

Research Article

Adiabatic Gasification and Pyrolysis of Coffee Husk Using Air-Steam for Partial Oxidation

Catalina Rodriguez and Gerardo Gordillo

Conversion Energy Research Group, Mechanical Engineering Department, Universidad de los Andes, Kr 1 E No. 19A-40, Office ML 652, Bogotá, Colombia

Correspondence should be addressed to Gerardo Gordillo, g.gordillo43@uniandes.edu.co

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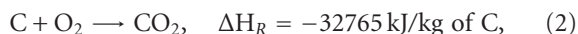
Colombian coffee industry produces about 0.6 million tons of husk (CH) per year which could serve as feedstock for thermal gasification to produce gaseous and liquid fuels. The current paper deals with: (i) CH adiabatic gasification modeling using air-steam blends for partial oxidation and (ii) experimental thermogravimetric analysis to determine the CH activation energy (E). The Chemical Equilibrium with Applications Program (CEA), developed by NASA, was used to estimate the effect of equivalence ratio (ER) and steam to fuel ratio (S:F) on equilibrium temperature and gas composition of ~ 150 species. Also, an atom balance model was developed for comparison purposes. The results showed that increased ER and (S:F) ratios produce mixtures that are rich in H_2 and CO_2 but poor in CO. The value for the activation energy was estimated to be 221 kJ/kmol.

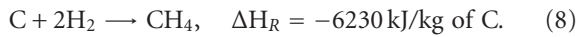
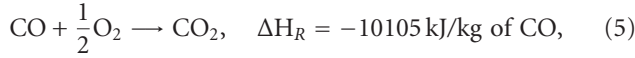
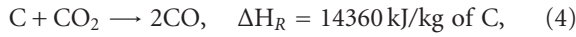
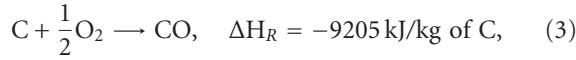
1. Introduction

Combusting fossil fuels produce green house emissions which cause a negative environmental impact. There are various fuel alternative technologies which can be developed in order to mitigate both the dependence on fossil fuels and the negative impact caused by its emissions. Biomass sources, for example, energy crops and wastes, can be used as feedstock in thermal processes such as direct combustion to produce heat, or gasification and pyrolysis to produce gaseous and liquid fuels. The coffee agriculture industry around the world produces a great amount of wastes, for example, only in Colombia about 13 million tons of coffee grain are produced per year, which result in 0.6 tons of coffee husk (see mass balances from coffee processing in Table 1) [1]. These residues can cause pollution of natural sources (land, water, and air) if treatment and storage systems are not correctly managed.

In thermochemical gasification processes biomass feedstock undergoes thermal degradation in an inert medium (pyrolysis, (1)) or partial oxidation in an oxidizing medium (gasification, (2)–(8)) to produce liquid or gaseous fuels,

respectively [2]. The oxidizing source can be air, pure oxygen, or a mixture of those with steam. Also, pure steam is used in reforming processes in which the biomass is heated to strip the H_2 from the H_2O through the reaction $C + H_2O \rightarrow CO + H_2$. Subsequently, the produced CO reacts with the remaining H_2O ($CO + H_2O \rightarrow CO_2 + H_2$) to produce more H_2 and CO_2 . The gas composition from partial oxidation of biomass depends upon the type of biomass and oxidizing source, as well as on the rate at which both biomass and oxidizer are simultaneously supplied to the gasifier. In general, gasification with air and pure oxygen produces mixtures rich in CO, whereas gasification with air-steam and pure steam produce gases high in H_2 [3]. In biomass gasification many reactions occur simultaneously; however, the global process can be modeled using reactions (1) through (8) as shown below [4]:





Reaction (1) corresponds to any biomass pyrolysis, in which the biomass is heated to volatilize the volatile matter. Subsequently, the products released in pyrolysis (C and light gases) react with the oxidizer supplied and other gases generated to produce more products (reactions (2) to (8)). Reactions with $\Delta H_R > 0$ are endothermic, and those with $\Delta H_R < 0$ are exothermic. According to Annamalai and Puri, [5], reaction (2) dominates at low temperatures (below 800°K) while reaction (3) dominates at higher temperatures. In gasification processes, the reactions (4), (6), and (7) are important due to low oxygen and high steam contents in the oxidizing source.

In 2006, Xu et al. [6] reported experimental results on the effects that gasifier temperature, fuel particle size, steam/fuel ratio, residence time, and air supplied to the gasifier have on product gas compositions from gasification coffee grounds. The study was performed in a dual fluidized bed gasifier. In 2009, Gordillo and Annamalai [3] used chemical equilibrium and atom balance modeling to estimate the effect of modified equivalence ratio and S:F ratio on the composition of gases produced from air-steam gasification of dairy biomass (DB). In 2009, Velez et al. [7] studied the effect of the steam/fuel ratio on the production of CO, H₂, and CO₂ for fluidized bed cogasification of coal with coffee husk. In 2010, Lugano et al. [8] studied the effect of gasification temperature (700, 800, and 900°C) on coffee husk gasification rate under inert nitrogen conditions and oxygen concentrations ranging between 2% and 4%. Also, using the fitting kinetics analysis method for a single heating rate (210°C·min⁻¹) in a furnace at 900°C and the coats approximation algorithm [9], and assuming a reaction model of first order, these researchers estimated the activation energy, E, and the pre-exponential factor, A, of the Arrhenius's equation.

The current paper deals with (i) CH adiabatic gasification modeling using air-steam blends for partial oxidation and (ii) pyrolysis kinetic model to determine, by thermogravimetric analysis (TGA), the CH activation energy (*E*). The Chemical Equilibrium with Applications program (CEA), developed by NASA, was used to estimate the effect of both the equivalence ratio (ER) and steam to fuel ratio (S:F) on adiabatic temperature and gas composition of an unlimited number of species (~150), whereas atom

TABLE 1: Mass balance of products obtained from coffee grain pre-treatment.

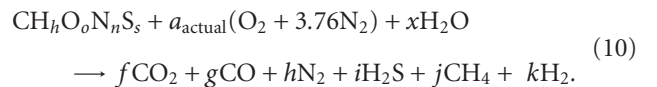
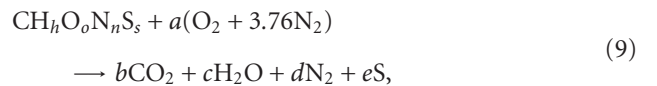
Part	Percentage %
Red Coffee grain	100%
Pulp	43.6%
Mucilage	14.9%
Water	17.1%
Husk	4.2%
Coffee (drink)	5.8%
Coffee waste	10.4%
Other	4.0%

balance was developed to estimate gas composition of a reduced number of species (CH₄, CO₂, CO, N₂, and H₂) and for comparison purposes. Thermogravimetric analysis (TGA) was carried out using N₂ as carrier gas and under different heating rates (β : 5, 10, 20, and 40°C/min), while the isoconversional method (i.e., free model) was used to estimated the activation energy (*E*).

2. Adiabatic Gasification Modeling

The gas composition of the mixtures produced by gasification of biomass can be predicted using chemical equilibrium for a larger number of species or atom balance on components for a reduced number of species (CO₂, CO, CH₄, H₂, and N₂). In general, biomass gasification using air-steam mixtures as oxidizing source produces gas mixtures (dry basis) composed mostly by CO₂, CO, CH₄, H₂, N₂, and other species in trace amounts [3].

2.1. Atom Balance Model. Combustion processes can be classified as complete (stoichiometric), when the reactants undergo complete oxidation, or incomplete, when the reactants do not oxidize totally. Equation (9) shows the stoichiometric reaction of any biomass with air as oxidizing source, while (10) presents the incomplete reaction of any biomass with air-steam as oxidizing source. In this last equation, only the most important products are shown



The equivalence ratio (ER) is a parameter which establishes the ratio between the stoichiometric oxygen and the actual oxygen supplied to the combustor. In the case of gasification with air-steam, the steam to fuel ratio (S:F) is also an important parameter since it determines the amount of steam supplied to the gasifier per fuel unit. Because both ER and S:F establish the ratio between the rate of biomass and oxidizer supplied simultaneously to the gasifier, they

have a strong effect on the quality of gases produced. They can be defined as follows:

$$\text{ER} = \frac{\text{Stoichiometric air moles}}{\text{actual air moles}} = \frac{a}{a_{\text{actual}}}, \quad (11)$$

$$\text{S : F} = \frac{\text{Steam moles}}{\text{Fuel moles}} = x. \quad (12)$$

Adiabatic gasification implies equal reactant and product energy. Therefore, the total enthalpy of the reactants (HR), at inlet temperature (T_{in}), equals the total enthalpy of the products (HP), at outlet temperature (T_{out}) (13)

$$\sum_{j=1}^m N_j h_{T(T_{\text{in}})} = \sum_{i=1}^n N_i h_{T(T_{\text{out}})}, \quad (13)$$

where N_j and $h_{T(T_{\text{in}})}$ are the moles and total enthalpies of the reactants j , at temperature (T_{in}), and N_i and $h_{T(T_{\text{out}})}$ are the moles and total enthalpies of the product i , at T_{out} . Using (11) through (13), along with atom balance on components (C, H, O, N, and S), the values of the (8) coefficients (a_{actual} , x , f , g , h , i , j , and k) in (10) can be estimated, as a function of the ER, S : F, and T_{out} . The HHV or energy density of the gases produced can be calculated using (14)

$$\text{HHV}_{\text{gases}} = \sum_{i=1}^n (X_i * \text{HHV}_i), \quad (14)$$

where X_i and HHV_i are mole fraction and gross heating value (kJ per SATP m^3) on a dry basis of each fuel gas produced, respectively, $i = \text{CO}$, CH_4 , H_2 , and so forth, and $\text{HHV}_{\text{gases}}$ is the energy density or HHV (kJ per standard ambient temperature and pressure (SATP) m^3) of the product gases.

Although the energy density or HHV of the products gives information on the amount of energy per unit of gas produced, it does not provide information on the fraction of energy recuperated as fuel gases per each fuel unit gasified. The fraction of energy recuperated in air-steam gasification processes can be estimated using (15)

$$\text{ECE}_{\text{gases}} = \frac{\text{HHV}_{\text{Gases}}}{N_{\text{Fuel}} * \text{HHV}_{\text{Fuel}} + N_{\text{steam}} * 18 * (\tau + 4.18(373 - 298))}, \quad (15)$$

where, N_{Fuel} and N_{steam} correspond to the moles of fuel and steam supplied, respectively, to the gasifier by each normal m^3 of dry product gases, τ is the latent heat of steam, HHV_{Fuel} is the gross heat value (kJ/kmol of DAF fuel) of the fuel, and $\text{ECE}_{\text{Gases}}$ is the energy conversion efficiency (ECE) or energy recovery.

2.2. Chemical Equilibrium Model. The Chemical Equilibrium with Applications program (CEA), developed by NASA, was used under adiabatic conditions to solve for about 150 species (including pure carbon) and adiabatic temperature. The CEA uses chemical equilibrium to estimate the species which are produced from a certain chemical

TABLE 2: Conditions used in atom and equilibrium modeling.

Parameter	Coffee husk (CH)
Fuel	Coffee husk (CH)
Pressure (bar)	1
Air temperature ($^{\circ}\text{K}$)	273
Vapor temperature ($^{\circ}\text{K}$)	373
Equivalence ratio (ER)	1–6
steam-fuel ratio (S : F)	0.3–0.8

reaction. If the reaction is adiabatic, the program requires as input data the reaction pressure and the composition and enthalpy of the reactants. In case of a nonadiabatic reaction, the input data required are the reactant composition and the temperature and pressure of the reaction. Atom and equilibrium models were developed under the conditions shown in Table 2.

3. Pyrolysis Kinetic Model Based on Thermogravimetric Analysis

Model-free and model-fitting have been applied to estimate the kinetics parameters based on thermogravimetric analysis data. In this section a kinetic model based on the isoconversional method (model-free) proposed by Ozawa [10] is presented. This method requires carrying out a series of experiments at different heating rates and assumes basically that the reaction of any solid as shown in (16) is independent of temperature [11]. The reaction rate of solids is usually based on a single step reaction which can be expressed as

$$\frac{d\alpha}{dt} = A e^{-E/RT} f(\alpha), \quad (16)$$

where α is the extent of conversion, t is time, A the pre-exponential factor of the Arrhenius's equation, E the activation energy, and $f(\alpha)$ a particular function, called the reaction model, which describes the dependence of the reaction rate on the degree of conversion α . The isoconversional method assumes that A , $f(\alpha)$, and α are independent of temperature and that A and E are independent of α . Under no isothermal conditions, (16) can be expressed as follows:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} f(\alpha), \quad (17)$$

where $\beta = dT/dt$ is the heating rate and T is the temperature. Integrating (17) and taking natural logarithm gives

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T e^{-E/RT} dT = \frac{AE}{\beta R} f\left(\frac{E}{RT}\right), \quad (18)$$

$$\ln g(\alpha) = \ln\left(\frac{AE}{R}\right) - \ln \beta + \ln f\left(\frac{E}{RT}\right). \quad (19)$$

TABLE 3: Ultimate (DAF basis) and proximate analysis of coffee husk biomass.

	Coffee husk
C%	46.51
H%	6.77
O%	46.20
N%	0.43
S%	0.09
Ash%	0.68
Moisture%	7.22
FC%	15.5
VM%	76.6
HHV (kJ/kg)	17 945
HHV _{DAF} (kJ/kg)	18 068
Empirical formula	$\text{CH}_{1.746}\text{O}_{0.75}\text{N}_{0.008}\text{S}_{0.0007}$

TABLE 4: Conditions used in thermogravimetric analysis.

Parameter	
Atmosphere	Inert (N_2)
Heating rate ($^{\circ}\text{C}/\text{min}$)	5, 10, 20 y 40
Final temperature ($^{\circ}\text{C}$)	950
Particle size	Lesser than $425\ \mu\text{m}$
Repetitions	2 for each heating rate
Sample amount	Lesser than 25 mg

Using Doyle's approximation algorithm [12], Equation (19) can be expressed as

$$\ln g(\alpha) = \ln\left(\frac{AE}{R}\right) - \ln \beta - 5.331 - 1.052 \frac{E}{RT}, \quad (20)$$

$$\ln \beta = \ln\left(\frac{AE}{Rg(\alpha)}\right) - 5.331 - 1.052 \frac{E}{RT}. \quad (21)$$

Since A , E , and β are assumed independent of T , the activation energy, E , can be estimated from the slope of the linear curves which result of plotting $\ln \beta$ versus $1/T$ for a constant extent of conversion (α) and the corresponding temperatures of the different heating rates (β) [13].

4. Materials and Methods

Coffee husk samples were obtained from Colombian coffee industry and were characterized by ultimate and proximate analysis including heating value. Table 3 shows the results from those analyses (DAF basis). The empirical formula was derived using chemical composition and atom balance on compounds. The samples analyzed by thermogravimetric analysis were crushed in order to reduce the particle size to $\leq 425\ \mu\text{m}$.

The thermogravimetric analysis was carried out using a NETZSCH STA 409 PC Luxx calorimeter and the software NETZSCH Proteus for MS Windows and under the conditions listed in Table 4.

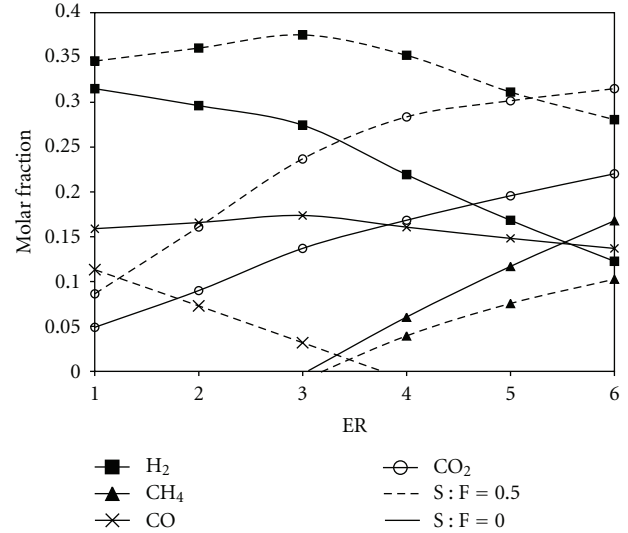


FIGURE 1: Effect of the ER on the Production of H_2 , CH_4 , CO , and CO_2 for $\text{S:F} = 0$, $\text{S:F} = 0.5$, and $T = 873\ \text{K}$, estimated by Atom balance model.

5. Results and Discussion

5.1. Atom Balance Model. This section discusses the effect of the operating parameters (ER and S:F), estimated by atom balance, on the production of CO , CO_2 , CH_4 , and H_2 . Others species such as N_2 (present in large amounts) and H_2S (and many others present in trace amounts) are not shown.

Figure 1 shows the effect of ER and S:F on the H_2 , CH_4 , CO , and CO_2 production for a product temperature of $873\ \text{K}$. At constant ER, increasing S:F implies more steam moles in the oxidizer source per each mol of air entering the gasifier; hence, the gasification process occurs in an ambient rich in H_2O , which favors the production of H_2 and CO_2 via the following reactions: $\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$ and $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$. More C and H atoms producing CO_2 and H_2 mean less C and H atoms available to produce CH_4 and CO , which leads to decreased CO and CH_4 production. From Figure 1, it is apparent that gasification with only air ($\text{S:F} = 0$) produces more CO and CH_4 and less H_2 than gasification with air-steam ($\text{S:F} = 0.5$).

5.2. Equilibrium Model. The effects of ER and S:F on adiabatic temperature and gas composition, estimated by equilibrium model, is presented in this section. Although, about 150 species were analyzed, only results on the more relevant species (H_2 , CO , CH_4 , and CO_2) are presented here. With exception of N_2 , other species were in trace amounts. The effect of the ER on adiabatic temperature (T_{ad}) is illustrated in Figure 2 for various S:F ratios. At constant S:F ratio, increase in ER results in decrease in the oxygen entering the gasifier; therefore, there are less O atoms available for the oxidation of C via the reactions (2) and (3) which are exothermic. Consequently, less heat is released, which leads to lower adiabatic temperatures. Furthermore, the results show that decreased S:F ratios increase the adiabatic

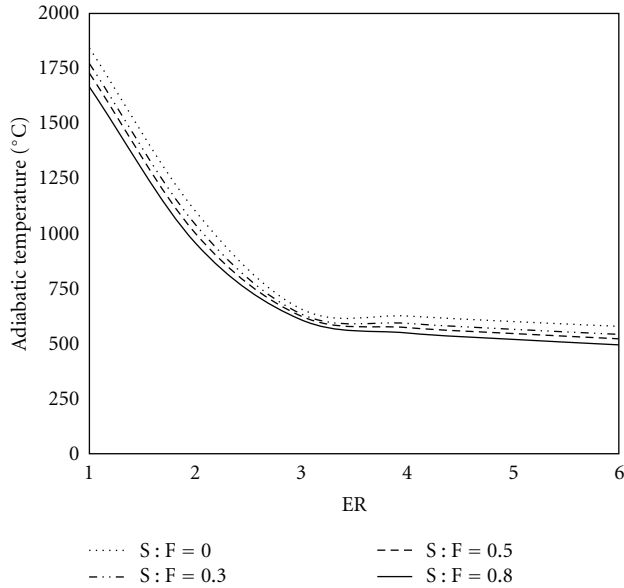


FIGURE 2: Adiabatic temperature estimated with equilibrium model for various S:F ratios, adopted from [14].

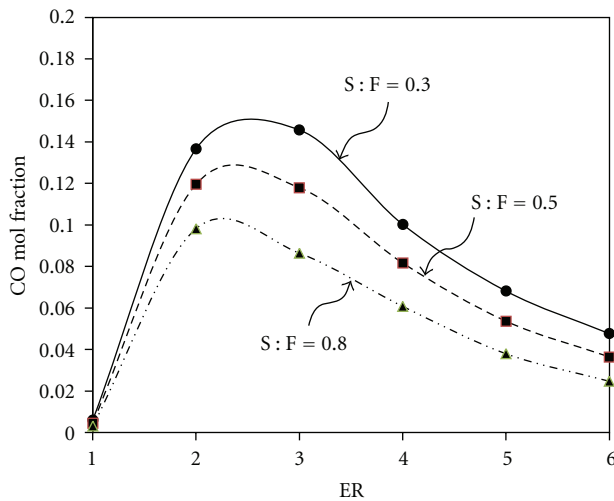


FIGURE 3: Effect of ER on CO production for various S:F, estimated with chemical equilibrium.

temperature. In general, the maximum temperatures were attained for gasification with only air (S:F = 0) while the minimum temperatures were obtained at S:F = 0.8. At ER > 3.5 the effect of the ER on T_{ad} is negligible. This suggests that gasification of CH at ER > 3.5 tends to be pure pyrolysis.

Figures 3, 4, 5, 6 show the effect of ER, on CO, CO₂, H₂, and CH₄ for various S:F. At constant S:F, higher ERs imply less oxygen entering the gasifier for the reaction $C + (1/2) O_2 \rightarrow CO$; thus, there are more C atoms available to react with the steam to produce H₂ via the reaction $C + H_2O \rightarrow CO + H_2$. The CO produced by the reactions of C with steam and C with oxygen reacts with the remaining steam to produce more H₂ and CO₂ (shift reaction). More C

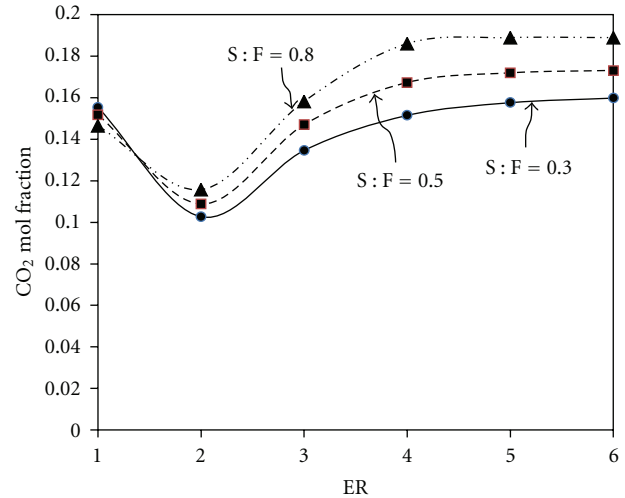


FIGURE 4: Effect of ER on CO₂ production for various S:F, estimated with chemical equilibrium.

atoms consumed by the shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) imply less C atoms leaving as CO.

The CO and H₂ curves show a peak with the ER (Figures 3 and 5). The CO mole fraction increases with increased ER until ER ≈ 2.5 beyond which it starts to decrease. The lowest value of CO is reached at ER = 1 (stoichiometric reaction) while the maximum ($\sim 16\%$) is attained at ER ≈ 2.5 and S:F = 0.30 (Figure 3). The concentration of H₂ also shows an inflection point at ER = 3.2. At ER < 3.2, increased ER increases very strongly the concentration of H₂ but at ER > 3.2, the effect of the ER on the fraction of H₂ is rather weak (Figure 5). Although, the effect of S:F on the H₂ concentration is insignificant the results suggest that the steam-to-air ratio entering the gasifier affects the H₂/CO ratio leaving the gasifier. At constant S:F, increasing the ER (decreased oxygen supplied through air) increases steam-to-air ratios. From these results, it is evident that higher S:F ratios increase the H₂/CO ratio. At ER < 2, the CO₂ decreases with increased ER and S:F ratios whereas at ER > 2.0 increasing both ER and S:F produces mixtures rich in CO₂. This is because of the higher steam concentration in the reactor, which favors the reaction of CO with steam (shift reaction) to produce more H₂ and CO₂. As shown in Figure 6, more available H atoms in the gasifier lead to CH₄-rich concentrations. From Figure 6, it is evident that at ER < 3.3, the effect of the S:F ratio on the concentration of CH₄ is practically negligible and that the production of CH₄ is only possible at ER $\gtrsim 2.0$. In general, these results show that at ER < 2.0 (increased oxygen through air), the concentration of CO and H₂ increases and that the concentration of CO₂ and adiabatic temperature decrease with increased ER (Figure 3 through 6), indicating that the heterogeneous $C + H_2O \rightarrow CO + H_2$ reaction (which is endothermic, $\Delta H_R = 10,390 \text{ kJ kg}^{-1}$ of C) is more important than the homogeneous $CO + H_2O \rightarrow H_2 + CO_2$ reaction, which is a slightly exothermic ($\Delta H_R = -1470 \text{ kJ kg}^{-1}$ of CO). At $2.0 < ER < 3.0$ (less O₂ supply), the shift reaction begins to

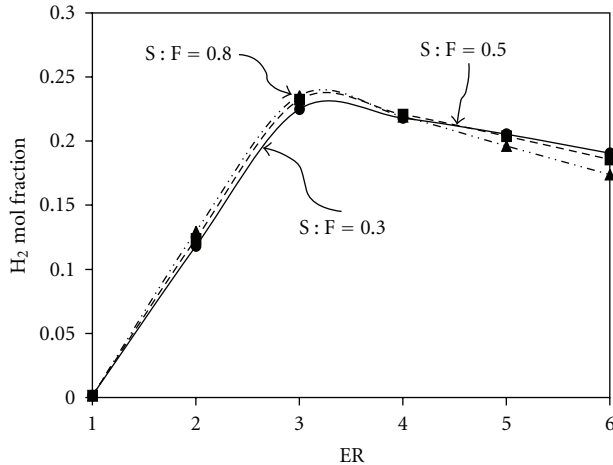


FIGURE 5: Effect of ER on H₂ production for various S:F, estimated with chemical equilibrium.

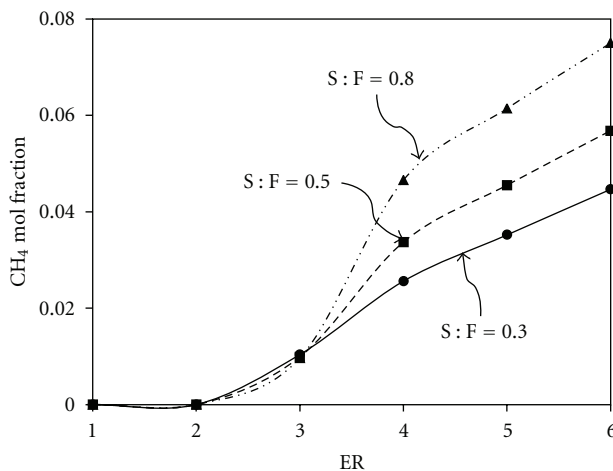


FIGURE 6: Effect of ER on CH₄ production for various S:F, estimated with chemical equilibrium.

be important because the H₂O concentration in the reactants is much higher. Hence, CO production starts to decrease whereas the production of H₂ increases.

The molar fraction of carbon estimated with equilibrium model is presented in Figure 7 as a function of ER and various S:F. It is evident that the production of carbon (C) is possible only at ER > 3. This suggests that at those ER the oxygen supplied is not enough to burn completely the carbon atoms through the reactions (2) and (3). On the other hand, at constant S:F and ER > 3, increasing ER increases carbon production, because of the less oxygen supplied for each kg of fuel gasified. Also, the results show that at constant ER, increased S:F ratios produce lower carbon indicating that the more H₂O in the reactant react with char. In general, the results on C production indicate that at ER > 3 the pyrolysis tend to be important.

The results from chemical equilibrium modeling and atom modeling are compared in Table 5 showing that the

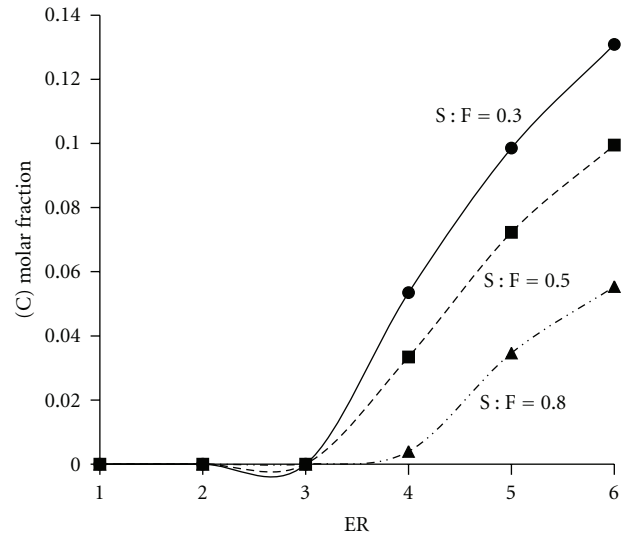


FIGURE 7: Effect of ER on Char (C) production for various S:F, estimated with chemical equilibrium.

gas composition (except CH₄ and CO), predicted with atom-balance and equilibrium model are almost similar. The difference in CH₄ and CO is due to the fact that the equilibrium model includes a larger number of species (~150) compared to atom balance that includes the production of only 6 species (CO, CO₂, CH₄, H₂, N₂, and H₂S). The lower amount of species estimated with atom balance is due to the lower number of available equations. Also, due to the low number of species, atom balance supposes that all the fixed carbon (FC) contained in CH and all H atoms contained in both CH and oxidizer reacts completely, through the reactions (2), (3), (4), (6), and (8), to produce the secondary products (CO, CH₄, CO₂, and H₂) shown in the global reaction (10). Thus, there is no presence of C and H₂O in the products. However, equilibrium model includes in the products pure carbon (Figure 7) and H₂O.

5.3. HHV of Gases. Table 6 presents the energy density of the gases at $2 < ER < 6$ and $0.3 < S:F < 0.8$. At $ER \leq 3.0$, increasing S:F decreases the HHV. In contrast, at $ER > 3$, the HHV of gaseous fuel increases with increased S:F ratios. As discussed earlier, increased S:F decreases the production of CO (Figure 3); thus, the HHV tend to decrease. Although, at $ER > 3$, increasing S:F decrease CO, the gas HHV increases due to more production of CH₄ (Figure 6) which has a higher HHV (~38000 kJ/SATP) as compared to that of the CO (~11000 kJ/SATP m³). In general, at constant S:F, increasing the ER tends to increase the HHV. The HHV for the selected operating conditions varied from 2643 to 5037 kJ/SATP m³. The highest HHV (5037 kJ/SATP m³) was achieved for a ER = 6 and S:F = 0.80, whereas the lowest HHV (2643 kJ/SATP m³) was attained at ER = 2 and S:F = 0.8. From Table 6, it is evident that the effect of ER ratio on gas HHV is stronger than that of the S:F.

Table 7 presents the energy conversion efficiency (ECE) estimated with equilibrium model for the range of operating

TABLE 5: Comparison of results on gas composition (mole fraction on a dry basis) obtained by atom and equilibrium model, adopted from [14].

	S:F = 0			S:F = 0.5		
	Chemical equilibrium	Atom balance	Difference (%)	Chemical equilibrium	Atom balance	Difference (%)
Temp. (°K)	873	873	0.06	873	873	0.02
ER	3.74	3.73	0.27	3.22	3.23	0.16
CH ₄	0.045	0.044	2.76	0.0017	0.002	15.96
CO	0.163	0.164	0.85	0.024	0.022	5.60
CO ₂	0.162	0.161	0.65	0.252	0.253	0.39
H ₂	0.232	0.234	0.88	0.377	0.377	0.08

TABLE 6: HHV of gases (kJ/SATP m³).

S:F	ER				
	2	3	4	5	6
0.30	2956	4687	4632	4413	4396
0.50	2823	4431	4742	4649	4642
0.80	2643	4095	4948	4957	5037

TABLE 7: Energy conversion efficiency (ECE) estimated with equilibrium model.

S:F	ER				
	2	3	4	5	6
0.30	0.61	0.81	0.71	0.65	0.60
0.50	0.56	0.75	0.72	0.66	0.62
0.80	0.49	0.67	0.72	0.68	0.56

parameters studied ($2 < ER < 6$ and $0.3 < S:F < 0.8$). Even though at $ER > 3$ the energy density of the gases increases with increased ER, ECE decreases with increased ER. This is because under those operating conditions ($ER > 3$) there is more production of carbon and the gasification tends to be near pyrolysis that produces lesser amount of combustible gases and more combustible loss through char. On the other hand, at $ER < 3$, increased ER tends to increase the ECE. For the range of the operating conditions studied, ECE ranged from 0.56 to 0.81; the remaining fraction corresponds to the energy returned in char and sensible heat of gases leaving the gasifier.

The results on gas composition and ECE show that the highest productions of H₂ (23%) and CO (~15%) and the highest ECE (81%) are achieved at $ER = 3$ and $S:F = 0.3$, which suggests that those are the best operating conditions.

5.4. Kinetics Model. This section presents results obtained from the kinetic analysis. Figure 8 illustrates the thermogravimetric analysis (TGA) of the coffee husk pyrolysis for four different heating rates (5, 10, 20, and 30°C/min). Also, in Figure 8, the different conversion degrees (α : 20, 30, 40, and 50%) used to estimate the activation energy (E) are pointed out.

The mass released between 300°K and 400°K corresponds to the moisture content (~7.5%) in CH. On the other hand, the results from Figure 8 indicate that most of the

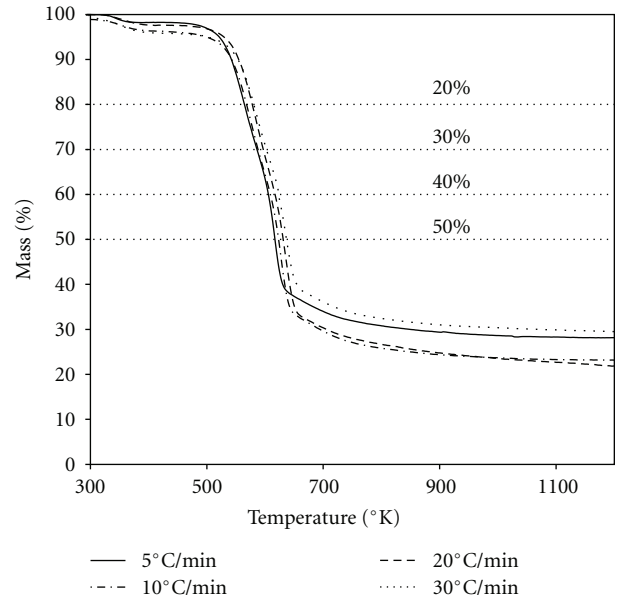


FIGURE 8: Thermogravimetric analysis of the coffee husk pyrolysis at different heating rates, adapted from [14].

volatile matter (VM) content in CH is volatilized between ~500 K and 700 K (higher slope of the curves). After ~700 K, the mass tends to remain constant, indicating that most of this mass corresponds to char (fixed carbon and ash contents in HC biomass). In general, the results from TGA show that the volatilization of VM is very important at $500 \text{ K} < T < 700$. Conversely, at $T > 700 \text{ K}$ the rate of VM released is negligible, which indicates that the CH pyrolysis process occurs at temperatures ranging between 500 and 700 K.

Figure 9 shows the plots of $-\ln \beta$ versus $10^{-3} T$ for conversion degrees (α) of 20, 30, 40, and 50% and the corresponding heating rates (β) of 5, 10, 20, and 40°C·min⁻¹. The activation energy was estimated from the slopes of linear curves which match the experimental results.

Table 8 illustrates the slopes and the activation energies of the thermal decomposition kinetics of CH for different conversion degrees. Also, the arithmetic average of all conversion degree studied and the standard deviation are presented.

The average activation energy discussed here for the CH pyrolysis (211 kJ/kmol) is higher than those presented by

TABLE 8: Slope, correlation coefficient, and activation energy obtained from 9 for various conversion degrees, adapted from [14].

Conversion (%)	Slope	R^2	E (kJ/mol)	E_{average} (kJ/mol)	Std. Dev. (kJ/mol)
20	33.99	0.82	273.15		
30	30.64	0.71	245.09	221	46.87
40	24.84	0.70	196.71		
50	21.58	0.81	169.02		

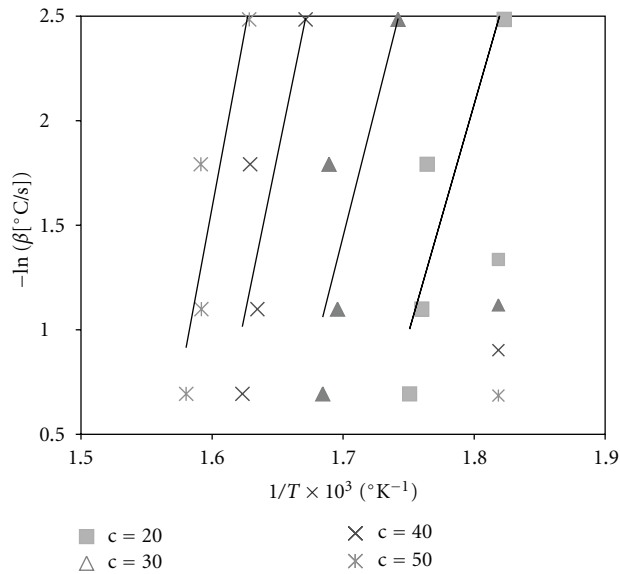


FIGURE 9: Curves to determine the activation energy of CH, based on the kinetic model proposed by [13], for various conversion degrees, adapted from [14].

Lugano et al. [8] for CH (161 kJ/kmol) and Sanchez et al. [15] for combustion of biowastes (143 kJ/kmol), but it is a little lower than that presented by Garcia-Pérez et al. [16] for sugarcane bagasse pyrolysis (235 kJ/kmol). The difference between the value of the activation energy presented here and that presented by Lugano et al. [8] is due to the use of different methods to estimate E . In this study, the isoconversional (free) method was used for different heating rates (5, 10, 20, and 30°C/min), while Lugano et al. [8] used the fitting method for a single heating rate (210°C/min). Also, the fitting method, for a single heating rate, requires assuming previously a particular function ($f(\alpha)$), which depends on the reaction's mechanism, in order to estimate the activation energy, whereas the isoconversional method (i.e., free-model) does not require assuming previously any particular function to estimate the activation energy.

6. Conclusions

The results suggest that gasification of CH with air-steam could produce gaseous combustibles with H_2 concentrations from 0 to ~25%, CO from 0 to ~16%, and CH_4 from 0 to ~7%.

Equilibrium temperature decreases with increased ER until $ER = 3.5$. At $ER \gtrsim 3.5$, the effect of ER on

equilibrium temperature is negligible, indicating that under these operating conditions the process tends to be near pyrolysis.

Increased ER increases both the production of CO until $ER \cong 2.5$ after which it starts to decrease and the production of H_2 until $ER \cong 3.2$ after which it tends to be constant, indicating that at $ER > 3.2$ the effect of the ER on the fraction of H_2 is rather weak.

In general, increasing S:F ratio tends to produce richer mixtures in CO_2 and CH_4 but poorer in CO. On the other hand, the effect of the S:F on the H_2 production is negligible.

The activation energy of the CH pyrolysis (211 kJ/kmol) is higher than those presented by [8, 15] for CH and combustion of biowastes, respectively, but it is a little lower than that presented by [16] for sugarcane bagasse pyrolysis (235 kJ/kmol). The difference between the activation energy presented here and that presented by [8] is due to the use of different methods to estimate it. According to [11], the kinetics parameters of the Arrhenius's equation, estimated using the fitting method, are different to those estimated using the free method.

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