Effect of Torrefied Wood Biomass under an Oxidizing Environment in a Downdraft Gasification Process

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The effect of composition and heating value of torrefied biomass under an oxidizing atmosphere at different conditions (180, 210, and 240 °C during 30, 75, and 120 minutes) was studied relative to downdraft gasification performance. An extended model for gasification in thermochemical equilibrium was used to evaluate the effect of pretreated biomasses, fuel-to-air equivalence ratio, and char byproduct production on the producer gas composition, reaction temperature, cold gas efficiency (CGE), and the engine fuel quality (EFQ). The model was validated with experimental data, reaching a global relative error of 8.5%. For raw or torrefied biomasses, with regard to char production, the CGE decreases if char increases; this is due to the fact that the process tends to combustion regimes when a lower amount of carbon is involved in the gasification reaction. Otherwise, the CGE and EFQ increase (up to 80% and 2.5 MJ/kg, respectively) if fuel-to-air ratio increases. With regard to the torrefied biomass, it is highlighted that CGE and EFQ increase from 77% to 82% and from 2.2 MJ/kg to 2.5 MJ/kg, respectively, when the torrefaction conditions (temperature and/or time) increase. This behavior is related to the increase of the autothermal zones in the gasification process and due to the higher heating value of torrefied biomass.

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INTRODUCTION

Biomass is a source of renewable energy that has great potential to reduce our dependence on fossil fuels, mainly due to its highly decentralized availability (Martínez *et al.* 2012; Díez and Pérez 2017). Biomass can be converted to solid, liquid, and gaseous products, which are useful to other thermochemical or industrial processes (Puig-Arnavat *et al.* 2010). Moreover, the use of biomass as energy resource has a minimum impact on the environment, which follows the goals proposed by the United Nation's Framework Convention on Climate Change (UNFCCC 2015). However, biomass as feedstock has several disadvantages, such as high moisture content, low energy content, and high transportation and storage costs (Berrueco *et al.* 2014).

Several strategies have been studied in order to upgrade biomass properties, such as torrefaction. Torrefaction can be regarded as a mild pyrolysis process (200 to 300 °C) that is conducted under an inert environment for less than 1 h (Prins *et al.* 2006; Couhert *et al.* 2009; Ramos-Carmona *et al.* 2017b). A torrefied biomass exhibits better properties than the raw material due to its lower moisture content and its lower O/C ratio caused by the thermal decomposition of hemicelluloses (Wei-Hsin Chen *et al.* 2010; Pelaez-Samaniego *et al.* 2014; Ramos-Carmona *et al.* 2017). With the pretreatment, the biomass'

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heating value increases and a lower grinding energy is required; it is also less hydroscopic. (Repellin *et al.* 2010; Ibrahim *et al.* 2013).

The use of an inert gas during torrefaction increases its operation costs. An alternative way to reduce this cost is to use air as a carrier gas for oxidative torrefaction (Lu *et al.* 2012). The effect of changing the torrefaction atmosphere on the properties of the pretreated biomass has been studied by several investigators (Rousset *et al.* 2012; Chen *et al.* 2013b; Chen *et al.* 2014; Uemura *et al.* 2015). It has been reported that torrefaction under an oxidizing environment favors oxidation reactions on the biomass surface, as well as oxidized volatile matter being released during the process (Chen *et al.* 2013b). The main constituent that is thermally degraded during the pretreatment is the cellulose, instead of the hemicelluloses, according to Rousset *et al.* (2012). Additionally, the authors stated that the change of environment is suitable for torrefaction of lignocellulosic biomass because its cell wall structure is relatively insensitive to the oxidation reactions (Lu *et al.* 2012; Chen *et al.* 2014).

Torrefied biomass is often burned in combination with other fuels, such as coal and gas. Several studies reported that the electrical efficiency decreases for co-firing torrefied biomass when the torrefaction temperature is high or the amount of biomass substitution is high. Moreover, severe torrefaction temperatures were not feasible because the power consumption saved during grinding does not compensate the heat consumed during the torrefaction (Li *et al.* 2014). On the other hand, NO_x and SO_x emissions are diminished when torrefied biomass is co-fired with coal; this is due to the lower sulfur and nitrogen levels contained in the biomass.

Gasification is a process that converts a solid feedstock into a gaseous fuel through its partial oxidation with a gasifying agent (*e.g*., air, oxygen, water vapor, and mixtures thereof) (Martínez *et al.* 2012). The resulting gasified product can be burned in turbines or internal combustion engines for power generation, or be used for the production of value-added chemicals (Pérez *et al.* 2016). The process of using a torrefied biomass as a feedstock has been studied for various gasification technologies. For entrained flow gasifiers, torrefied biomass tended to produce more syngas with higher H_2 and CO levels; therefore, due to the higher concentration of these gaseous fuels, higher producer gas (PG) heating value and gasification efficiencies were achieved (Couhert *et al.* 2009; Chen *et al.* 2011; Chen *et al.* 2013a). Also, depending on the severity of the torrefaction conditions, higher carbon conversion efficiencies have been reported (Weiland *et al.* 2014). Higher gas yield, gasification temperatures, PG heating value, and overall efficiencies were obtained in fluidized bed reactors using torrefied biomass as feedstock (Prins *et al.* 2006; Berrueco *et al.* 2014; Xue *et al.* 2014). Otherwise, lower tar yields and lower energy efficiencies have been reported for this technology if the volatiles released during torrefaction are not used (Prins *et al.* 2006; Berrueco *et al.* 2014).

For fixed bed gasifiers, several investigators have stated that torrefied biomass leads to higher syngas yields, and to higher H_2 and CO levels, higher cold gas efficiencies, and lower tar yields (Kuo *et al.* 2014; Sarkar *et al.* 2014; Tapasvi *et al.* 2015). Nevertheless, these findings were obtained under isothermal conditons (Sarkar *et al.* 2014) or under simulated conditions (Kuo *et al.* 2014; Tapasvi *et al.* 2015). For an autothermal gasification process, the reaction temperature is affected by the feedstock's heating value and the fuel-to-air ratio (Melgar *et al.* 2007).

The aim of this work was to study the effect of torrefied biomass produced under an oxidizing environment on downdraft gasification performance under autothermal conditions, *i.e*., the reaction temperature is calculated in function of the heat produced by

the gasification reaction assuring that the process will not be extinguished. The reaction temperature is not an input parameter. An extended model in thermochemical equilibrium was used to evaluate the effect of chemical composition (ultimate analysis) and heating value of biomasses subject to different torrefaction conditions, fuel-to-air equivalence ratio, and char production as a by-product of the gasification process. Char production is a measure of the fraction of initial biomass feed into the gasifier that is not converted to syngas; this results in a gasification process that is inefficient (Martínez *et al.* 2012, Lenis *et al.* 2016). The response variables analyzed were the syngas composition, reaction temperature (gasification process temperature), and other thermodynamic parameters of the gasification process, such as the generated syngas heating value and cold gas efficiencies. Additionally, the quality of the generated syngas for internal combustion engines is evaluated.

EXPERIMENTAL

Model Description

The model used in this work is an extended version of the model developed by Melgar *et al.* (2007). It models the overall gasification reaction in terms of mass and energy balances. This model is a helpful tool to predict producer gas (PG) composition and the reaction temperature of the gasification process (Table 1). Furthermore, it is possible to determine other important parameters such as lower heating value (LHV$_{pg}$), cold gas efficiency (CGE), and engine fuel quality (EFQ) from the composition of the gasification products (Melgar *et al.* 2007; Pérez *et al.* 2016). These parameters define the fuel quality of the PG for direct combustion or internal combustion engine applications. Therefore, the model is useful for studying gasification performance in terms of biomass composition, biomass moisture content, and fuel-to-air equivalence ratio (F_r) (Melgar *et al.* 2007; Pérez *et al.* 2016).

One of the hypotheses used as a basis of this work to model the downdraft gasification process states that the producer gas from downdraft reactors contains a low concentration of tars, lower than 1 mg/Nm^3 (Gagliano *et al*. 2016). This is due to the synergy between the low volatile matter content of torrefied biomass and the cracking of tars in downdraft gasification oxidation and reduction stages; consequently, the tars formation in the global equation is not meaningful (Kuo *et al*. 2014; Patra and Sheth 2015; Gagliano *et al*. 2016).

Modifications were made to the thermodynamics of the model to take into account other gasification products due to the sulfur present in biomass, as well as the resulting solid fraction after gasification (*i.e.* char). PG is modeled as an ideal gas mixture, and reactor operates at atmospheric pressure (Melgar *et al.* 2007). Therefore, a new global reaction of the modified gasification model was employed:

$$CH_mO_pN_qS_r + wH_2O + x(O_2 + 3.76N_2) \rightarrow (1-i)\cdot[aCO + bCO_2 + dCH_4]$$
$$+ cH_2 + eH_2O + fN_2 + gO_2 + lSO_2 + jH_2S + kCOS + i\cdot Char \tag{1}$$
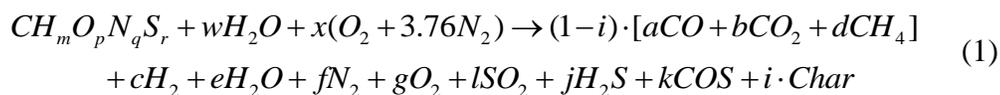
The equilibrium models are based on solving a system of algebraic linear or nonlinear equations systems. The atomic balance and auxiliary equations are required to solve the producer gas composition. Equations 5 and 6 were employed in this work as auxiliary equations to solve the nonlinear equations system. These two reactions have been

taken into account by Gagliano *et al.* (2016) and Aydin *et al.* (2017) to solve downdraft gasification models based on equilibrium assumptions. Additional gasification products, H2S and COS, are added to the model that are associated with the sulfur contained in the biomass. Álvarez-Rodríguez and Clemente-Jul (2008) reported that these are the main products resulting from the thermochemical conversion of the sulfur in lean-oxygen environments (*i.e.* gasification regimes). Since two compounds are incorporated into the model, there are two new thermodynamic equilibrium expressions needed. Martínez *et al.* (2014) used these reactions in their work about syngas generated from the volatiles released during waste tire pyrolysis (Table 1, Eqs. 7 and 8). Additionally, the resulting solid fraction after gasification -char- is modeled as pure carbon (Table 1, Eq. 9), which is a byproduct of a real gasification process (Martínez *et al.* 2011; Lenis *et al.* 2016).

Table 1. Thermodynamic Equilibrium Reactions of Biomass Gasification Related to Stoichiometric Eq. 1.

Thermochemical equilibrium model	Equation
$F_{stq,bms} = \dfrac{1\ mol_{bms} \cdot (1 + m + 16p + 14q + 32r)(kg/kmol)}{\left(1 + \frac{m}{4} + \frac{r}{2} - \frac{p}{2}\right) mol_{air} \cdot M_{air}(kg/kmol)}$	2
$F_r = \dfrac{(m_{bms}/m_{air})_{real}}{F_{stq,bms}}$	3
$x = \dfrac{1}{F_r F_{stq,bms}}$	4
$C + 2H_2 \leftrightarrow CH_4$ $\therefore K_1 = \dfrac{(P_{CH_4}/P_0)}{(P_{H_2}/P_0)} = \dfrac{dn_T}{c^2}$	5
$CO + H_2O \leftrightarrow CO_2 + H_2$ $\therefore K_2 = \dfrac{(P_{CO_2}/P_0)(P_{H_2}/P_0)}{(P_{CO}/P_0)(P_{H_2O}/P_0)} = \dfrac{bc}{ae}$	6
$CO + H_2S \leftrightarrow COS + H_2$ $\therefore K_3 = \dfrac{(P_{COS}/P_0)(P_{H_2}/P_0)}{(P_{CO}/P_0)(P_{H_2S}/P_0)} = \dfrac{kc}{aj}$	7
$COS + 2CO_2 \leftrightarrow 3CO + SO_2$ $\therefore K_4 = \dfrac{(P_{CO}/P_0)(P_{SO_2}/P_0)}{(P_{COS}/P_0)(P_{CO_2}/P_0)} = \dfrac{al}{kb}$	8
$i = \dfrac{unreacted\ carbon\ moles}{carbon\ moles\ in\ biomass} \quad \therefore\ 0 \leq i < 1$	9
$T_{k+1} = T_k + \dfrac{h_{react} - h_{prod}(T_k)}{C_{p,prod}(T_k)}$	10

Input parameters required by the model are the ultimate analysis of the biomass, along with its moisture content level. These are used to calculate the elemental formula for

the biomass ($CH_mO_pN_qS_r$), as well as the molar amount of water (Melgar *et al.* 2007). With this information, the fuel-to-air ratio under stoichiometric conditions is determined by means of Eq. 2. Thereby, from this stoichiometric parameter ($F_{stq,bms}$) and by fuel-to-air equivalence ratio (F_r, see Eq. 3), the real air molar quantity is calculated (Eq. 4). Next, the enthalpies of the reactants are estimated.

To solve the moles of each specie and the gasification process temperature (Eq. 1), an iterative process in function of the reaction temperature was conducted (Pérez *et al.* 2016). PG composition was determined by solving the nonlinear system equations using the Newton-Raphson method with an initial reaction temperature guessing. Subsequently, the reaction temperature (T_{k+1}) was calculated from the energy balance between reactants (h_{react}, biomass, moisture, and air) and gasification products (h_{prod}, PG, biochar), see Eq. 10. The calculated temperature was used in the next iterative step until the heat and mass balances were obtained. The model has been developed with Matlab$^®$ software (version R2013b, MathWorks, Natick, US). A detailed procedure for solving the model and auxiliary equations are reported by Pérez *et al.* (2016).

Although the thermo equilibrium calculations may identify the maximum yield of producer gas that can be attained at the reaction temperature, they have some limitations. The most important one is that the kinetics of reactions is assumed to be fast and is also assumed that all the species are available for reaction. Moreover, as the global equilibrium is considered, no gradient of temperature and species are taken into account in the calculation and the system is considered homogeneously mixed. Therefore, these limitations affect the model results than can be used only to predict the maximum achievable yield of a desired product (gaseous fuel) and the reaction temperature in function of process parameters such as type of gasifying agent, carbonaceous feedstock composition, and fuel-air equivalence ratio. Additionally, this gasification model does not provide a detailed description of physical and chemical mechanisms inside the gasifier. The results are considered as a general energy information that may assist the exploration of the thermodynamic operational limits of the gasification process (Patra and Sheth 2015). However, to improve the model capacities in this work, the char byproduct is an approach of the carbon conversion efficiency to consider that not all carbon in the solid fuel reacts to produce carbonaceous gases, such as CO, CO_2, and CH_4.

Model Validation

The purpose of the present study was to evaluate the gasification performance of torrefied biomass as a feedstock under autothermal conditions. Therefore, the experimental data reported by Bibens (2010) were used to validate the accuracy of the extended gasification model when operated in downdraft conditions with torrefied wood as the biofuel. Bibens (2010) evaluated the effect of torrefied pine chips on gasification performance by yields measure, efficiencies, and tar production levels during the process. The gasification facility used in his work is a two-stage downdraft fixed bed gasifier. Pine torrefaction was conducted under an inert gas environment in a batch rotary kiln at different temperature levels and at various residence times. Table 2 shows the different composition and heating values for raw and torrefied biomasses evaluated by Bibens (2010). Torrefaction conditions are coded as temperature-time sample tags (*e.g.*, 250-30 means a torrefaction temperature of 250 °C for 30 minutes of treatment). Moreover, gasification parameters such as fuel-to-air equivalence ratio and char yield are shown. These values are used as input data to validate the model.

Gasification tests carried out by Bibens (2010) were used as the basis for specifying

input parameters, such as the fuel-to-air equivalence ratio to select values and the gasification zone temperature fixed at approximately 800 °C, in order to maintain consistency. The steady-state of the process was defined when the output PG temperature reached 400 °C. The PG composition was determined by gas chromatography; biochar samples were taken at two hours interval during the gasification operation. Additional details of the gasification experimental design are given by Bibens (2010).

Table 2. Experimental Data from Bibens (2010) Used for Model Validation

Sample	Ultimate Analysis [wt. % daf[a]]				Moisture [wt. %]	LHV$_{bms}$ [kJ/kg]	F_r	Char Yield [wt. %]
	C	H	N	O				
Raw	49.14	5.59	0.16	45.11	4.43	17470	3.13	1.02
Raw	49.14	5.59	0.16	45.11	9.35	17470	3.03	0.53
250-30	54.83	5.77	1.03	38.37	1.83	20960	2.94	0.30
250-60	55.23	5.94	0.81	38.02	2.15	21410	2.94	3.69
275-30	59.39	5.53	0.21	34.87	3.33	22660	2.70	0.30
275-60	60.78	5.60	0.23	33.39	3.08	23380	2.56	0.34
300-30	68.86	5.26	0.52	25.36	2.01	26670	2.78	3.71
300-60	73.04	5.06	0.29	21.61	1.18	28350	1.69	1.10
[a]dry ash free								

Wood Analysis

Patula pine wood was selected due to its silvicultural potential in Colombia. This pine species grows fast and exhibits favorable forest characteristics such as large planted areas (3849 ha), high mean annual increment (20 m³/ha/year), and short harvest time (13 years). Properties of pine as a biofuel have been enhanced by a torrefaction pretreatment process under an oxidizing environment (*i.e*., air) in a rotary kiln (Ramos-Carmona *et al*. 2017a).

Table 3 shows how different torrefaction conditions (coded as temperature-time) affect the elemental analysis and lower heating value of the pretreated pine. Heating values of the different samples are estimated using the correlation given by Friedl *et al.* (2005) based on the ultimate analysis of biomass. Sulfur levels in Patula pine were not detected.

The torrefaction process with air as oxidizing environment increases the carbon content while decreasing the hydrogen and the oxygen content. Samples 180-30 and 180-75 have chemical compositions that are similar to raw pine. For torrefaction at 240 °C, the chemical composition of the pretreated pine is similar to a biochar obtained by carbonization due to oxidation reactions during the pretreatment (Chen *et al.* 2014). The heating value of the pretreated material increases with torrefaction severity. Similar results have been reported for torrefied biomass specimens conducted under inert and oxidizing environments (Lu *et al.* 2012; Uemura *et al.* 2013; Chen *et al.* 2014). Changes in biomass composition are related to the thermal degradation of main constituents (cellulose and hemicelluloses) during torrefaction (Chen *et al.* 2010; Rousset *et al.* 2012). The composition of the torrefied biomasses, their experimental conditions and characterization were taken from Ramos-Carmona *et al*. (2017a). The objective of this study was to analyze the effect of torrefaction temperature and residence time under an oxidizing atmosphere (air) on the physicochemical and fuel properties of Patula pine wood chips and to characterize the pretreatment process from the thermodynamic point of view.

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Table 3. Chemical Compositions and Heating Values of the Raw and the Torrefied Patula Pine*

Sample	Ultimate analysis [wt. % daf [a]]				O/C	H/C	LHV_{bms} [MJ/kg]	$F_{stq,bms}$ [kg_{bms}/kg_{air}]
	C	H	N	O				
Raw	55.70 (0.21)	7.14 (0.07)	0.19 (0.01)	36.97 (0.28)	0.664	0.128	16.85	0.180
180-30	55.15 (0.24)	7.20 (0.07)	0.15 (0.15)	37.50 (0.21)	0.680	0.131	15.94	0.194
180-75	55.40 (0.46)	6.96 (0.24)	0.00 (0.00)	37.64 (0.22)	0.679	0.126	16.30	0.192
180-120	56.45 (0.19)	6.60 (0.03)	0.48 (0.03)	36.47 (0.25)	0.646	0.117	17.12	0.184
210-30	56.91 (0.02)	6.74 (0.19)	0.44 (0.02)	35.91 (0.19)	0.631	0.118	17.25	0.181
210-75	58.15 (0.06)	6.59 (0.01)	0.22 (0.01)	35.04 (0.07)	0.603	0.113	17.76	0.176
210-120	57.68 (0.51)	6.51 (0.06)	0.00 (0.00)	35.81 (0.57)	0.621	0.113	17.19	0.185
240-30	76.03 (0.05)	3.75 (0.06)	0.35 (0.04)	19.87 (0.06)	0.261	0.049	23.90	0.133
240-75	72.58 (0.23)	2.49 (0.02)	0.02 (0.02)	24.91 (0.23)	0.343	0.034	21.08	0.159
240-120	71.17 (0.17)	2.65 (0.19)	0.08 (0.01)	26.10 (0.01)	0.367	0.037	21.16	0.158

*Values in bracket correspond to ±Standard deviations
[a]dry ash free

RESULTS AND DISCUSSION

In this section, the validation model with experimental data, and a sensitivity analysis to study how the gasification performance is affected in function of biochar production, fuel-to-air equivalence ratio, and the torrefaction conditions of pine wood is presented. The main parameters of analyzed gasification process were PG composition and LHV, gasification reaction temperature, CGE, and EFQ.

Model Validation

Figure 1 compares the observed experimental data to the predicted values by the gasification model. Predictions for PG composition, heating value, and CGE from the model were in good agreement with the measured experimental data. The model tended to slightly overestimate the CO and to underestimate the CO_2 levels, while the H_2 and CH_4 levels were underestimated; thus, the LHV_{pg} values were slightly overestimated due to the higher CO levels calculated by the model.

Model predictions did not agree with measured experimental data when the torrefaction conditions were severe (*i.e.*, 300 °C). The chemical composition of the 300 °C torrefied biomass had a higher carbon content (Table 2). Thus, it is expected that CO and CO_2 concentrations in the PG increase when the torrefaction pretreatment of the feedstock is 300 °C. Nevertheless, Bibens (2010) reported lower CO and CO_2 concentrations (15 % vol and 4.12 % vol, respectively) using the pretreated biomass when compared to the untreated raw material (23.84 % vol and 10.73 % vol, respectively). Yang *et al.* (2006) reported experimental and simulated data for air gasification of char. Their observations, however, showed higher CO concentration with respect to H_2 for all gasification conditions. These observations agreed with the results of the present model.

a) Producer gas (PG) composition   b) LHVpg and CGE
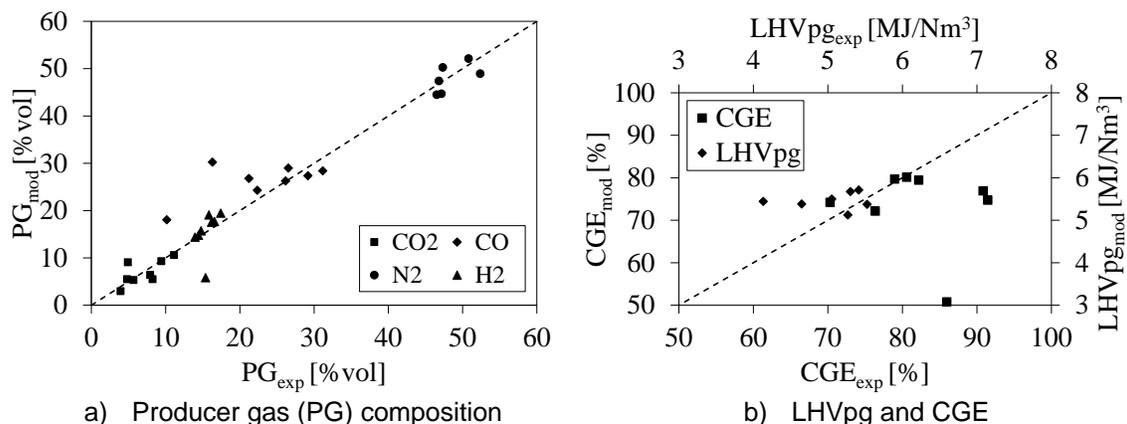
Fig. 1. Model validation using the experimental data from Bibens (2010) for torrefied wood gasification.

Table 4 shows the root mean square error (RMSE) and the relative error (RE) of the prediction values (*i.e.*, response variables) from the model for different pretreatment conditions of Table 2. Two columns of the Table 4 (named "All torrefaction conditions") show the model accuracy comparing all experimental data against the model response in function of all torrefaction conditions (Fig. 1). The average relative error of the model is 24.8%, and without CH_4, the relative error diminishes up to 16%. Otherwise, the other two

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columns of Table 4 (named "All except 300 °C data") show the errors excluding the data of torrefaction conditions at 300 °C, thereby, the average relative error is 17.6%, and without CH_4, the relative error decreases up to 8.5%. The experimental data associated with the gasification process using torrefied biomass at 300 °C increased both RMSE and RE for all predicted values. The exclusion of these extreme torrefaction conditions leads to reduce errors of predicted values by the model. Except for the CH_4, due to the lower concentration of this gaseous species (< 2.0 % vol). The accuracy of predicted values showed that the model is able to simulate gasification process with torrefied biomass. Therefore, the model can be used as a tool to study the effects of torrefaction pretreatment conditions on the gasification of wood under an oxidizing environment while producing biochar as a byproduct.

Table 4. Error Estimates for Prediction Values from Biomass Gasification Model for Table 2

Response variable	All torrefaction conditions		All except 300 °C data	
	RMSE [± units]	RE [%]	RMSE [± units]	RE [%]
CO [% vol]	6.21	27.88	2.94	9.96
CO_2 [% vol]	1.90	23.41	1.33	13.06
H_2 [% vol]	3.71	15.24	1.78	9.45
N_2 [% vol]	4.26	5.48	2.33	4.36
CH_4 [% vol]	1.84	77.95	1.28	71.78
LHVpg [MJ/Nm³]	0.67	12.29	0.41	7.12
CGE [%]	14.79	11.30	9.11	7.31
RMSE – Root mean square error				
RE – Relative error				

Effect of Biochar Production and Fuel-to-Air Equivalence Ratio

The veracity of the model was validated using experimental data obtained from biomass gasification, which had undergone torrefaction pretreatment. Therefore, the model could be used to study the effect of biochar byproduct production and fuel-to-air equivalence ratio on gasification performance from torrefied wood. Carbon conversion efficiencies can reach as high as 70 to 95%, and fuel-to-air equivalence ratios are commonly between 2 to 4 for gasification processes (Di Blasi and Branca 2013; Guizani *et al.* 2015; Pérez *et al.* 2016). The proportion of unreacted carbon, *i*, in Eqs. 1 and 9 was varied from 0 to 0.30. The ideal thermodynamic behavior of gasification process is considered when all carbon in biomass is converted to gas (*i*=0) with no char formation. The fuel-to-air equivalence ratio (F_r) was varied from 2 to 4. The results shown in Figs. 2 to 5 represent a function *z=f(x,y)* that depicts the effect of two independent variables on the dependent one. Herein, *z* is the answer calculated by the model (reaction temperature, producer gas composition, and CGE), and *x* and *y* are the input parameters to be studied in the way they affect the gasification process. The input variables analyzed are fuel-air equivalence ratio and the amount of char produced.

Figure 2 illustrates how the gasification reaction temperature is affected by char conversion and by fuel-to-air equivalence ratio for various torrefaction pretreatments of the pine. Only the results for 75 minutes of torrefaction time are shown, since the results of the other torrefaction times were similar. The reaction temperature increased by increasing char production and decreased by increasing fuel-to-air equivalence ratio. For these conditions, the actual (or real) fuel-to-air ratio of the process tended to decrease; the thermochemical gasification process tended to move to combustion regimes, which led to

an increase in the gasification reaction temperature. This behavior is associated with the model considerations, where all input air model reacts with the remaining biomass under steady state. For high fuel-to-air equivalence ratios and high char conversion (low *i*), the model showed gasification reaction temperatures around 400 to 600 °C; however, these temperatures did not approach autothermal conditions in an actual gasification facility. For lower gasification temperatures, there was not heat generated in the reaction front to favor the endothermic stages of the gasification process (*e.g.*, drying, pyrolysis, and reduction) (Melgar *et al.* 2007; Caton *et al.* 2010). Thus, a limit is needed to describe the autothermal process conditions (Caton *et al.* 2010).
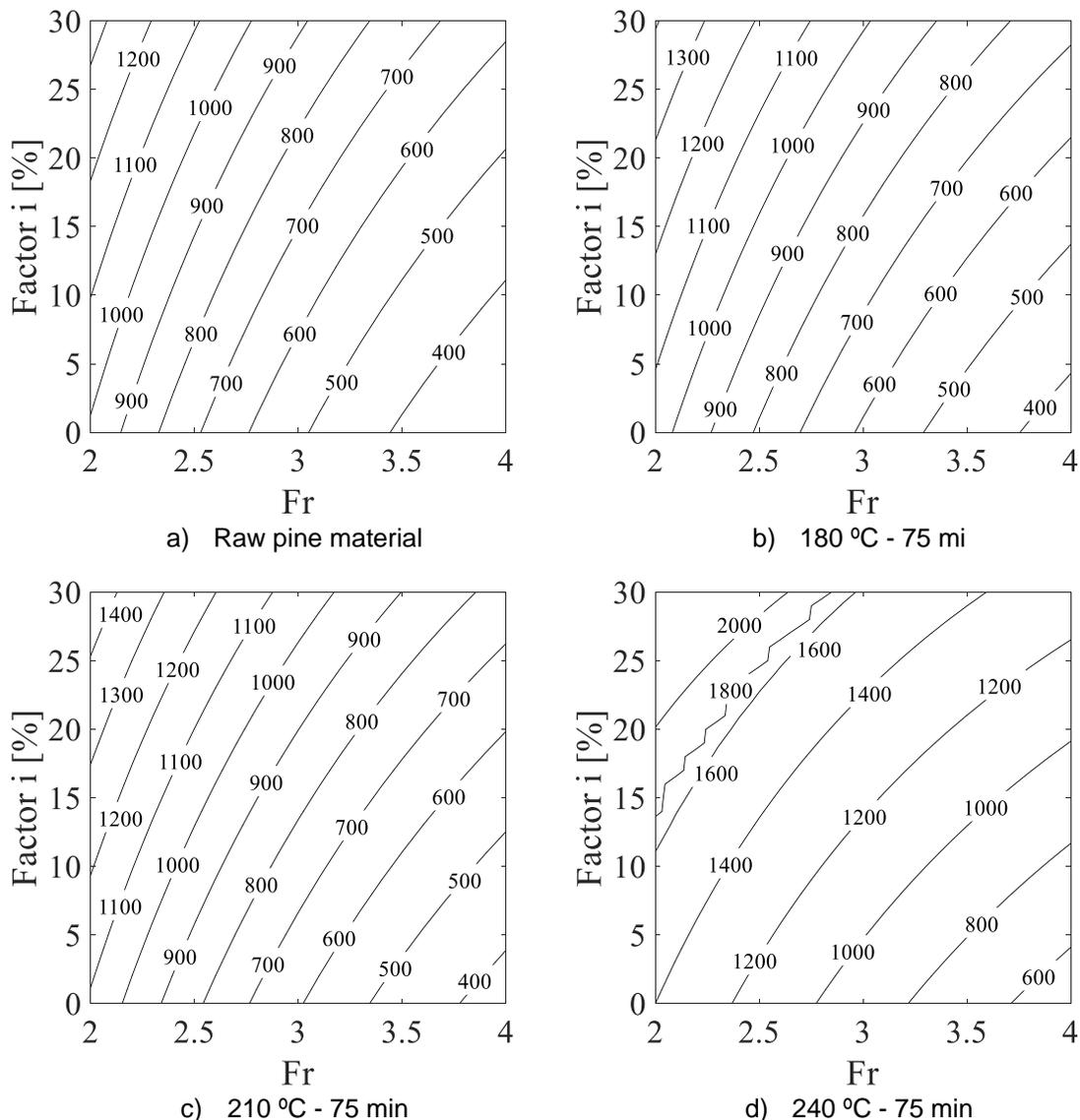
Fig. 2. The gasification reaction temperature [°C] for raw and torrefied pine as a function of biochar conversion (Factor "*i*") and F_r.

Figure 3 shows the autothermal zones for the gasification process that are calculated by the model based on char conversion and F_r values for the torrefied pine. The autothermal zone limits are defined when the reaction temperature is equal to or higher than 650 °C

(Caton *et al.* 2010). Increasing the degree of torrefaction, temperature and/or residence time caused the autothermal zone to become wider; *i.e.*, the gasification process became stable at higher F_r values and resulted in higher carbon conversion (or lower unconverted carbon). This behavior is associated with the increase in the heating value of the torrefed pine, which is caused by the thermal degradation of wood constituents (Lu *et al.* 2012). Thus, more energy is available in the gasification process, which results in a higher reaction temperature for a given fuel-to-air equivalence ratio (

Fig. 2). These limits are taken into account to analyze the other predicted responses of the model that consider the autothermal behavior (such as cold gas efficiency (CGE) and CO-to-CO_2 ratio).
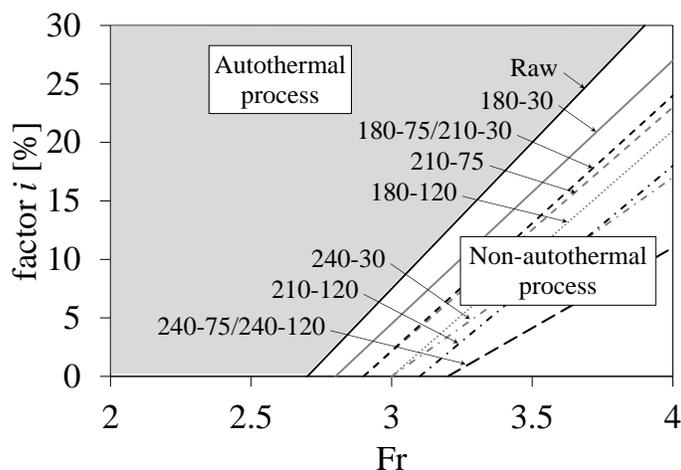
Fig. 3. Autothermal zones in the gasification process in function of torrefaction conditions of wood biomass

Figures 4 and 5 show the CGE and the CO-to-CO_2 ratio in the gasification syngas as a function of biochar production (factor "i") and fuel-to-air equivalence ratio (Fr), respectively. The results are shown under autothermal conditions of the process for different levels of pine torrefaction. CGE value provided information about the energy conversion of the biomass during the gasification process; *i.e.*, the ratio between the energy content of the PG and the energy supplied by biomass (Melgar *et al.* 2007). For raw and torrefied pine, the CGE value decreased as char production increased, and as fuel-to-air equivalence ratio decreased (Fig. 4). As stated above, the gasification process approaches to combustion regimes if *Fr* diminishes; therefore, the production of CO_2 during the gasification increases (Fig. 5). Thus, CO_2 and N_2 concentrations in the PG increased, which resulted in a reduction in the heating value of the syngas. This finding agreed with the results reported by Lenis *et al.* (2016) for an experimental fixed bed reactor that afforded higher biochar conversions and lower CGE values.

CGE values increased with F_r due to the higher fuel-rich conditions. A higher amount of carbon monoxide (CO) is produced (Fig. 5). CO is the more abundant gaseous species in the PG (25 to 40% vol); thus, the heating value of the PG increased with F_r, which resulted in higher CGE values. Figure 5 shows that the autothermal gasification zone increases with torrefaction conditions. It is possible to achieve higher efficiencies regarding the raw material if the process is conducted at higher F_r; at this gasification condition ($F_r > 3.0$; Fig. 5d) the CGE can reach values up to 80% (Fig. 4). Tapasvi *et al.* (2015) reported

similar results for torrefied biomass using an inert atmosphere with a two-stage gasification model.
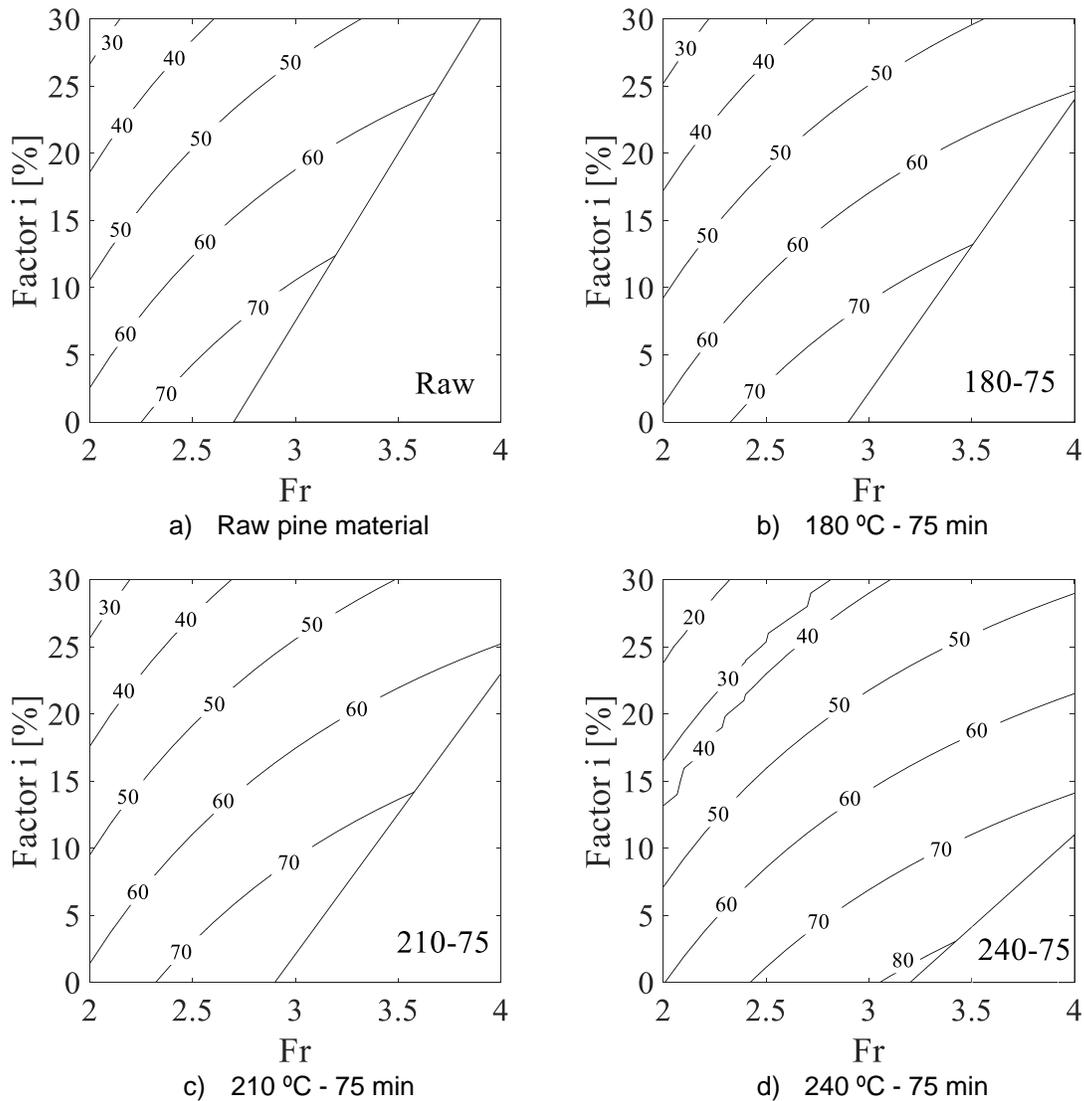
Fig. 4. CGE [%] for raw and torrefied pine as a function of biochar conversion (Factor "*i*") and F_r. Zones without z-values: non-autothermal process

As the torrefaction severity increased, the gasification process reached autothermal conditions at higher F_r, if a lower amount of biochar is produced as byproduct in the gasification process (lower factor *"i"*). Under this regime, the CGE value and gasification reaction temperature increased due to the higher heating value of the torrefied biomass (Table 3). Thus, higher gasification temperatures favored the auxiliary reactions (Eqs. 5 and 6) to produce higher concentrations of gaseous fuels, which led to higher efficiencies under stable conditions.
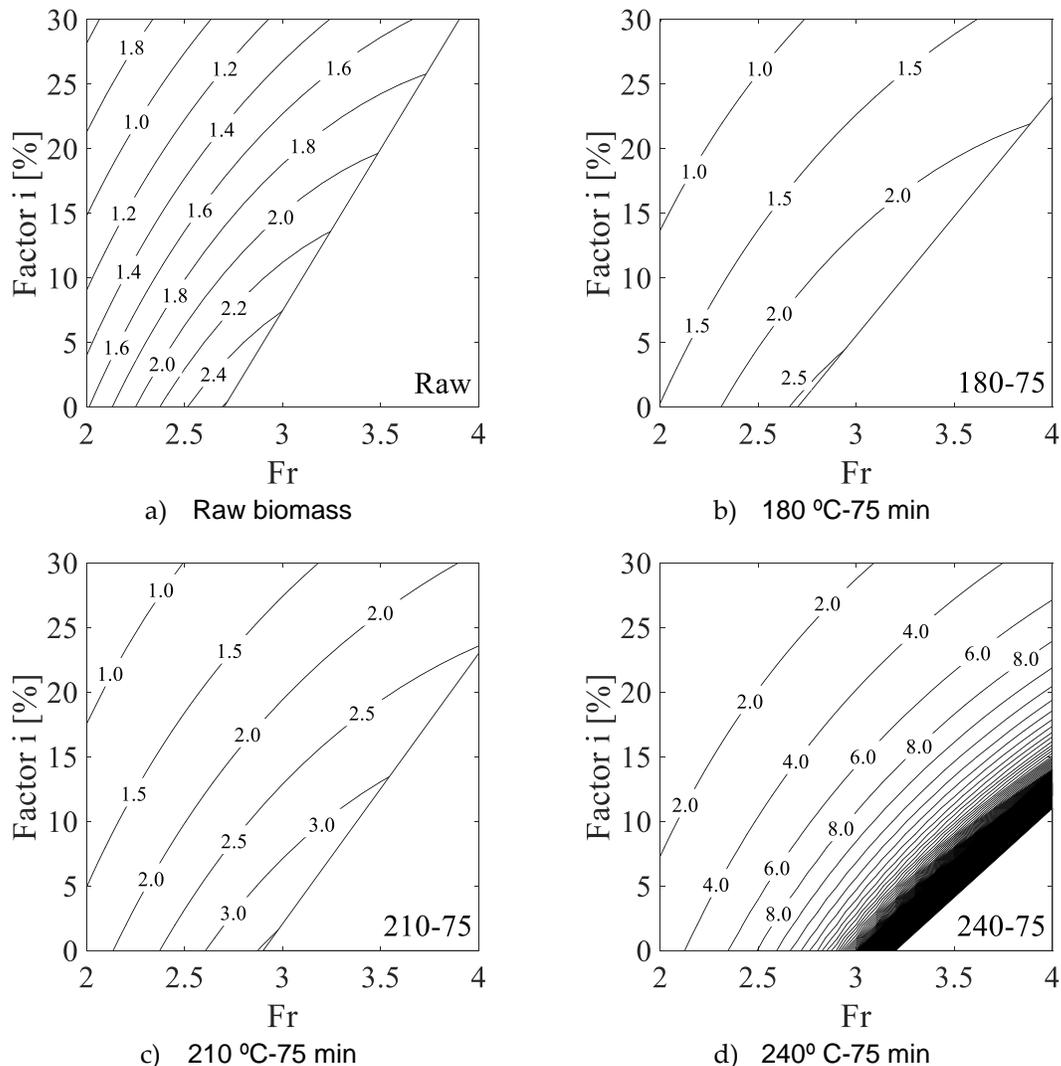
Fig. 5. CO-to-CO$_2$ ratio for the gasification of raw and torrefied pine as a function of biochar conversion (Factor "*i*") and F_r. Zones without z-values: non-autothermal process

Effect of Torrefaction under an Oxidizing Environment

The developed model was used with appropriate inputs for chemical reactions and thermodynamic data in order to evaluate the effect of the torrefaction pretreatment under an oxidizing environment on the gasification reactor performance. The moisture contents of the raw and the torrefied wood were not considered during the model simulations. All simulations were conducted with no biochar conversion of the biomass (*i.e., i* equals zero) (Prins *et al.* 2006), and with fuel-to-air equivalence ratios between 2 and 3.2 (Di Blasi and Branca 2013; Guizani *et al.* 2015; Pérez *et al.* 2016). For the torrefaction conditions, their response variables reached different autothermal zones in function of F_r, which was stated in the previous section (Fig. 3).

Reaction temperature

Figure 6 shows the reaction temperature for raw and torrefied pine as a function of F_r. For all samples, the gasification reactor temperature decreased as F_r increased, which

was due to sub-stoichiometric amount of air for complete combustion in the reactor. Thus, if less air is involved in the gasification process, the amount of energy released decreases, which results in a lower gasification reaction temperature (Melgar *et al.* 2007).
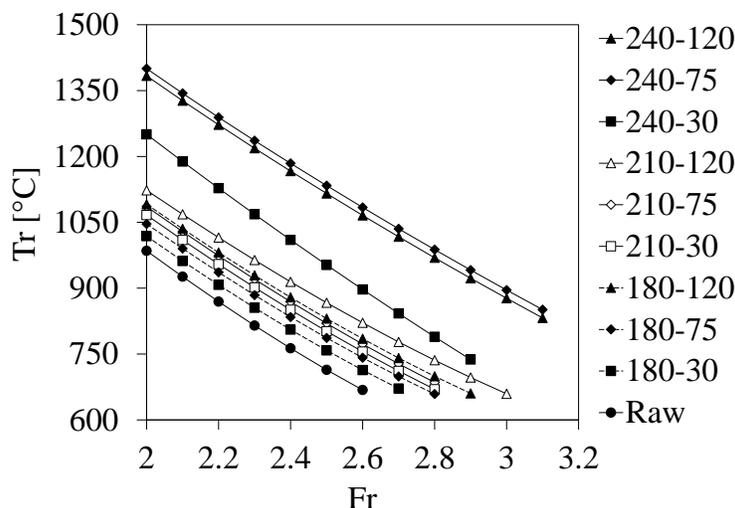
Fig. 6. Gasification reaction temperature for raw and torrefied pine

The gasification reaction temperature of the torrefied pine depended on two biomass properties, namely the heating value and fuel-to-air stoichiometric ratio. Higher torrefaction severity resulted in higher heating value; thus, the energy released during the gasification process was higher, which increased the reaction temperature. However, the torrefied biomass with the highest heating value (Sample 240-30 of Table 3) did not reach the highest reaction temperature. The highest temperature condition was reached for a gasification process using pine that is torrefied at 240 °C for 75 minutes. This was due to Sample 240-30 having a higher carbon content, a lower oxygen content and a lower fuel-to-air stoichiometric ratio than Sample 240-75 (Table 3). Therefore, Sample 240-30 required a higher amount of air to reach a given F_r in the gasification process. This led to increase the nitrogen content in the global gasification reaction (Eq. (1)). This inert gas was heated by a fraction of the energy released during the gasification, which resulted in a decrease of the gasification reaction temperature (Pérez *et al.* 2016). Prins *et al.* (2006) also reported an increase in the reaction temperature when torrefied biomass was used as feedstock in the gasification processes. Reaction temperatures for torrefied pine at 210 °C for 30 and 75 minutes were lower than the reaction temperature for torrefied pine at 180 °C for 120 minutes due to their lower fuel-to-air stoichiometric ratios (Table 3).

PG composition and heating value
Figure 7 shows the PG composition and heating value as function of the torrefaction pretreatment conditions. As mentioned before, (see "Effect of biochar production and fuel-to-air equivalence ratio"), increasing the F_r value led to higher fuel-rich conditions in the gasification process; thus, more CO, H_2, and CH_4 gases that have high heating values are generated, which resulted in an increase of the overall syngas heating value. Pérez *et al.* (2016) stated that equilibrium constants for the hydrogen reduction with char (Eq. 5) and the water-gas shift reaction (Eq. 6) increases with lower gasification reaction temperature. This favors the production of H_2 and CH_4.

a) CO dry base

b) H₂ dry base

c) CH₄ dry base

d) LHVpg

→ Raw   ▪ 180-30   ▾ 180-75   ▴ 180-120   □ 210-30
◦ 210-75   ▵ 210-120   ◆ 240-30   ◆ 240-75   ▴ 240-120
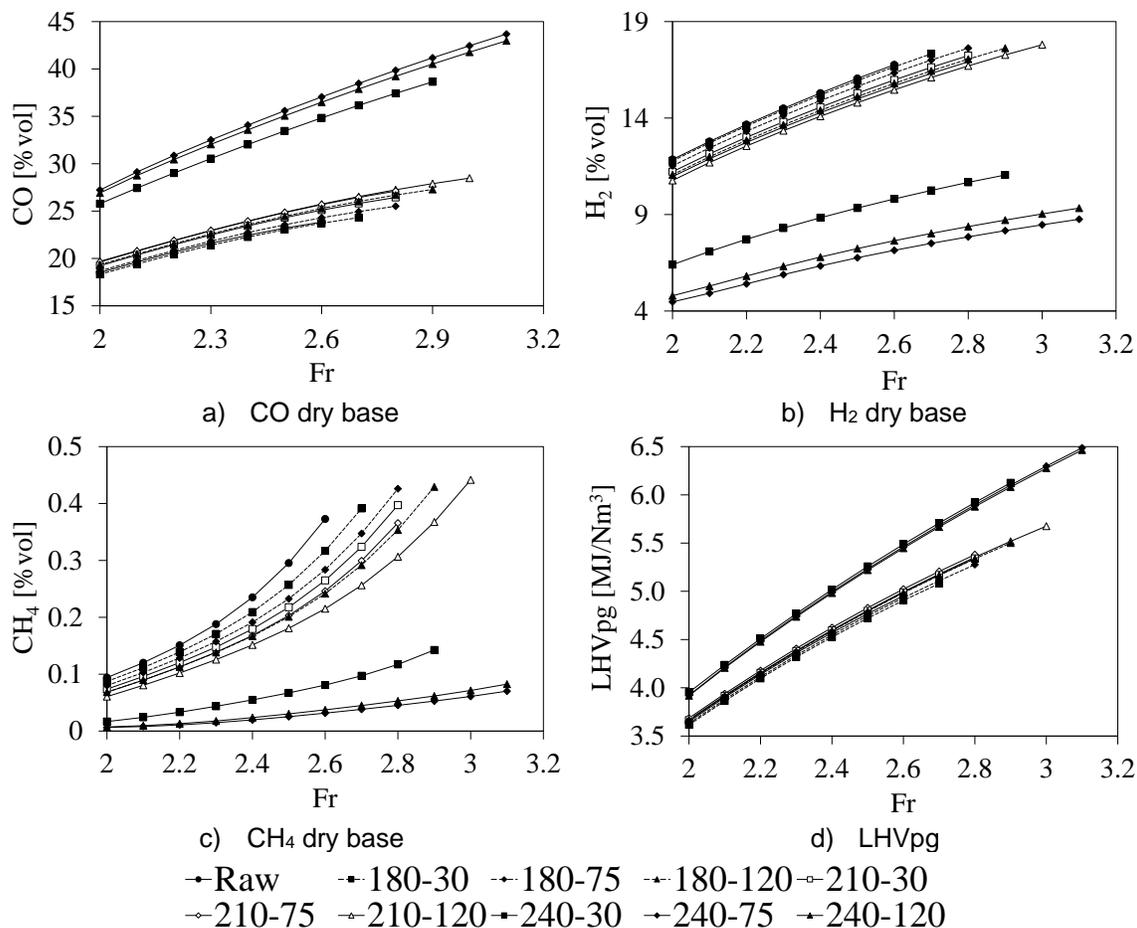
Fig. 7. PG composition and heating values from raw and torrefied pine

CO concentration tended to increase while H_2 and CH_4 decreased as the level of torrefaction severity increased, which was due to the reduction in H/C and O/C ratios of treated biomasses (Table 3). As expected, torrefied biomass at 240 °C had the highest concentration of CO in the PG. This result is related to the high carbon content of these materials. However, despite the difference in PG compositions of the different materials, the syngas heating value was similar for raw pine and pine torrefied up to 210 °C for 120 minutes (with a 2% variation regardless of the F_r). Moreover, the PG heating value from the torrefied pine at 240 °C was higher, and this heating value decreased slightly as the torrefaction residence time increased. Pretreated pine at this temperature (240 °C) exhibited a higher carbon content, which decreases with residence time due to oxidation reactions that occur during the process (Chen *et al.* 2014). Studies of gasification processes using torrefied biomass reported similar observations noted in the present work (Prins *et al.* 2006; Chen *et al.* 2011).

Cold gas efficiency and engine fuel quality

Figure 8 shows the CGE values for the raw and torrefied pine. Increasing F_r results in an increase in the CGE value for all feedstocks for the gasification process of this study. As mentioned before (see "PG composition and heating value"), syngases with high energy

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content, such as CO, CH$_4$, and H$_2$, have higher concentrations in the PG as F_r increases. This enhances the PG-heating value (Fig. 7d), resulting in increased (Fig. 8).

CGE values tended to decrease as the torrefaction severity increased for a given F_r, except for Sample 240-30. The heating value of the PG slightly increased (around 3%) for torrefied pine up to 210 °C and 120 minutes of pretreatment. However, the energy input for torrefaction was higher (around 5%) due to the energy gained from pine pretreatment. Thus, a lower CGE value is obtained for torrefied biomass used for gasification. The CGE value for torrefied pine Sample 240-30 was similar to the CGE value of the raw pine. This is because Sample 240-30 reached the maximum PG heating value regardless the F_r of the process. Its heating value was about 15.5% higher *versus* raw pine (Fig. 7d). Thus, the energy output of the PG increases, leading to a higher CGE. For achieving higher CGE values using torrefied biomass, it is necessary to shift towards more fuel-rich conditions (*i.e.* higher F_r) in the gasification process with a lower amount of solid byproduct (see "Effect of biochar production and fuel-to-air equivalence ratio"). Kuo *et al.* (2014) reported lower CGE values for torrefied biomass at high temperatures (300 °C) due to similarities in the PG heating values for the raw and torrefied materials.
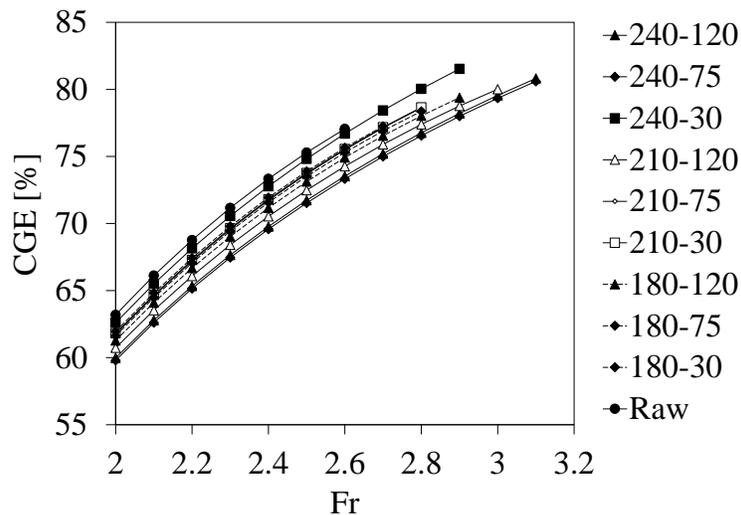
Fig. 8. CGE for the raw and torrefied pine

PG from gasification can be used for heat or power generation with internal combustion engines (Martínez *et al.* 2012). Therefore, it is necessary to evaluate PG for its suitability for these applications. The effective power (N_e) of an engine is estimated by Eq. 11 (Tinaut *et al.* 2006):

$$N_e = K_D \cdot K_o \cdot EFQ \tag{11}$$

K_D and K_0 are parameters that are related to engine design and operating conditions, respectively. The engine fuel quality (*EFQ*) is related to the heating value (LHV_{pg}) of the PG, the fuel-to-air stoichiometric ratio ($F_{stq,pg}$), and the air mole fraction in the PG-air mixture (Y_{air}) (Tinaut *et al.* 2006), see Eqs. 12 and 13.

$$EFQ = LHV_{pg} \cdot Y_{air} \cdot F_{stq,pg} \tag{12}$$

$$F_{stq,pg} = \frac{2}{4.76 \cdot (a + 4d + c)} \tag{13}$$

For a stationary engine in a power plant, K_D and K_0 are constants (Pérez *et al.* 2016); therefore, the effective power depends on PG composition and its heating value. Figure 9a shows the *EFQ* for raw and torrefied pine as function of F_r. Higher F_r in the gasification process led to higher *EFQ* values for all gasification materials; this was due to the higher concentration of gaseous fuels in the PG with higher F_r values; therefore, the PG heating value increases and favors to achieve higher *EFQ* in function of *Fr* (Eq. 12, Fig. 9a). Likewise, $F_{stq,pg}$ tended to decrease with *Fr*, because more air was needed to burn the PG under stoichiometric conditions; hence, the air fraction in the mixture also increased with F_r. Therefore, higher air fraction in the mixture and higher PG heating value resulted in an increase in the energy density of the stoichiometric mixture PG-air (*i.e.,* higher *EFQ* values) (Pérez *et al.* 2016). Pérez *et al.* (2016) obtained lower *EFQ* values for gasification for different Colombian wood species. However, the cited authors reported similar trends to the ones reported in this work (*i.e.,* increasing *EFQ* with F_r). This result showed that torrefaction of pine under an oxidizing environment is suitable to produce gaseous fuels with acceptable quality for internal combustion engine applications.
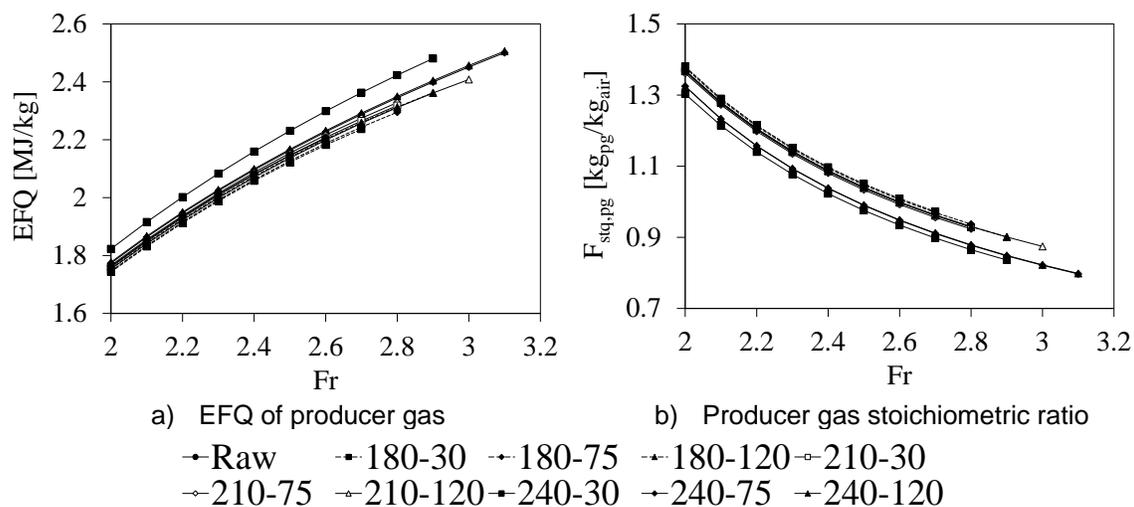
Fig. 9. EFQ and fuel-to-air stoichiometric ratio of PG from raw and torrefied pine

For a given value of F_r, the *EFQ* value was similar for raw and torrefied pine, with the exception of Sample 240-30. There was a slight increasing trend with increasing torrefaction severity (*i.e.*, lower O/C ratio). The share of PG heating value and air fraction in PG-air mixture prevailed on *EFQ*, over the reduction in the fuel gas-to-air stoichiometric ratio. The highest *EFQ* values obtained for a PG from torrefied pine sample 240-30 were due to this feedstock and its PG have the highest heating value (Table 3; Fig. 7d). The *EFQ* results also support that the torrefaction is a suitable process to upgrade biomass properties for power generation by means of gasification processes coupled to internal combustion engines.

CONCLUSIONS

1. Gasification performance of torrefied biomass under an oxidizing environment was studied by a model under a thermochemical equilibrium. The model was extended from

a previous version to take into account new products associated with sulfur species in the biomass, as well as biochar conversion as a byproduct. Furthermore, the modified model was validated using experimental data of a gasification process using a torrefied biomass. The errors in the predicted values from the model in comparison to measured experimental data were small, especially for the heating value of the producer gas and for the cold gas efficiency value. The global relative error of the model was 8.5%. Therefore, the model is a useful tool to study the gasification performance of upgraded biomass by torrefaction pretreatment.

2. The biochar conversion has a direct influence on the gasification performance since it modifies the real fuel-to-air equivalence ratio. Higher biochar production increases the availability of air to react with the biomass in the gasification process; hence, fuel-to-air ratio tends to combustion conditions reducing the concentration of gasses with energy content such as CO, H_2, and CH_4 and increasing the concentration of others such as CO_2 and H_2O in the PG. Using torrefied biomass results in higher gasification reaction temperatures for a given fuel-to-air equivalence ratio. Therefore, higher process efficiencies can be achieved using upgraded biomass as a feedstock.

3. Thermodynamic parameters of the gasification process are enhanced when using a higher fuel-to-air equivalence ratio (F_r). Higher F_r values increase the amounts of gases with high energy content (e.g. CO, H_2, and CH_4) in the producer gas; therefore, higher heating value, cold gas efficiency, and *EFQ* are obtained. Regarding torrefaction conditions for treated biomasses up to 210 ° for 120 min, the process efficiencies slightly decrease with torrefaction severity; this result is due to the fact that PG heating value does not significantly change regarding the raw material, while heating values of biomasses increase. However, the heating value of the pine material tended to increase with increasing torrefaction severity, especially for 240 °C torrefaction. This higher energy content of PG leads to improvement of the quality of the PG for internal combustion engine applications. Thus, torrefaction pretreatment of a biomass with an oxidizing environment can be used to upgrade a material to be used in gasification while improving the resulting producer gas as a fuel for internal combustion engines.

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