.34	Rice husk	Pilot	864	0.34	[47]
CP	CP0.35	Wood pellets	Pilot	812	0.35	[48]
GE-CE	GE-CE-1	RFB eucalyptus type A	Pilot	804	0.22	[27]
	GE-CE-2	RFB eucalyptus type A	Pilot	798	0.24	[27]
	GE-CE-3	RFB eucalyptus type A	Pilot	812	0.25	[27]
	GE-CE-4	RFB eucalyptus type A	Pilot	810	0.26	[27]
	GE-CE-5	RFB eucalyptus type A	Pilot	818	0.28	[27]
	GE-CE-6	RFB eucalyptus type B1	Pilot	706	0.28	[27]
	GE-CE-7	RFB eucalyptus type B1	Pilot	714	0.30	[27]
	GE-CE-8	RFB eucalyptus type B1	Pilot	700	0.36	[27]
	GE-CE-9	RFB eucalyptus type B2	Pilot	736	0.17	[27]
	GE-CE-10	RFB eucalyptus type B2	Pilot	709	0.18	[27]
	GE-CE-11	RFB eucalyptus type B2	Pilot	719	0.20	[27]
	GE-CE-12	RFB eucalyptus type B2	Pilot	800	0.25	[27]
	GE-CE-13	RFB eucalyptus type B2	Pilot	813	0.35	[27]
GE-CP	GE-CP-1	RFB pine	Pilot	786	0.23	[27]
	GE-CP-2	RFB pine	Pilot	811	0.26	[27]
	GE-CP-3	RFB pine	Pilot	830	0.30	[27]
	GE-CP-4	RFB pine	Pilot	824	0.29	[37]
	GE-CP-5	RFB pine	Pilot	786	0.24	[37]
	GE-CP-6	RFB pine	Pilot	798	0.19	[37]
GE-WP	GE-WP-1	Wood pellets	Pilot	816	0.22	[27]
	GE-WP-2	Wood pellets	Pilot	802	0.24	[27]
	GE-WP-3	Wood pellets	Pilot	854	0.25	[27]
	GE-WP-4	Wood pellets	Pilot	833	0.30	[27]
	GE-WP-5	Wood pellets	Pilot	793	0.24	[37]

Table 1 – (continued)

Experiment reference		Biomass type	BFB Scale	T [°C]	ER	Ref
GE-WP	GE-WP-6	Wood pellets	Pilot	828	0.21	[37]
IPE	IPE0.29	Torrefied woodchips	Bench	760	0.29	[50]
IPP	IPP0.24	Straw pellets	Bench	780	0.24	[50]
IPPC	IPPC0.21	Softwood pellets	Bench	760	0.21	[50]
KC	KC0.25 - 650	Rice husk	Pilot	650	0.25	[16]
	KC0.25 - 675	Rice husk	Pilot	675	0.25	[16]
	KC0.25 - 700	Rice husk	Pilot	700	0.25	[16]
	KC0.25 - 725	Rice husk	Pilot	725	0.25	[16]
	KC0.35 - 600	Rice husk	Pilot	600	0.35	[16]
	KC0.35 - 650	Rice husk	Pilot	650	0.35	[16]
	KC0.35 - 700	Rice husk	Pilot	700	0.35	[16]
	KC0.35 - 725	Rice husk	Pilot	725	0.35	[16]
	KC0.35 - 750	Rice husk	Pilot	750	0.35	[16]
	KC0.45 - 600	Rice husk	Pilot	600	0.45	[16]
	KC0.45 - 650	Rice husk	Pilot	650	0.45	[16]
	KC0.45 - 700	Rice husk	Pilot	700	0.45	[16]
	KC0.45 - 725	Rice husk	Pilot	725	0.45	[16]
	KC0.45 - 800	Rice husk	Pilot	800	0.45	[16]
	KCA	KCA0.36	Cotton stalk	Bench	770	0.36
KCA0.71		Cotton stalk	Bench	770	0.71	[51]
KCS	KCS0.25	Hazelnut shell	Bench	775	0.25	[51]
	KCS0.68	Hazelnut shell	Bench	775	0.68	[51]
KE	KE0.32	Rubber woodchip	Pilot	750	0.32	[54]
	KE0.36	Rubber woodchip	Pilot	770	0.36	[54]
	KE0.38	Rubber woodchip	Pilot	790	0.38	[54]
	KE0.41	Rubber woodchip	Pilot	810	0.41	[54]
	KE0.43	Rubber woodchip	Pilot	840	0.43	[54]
KP	KP0.19	Wood pellets	Pilot	775	0.19	[45]
	KP0.24	Wood pellets	Pilot	775	0.24	[45]
	KP0.27	Wood pellets	Pilot	775	0.27	[45]
	KP0.32	Wood pellets	Pilot	775	0.32	[45]
KWP	KWP0.19	Pistachio shell	Bench	770	0.19	[52]
	KWP0.37	Pistachio shell	Bench	770	0.37	[52]
KWS	KWS0.19	Walnut shell	Bench	770	0.19	[52]
	KWS0.37	Walnut shell	Bench	770	0.37	[52]
MC	MC0.25 - 670	Rice husk	Pilot	670	0.25	[53]
	MC0.25 - 700	Rice husk	Pilot	700	0.25	[53]
	MC0.25 - 665	Rice husk	Pilot	665	0.25	[53]
	MC0.30 - 744	Rice husk	Pilot	744	0.30	[53]
	MC0.30 - 750	Rice husk	Pilot	750	0.30	[53]

Table 1 – (continued)

Experiment reference	Biomass type	BFB Scale	T [°C]	ER	Ref	
MC	MC0.30 - 766	Rice husk	Pilot	766	0.30	[53]
	MC0.35 - 811	Rice husk	Pilot	811	0.35	[53]
	MC0.35 - 822	Rice husk	Pilot	822	0.35	[53]
	MC0.35 - 828	Rice husk	Pilot	828	0.35	[53]
MM	MM0.18	<i>Miscanthus</i>	Pilot	750	0.18	[38]
	MM0.26	<i>Miscanthus</i>	Pilot	800	0.26	[38]
	MM0.27	<i>Miscanthus</i>	Pilot	750	0.27	[38]
	MM0.30	<i>Miscanthus</i>	Pilot	800	0.30	[38]
	MM0.31	<i>Miscanthus</i>	Pilot	850	0.31	[38]
	MM0.37	<i>Miscanthus</i>	Pilot	850	0.37	[38]
NS	NS0.26	Pine sawdust	Bench	800	0.26	[39]
	NS0.32	Pine sawdust	Bench	800	0.32	[39]
	NS0.36	Pine sawdust	Bench	790	0.36	[39]
	NS0.37	Pine sawdust	Bench	800	0.37	[39]
	NS0.47	Pine sawdust	Bench	810	0.47	[39]
SB	SB0.27	Sugarcane bagasse	Bench	800	0.27	[40]
SC	SC0.30	Rice husk	Pilot	850	0.30	[41]
	SC0.40	Rice husk	Pilot	860	0.40	[41]
	SC0.50	Rice husk	Pilot	870	0.50	[41]
SCT	SCT0.26	Bana grass	Bench	800	0.26	[40]
	SCT0.27	Bana grass	Bench	800	0.27	[40]
	SCT0.30	Bana grass	Bench	800	0.30	[40]
	SCT0.33	Bana grass	Bench	800	0.33	[40]
SF	SF0.30	Coir pith	Pilot	750	0.30	[41]
	SF0.40	Coir pith	Pilot	760	0.40	[41]
	SF0.50	Coir pith	Pilot	770	0.50	[41]
SP	SP0.25	Alfalfa pellets	Pilot	-	0.25	[42]
	SP0.30	Alfalfa pellets	Pilot	-	0.30	[42]
SS	SS0.30	Sawdust	Pilot	840	0.30	[41]
	SS0.40	Sawdust	Pilot	860	0.40	[41]
	SS0.50	Sawdust	Pilot	880	0.50	[41]
VC	VC0.20 - 750	Olive kernel	Bench	750	0.20	[43]
	VC0.20 - 800	Olive kernel	Bench	800	0.20	[43]
	VC0.20 - 850	Olive kernel	Bench	850	0.20	[43]
	VC0.30 - 750	Olive kernel	Bench	750	0.30	[43]
	VC0.30 - 800	Olive kernel	Bench	800	0.30	[43]
	VC0.30 - 850	Olive kernel	Bench	850	0.30	[43]
	VC0.40 - 750	Olive kernel	Bench	750	0.40	[43]
	VC0.40 - 800	Olive kernel	Bench	800	0.40	[43]
	VC0.40 - 850	Olive kernel	Bench	850	0.40	[43]

Table 1 – (continued)

Experiment reference	Biomass type	BFB Scale	T [°C]	ER	Ref	
XM	XM0.23	<i>Miscanthus</i>	Pilot	639	0.23	[44]
	XM0.26	<i>Miscanthus</i>	Pilot	645	0.26	[44]
	XM0.28	<i>Miscanthus</i>	Pilot	693	0.28	[44]
	XM0.37	<i>Miscanthus</i>	Pilot	723	0.37	[44]

Journal Pre-proof

Table 2 – Proximate and ultimate analysis of the biomass samples used for the models

Biomass	% wt, daf					% wt, db	Reference
	C	H	N	S	O	Ash	
CEM							
Cellulose (C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> )	44.45	6.22	0.00	0.00	49.34	-	-
Lignin	63.77	5.99	0.27	0.32	29.45	-	[18]
Miscanthus	49.20	6.00	0.40	0.15	44.20	3.00	[55]
Rice husk	49.30	6.10	0.80	0.08	43.70	18.00	[55]
RFB from eucalyptus	49.66	6.53	0.07	0.00	43.74	1.19	[27]
Empirical model							
Alfalfa pellets	50.10	5.90	2.88	0.30	40.88	16.98	[42]
Bana grass	49.33	5.54	0.46	0.17	43.89	4.50	[40]
Coir pith	47.18	3.60	1.01	0.01	48.20	6.00	[41]
Cotton stalk	52.80	5.62	1.00	0.18	40.71	6.91	[51]
Hazelnut shell	56.96	5.05	0.43	0.13	37.42	2.60	[51]
Miscanthus-1	44.50	5.20	5.30	0.00	45.00	-	[38]
Miscanthus-2	47.63	6.19	0.40	0.00	45.78	4.47	[44]
Olive kernel	48.59	5.73	1.57	0.05	44.06	2.17	[43]
Pine sawdust	50.42	5.75	0.20	0.03	44.47	0.85	[39]
Pistachio shell	50.03	5.93	0.40	0.10	43.55	0.27	[52]
RFB from eucalyptus-1	47.08	6.29	0.36	0.00	46.00	2.60	[27]
RFB from eucalyptus-2	49.66	6.53	0.07	0.00	43.74	1.19	[27]
RFB from pine	51.42	6.58	0.25	0.01	41.75	1.20	[27]
Rice husk-1	45.41	7.23	4.11	0.01	43.24	19.40	[47]
Rice husk-2	47.00	6.78	0.48	0.04	45.70	20.00	[53]
Rice husk-3	49.07	3.79	0.63	0.01	46.42	21.68	[16]
Rice husk-4	38.92	5.10	2.17	0.12	53.69	19.33	[41]
Rubber woodchip	46.40	5.70	0.20	0.00	47.70	1.10	[54]
Sawdust	51.33	6.13	0.12	0.02	41.97	1.80	[41]
Softwood pellets	54.61	5.83	0.00	0.03	39.53	0.57	[50]
Straw pellets	52.86	6.11	0.82	0.14	40.07	6.32	[50]
Sugarcane bagasse	49.15	5.59	0.13	0.05	45.01	5.80	[40]
Torrefied woodchips	58.77	5.53	0.15	0.01	35.50	0.18	[50]
Walnut shell	54.84	5.50	0.44	0.12	39.10	1.95	[52]
Wood pellets-1	47.65	6.22	0.09	0.00	46.04	0.32	[27]
Wood pellets-2	51.02	7.16	0.09	0.00	41.73	0.80	[45]

development

daf – dry ash free  
db – dry basis



The database information was processed for equivalent units and basis, namely: i) biomass composition was expressed by mass fractions in dry ash-free fuel basis (C,H,O,N,S, kg i/kg daf fuel) and by mass fractions in dry basis (ash content, kg ash/kg dry fuel), ii) gas composition was expressed in volumetric dry basis (%v, dry gas). Conversions between basis were performed as deemed necessary. The recorded data comprises the following parameters:

1. Biomass feedstock characteristics:
  - a. Category (woody or non-woody) and type (miscanthus, rice husk, wood pellets, sawdust, bagasse, etc.);
  - b. Elemental composition (C,H,N,O,S);
  - c. Ash content.
2. BFB characteristics and operating parameters:
  - a. Scale (bench or pilot);
  - b. Average bed temperature (600-880°C);
  - c. ER (0.17-0.71).
3. Experimental results:
  - a. Producer gas composition (CO<sub>2</sub>, CH<sub>4</sub>, CO and H<sub>2</sub>);
  - b. Producer gas LHV;
  - c. Efficiency parameters ( $Y_{\text{gas}}$ , CGE and CCE).

Additional operating parameters, such as the fluidization velocity, residence time of gases and biomass, particle size of the biomass or heat supply, were not considered for the empirical model development because they are seldom detailed in the literature. Furthermore, the CEM approach, whose comparison with empirical modelling was the main focus of this work, only requires the knowledge of the feedstock and gasifying agent composition and the definition of the temperature, pressure and most common products. Accordingly, the strict CEM approach is a function of these parameters and is independent of the reactor design, and its hydrodynamics.

The methodologies used in the studies organized in this database were also briefly addressed for comparison purposes. In the analyzed literature, distinct measurement techniques are referred for determining the producer gas composition, for example infrared analysis for determination of CO, CO<sub>2</sub> and CH<sub>4</sub> concentration, thermal conductivity measurement for determination of H<sub>2</sub> concentration and paramagnetic analysis for determination of O<sub>2</sub> concentration [27,40,50,51]. N<sub>2</sub> concentration determination by mass balance is referred in some works [27,37,50,51]. Collection of gas samples in sampling bags, such as *Flexfoil* bags [27], with the objective of determining the producer gas composition (H<sub>2</sub>, CO<sub>2</sub>, CO, CH<sub>4</sub>, etc.) in GC-TCD equipment is also commonly referred [16,27,37,40,42,44]. Chemiluminescence analysis for detection of nitrogen oxides as NO was referred by one author [40]. The flow rate of the producer gas is determined by mass flow meters by some authors, such as Coriolis mass flow meters [44], and by calculation methodologies by other authors, namely nitrogen mass balances [27,37,42]. Regarding the necessary producer gas conditioning measures for sampling and equipment analysis, it is commonly referred tar condensation and particle removal by moisture traps, impinger bottles filled with isopropanol, ceramic filters, among other equipment [27,43,44].

Some parameters were not reported in all the analyzed studies; thus, their determination was performed as necessary when the required data was available. The LHV of the distinct types of biomass was determined according to the correlation developed by Parikh et al., [56]. The LHV of the producer gas was determined based on the relative abundance of combustible gases components (H<sub>2</sub>, CO, CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>) and their respective LHV (at reference conditions, 273K and 101 kPa) [57]. Some deviations can occur due to some authors including other combustible gaseous species in the LHV calculation formula (e.g., propane). In this work, the gaseous species considered for the determination of the LHV were CO, H<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>. The reasoning behind this consideration results from the concentration of other minor components (e.g., propane) seldom being available in the published works and their

abundance being relatively low, consequently presenting low contribution to the LHV value. Efficiency parameters, namely  $Y_{\text{gas}}$ , CGE and CCE, were also determined when the data necessary for their calculation was accessible in the published works. The following equations were used:

$$Y_{\text{gas}} = \frac{V_G}{m_F} \quad (\text{Equation 1, [39]})$$

$$\text{CGE [\%]} = \frac{V_G \times \text{LHV}_G}{m_F \times \text{LHV}_F} \times 100 \quad (\text{Equation 2, [58]})$$

$$\text{CCE [\%]} = \frac{V_G \times \frac{P_G}{R \times T_G} \times M_C \times \sum_i \epsilon_{C,i} \times y_{i,db}}{m_F \times w_{CF}} \times 100 \quad (\text{Equation 3, [59]})$$

The CEM was developed considering the biomass and gasifying agent composition (CHNOS) and the chemical products of the process containing these elements; the products selected are the most commonly reported in biomass gasification processes. Other minor elements, such as Chlorine, were not considered. Thus, a total of 13 compounds in the products of gasification were considered:  $\text{N}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$  and unconverted solid carbon ( $\text{C}_{(s)}$ ). All products were assumed to act as ideal gases, except for  $\text{C}_{(s)}$ . Steady state conditions of operation were assumed. Tar formation was neglected and ash in the feedstock was assumed to be inert. All the reactants were assumed to enter and leave the reactor at process temperature. The process temperature is assumed as homogeneous inside the gasifier, which is a common procedure in other non-stoichiometric thermodynamic models [11]. Hydrodynamics and kinetics were not considered.

The CEM was applied to calculate the composition of the producer gas for distinct direct (air) gasification parameters. Then, the respective efficiency parameters were calculated based on the obtained compositions. The software tool used for the model development was GASEQ (<http://www.gaseq.co.uk/>). The following parameters were used as input in the model:

- Feedstock: RFB from eucalyptus, rice husk, *miscanthus*, cellulose ( $\text{C}_6\text{H}_{10}\text{O}_5$ ) and lignin (Table 2);

- Bed temperature: 600°C, 700°C, 800°C and 900°C;
- ER: 0 (pyrolysis), 0.10, 0.20, 0.25, 0.30 and 0.40;
- Pressure: 1 atm.

The compiled experimental database and the CEM predictions were analyzed using multiple regression tools in Microsoft Excel. This type of regression describes the relationship between the analyzed data and outputs functions for the determination of process parameters. Linear empirical and CEM correlations were developed due to finding similar coefficients of determination (R-Squared and adjusted R-Squared) for distinct regressions (e.g., linear, polynomial) for the experimental and CEM data. Thus, linear correlations were adopted due to their simplicity and easier interpretation. The prediction capability of the correlations was briefly addressed by comparison with experimental biomass gasification data obtained in an 80kWth BFB direct (air) gasifier.

Pearson's correlation test was used to measure the strength of the correlation between two variables. It is important to note that correlation does not imply causation [60]. Pearson-R correlation coefficient (PCC) was determined between inputs and outputs for both experimental and CEM results and between actual and predicted outputs for both empirical and CEM correlations.

### 3. Experimental and CEM results comparison

In this section, the experimental results reported in the literature and the CEM predictions are compared, and correlations based on these data were developed and evaluated. The objective of these correlations is to serve as simple and immediate tools for determining first estimates of gasification products. The main parameters of the gasification process were considered, namely the reactor bed temperature and ER. The comparison between reported experimental results and CEM predictions is performed for similar operating conditions: ER between 0.20 and 0.40 and bed temperature between 600 and 900°C. Accordingly, both empirical and CEM correlations were developed for those conditions. Reported experimental results with other conditions and CEM predictions for pyrolysis conditions (ER=0) and gasification under unsuitable low ER (ER=0.10) are shown for comparison purposes, but not used in the correlations development. The CEM results for lignin and cellulose were not included in the correlations development and are analyzed separately. Pearson's correlation test was performed to measure the strength of the correlation between operating parameters and results.

#### 3.1. Properties of the producer gas

##### 3.1.1. Combustible gases yield ( $H_2$ , CO and $CH_4$ )

The influence of the reactor bed temperature and ER in the hydrogen concentration in the producer gas is shown in Figure 1. For similar operating conditions, the experimental  $H_2$  results (2.0 to 24.0%v) are lower than those predicted by the CEM (12.9 and 29.1%v). Furthermore, the relation between  $H_2$  concentration and reactor bed temperature or ER is distinct for both CEM and experimental results. The CEM shows that  $H_2$  concentration is dependent on the employed ER, while the experimental results do not show any evident relation for both ER and temperature. Accordingly, PCC was found close to -1 for the relation of  $H_2$  concentration and ER in the CEM results (Table 3).

Table 3 – PCC values for the correlation between operating conditions (temperature (T) and equivalence ratio (ER)) and the producer gas composition ( $H_2$ , CO and  $CH_4$ ), LHV,  $Y_{gas}$ , CGE and CCE, for the experimental results reported in the literature and CEM predictions.

PCC	$H_2$		CO		$CH_4$		LHV		$Y_{gas}$		CGE		CCE	
	Exp	CEM	Exp	CEM	Exp	CEM	Exp	CEM	Exp	CEM	Exp	CEM	Exp	CEM
T	-0.2	0.2	-0.4	0.8	0.2	-0.9	-0.2	0.6	0.3	0.4	-0.2	0.8	0.0	0.8
ER	0.0	-0.9	-0.3	-0.4	-0.4	-0.3	-0.5	-0.7	0.5	0.7	0.1	-0.3	0.3	0.3

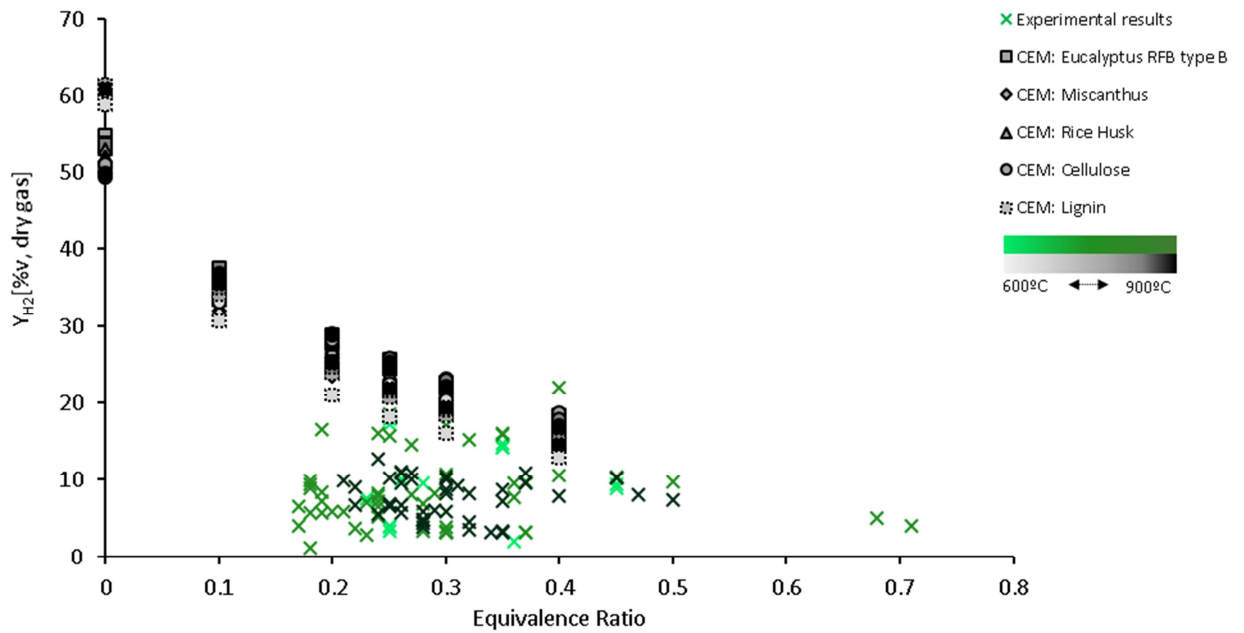
\*- Exp refers to the experimental results reported in the literature; CEM refers to the chemical equilibrium model predictions.

Journal Pre-proof

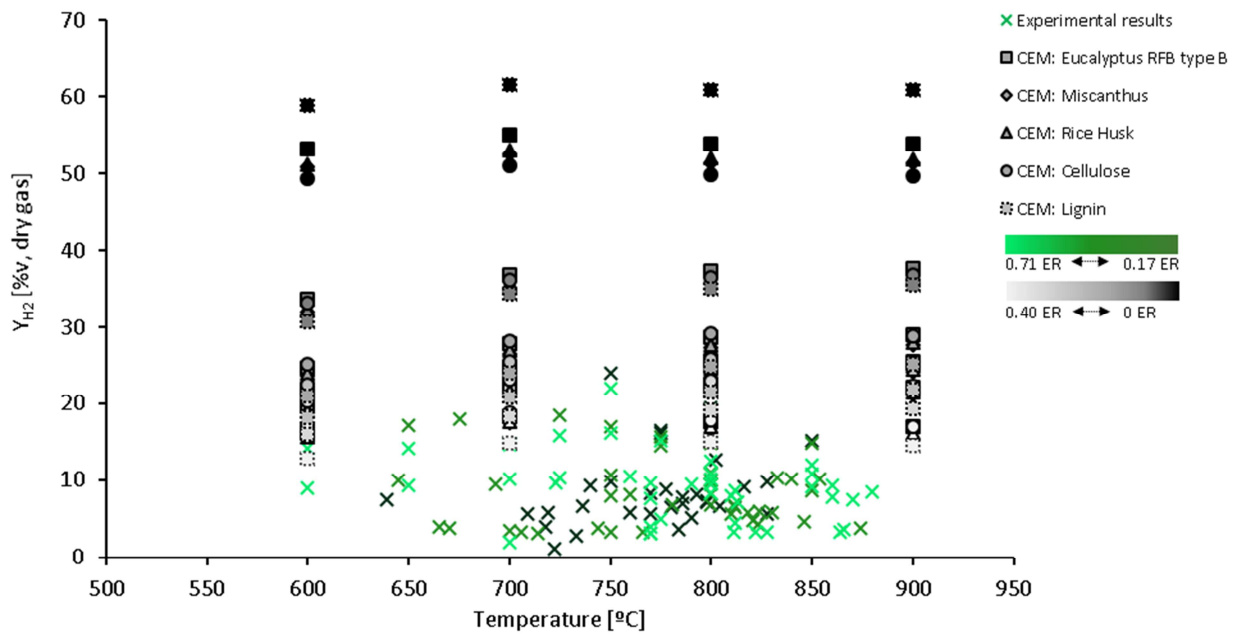
These differences may be justified by the impact of other parameters that were not analyzed in this work and are not related to chemical equilibrium, e.g., the physical properties of the biomass feedstock.

For pyrolysis conditions (ER=0) and gasification conditions with ER=0.10, the CEM results show H<sub>2</sub> concentration values between 32.0 and 54.9 %v for the range of temperatures considered (600°C to 900°C). Thus, higher production of H<sub>2</sub> is expected for pyrolysis conditions and gasification conditions with lower ER than that typically employed in practical gasifiers. The maximum value of H<sub>2</sub> concentration was found for pyrolysis of RFB from eucalyptus (T=700°C).

The CEM results for lignin conversion indicate higher H<sub>2</sub> concentration values in the producer gas than those predicted for the biomass feedstocks studied (miscanthus, rice husk and RFB from eucalyptus), predicting a maximum of 61.4%v for pyrolysis condition (T=700°C, Figure 1).



(a)

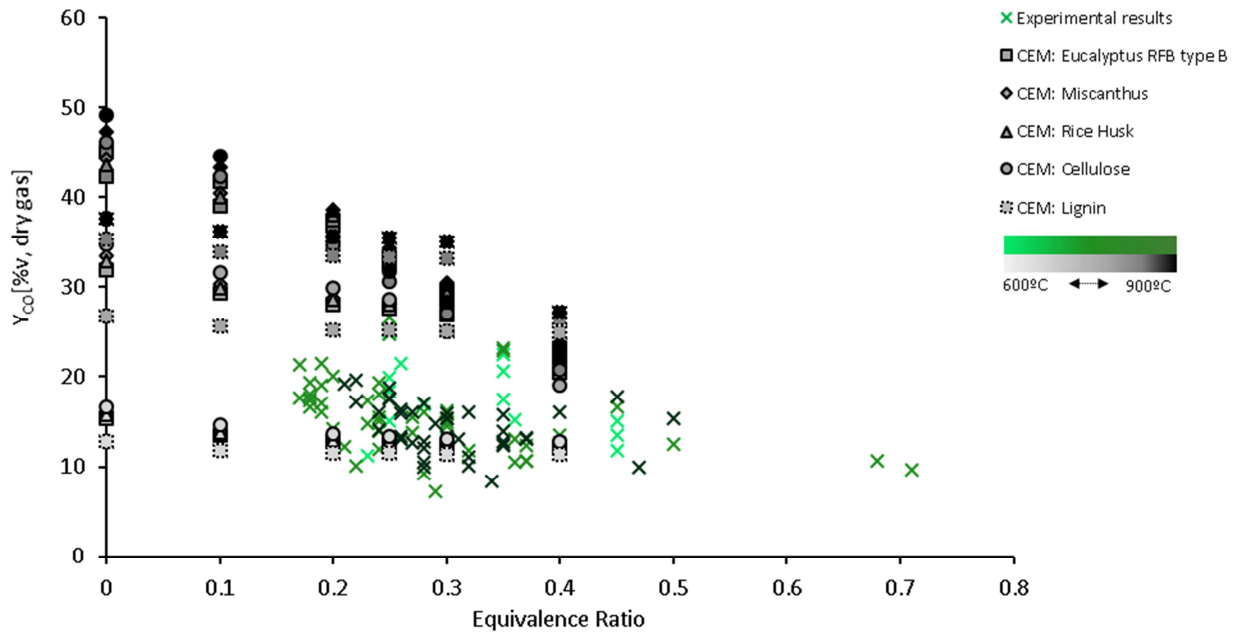


(b)

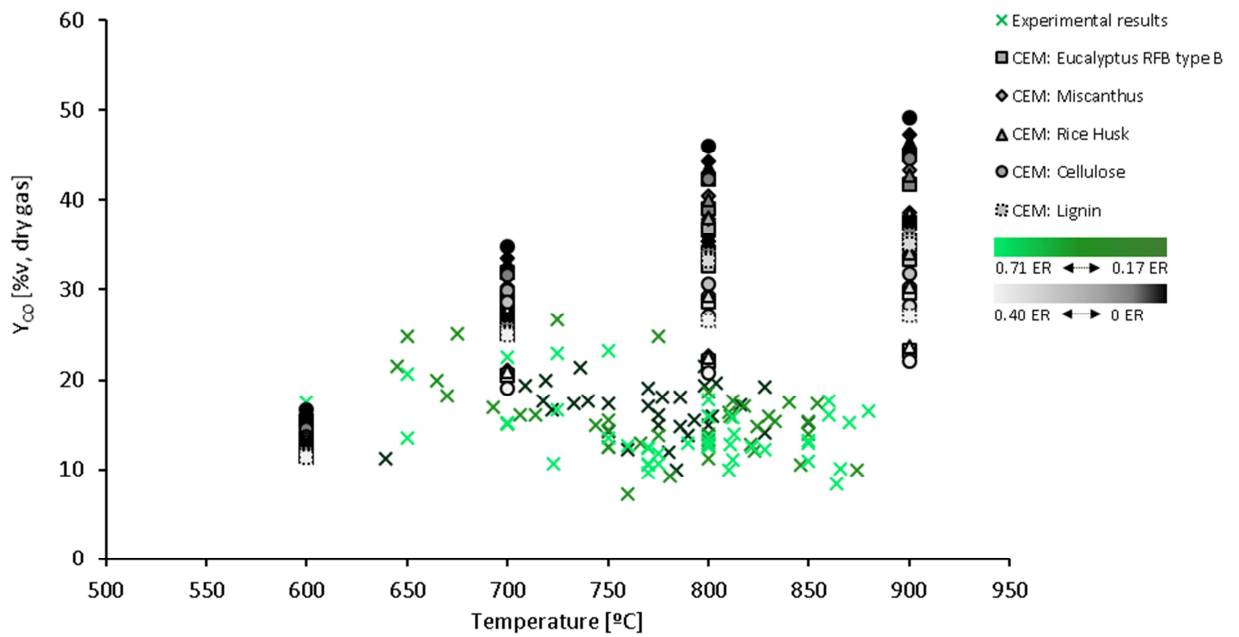
Figure 1 – Influence of the ER (a) and bed temperature (b) on the  $H_2$  concentration in the producer gas for the experimental results reported in the literature and CEM results.



In Figure 2, it is observed that the CO concentration values predicted by the CEM are higher than the CO concentration values found in the experimental results. For similar operating conditions, experimental results show CO concentration values between 7.2 and 26.6%v, while the CEM results show CO concentration values between 11.3 and 38.6%v. Furthermore, the CEM results show that CO concentration increases significantly with temperature increase, which is a phenomenon not observed in the experimental results (Figure 2 (b)). The PCC value for the relation between the predicted CO concentration value in the CEM and the process temperature is close to 0.8, showing positive correlation between these variables (Table 3). On the other hand, the PCC value for the relation between the CO concentration value found in the experimental results and the process temperature is close to -0.4, showing a slightly negative correlation. The reasoning behind this difference may be associated to the fact that in practical autothermal direct (air) gasifiers, the increase of bed temperature is associated to the increase of ER, which is known to lower CO concentration in the producer gas. In fact, in the developed database in the present work, the average ER for experimental studies with bed temperature above 800°C is 0.32 (Table 1). Nonetheless, it is observed a similar tendency for the decrease of CO with the increase of ER in both experimental and CEM results (Figure 2 (a)).



(a)

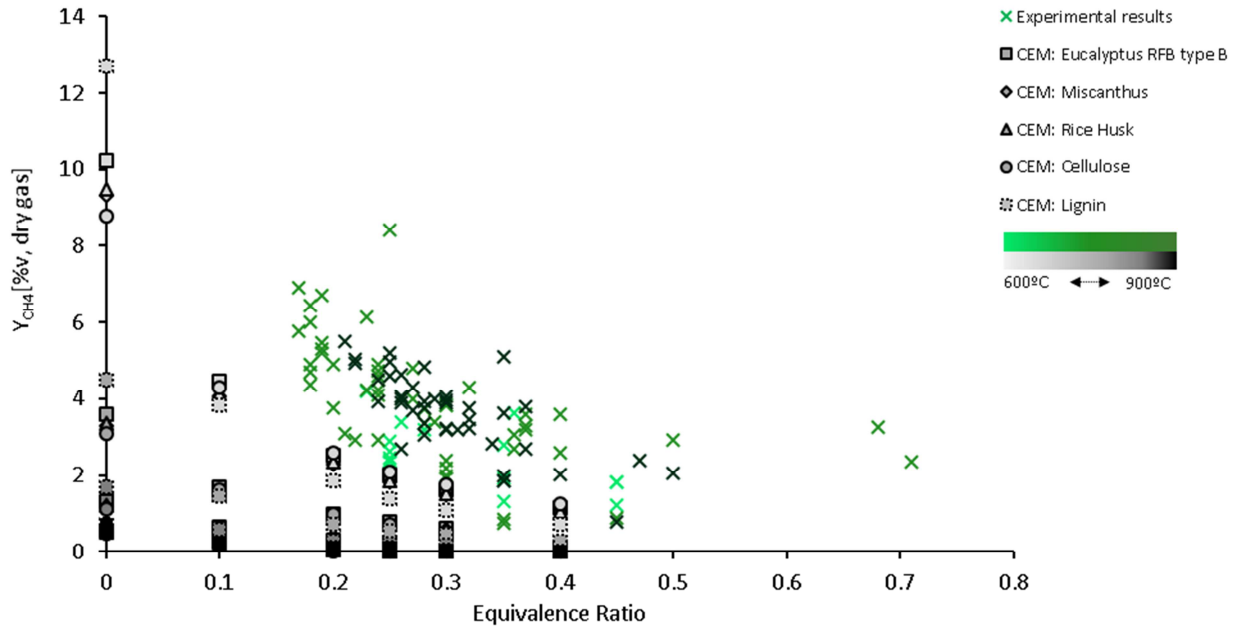


(b)

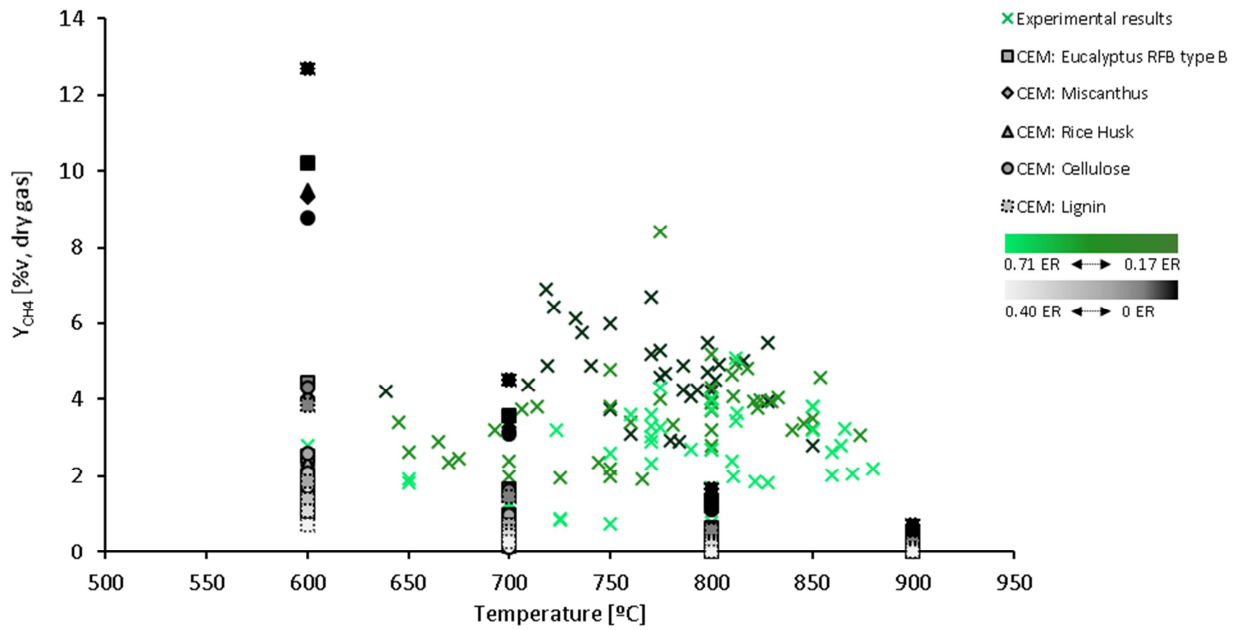
Figure 2 – Influence of the ER (a) and bed temperature (b) on the CO concentration in the producer gas for the experimental results reported in the literature and CEM results.

Analogous to the observations previously made regarding  $H_2$  concentration, higher concentration values of CO were predicted by the CEM for pyrolysis conditions and gasification with  $ER=0.10$ . For these conditions, the CEM results show CO concentration values between 13.8 and 47.3 %v, with the maximum value found for the pyrolysis of miscanthus at  $900^\circ\text{C}$ . Nonetheless, a higher CO concentration value (49.21 %v) was predicted for the pyrolysis of cellulose at  $900^\circ\text{C}$ .

In contrast to the observations made regarding the concentration of CO and  $H_2$ , the concentration of  $CH_4$  is typically higher in the reported experimental results than in the CEM results (Figure 3). For similar operating conditions, experimental results show  $CH_4$  concentration between 0.7 and 8.4%v, while the CEM results show  $CH_4$  concentration between 0.0 and 2.6%v. A similar negative correlation between  $CH_4$  concentration and ER is observed in both experimental and CEM results (Figure 3 (a)). However, CEM results shows a significant decrease of  $CH_4$  concentration with temperature increase, which is not observed in the experimental results (Figure 3 (b)). The determined PCC values are in accordance with this analysis (Table 3).



(a)



(b)

Figure 3 – Influence of the ER (a) and bed temperature (b) on the CH<sub>4</sub> concentration in the producer gas for the experimental results reported in the literature and CEM results.

CEM results for biomass pyrolysis conditions shows CH<sub>4</sub> concentration values between 0.3 and 10.2 %v, with the highest value predicted for the pyrolysis of RFB from eucalyptus at 600°C; this concentration value is higher than the values typically found in the experimental results analyzed. Furthermore, CEM results for lignin conversion show even higher values of CH<sub>4</sub> concentration, attaining a maximum value of 12.7%v for pyrolysis conditions at 600°C (Figure 3).

The developed empirical correlations based on experimental results reported in the literature (Equations 4, 5 and 6) show a significantly lower R<sup>2</sup> and observable deviations from the correlations developed using the CEM results (Equations 7, 8 and 9). This shows the high variability of the values reported in the literature regarding the composition (e.g., H<sub>2</sub>, CO and CH<sub>4</sub>) of the producer gas obtained in biomass direct (air) gasification processes in BFB reactors, and their significant differences from chemical equilibrium predictions, for similar operating conditions.

$$Y_{H_2,exp} = -0.01564 \times T - 0.65738 \times ER + 21.45107 \quad (\text{Equation 4})$$

$$R^2 = 0.04$$

$$Y_{CO,exp} = -0.02735 \times T - 15.3379 \times ER + 41.0061 \quad (\text{Equation 5})$$

$$R^2 = 0.23$$

$$Y_{CH_4,exp} = 0.005132 \times T - 9.99971 \times ER + 2.401523 \quad (\text{Equation 6})$$

$$R^2 = 0.26$$

$$Y_{H_2,eq} = 0.008173 \times T - 49.5472 \times ER + 30.2562 \quad (\text{Equation 7})$$

$$R^2 = 0.93$$

$$Y_{CO,eq} = 0.060842 \times T - 47.7011 \times ER - 6.70893 \quad (\text{Equation 8})$$

$$R^2 = 0.79$$

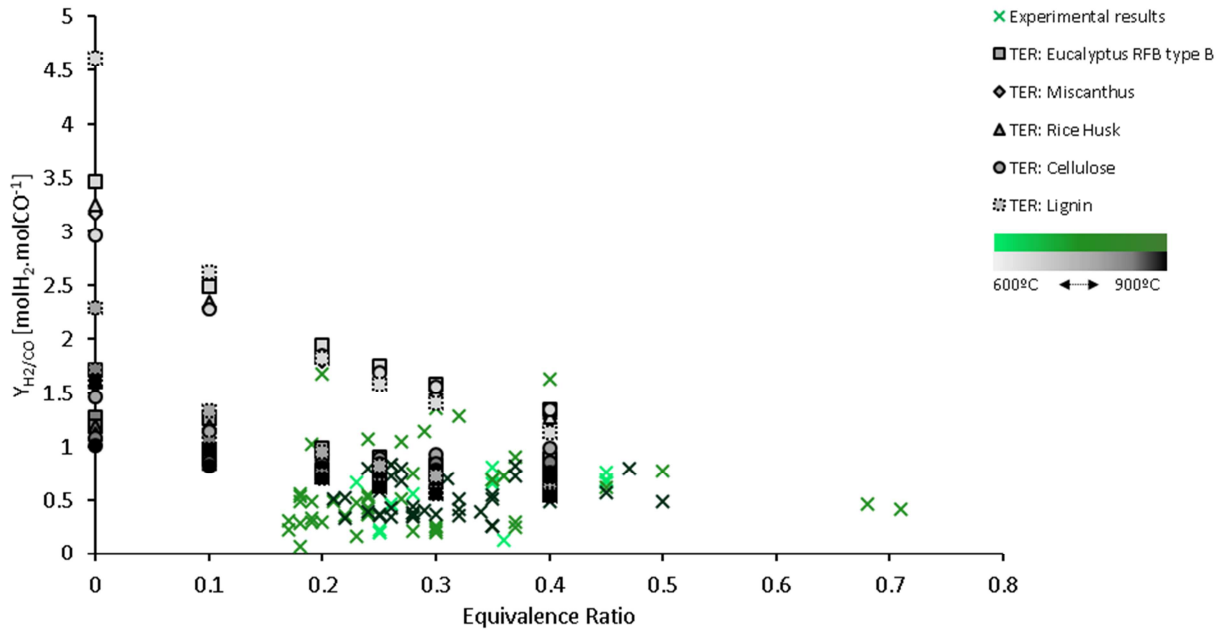
$$Y_{CH_4,eq} = -0.00563 \times T + -2.91807 \times ER + 5.6700002 \quad (\text{Equation 9})$$

$$R^2 = 0.81$$

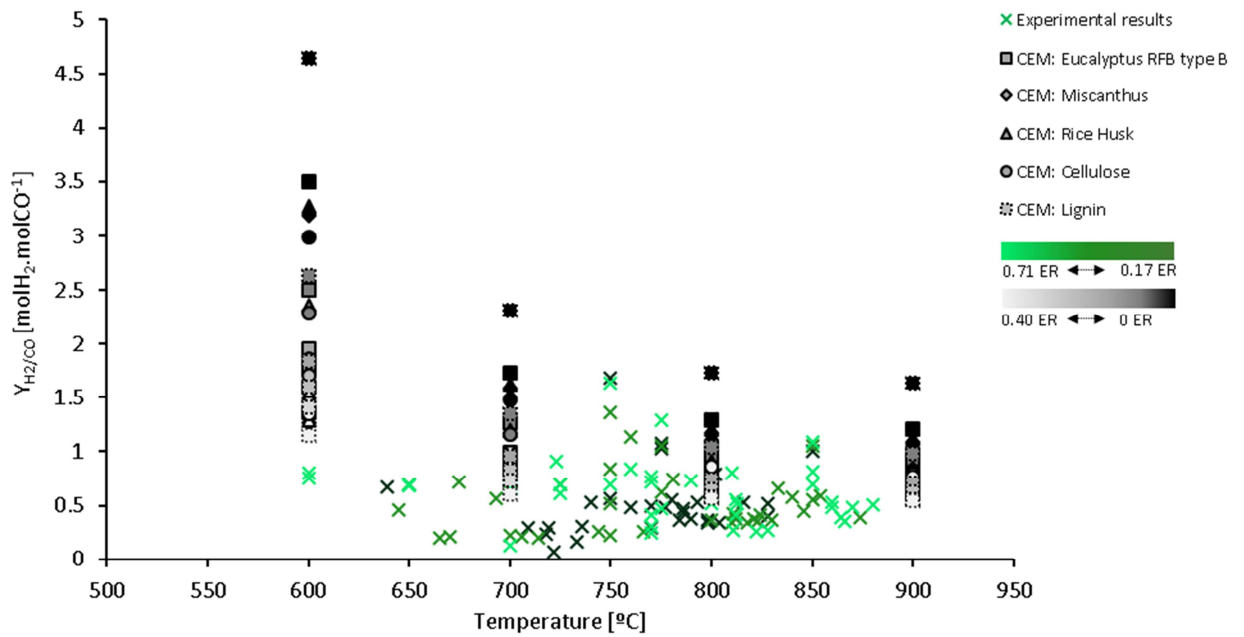
### 3.1.2. Gas phase products yield ratios

The relation between H<sub>2</sub>:CO molar ratios and the temperature and ER is shown in Figure 4. This ratio is relevant for the configuration of gasification processes for production of fuel gas for advanced applications that require specific H<sub>2</sub>:CO molar ratios, such as methanol production (2 mol.mol<sup>-1</sup>), synthetic fuels production through Fischer-Tropsch (FT) synthesis (0.6 mol.mol<sup>-1</sup>) and dimethyl ether (DME) production (1 mol.mol<sup>-1</sup>) [61–64]. Figure 4 shows that the H<sub>2</sub>:CO molar ratios for the CEM results are typically higher than the H<sub>2</sub>:CO ratios found in the experimental results. This is a consequence of the H<sub>2</sub> experimental yield being further away from equilibrium than the CO experimental yield, as observed in the previous section 3.1.1.

For similar operating conditions, the H<sub>2</sub>:CO molar ratio was found between 0.1 and 1.7 for the experimental results, which is in accordance with typical values referred for gasification processes in BFBs [63], and between 0.7 and 1.9 for the CEM results. Thus, concerning H<sub>2</sub>:CO molar ratio requirements, it can be observed that the producer gas from direct (air) gasification in BFB might be potentially used for FT synthesis but need further refinement to be used in other advanced applications, such as methanol synthesis. CEM results for pyrolysis conditions and gasification with ER=0.10 show higher H<sub>2</sub>:CO molar ratios, namely between 0.8 and 3.5, with the maximum value observed for the pyrolysis of RFB from eucalyptus at 600°C. Furthermore, CEM results for lignin conversion show an even higher H<sub>2</sub>:CO molar ratio, with a maximum value of 4.6 predicted for lignin pyrolysis at 600°C (Figure 4).



(a)



(b)

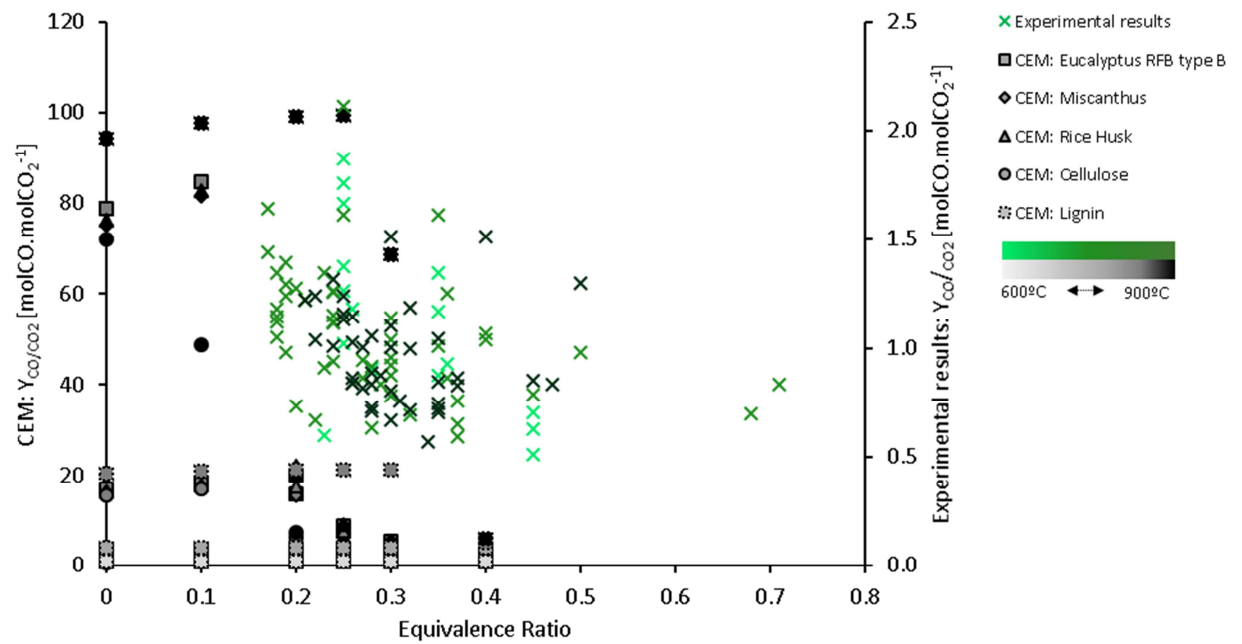
Figure 4 – Influence of the ER (a) and bed temperature (b) on the  $H_2:CO$  molar ratio in the producer gas for the experimental results reported in the literature and CEM results.

In Figure 4 (a), it can be observed a tendency for the decrease of the H<sub>2</sub>:CO molar ratio with the increase of ER for the CEM results, which is not observed in the experimental results. Furthermore, in the CEM results, it is also observed a significant decrease of this molar ratio with temperature increase, which is not observed in the analyzed experimental results (Figure 4 (b)). A decrease of H<sub>2</sub>:CO molar ratio with temperature increase has also been discussed in the literature [65] and can be justified by the occurrence of the exothermic water gas shift reaction (Equation 10); thus, high temperatures do not favor the CO conversion rate, leading to lower H<sub>2</sub>:CO molar ratio values [65].

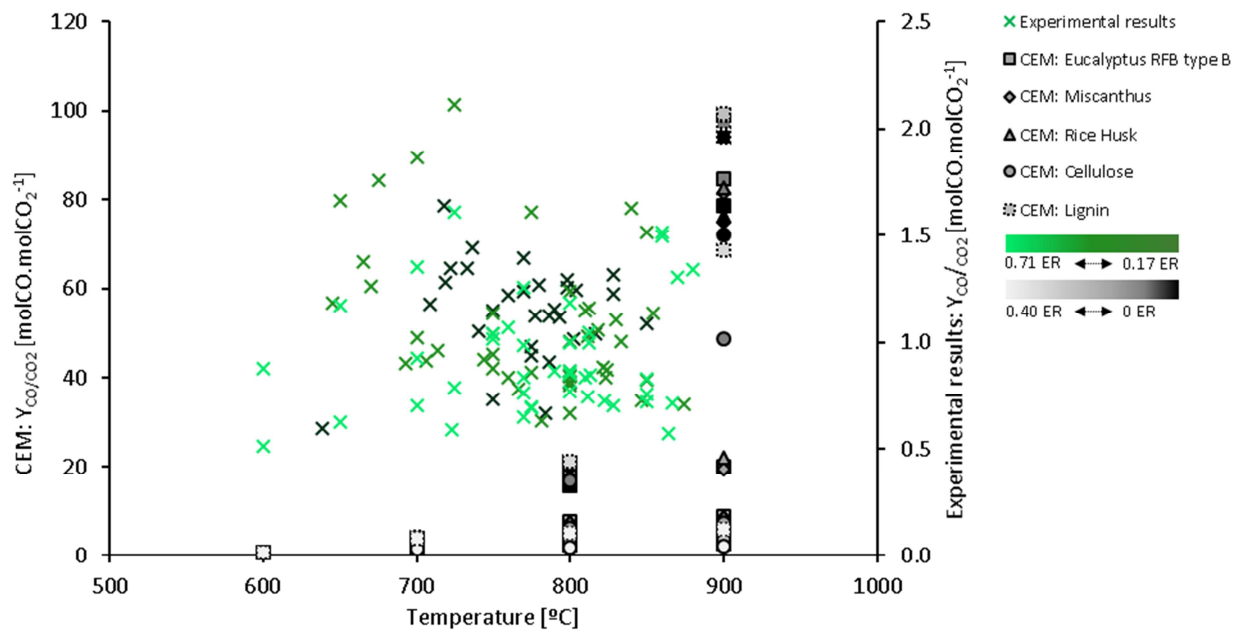


The CO:CO<sub>2</sub> molar ratio is shown in Figure 5, and although this ratio is not commonly referred in the literature, it can be used as an indicator of the efficiency of the process and the balance between the occurrence of gasification/combustion reactions [67]. It can be noticed that the experimental CO:CO<sub>2</sub> molar ratio values are significantly lower than the ones predicted by the CEM (Figure 5). For similar operating conditions, experimental results show CO:CO<sub>2</sub> molar ratios between 0.6 and 2.1, while CEM results show CO:CO<sub>2</sub> molar ratios between 0.7 and 22.1. Furthermore, CEM results show higher CO:CO<sub>2</sub> molar ratios, between 0.7 and 84.7, for pyrolysis and gasification with ER=0.10, with the maximum value obtained for gasification of RFB from eucalyptus at ER=0.10 and 900°C.





(a)



(b)

Figure 5 – Influence of the ER (a) and bed temperature (b) on the CO:CO<sub>2</sub> molar ratio in the producer gas for the experimental results reported in the literature and CEM results.

The influence of ER and bed temperature on the experimental CO:CO<sub>2</sub> molar ratios is not evident (Figure 5). On the other hand, the CEM results show that there is an increase of this molar ratio with temperature increase and ER decrease. For similar operating conditions, it is also observed that biomass with higher total carbon content typically leads to higher CO:CO<sub>2</sub> molar ratio in the producer gas for both CEM and experimental results. The reasoning behind this phenomenon may be related to a higher occurrence of carbon gasification by CO<sub>2</sub> (Boudouard reaction, Equation 11).



### 3.2. Process efficiency parameters

#### 3.2.1. LHV and $Y_{\text{gas}}$

The LHV of the producer gas for the experimental results reported in the literature and CEM results is shown in Figure 6. It is observed that the experimental LHV values are slightly lower than the LHV values predicted by the CEM. For similar operating conditions, the experimental and CEM results show LHV between 2.4 and 7.8 MJ/Nm<sup>3</sup> and between 3.6 and 7.9 MJ/Nm<sup>3</sup>, respectively. Pyrolysis conditions and gasification with ER=0.10 show a higher LHV, namely between 6.7 and 11.7 MJ/Nm<sup>3</sup>, with the maximum value obtained for the pyrolysis of RFB from eucalyptus at 900°C. For lignin conversion, an even higher LHV value (12.5 MJ/Nm<sup>3</sup>), is observed in the CEM results for pyrolysis conditions and 600°C.

Regarding the variation of LHV with the operating parameters, there is an evident trend for the decrease of LHV with ER increase for both experimental and CEM results (Figure 6 (a)). The influence of temperature on LHV is not evident for the experimental results (Figure 6 (b)). For the CEM results, there is an observable tendency for the increase of LHV with temperature increase. PCC values are in concordance with this analysis and indicate that the CEM results present less dispersion (Table 3). Accordingly, the empirical correlation (developed based in experimental data) for LHV (Equation 12) presents a lower R<sup>2</sup> value than the correlation developed based in the CEM results (Equation 13).

$$LHV_{exp} = -0.00299 \times T + -8.87018 \times ER + 9.637507 \quad (\text{Equation 12})$$

$$R^2 = 0.24$$

$$LHV_{eq} = 0.006549 \times T + -12.4161 \times ER + 4.339622 \quad (\text{Equation 13})$$

$$R^2 = 0.85$$

Journal Pre-proof

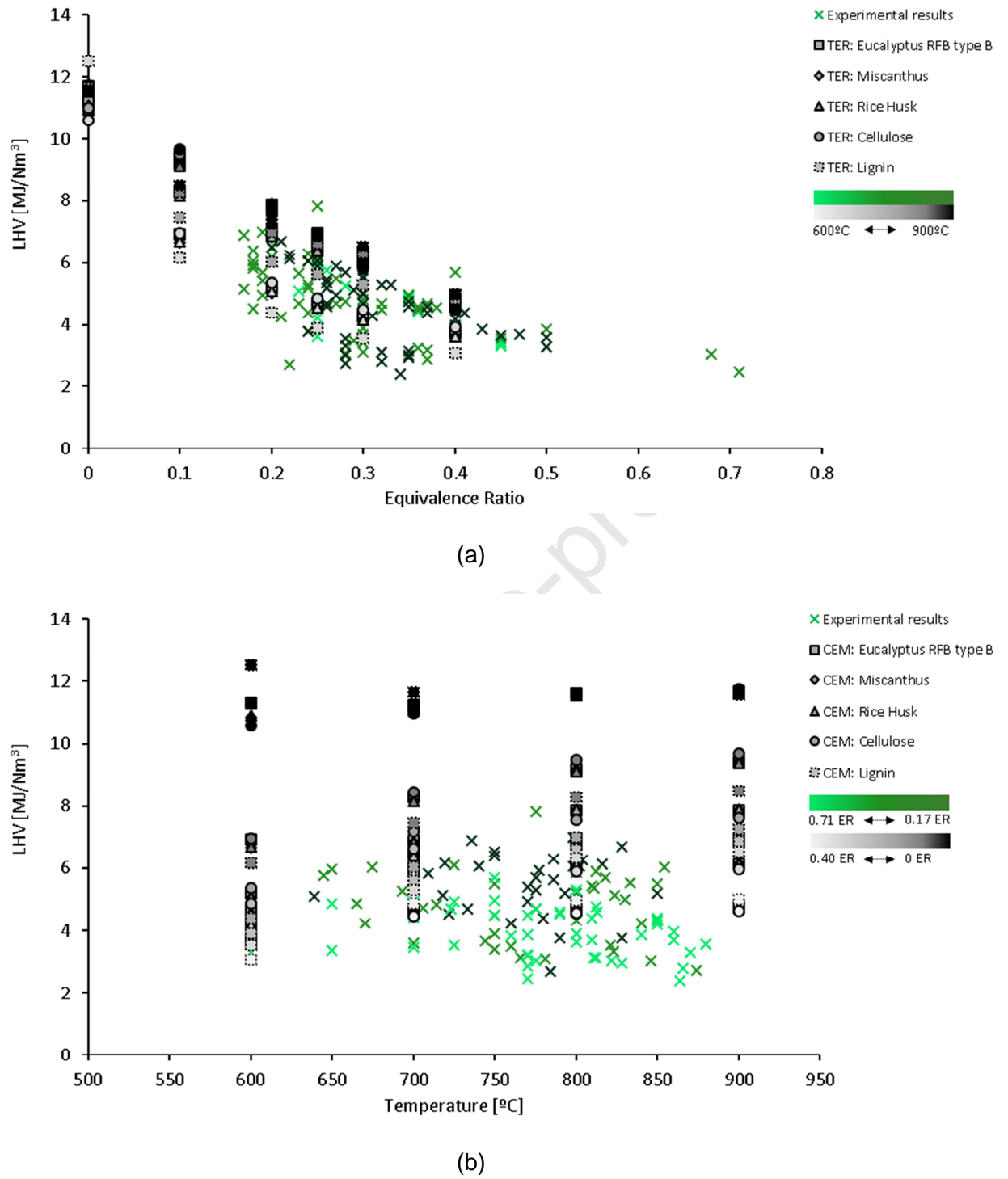


Figure 6 – Influence of the ER (a) and bed temperature (b) on the LHV of the producer gas for the experimental results reported in the literature and CEM results.

The  $Y_{gas}$  for both experimental and CEM results is shown in Figure 7. For similar operating conditions, the experimental and CEM results show  $Y_{gas}$  values between 1.2 and 3.5 Nm<sup>3</sup>/kg biomass db and 1.4 and 2.9 Nm<sup>3</sup>/kg biomass db, respectively. CEM results for pyrolysis conditions and gasification with unusually low ER (ER=0.10), show significantly lower  $Y_{gas}$ , namely between 0.6 and 1.8 Nm<sup>3</sup>/kg biomass db. Nonetheless, the maximum  $Y_{gas}$  value (3.7 Nm<sup>3</sup>/kg biomass db) was found in the CEM results for lignin gasification with ER=0.40 and 800°C. In the experimental results, a higher  $Y_{gas}$  value is referred in the literature, namely 4.1 Nm<sup>3</sup>/kg biomass db during gasification of sawdust with ER=0.50 and T=880°C [41]. However, these conditions are not suitable for typical direct (air) biomass gasification processes in BFB reactors due to the high ER employed, which leads to excessive combustion and low producer gas quality.

In Figure 7 (a), it can be observed an evident tendency for the increase of  $Y_{gas}$  with the ER for both experimental and CEM results. This can be explained by the higher ratio of gasifying agent per unit of biomass, which results directly from the increase of ER. A slight positive tendency is also observed between  $Y_{gas}$  and temperature increase, for both experimental and CEM results (Figure 7 (b)). Accordingly, the developed empirical and CEM correlations for  $Y_{gas}$  determination (Equations 14 and 15) present closer  $R^2$  values than the correlations developed for other parameters.

$$Y_{gas,exp} = 0.001936 \times T + 4.630323 \times ER - 0.97472 \quad (\text{Equation 14})$$

$$R^2 = 0.30$$

$$Y_{gas,eq} = 0.001246 \times T + 3.400375 \times ER + 0.31634 \quad (\text{Equation 15})$$

$$R^2 = 0.62$$

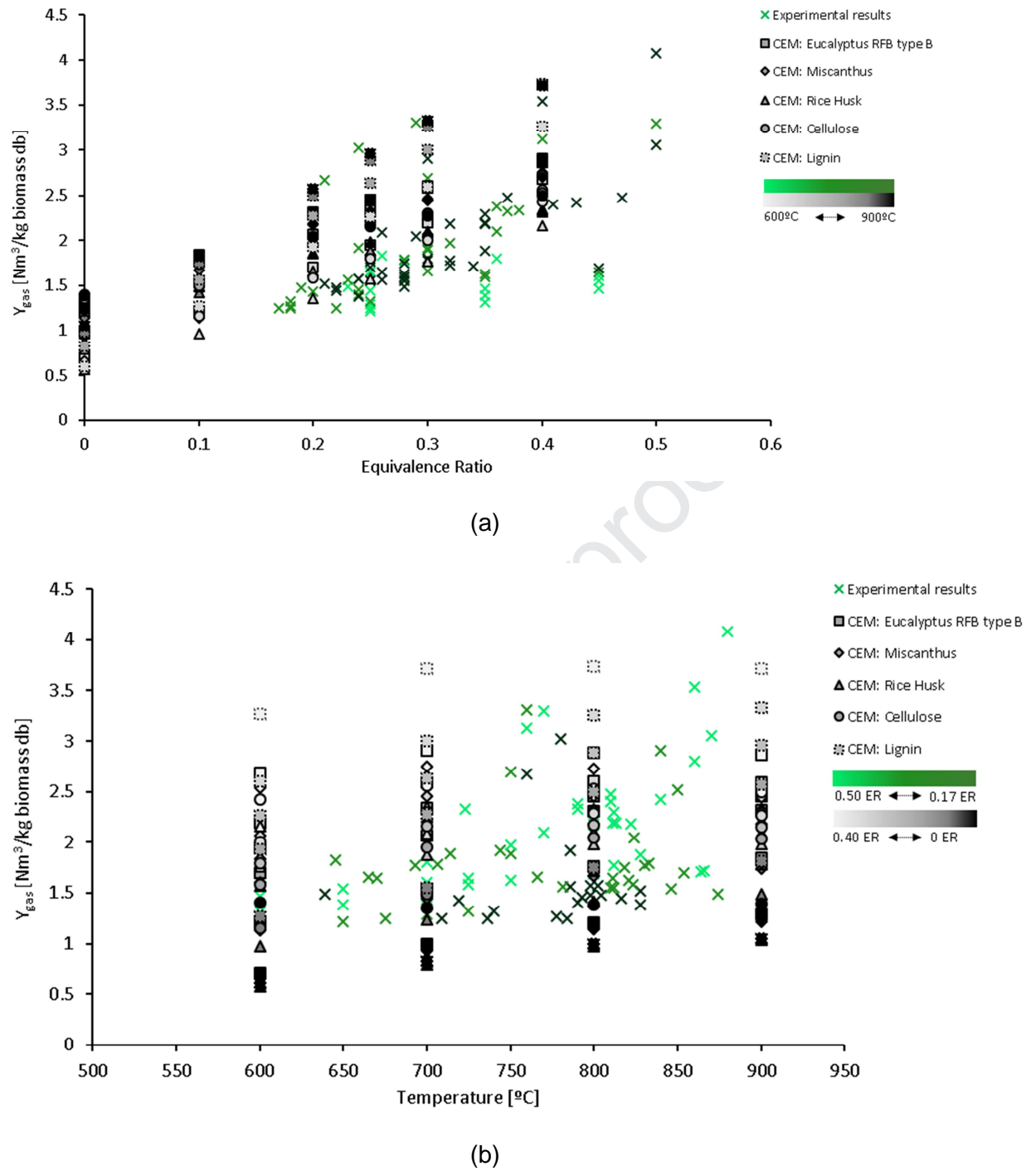


Figure 7 – Influence of the ER (a) and bed temperature (b) on the  $Y_{gas}$  for the experimental results reported in the literature and CEM results.

### 3.2.2. CGE and CCE

The CGE and CCE are parameters typically used in the literature to evaluate the efficiency of biomass gasification processes [27,37].

Regarding CGE, the experimental results show significantly lower values than the CEM predictions (Figure 8). For biomass gasification processes under similar operating conditions, CGE values are between 23.5 and 78.8% for experimental results and between 45.1 and 98.7% for CEM results. The CEM results for pyrolysis conditions and gasification with unsuitable low ER (ER=0.10) show lower CGE values, namely between 24.8 and 93.6%. Nonetheless, a maximum CGE value of 105.9% was predicted by the CEM for cellulose gasification with ER=0.10 at 900°C; this value means that the producer gas has higher energy content than the initial biomass, which is not possible according to the laws of thermodynamics. This inconsistency may be related to the equation used to estimate the LHV of the distinct biomass types [56] (see Section 2. Methods).

The CEM results show a tendency for the increase of CGE with temperature increase, whereas no clear tendency is observed in the experimental results (Figure 8 (b)). No evident tendency is observed between CGE and ER for both experimental and CEM results (Figure 8 (a)). This may be related to the fact that low ER favor the concentration of combustible gases in the producer gas but also favor a decrease in gas production, thus creating a trade-off between these parameters, as it has been previously suggested by the authors [27]. Accordingly, PCC values for the relation between CGE and the operating parameters typically indicate high dispersion (Table 3), except for the PCC value found for the relation between the CGE predicted by the CEM and the process temperature (0.8). Thus, the developed empirical correlation (Equation 16) present a significantly lower  $R^2$  value than the correlation developed based on CEM results (Equation 17).

$$CGE_{exp} = -0.03761 \times T + 15.64463 \times ER + 73.98776 \quad (\text{Equation 16})$$

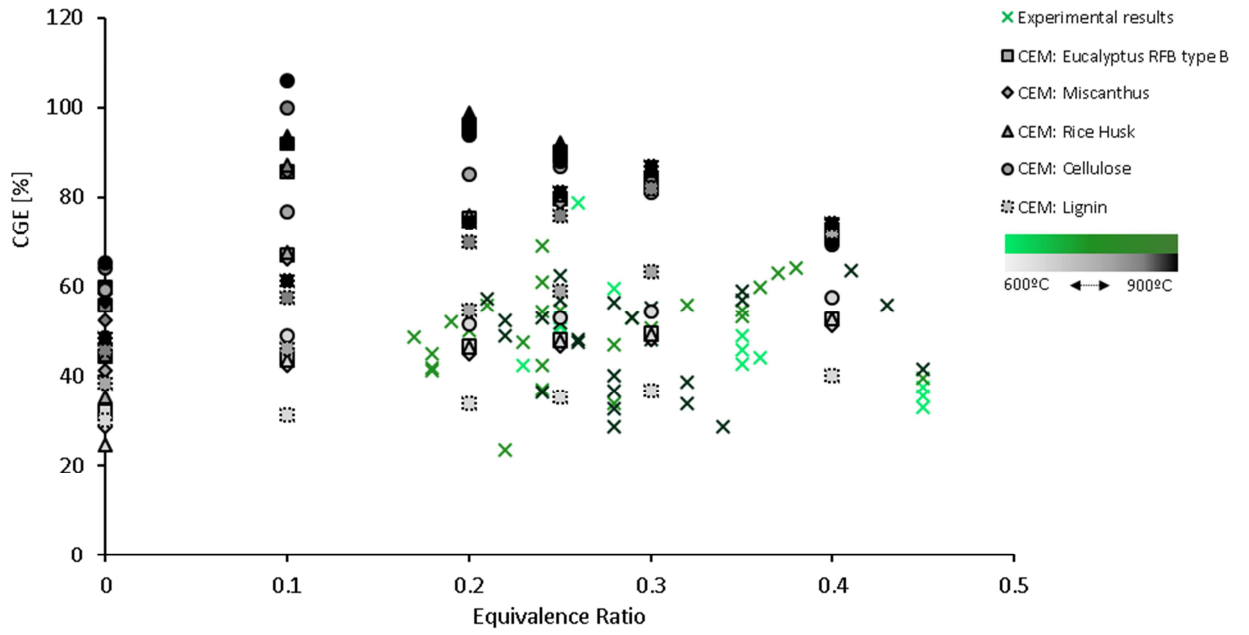
$$R^2 = 0.06$$

$$CGE_{eq} = 0.12096 \times T + -59.3921 \times ER + 0.916735 \quad (\text{Equation 17})$$

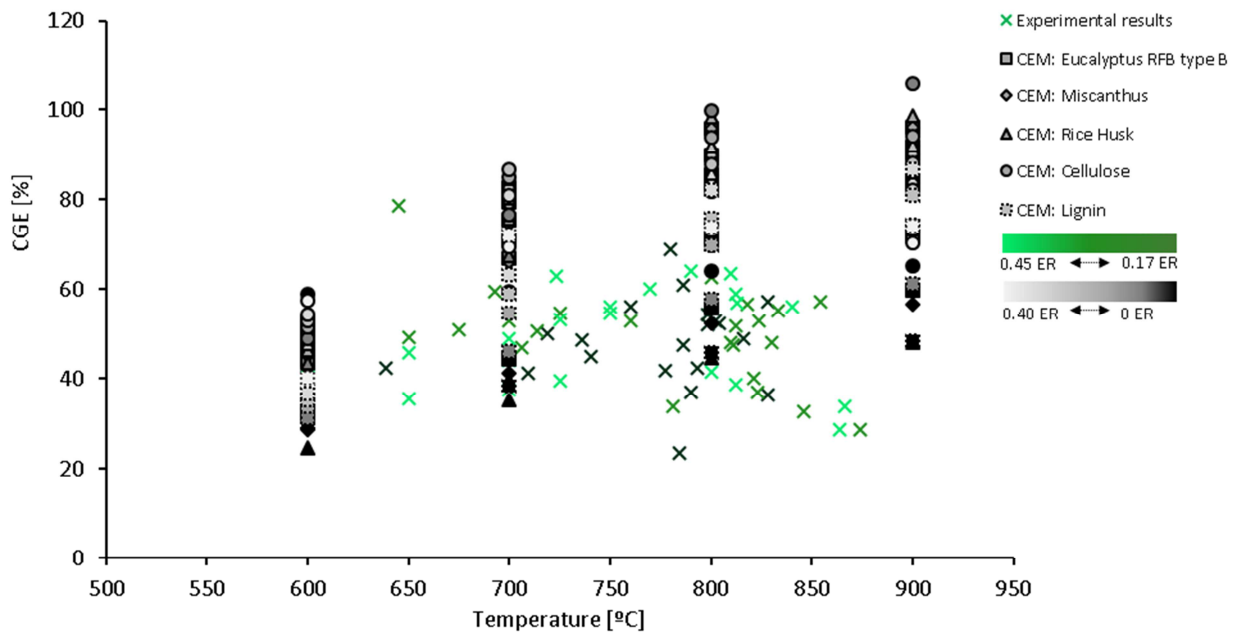
$$R^2 = 0.71$$

Journal Pre-proof





(a)



(b)

Figure 8 – Influence of the ER (a) and bed temperature (b) on the CGE for the experimental results reported in the literature and CEM results.

The influence of temperature and ER in the CCE, for both CEM and experimental results, is shown in Figure 9. For biomass gasification under similar operating conditions, the experimental and CEM results show similar values for CCE, namely between 55.0 and 94.8% and 59.0 and 99.5%, respectively. The CEM results for pyrolysis conditions and gasification with unsuitable low ER (ER=0.10) show lower CCE values, namely between 22.9 to 86.3%, depending on biomass type and temperature. The CEM results for lignin and cellulose also show similar CCE values (20.5 to 99.5%). The highest CCE value (99.5%) was predicted by the CEM for various conditions, for example RFB from eucalyptus gasification with ER=0.20 and 800°C.

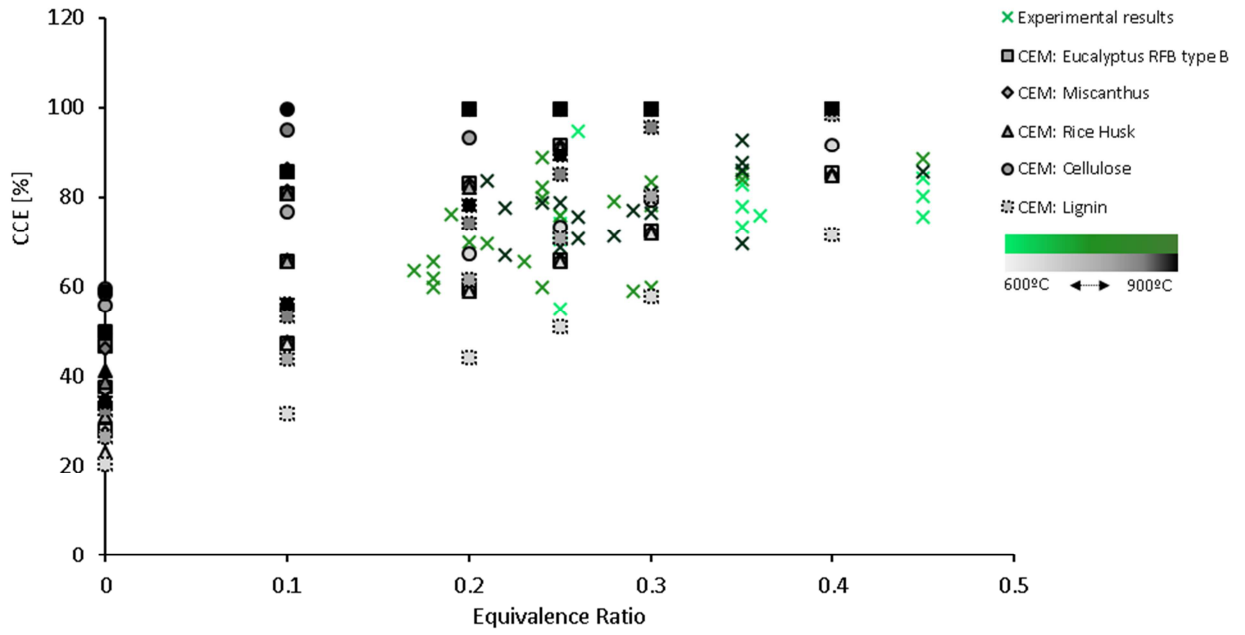
A tendency for the increase of CCE with ER is observed for both experimental and CEM results (Figure 9 (a)). A tendency for the increase of CCE with temperature can also be observed for the CEM results (Figure 9 (b)), which is in accordance with some other works [68]. For the experimental results, no evident tendency for the relation between CCE and temperature is observed. Accordingly, PCC values for the experimental results are significantly low and indicate high dispersion (Table 3) and the developed empirical correlation (Equation 18) has a significantly lower  $R^2$  value than the correlation developed based on CEM results (Equation 19).

$$CCE_{exp} = 0.005378 \times T + 45.36009 \times ER + 58.86143 \quad (\text{Equation 18})$$

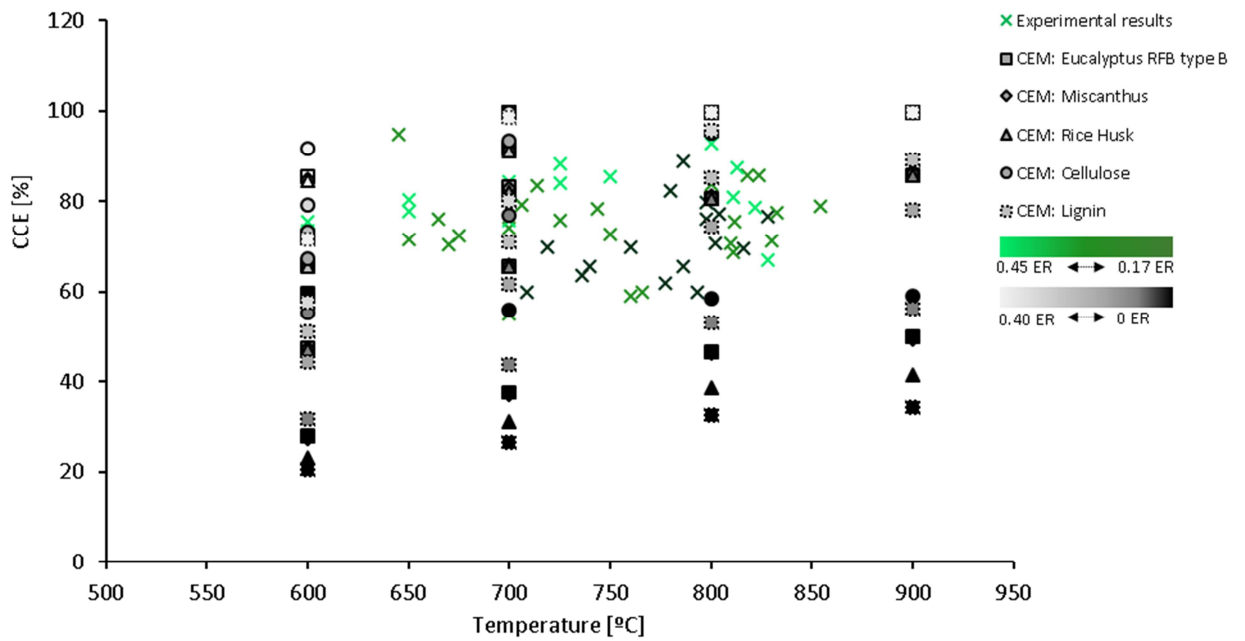
$$R^2 = 0.07$$

$$CCE_{eq} = 0.093148 \times T + 52.28168 \times ER + 5.825285 \quad (\text{Equation 19})$$

$$R^2 = 0.7$$



(a)



(b)

Figure 9 – Influence of the ER (a) and bed temperature (b) on the CCE for the experimental results reported in the literature and CEM results.

#### 4. Empirical and CEM correlations evaluation

In this section, the empirical and CEM correlations prediction capability was briefly evaluated. For this purpose, direct (air) gasification experiments were performed in a pilot-scale BFB gasifier (80 kWth) with distinct biomass types and operating conditions. The pilot-scale gasifier was operated at atmospheric pressure, with superficial gas velocity around 0.27 – 0.30 m/s (depending on the bed temperature) and under bubbling fluidization regime. A more detailed description of the experimental infrastructure can be found in other works [27,37,69,70]. The operating conditions of the gasification experiments performed are detailed in Table 4. The correlations were evaluated by using these operating conditions (ER and bed temperature) as inputs and comparing the predicted results with the experimental results.

In Table 5, the experimental results and the empirical and CEM correlations predictions are summarized and compared. The composition of the producer gas ( $H_2$ , CO and  $CH_4$ ), LHV,  $Y_{gas}$ , CGE and CCE are considered as parameters. Pearson's correlation test was performed to measure the strength of the correlation between the empirical and CEM correlations predictions and the experimental results, thus characterizing the accuracy of the predictions. In this analysis, a PCC value of 1 indicates that the values predicted by the correlations are perfectly linearly correlated with the observed experimental results [71].

The comparison between the empirical correlations predictions and the experimental results (Table 5) allowed the following general observations:

- Prediction of  $CH_4$  concentration,  $H_2/CO$  molar ratio, LHV,  $Y_{gas}$  and CCE with low relative errors;
- Overestimation of  $H_2$  and CO concentration and slight overestimation of CGE;
- Maximum relative mean error associated to the prediction of  $H_2$  and CO concentration (16.9 and 13.2%, respectively), with the remaining relative mean errors being lower than 8.0% (CGE).

Table 4 – Operating conditions during the biomass gasification experiments performed in the pilot-scale BFB

Biomass feedstock	Average bed temperature [°C]	ER	Biomass feed rate [kg/h]	Air feed rate [L NPT/min]
Eucalyptus RFB	747	0.26	11.1	200
Eucalyptus RFB	754	0.26	11.1	200
Eucalyptus RFB	775	0.26	11.1	200
Wood pellets	814	0.33	8.7	200
Wood pellets	815	0.32	8.9	200
Eucalyptus RFB	816	0.28	10.5	200
Eucalyptus RFB	816	0.20	14.8	200
Wood pellets	817	0.33	8.8	200
Eucalyptus RFB	825	0.26	11.1	200

Table 5 – Comparison between obtained results in direct (air) gasification of biomass experiments in a BFB reactor and predicted by the empirical correlations and CEM correlations for the same operating conditions (Table 4).

		% vol, db			Mol.mol <sup>-1</sup>	MJ/Nm <sup>3</sup>	Nm <sup>3</sup> /kg biomass db	%	
		H <sub>2</sub>	CO	CH <sub>4</sub>	H <sub>2</sub> /CO	LHV	Y <sub>gas</sub>	CGE	CCE
Experimental results	$\bar{x}$	7.3	12.9	3.8	0.6	4.6	1.8	44.5	73.2
	$\sigma$	1.0	1.7	0.4	0.1	0.5	0.2	7.8	10.2
Empirical correlations	$\bar{x}$	8.8	14.9	3.7	0.6	4.8	1.9	48.4	75.8
	Error $\bar{x}$ [%]	16.9	13.2	-2.0	4.1	3.0	5.3	8.0	3.5
	$\sigma$	0.5	1.1	0.4	0.0	0.4	0.2	1.1	1.9
	Error $\sigma$ [%]	-114.8	-48.1	2.2	-142.5	-21.2	1.4	-602.5	-432.1
	PCC	-0.9	-0.5	0.6	0.7	0.0	1.0	-0.3	0.9
CEM correlations	$\bar{x}$	22.9	28.5	0.4	0.8	6.2	2.3	85.7	94.7
	Error $\bar{x}$ [%]	68.1	54.6	-926.0	29.7	25.4	22.0	48.1	22.8
	$\sigma$	2.0	2.3	0.2	0.1	0.5	0.2	3.5	3.8
	Error $\sigma$ [%]	51.2	27.3	-76.2	-16.0	4.1	-36.3	-125.3	-166.9
	PCC	-0.4	0.8	-0.2	-0.4	0.5	1.0	0.8	0.9

High positive PCC values were found for  $\text{CH}_4$ ,  $\text{H}_2/\text{CO}$  molar ratio,  $Y_{\text{gas}}$  and CCE, showing positive correlations between the experimental results and the empirical correlations predictions. However, a significantly lower PCC value was found for LHV (close to 0), despite this parameter prediction average relative error being low. Furthermore, PCC values were found negative for  $\text{H}_2$  (-0.9), CO (-0.5) and CGE (-0.4), showing negative correlations. These phenomena can be related to the high dispersion of values found in the literature for similar operating conditions, which were used in the development of the empirical correlations, as indicated by the low  $R^2$  values found previously (see Section 3. Experimental and CEM results comparison). Thus, for direct (air) gasification processes in BFB reactors, the developed empirical correlations show capacity to predict first estimates of gasification products and process efficiency parameters, specifically  $\text{CH}_4$  concentration,  $\text{H}_2/\text{CO}$  molar ratio,  $Y_{\text{gas}}$  and CCE, however, require further improvement for higher reliability.

Regarding the comparison between the CEM correlations predictions and the experimental results (Table 5), the following general observations can be made:

- Significant overestimation of  $\text{H}_2$  and CO concentration and CGE, and significant underestimation of  $\text{CH}_4$  concentration;
- Overestimation of  $\text{H}_2/\text{CO}$  molar ratio, LHV,  $Y_{\text{gas}}$  and CCE.
- Maximum relative mean error associated to  $\text{CH}_4$  prediction (-926 %) and minimum associated to  $Y_{\text{gas}}$  prediction (22 %).

The lack of accuracy of the CEM correlations to determine gasification products was expected due to the previously noticed difference between the producer gas composition predicted by the CEM and the gas composition reported in the literature regarding direct (air) biomass gasification in BFB reactors (see Section 3. Experimental and CEM results comparison). These combined observations prove that chemical equilibrium is not attained in practical BFB direct (air) gasifiers. Nonetheless,  $\text{H}_2/\text{CO}$  molar ratio values obtained through the CEM are significantly closer to the values observed experimentally (relative mean error of 29.7%). A positive PCC value (0.8)

was found for the correlation between CO concentration found in the experimental results and predicted by the CEM, however, negative correlations were found for H<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>/CO molar ratio (PCC = -0.2 to -0.4). Positive PCC values (0.5 to 1.0) were also found for LHV, Y<sub>gas</sub>, CGE and CCE.

Thus, these results indicate that the developed CEM correlations are not suited to characterize and predict gasification products from direct (air) biomass gasification processes in BFBs reactors. Nevertheless, these correlations present higher accuracy for the prediction of H<sub>2</sub>/CO molar ratios and efficiency parameters, than for the prediction of the volumetric concentration of major combustible gases (CO, H<sub>2</sub> and CH<sub>4</sub>) present in the producer gas. The lack of accuracy of CEMs for the prediction of the producer gas composition under certain operating conditions has also been recognized in other works [7,10,11,25], nonetheless, chemical equilibrium modelling is still the most commonly used approach for determining producer gas composition in biomass gasification [4,13], and has been intensively used for fluidized beds in recent years [10,13,24,34–36,72]. Therefore, these results also indicate that the focus of modelling studies should be shifted from black-box chemical equilibrium modelling to other modelling approaches, such as approaches that integrate experimental knowledge. In this respect, integrating chemical equilibrium modelling with experimental knowledge, for example an integration between the CEM and empirical model developed in this work, may allow higher agreement between the model predictions and experimental data. These aspects are relevant to increase confidence in the predicted results from numerical tools and consequently facilitate the upscaling of biomass gasification technologies to the industrial level.



## 5. Conclusions

This work shows that the producer gas composition reported in the literature regarding direct (air) biomass gasification in BFB gasifiers has significant deviations from the one predicted by chemical equilibrium. In fact,  $H_2$  and CO concentrations are grossly overestimated by the CEM predictions, while  $CH_4$  is largely underestimated. Furthermore, in some cases, the effect of temperature and ER on these concentration values is distinct for the reported experimental results and the CEM predictions. For example, the CEM predicted a significant decrease of  $H_2$  concentration with ER increase and this phenomenon was not observed in the reported experimental results. Regarding typical gasification efficiency parameters (LHV,  $Y_{gas}$ , CGE and CEE), it was also observed deviations from the CEM predictions, however, these were not as significant as the ones observed for the producer gas composition. Thus, for the analyzed operating conditions, it is considered that non-stoichiometric chemical equilibrium modelling is not suited to predict gasification products and support the design and operation of BFB reactors in direct (air) biomass gasification. At most, black-box chemical equilibrium modelling should be used to obtain first estimates of LHV,  $Y_{gas}$  or CCE.

On the other hand, the empirical model development was hindered by the variability of the experimental results (for similar operating conditions) reported in the literature and by the lack of information regarding the specific design and operating conditions of the BFB gasifiers. Nonetheless, the empirical model showed moderate accuracy for the prediction of preliminary estimates of gasification products and process efficiency parameters, specifically  $CH_4$  concentration,  $H_2/CO$  molar ratio,  $Y_{gas}$  and CCE. However, further development is necessary to improve the accuracy of the model predictions (with special emphasis on the prediction of  $H_2$  and CO concentration), and consequently increase its reliability in the design, up-scale and operation of direct (air) BFB gasifiers. For this purpose, outlier exclusion, increase of database size and the

inclusion of the biomass feedstock elemental composition in the correlations development, may be beneficial.

Currently, despite some studies revealing the flaws of the CEM approach, this is still the most commonly used technique to predict the products composition from biomass gasification and has been intensively used for simulating fluidized bed gasification in recent years. Accordingly, this work clearly shows that using CEMs to predict producer gas composition from direct (air) biomass gasification processes in BFBs can result in significant deviations from practical experimental results. Thus, alternative modeling techniques, for example approaches that integrate theoretical and experimental knowledge, such as integrating CEMs with empirical modelling, could be more reliable for the up-scale, design and operation of gasification technologies.

Biomass gasification technologies still require significant improvements to be cost-competitive and to be able to compete with conventional technologies based on fossil fuels. In this respect, modelling approaches are less expensive and time consuming than experimental research, and may improve the research progress of biomass gasification technologies and optimize the operation and design of gasification plants, leading to reduced costs. For this purpose, models based on suitable modelling approaches must be developed, for example by integrating practical knowledge from available experimental works. Accordingly, this paper results give a relevant insight on the variability of reported experimental results regarding direct (air) biomass gasification in BFBs and the applicability and accuracy of empirical and chemical equilibrium modelling approaches. In result, adopting and developing suitable modelling approaches is facilitated.

**Acknowledgments**

The authors acknowledge the Portuguese Foundation for Science and Technology for the financial support provided through the project POCI-01-0247-FEDER-021874 - INPACTUS – Innovative Products and Technologies from Eucalyptus and project “SusPhotoSolutions - Soluções Fotovoltaicas Sustentáveis”, PO Centro 2020 (ref. CENTRO-01-0145-FEDER-000005). Thanks are due for the financial support to CESAM (UID/AMB/50017/2019), to FCT/MCTES through national funds, and the co-funding by the FEDER, within the PT2020 Partnership Agreement and Compete 2020, and Compete 2020. The authors also acknowledge the Portuguese Foundation for Science and Technology and The Navigator Company for providing financial support to the PhD scholarship granted to Daniel Pio (ref. PD/BDE/128620/2017).

**References**

- [1] Mirmoshtaghi G, Li H, Thorin E, Dahlquist E. Evaluation of different biomass gasification modeling approaches for fluidized bed gasifiers. *Biomass and Bioenergy* 2016;91:69–82. doi:10.1016/j.biombioe.2016.05.002.
- [2] Higman C, Burgt M van der. *Gasification*. Gulf Professional Publishing; 2011.
- [3] La Villetta M, Costa M, Massarotti N. Modelling approaches to biomass gasification: A review with emphasis on the stoichiometric method. *Renew Sustain Energy Rev* 2017;74:71–88. doi:10.1016/j.rser.2017.02.027.
- [4] Safarian S, Unnpórsson R, Richter C. A review of biomass gasification modelling. *Renew Sustain Energy Rev* 2019;110:378–91. doi:10.1016/j.rser.2019.05.003.
- [5] Baruah D, Baruah DC, Hazarika MK. Artificial neural network based modeling of biomass gasification in fixed bed downdraft gasifiers. *Biomass and Bioenergy* 2017;98:264–71. doi:10.1016/j.biombioe.2017.01.029.
- [6] Meenaroch P, Kerdsuwan S, Laohalidanond K. Development of Kinetics Models in Each Zone of a 10 kg/hr Downdraft Gasifier using Computational Fluid Dynamics. vol. 79. Elsevier B.V.; 2015. doi:10.1016/j.egypro.2015.11.485.
- [7] Zhao M, Sikarwar S, S.Fennell P, Shah N, J.Anthony E. Progress in biofuel production from gasification 2017;61. doi:10.1016/j.pecs.2017.04.001.
- [8] Gómez-Barea A, Leckner B. Modeling of biomass gasification in fluidized bed. *Prog Energy Combust Sci* 2010;36:444–509. doi:10.1016/j.pecs.2009.12.002.
- [9] Fortunato B, Brunetti G, Camporeale SM, Torresi M, Fornarelli F. Thermodynamic model of a downdraft gasifier. *Energy Convers Manag* 2017;140:281–94. doi:10.1016/j.enconman.2017.02.061.
- [10] Puig-Arnavat M, Bruno JC, Coronas A. Review and analysis of biomass gasification models. *Renew Sustain Energy Rev* 2010;14:2841–51. doi:10.1016/j.rser.2010.07.030.
- [11] Gambarotta A, Morini M, Zubani A. A non-stoichiometric equilibrium model for

- the simulation of the biomass gasification process. *Appl Energy* 2017;227:119–27. doi:10.1016/j.apenergy.2017.07.135.
- [12] Baruah D, Baruah DC. Modeling of biomass gasification: A review. *Renew Sustain Energy Rev* 2014;39:806–15. doi:10.1016/j.rser.2014.07.129.
- [13] Acar MC, Böke YE. Simulation of biomass gasification in a BFBG using chemical equilibrium model and restricted chemical equilibrium method. *Biomass and Bioenergy* 2019;125:131–8. doi:10.1016/j.biombioe.2019.04.012.
- [14] Basu P. *Biomass Gasification, Pyrolysis and Torrefaction: Practical Design and Theory*. 2013.
- [15] Knoef H. *Handbook of Biomass Gasification*. BTG Gr 2005:378.
- [16] Karmakar MK, Mandal J, Haldar S, Chatterjee PK. Investigation of fuel gas generation in a pilot scale fluidized bed autothermal gasifier using rice husk. *Fuel* 2013;111:584–91. doi:10.1016/j.fuel.2013.03.045.
- [17] Jarungthammachote S, Dutta a. Equilibrium modeling of gasification: Gibbs free energy minimization approach and its application to spouted bed and spout-fluid bed gasifiers. *Energy Convers Manag* 2008;49:1345–56. doi:10.1016/j.enconman.2008.01.006.
- [18] Neves D. *Evaluation of thermochemical conversion in fluidized bed*. PhD thesis, University of Aveiro; 2013.
- [19] Lim Y II, Lee U Do. Quasi-equilibrium thermodynamic model with empirical equations for air-steam biomass gasification in fluidized-beds. *Fuel Process Technol* 2014;128:199–210. doi:10.1016/j.fuproc.2014.07.017.
- [20] Hannula I, Kurkela E. A semi-empirical model for pressurised air-blown fluidised-bed gasification of biomass. *Bioresour Technol* 2010;101:4608–15. doi:10.1016/j.biortech.2010.01.072.
- [21] Rodriguez-Alejandro DA, Nam H, Maglinao AL, Capareda SC, Aguilera-Alvarado AF. Development of a modified equilibrium model for biomass pilot-scale fluidized bed gasifier performance predictions. *Energy* 2016;115:1092–108.

- doi:10.1016/j.energy.2016.09.079.
- [22] Puig-Arnavat M, Bruno JC, Coronas A. Modified Thermodynamic Equilibrium Model for Biomass Gasification: A Study of the Influence of Operating Conditions. *Energy & Fuels* 2012;26:1385–94. doi:10.1021/ef2019462.
- [23] Sittisun P, Tippayawong N, Pang S. Biomass gasification in a fixed bed downdraft reactor with oxygen enriched air: A modified equilibrium modeling study. *Energy Procedia* 2019;160:317–23. doi:10.1016/j.egypro.2019.02.163.
- [24] Pala LPR, Wang Q, Kolb G, Hessel V. Steam gasification of biomass with subsequent syngas adjustment using shift reaction for syngas production: An Aspen Plus model. *Renew Energy* 2017;101:484–92. doi:10.1016/j.renene.2016.08.069.
- [25] Heidenreich S, Foscolo PU, Müller M, Foscolo PU. *Advanced Biomass Gasification: New Concepts for Efficiency Increase and Product Flexibility*. 2016.
- [26] Yu J, Smith JD. Validation and application of a kinetic model for biomass gasification simulation and optimization in updraft gasifiers. *Chem Eng Process - Process Intensif* 2018;125:214–26. doi:10.1016/j.cep.2018.02.003.
- [27] Pio DT, Tarelho LAC, Matos MAA. Characteristics of the gas produced during biomass direct gasification in an autothermal pilot-scale bubbling fluidized bed reactor. *Energy* 2017;120:915–28. doi:10.1016/j.energy.2016.11.145.
- [28] Gagliano A, Nocera F, Bruno M, Cardillo G. Development of an Equilibrium-based Model of Gasification of Biomass by Aspen Plus. *Energy Procedia* 2017;111:1010–9. doi:10.1016/j.egypro.2017.03.264.
- [29] Torres C, Urvina L, de Lasa H. A chemical equilibrium model for biomass gasification. Application to Costa Rican coffee pulp transformation unit. *Biomass and Bioenergy* 2019;123:89–103. doi:10.1016/j.biombioe.2019.01.025.
- [30] Antolini D, Shivananda AS, Patuzzi F, Grigiante M, Baratieri M. Experimental and modeling analysis of Air and CO<sub>2</sub> biomass gasification in a reverse lab scale downdraft gasifier. *Energy Procedia* 2019;158:1182–7.

- doi:10.1016/j.egypro.2019.01.304.
- [31] Zainal ZA, Ali R, Lean CH, Seetharamu KN. Prediction of performance of a downdraft gasifier using equilibrium modeling for different biomass materials. *Energy Convers Manag* 2001;42:1499–515. doi:10.1016/S0196-8904(00)00078-9.
- [32] Melgar A, Pérez JF, Laget H, Horillo A. Thermochemical equilibrium modelling of a gasifying process. *Energy Convers Manag* 2007;48:59–67. doi:10.1016/j.enconman.2006.05.004.
- [33] Brachi P, Chirone R, Miccio F, Miccio M, Ruoppolo G. Entrained-flow gasification of torrefied tomato peels: Combining torrefaction experiments with chemical equilibrium modeling for gasification. *Fuel* 2018;220:744–53. doi:10.1016/j.fuel.2018.02.027.
- [34] Doherty W, Reynolds A, Kennedy D. The effect of air preheating in a biomass CFB gasifier using ASPEN Plus simulation. *Biomass and Bioenergy* 2009;33:1158–67. doi:10.1016/j.biombioe.2009.05.004.
- [35] Zang G, Jia J, Shi Y, Sharma T, Ratner A. Modeling and economic analysis of waste tire gasification in fluidized and fixed bed gasifiers. *Waste Manag* 2019;89:201–11. doi:10.1016/j.wasman.2019.03.070.
- [36] Ruggiero M, Manfrida G. An equilibrium model for biomass gasification processes. *Renew Energy* 1999;16:11–1109.
- [37] Pio DT, Tarelho LAC, Pinto RG, Matos MAA, Frade JR, Yaremchenko A, et al. Low-cost catalysts for in-situ improvement of producer gas quality during direct gasification of biomass. *Energy* 2018;165:442–54. doi:10.1016/j.energy.2018.09.119.
- [38] Monteiro E, Brito P, Calado L. Gaseificação Térmica de Miscanthus. In: Presented at the 2nd Conference Bioenergia-Portugal; May 2015:1–7.
- [39] Narvaez I, Orrio A, Aznar MP, Corella J. Biomass Gasification with Air in an Atmospheric Bubbling Fluidized Bed . Effect of Six Operational Variables on the

- Quality of the produced raw gas. *Ind Eng Chem Res* 1996;35:2110–20.  
doi:10.1021/ie9507540.
- [40] Turn SQ, M.Kinoshita C, M.Ishimura D, Zhou J. The fate of inorganic constituents of biomass in fluidized bed gasification. *Fuel* 1998;77:135–46.  
doi:10.1016/S0016-2361(97)00190-7.
- [41] Subramanian P, Sampathrajan a., Venkatachalam P. Fluidized bed gasification of select granular biomaterials. *Bioresour Technol* 2011;102:1914–20.  
doi:10.1016/j.biortech.2010.08.022.
- [42] Sarker S, Bimbela F, Sánchez JL, Nielsen HK. Characterization and pilot scale fluidized bed gasification of herbaceous biomass: A case study on alfalfa pellets. *Energy Convers Manag* 2015;91:451–8. doi:10.1016/j.enconman.2014.12.034.
- [43] Skoulou V, Koufodimos G, Samaras Z, Zabaniotou a. Low temperature gasification of olive kernels in a 5-kW fluidized bed reactor for H<sub>2</sub>-rich producer gas. *Int J Hydrogen Energy* 2008;33:6515–24.  
doi:10.1016/j.ijhydene.2008.07.074.
- [44] Xue G, Kwapinska M, Horvat A, Li Z, Dooley S, Kwapinski W, et al. Gasification of miscanthus x giganteus in an air-blown bubbling fluidized bed: A preliminary study of performance and agglomeration. *Energy and Fuels* 2014;28:1121–31.  
doi:10.1021/ef4022152.
- [45] Kim YD, Yang CW, Kim BJ, Kim KS, Lee JW, Moon JH, et al. Air-blown gasification of woody biomass in a bubbling fluidized bed gasifier. *Appl Energy* 2013;112:414–20. doi:10.1016/j.apenergy.2013.03.072.
- [46] Lim MT, Alimuddin Z. Bubbling fluidized bed biomass gasification—Performance, process findings and energy analysis. *Renew Energy* 2008;33:2339–43. doi:10.1016/j.renene.2008.01.014.
- [47] Behainne JJR, Martinez JD. Performance analysis of an air-blown pilot fluidized bed gasifier for rice husk. *Energy Sustain Dev* 2014;18:75–82.  
doi:10.1016/j.esd.2013.11.008.



- [48] Campoy M, Gómez-Barea A, Vidal FB, Ollero P. Air-steam gasification of biomass in a fluidised bed: Process optimisation by enriched air. *Fuel Process Technol* 2009;90:677–85. doi:10.1016/j.fuproc.2008.12.007.
- [49] Ghani WAWAK, Moghadam RA, Salleh MAM, Alias a. B. Air gasification of agricultural waste in a fluidized bed gasifier: Hydrogen production performance. *Energies* 2009;2:258–68. doi:10.3390/en20200258.
- [50] Isik-Gulsac I, Gafarova-Aksoy P, Karatas H, Durak-Cetin Y, Sarioglan A. Biomass gasification in bubbling fluidized bed: Effect of biomass type on syngas properties. *Proceedings of the 23rd European Biomass Conference and Exhibition*, ISBN: 978-88-89407-516, Edited by ETA-Florence Renewable Energies, 01 to 04 June 2015, Vienna, Austria. Pg 828-833.
- [51] Karatas H, Olgun H, Akgun F. Experimental results of gasification of cotton stalk and hazelnut shell in a bubbling fluidized bed gasifier under air and steam atmospheres. *Fuel* 2013;112:494–501. doi:10.1016/j.fuel.2013.04.025.
- [52] Karatas H, Akgun F. Experimental results of gasification of walnut shell and pistachio shell in a bubbling fluidized bed gasifier under air and steam atmospheres. *Fuel* 2018;214:285–92. doi:10.1016/j.fuel.2017.10.061.
- [53] Mansaray KG, Ghaly a. E, Al-Taweel a. M, Hamdullahpur F, Ugursal VI. Air gasification of rice husk in a dual distributor type fluidized bed gasifier. *Biomass and Bioenergy* 1999;17:315–32. doi:10.1016/S0961-9534(99)00046-X.
- [54] Kaewluan S, Pipatmanomai S. Potential of synthesis gas production from rubber wood chip gasification in a bubbling fluidised bed gasifier. *Energy Convers Manag* 2011;52:75–84. doi:10.1016/j.enconman.2010.06.044.
- [55] Vassilev S V., Baxter D, Andersen LK, Vassileva CG. An overview of the chemical composition of biomass. *Fuel* 2010;89:913–33. doi:10.1016/j.fuel.2009.10.022.
- [56] Parikh J, Channiwala S a., Ghosal GK. A correlation for calculating HHV from proximate analysis of solid fuels. *Fuel* 2005;84:487–94.

- doi:10.1016/j.fuel.2004.10.010.
- [57] Waldheim L, Nilsson T. Heating value of gases from biomass gasification. IEA Bioenergy Agreement Task 20 – Thermal Gasification Biomass. 2001.
- [58] Basu P. Combustion and Gasification in Fluidized Beds. 2006.
- [59] Chen WH, Chen CJ, Hung CI, Shen CH, Hsu HW. A comparison of gasification phenomena among raw biomass, torrefied biomass and coal in an entrained-flow reactor. *Appl Energy* 2013;112:421–30.  
doi:10.1016/j.apenergy.2013.01.034.
- [60] Grech V. WASP (Write a Scientific Paper) using Excel – 13 : Correlation and Regression. *Early Hum Dev* 2018;122:60–3.  
doi:10.1016/j.earlhumdev.2018.04.009.
- [61] Saad JM, Williams PT. Manipulating the H<sub>2</sub>/CO ratio from dry reforming of simulated mixed waste plastics by the addition of steam. *Fuel Process Technol* 2017;156:331–8. doi:10.1016/j.fuproc.2016.09.016.
- [62] Tristantini D, Lögdberg S, Gevert B, Borg Ø, Holmen A. The effect of synthesis gas composition on the Fischer-Tropsch synthesis over Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Co-Re/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. *Fuel Process Technol* 2007;88:643–9.  
doi:10.1016/j.fuproc.2007.01.012.
- [63] Ciferno JP, Marano JJ. Benchmarking biomass gasification technologies for fuels, chemicals and hydrogen production. 2002.
- [64] Clausen LR, Elmegaard B, Houbak N. Design of novel DME/methanol synthesis plants based on gasification of biomass. 2011.
- [65] Lv P, Yuan Z, Wu C, Ma L, Chen Y, Tsubaki N. Bio-syngas production from biomass catalytic gasification. *Energy Convers Manag* 2007;48:1132–9.  
doi:10.1016/j.enconman.2006.10.014.
- [66] Ruiz J a., Juárez MC, Morales MP, Muñoz P, Mendivil M a. Biomass gasification for electricity generation: Review of current technology barriers. *Renew Sustain Energy Rev* 2013;18:174–83. doi:10.1016/j.rser.2012.10.021.

- [67] Ravaghi-Ardebili Z, Manenti F, Pirola C, Soares F, Corbetta M, Pierucci S, et al. Influence of the effective parameters on H<sub>2</sub>:CO Ratio Of Syngas At Low-Temperature Gasification. *Chem Eng Trans* 2014;37:253–8. doi:10.3303/CET1437043.
- [68] Timmer KJ. Carbon conversion during bubbling fluidized bed gasification of biomass. PhD Thesis, Iowa State University 2008.
- [69] Pio DT, Tarelho LAC, Tavares AMA, Matos MAA, Silva V. Co-gasification of refused derived fuel and biomass in a pilot-scale bubbling fluidized bed reactor. *Energy Convers Manag* 2020;206. doi:10.1016/j.enconman.2020.112476.
- [70] Pio DT, Tarelho LAC, Nunes TFV, Baptista MF, Matos MAA. Co-combustion of residual forest biomass and sludge in a pilot-scale bubbling fluidized bed. *J Clean Prod* 2019. doi:10.1016/j.jclepro.2019.119309.
- [71] Souza MB de, Couceiro L, Barreto AG, B. Quitete CP. Neural Network Based Modeling and Operational Optimization of Biomass Gasification Processes. *Gasif Pract Appl* 2012. doi:10.5772/48516.
- [72] Amaro J, Mendiburu AZ, Ávila I. Modeling of syngas composition obtained from fluidized bed gasifiers using Kuhn–Tucker multipliers. *Energy* 2018;152:371–82. doi:10.1016/j.energy.2018.03.141.

## Highlights


- Extended survey of experimental data on direct (air) biomass gasification
- New empirical modelling approach to predict gasification process parameters
- Literature data high variability is a barrier for empirical modelling
- Nonstoichiometric chemical equilibrium is not reliable to predict gasification products

Journal Pre-proof

**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:



Handwritten signatures of Daniel Louro Pereira and Yannis Tarelho.