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THERMOCHEMICAL EQUILIBRIUM MODELING FOR AIR GASIFICATION OF WASTE TIRES

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Abstract. *The disposal of waste tires is currently a challenge once its biological and chemical resistance to degradation results in a negative impact on the environment. In order to solve the environmental problems and to produce energy, waste tires can be disposed by thermochemical processes. Gasification is one of the thermochemical routes and so it is a method to obtain a syngas with a significant calorific value and a potential resource for electrical energy production. A suitable mathematical model can identify the behavior and the sensitivity of the performance of a gasifier to the variation of different operating conditions and design parameters, in other words, the effects of many parameters are speculated with few or no experimental data, and furthermore, the model can optimize an existing system with extrapolation of those conditions and parameters to achieve even better results. In this study, four thermochemical equilibrium models, reported in the literature, based on the equilibrium constant, for predicting the composition of syngas and process temperature in a downdraft gasifier were developed for waste tire, as feedstock. A comparative analysis of each model and its results is carried out. Accordingly, the effects of equivalence ratio (ER) and gasification temperature on syngas composition and low heating value (LHV) are investigated. The equivalence ratio varies from 0.35 to 0.45. An increase in the process temperature resulted in higher values for nitrogen and carbon dioxide, however, lower values for carbon monoxide and hydrogen were observed. Regarding the calorific value, lower ER values and lower temperatures resulted in higher LHV values. As expected, lower ER values resulted in lower* CO_2 *and higher* CH_4 *concentrations.*

Keywords: *waste tire, gasification, equilibrium modeling*

1. INTRODUCTION

Concerns regarding economic, geopolitical and environmental dimensions motivate the sustainable use of energy resources, the reduction of environmental pollution and the development of new technologies for obtaining renewable fuels.

Among the solid waste produced, waste tires play a prominent role in the discussion of health and environmental impacts, as their disposal is hampered due to biological and chemical resistance. Worldwide, it was estimated that around 2.9 billion units of tires would be produced by 2017 and 1 billion units would be discarded. Estimations of waste tires annually generation in Brazil vary between 17 and 20 million units, of which 6 million are related only to the state of São Paulo. At least 100 million units are accumulated in inadequate warehouses (WORLD TIRES, 2014).

Tires have a mixed conformation, formed by carbon black, elastomers compounds, steel and other different organic and inorganic constituents, but the main component of the tires is a cross-linked polymer, and therefore it is neither fusible nor soluble and consequently cannot be remodeled in other forms without severe degradation (ABDUL-RAOUF, 2010).

Generally, waste tires disposal occurs through incineration, the fastest and easiest discarding procedure. However, waste tires incineration produces a large number of emissions, including a broad set of hydrocarbons, and halogen-chlorinated compounds (chlorinated methanes, dioxins, and polychlorinated biphenyls - PCBs). Disposal of waste tires in landfills is environmentally harmful since they tend to return to the surface and break layer covers, damaging the land settlement in the long term and its rehabilitation (RECICLANIP, 2015). Currently, it is estimated that at least one car tire is discarded per person every year in developed countries, and also, approximately 4 billion waste tires are placed in landfills (FRIGO *et al.*, 2014).

In Brazil, the most common destination is the use of waste tires as an alternative fuel for the production of cement. The second most common is the granulation and spraying of rubber for rubber products or asphalt. The third most common is the lamination for later use in the manufacture of shoe soles and interior pipelines.

Waste tires have higher heating value, higher volatile content and lower ash content than coal and biomass, therefore, thermal treatment is a reasonable application for them. Among different thermochemical conversion techniques, the gasification process is used to obtain a gaseous product from solid feedstock and offers higher efficiencies compared to combustion and pyrolysis. This conversion process is considerably more complex than combustion and it is influenced by a number of factors, including the amount of oxidant, feedstock composition, gasifier temperature, reactor geometry and mode of gas-solid contact. The gaseous product is called producer gas or synthesis gas (*syngas)*. The producer gas can be used to generate electrical energy by using a fuel cell, gas turbine or gas engine. In addition to them, *char*, the solid product is also generated during the gasification of waste tires and it can be used as a carbon source in industrial processes (KARATAS *et al.,* 2013). Fixed bed gasification is the most common technology for the energy use of biomass and solid municipal wastes.

The modeling of gasification provides a better comprehension of physical and chemical mechanisms inside the gasifier constituting pyrolysis, combustion, reduction, and drying in the mathematical form. The whole process is represented as a system of equations that can provide valuable quantitative information about the process. Therefore, many researchers have been using the equilibrium model for the analysis of the gasification process.

The thermochemical equilibrium model is a tool to calculate the maximum yield that can be attained for the desired product in a reacting system. It is practically impossible to attain a chemical or thermodynamic equilibrium within the gasifier. However, this model provides the designer with a reasonable prediction of the maximum achievable yield of the desired product. The model calculations are independent of gasifier design and hence helpful for studying the influence of fuel and process parameters only (BASU, 2010).

There are two approaches to the equilibrium modeling. It can be determined by either the equilibrium constants (stoichiometric modeling) and minimization of the Gibbs free energy (non-stoichiometric modeling).

There are several published articles on stoichiometric equilibrium modeling for the gasification process, however not so many for the waste tires as feedstock in a downdraft gasifier. Therefore, in this work, a selection of four models previously published in the literature (ZAINAL *et al.,* 2001; BABU and SHETH, 2005; JARUNGTHAMMACHOTE and DUTTA, 2007**;** MENDIBURU *et al.,* 2014) is used to predict the performance of the gasification of waste tires.

2. MATHEMATICAL MODELING FOR GASIFICATION SYSTEMS

According to Basu (2006), mathematical modeling for gasification systems is an important tool for the design of systems of different sizes, but also to optimize an existing system with the extrapolation of conditions and parameters and so, achieve better results. A suitable model can identify the behavior and sensitivity of the performance of a gasifier due to the variation of different operating conditions and design parameters, therefore, the effects of many parameters are speculated with few or no experimental data.

The set of chemical reactions, the fluid dynamics and the heat and mass transfer phenomena involved in the process make the gasification modeling complex. Therefore, the modeling of the reaction system becomes an essential aspect for the understanding of gasification processes. According to Li (2002), biomass gasification models are divided into the kinetic model and the equilibrium model. Kinetic models approach the mechanisms, reaction rates and concentration of species produced at any point in time and space of a system. Equilibrium models predict the maximum attainable conversion and distribution of each species produced subjected to thermodynamic and mass transfer constraints. Equilibrium models do not require details of the geometry of the system nor do they predict the time required for equilibrium to be achieved and therefore are used to represent fixed bed and fluid bed gasifiers. Lower computational demand due to the need for small amount of data is an advantage of the use of equilibrium models, however, this approach becomes applicable only under conditions of chemical equilibrium, as the name itself suggests, that is, it presents a range of operation restricted On the other hand, the use of kinetic models to represent gasification processes requires an expressive number of empirical parameters that are specific to each reaction system. The parameters depend on experimental measurements that require time and resources, as well as a greater computational demand for numerical resolution due to its complex mathematical formulation (RODRIGUES, 2008).

The elaboration of a complete and detailed model that incorporates all areas of the gasifier for process description is a highly complex activity. Equilibrium models use the chemical and physical equilibrium relationships of the system for the prediction of the composition of the final product, they are simpler models and easy to apply for diverse cases, which is proven with the wide application in cases in the literature. Kinetic models are more rigorous phenomenological models that allow extending to the time and space of the modeled system. The kinetic approach is not so often found in the literature, but it has been developed quite a bit in recent decades culminating in applications with computational fluid dynamics (CFD) tools. Thus, kinetic models of the concurrent gasifier are still poorly practicable when compared to equilibrium models (RODRIGUES, 2008).

2.1 Equilibrium modeling for waste tires gasification

An equilibrium model is a type of mathematical model used to predict the behavior of the process in the gasifier. Generally, the model comprises sets of linear and non-linear species conservation equations and equations for the thermal equilibrium of the reactions that are also included in the model, which can be solved by using the method of Newton- Raphson or a mathematical software, for that work it was used routines in Matlab. There are not many studies about the numerical modeling of waste tires gasification (PIATKOWSKI and STEINFELD, 2011; KUZNETSOV *et al.*, 2012; JANAJREH *et al.*, 2013).

There are two approaches to equilibrium models: stoichiometric and non-stoichiometric. The stoichiometric approach is based on a well-defined mechanism, initial chemical compositions and determination of the equilibrium constants of a set of reactions, using Gibbs free energy data. The non-stoichiometric approach involves the minimization of Gibbs free energy subject to mass balance and non-negative constraints of the compositions (MENDIBURU *et al.*, 2014).

According to Cousins (1978), there is a considerable number of possible reactions to the gases formed in the gasifier reaction zone (CO, CO_2, CH_4, H_2, H_2O, and N_2), however, the heterogeneous reactions: Boudouard, Shift, and formation of methane are a good summarized representation of the process. Cousins (1978) also determined the compositions of CO, CO_2, CH_4, CO_2, H_2, and N_2 as a function of the reaction temperature in the gasification. Following the same stoichiometric methodology of chemical equilibrium presented by Cousins (1978), Zainal *et al.* (2001), considering only the interaction of the methane formation reaction and the homogeneous gas-water reaction or Shift reaction (a combination of the heterogeneous gas-water and Boudouard reactions), were able to predict the *syngas* composition generated by different biomass in a concurring flow gasifier, depending on their humidity and the reaction temperature.

In order to simulate the performance of a concurring gasifier, Babu and Chaurasia (2004) used the approach of Zainal *et al.* (2001) to study the effects of the gasifying agent injected in the system and the moisture content of the biomass on the *syngas* composition, reaction temperature, and calorific values. Babu and Sheth (2005) used the same methodology to study the effects of air enrichment with oxygen, air stream heating and the fraction of water vapor in the air on the same output variables.

Jarungthammachote and Dutta (2007) developed a stoichiometric model for predicting the *syngas* composition produced from domestic waste in a concurring gasifier in Thailand. The effects of the moisture content of the residue on the gasifier performance were studied and the model was validated and adjusted by means of several experimental literature data. They found that the reaction temperature, the calorific value and the efficiency decrease with increasing humidity. The results also showed that with increasing humidity, the molar amounts of CO_2, H_2 and CH_4 increase gradually, while those of CO and N_2 decrease.

The modeling of waste tire gasification process will be based only on equilibrium models with a stoichiometric approach and on equilibrium constants of the reactions. Therefore, the models for biomass gasification proposed by Zainal *et al*. (2001), Babu and Sheth (2005), Jarungthammachote and Dutta (2007) and Mendiburu *et al.* (2014) are used for waste tires, as feedstock.

2.2 Considerations upon modeling gasification processes

According to Rodrigues (2008), the equilibrium modeling with stoichiometric approach adopts the following considerations:

1. Dry biomass composed of only five elements: carbon, hydrogen, oxygen, nitrogen, and sulfur (CHONS system);
2. Non-dimensional and stationary system (0-D model);
3. The system formed by a single control volume so that variations of internal physical properties (temperature, pressure, and concentration) and the presence of intermediate chemical reactions are neglected;
4. Reagent residence time is assumed to be high enough to achieve chemical equilibrium;
5. All reactions are in chemical equilibrium, therefore, it is considered that the pyrolysis products are consumed and reach equilibrium in the reduction zone before they leave the gasifier.
6. The final gaseous product of gasification consists of only 8 chemical compounds: H_2O, O_2, N_2, CO, CO_2, CH_4, H_2, and SO_2;
7. All oxygen is consumed and all biomass carbon is gassed in the process, and thus the formation of residual carbon can be neglected;
8. Ashes are not involved in any chemical reaction or as a catalyst, therefore, it is considered an inert material, in the same way, the nitrogen present in the biomass and in the air;
9. All the biomass sulfur (S) is converted directly to sulfur dioxide (SO2);
10. The system behaves as an ideal gas.

After all considerations, the four models chosen for this paper set up Eq. 1, water-gas shift reaction, and Eq. 2, methane reaction, as the reactions considered in the process to calculate the equilibrium constants, which are a function of temperature.

$C + 2H_2 \rightarrow CH_4$ (Methane reaction formation) (1)

$CO + H_2O \rightarrow CO_2 + H_2$ (Shift reaction) (2)

3. METHODOLOGY: THE MODELS

3.1 Waste tires as feedstock in the gasification process

The mains species on the *syngas* are carbon monoxide (CO), hydrogen (H_2), methane (CH_4), carbon dioxide (CO_2), water vapor (H_2O), nitrogen (N_2). The composition of the waste tire used in this work is 73.8%, 6.8%, 9%, 0.3%, 1.3% for C, H, O, N and S respectively, and the percentage of ash (A) in the material given is 8.8% (JANAJREH *et al.*, 2013). The typical chemical formula of the material, based on a single carbon atom, can be expressed as $CH_{1,1057}O_{0,0915}N_{0,0035}S_{0,0066}$.

3.2 Model 1: Zainal *et al.* (2001)

Zainal *et al.* (2001) proposed an equilibrium model for a downdraft gasifier, for different types of biomass, assuming that all reactions are in thermodynamic equilibrium and the product of the pyrolysis burns and reaches equilibrium in the reduction zone before exiting the gasifier. It is also assumed that the system is adiabatic, thus, there is no loss of heat to the external environment. This model is able to predict the gas concentrations depending on the humidity and the reaction temperature.

The proportions of nitrogen and sulfur on the scrap tire composition are considerably small. Thus, in the model proposed by Zainal et al. (2001), the chemical formula of the material must be expressed only in terms of CHO, in this case $CH_{1,1057}O_{0,0915}$.

The overall gasification reaction is given by Eq. (3):

$$CH_{1,1057}O_{0,0915} + wH_2O + mO_2 + 3{,}76mN_2 \rightarrow x_1H_2 + x_2CO + x_3CO_2 + x_4H_2O + x_5CH_4 + 3{,}76mN_2 \quad (3)$$

As x_1, x_2, x_3, x_4, x_5 being the coefficients of the product compositions and m the amount of oxygen required per kmol of the waste tire. From the moisture content (MC%), the amount of water per kmol of the waste tire, given by w, can be calculated:

$$w = \frac{(MW_{tire})MC}{[(MW_{H_2O}(1 - MC)]} \quad (4)$$

Six equations are required to solve the six unknowns (x_1, x_2, x_3, x_4, x_5) of the system. The system of six linear and nonlinear equations formed by three equations obtained with the application of the conservation law for each element of the global gasification reaction (CHO), along with two equations from the equilibrium constant of methane formation and equilibrium constant of the Shift reaction and a last equation obtained with the energy balance, was used to solve the unknowns.

- Carbon balance

$1 - x_2 - x_3 - x_5 = 0$ (5)

- Hydrogen balance

$1{,}1057 + 2w - 2x_1 - 2x_4 - 4x_5 = 0$ (6)

- Oxygen balance

$0{,}0915 + w + 2m - x_2 - 2x_3 - x_4 = 0$ (7)

- Equilibrium constant of methane formation

$K_1(x_1^2) - x_5 = 0$ (8)

- Equilibrium constant of the Shift reaction

$$K_2(x_2x_4) = x_1x_3 \quad (9)$$

- Energy balance equation

$$\begin{aligned} H^o_{ftire} + w\left(H^o_{fH_2O_{(l)}} + H_{(vap)}\right) + mH^o_{fO_2} + 3{,}76mH^o_{fN_2} \\ = x_1H^o_{fH_2} + x_2H^o_{fCO} + x_3H^o_{fCO_2} + x_4H^o_{fH_2O_{(g)}} + x_5H^o_{fCH_4} \\ + (T_2 - T_1)(x_1Cp_{H_2} + x_2Cp_{CO} + x_3Cp_{CO_2} + x_4Cp_{H_2O} + x_5Cp_{CH_4} + 3{,}76mCp_{N_2}) \end{aligned} \quad (10)$$

In the system energy balance on Eq. (10), T_2 and T_1 refer to the gasification temperature in the reduction zone and room temperature, respectively.

Eq. (10) can be simplified as:

$$dH_{pneu} + wdH_{H_2O(l)} = x_1dH_{H_2} + x_2dH_{CO} + x_3dH_{CO_2} + x_4dH_{H_2O(g)} + x_5dH_{CH_4} + 3{,}76mdH_{N_2} \quad (11)$$

The waste tire enthalpy of formation is given by:

$$H^o_{f\,tire} = HHV + H^o_{f\,CO_2} + \frac{1{,}1057}{2}H^o_{f\,H_2O_{(l)}} \quad (12)$$

The high heat value (HHV) is calculated by the mass percentages of the tire components applied in the following Eq. (11) (CHANNIWALA and PARIKH, 2002):

$$HHV = 0{,}3491C + 1{,}1783H + 0{,}1005S - 0{,}10340 - 0{,}0151N - 0{,}0211A \quad (13)$$

The specific heat (Cp) depends on the temperature of the substance and it can be calculated using the following Eq. (14):

$$Cp = R(A + BT_{am} + \frac{C}{3}(4T_{am}^2 - T_1T_2) + \frac{D}{T_1T_2}) \quad (14)$$

R is the universal gas constant, 8.314 kJ/kmol.K. A, B, C and D are the coefficients of the specific heat equation expressed in Table 1. T_{am} is the mean value of T_1 and T_2.

Table 1 Coefficients for Cp calculation of various chemical compounds (Robert, 1984)

Compound	**Formula**	**T_{max}**	**A**	**10^3B**	**10^6C**	**10^{-5}D**
Methane	CH_4	1500	1,702	9,081	-2,164	
Hydrogen	H_2	3000	3,249	0,422		0,083
Carbon monoxide	CO	2500	3,376	0,557		-0,031
Carbon dioxide	CO_2	2000	5,457	1,047		-1,157
Nitrogen	N_2	2000	3,28	0,593		0,04
Water	H_2O	2000	3,47	1,45		0,121
Carbon	C	2000	1,771	0,771		-0,867

The equilibrium constant K is only a function of temperature and it is given by the following formula (Robert, 1984):

$$\ln K = -\frac{\Delta G^o}{RT} \quad (15)$$

Using the standard Gibbs function and some mathematical manipulations, as shown in Zainal et al. (2001), the equilibrium constants, K_1 and K_2, are functions of the gasification temperature, and they can be calculated using the general equations:

$$\ln K_1 = \frac{7082{,}848}{T} + (-6{,}567)\ln T + \frac{7{,}466.10^{-3}}{2}T + \frac{-2{,}164.10^{-6}}{6}T^2 + \frac{0{,}701.10^{-5}}{2T^2} + 32{,}541 \quad (16)$$

$$\ln K_2 = \frac{5870{,}53}{T} + 1{,}86\ln T + -2{,}7.10^{-4}T + \frac{-58200}{T^2} - 18{,}007 \quad (17)$$

Making m, x_4, and x_5 as a function of x_1 x_2 x_3 and rearranging the energy balance equation:

$$x_4 = w + 0{,}55285 - x_1 - 2x_5 \tag{18}$$

$$x_5 = 1 - x_2 - x_3 \tag{19}$$

Substituting Eq. (19) into Eq. (18):

$$x_4 = -x_1 + 2x_2 + 2x_3 + w - 1{,}44715 \tag{20}$$

From the oxygen balance in Eq. (7), and using equation (20):

$$m = \frac{1}{2}(-x_1 + 3x_2 + 4x_3 - 1{,}53865) \tag{21}$$

Simplifying Eq. (10), using Eq. (19), Eq. (20) and Eq. (21):

$$Ax_1 + Bx_2 + Cx_3 + Dw + E = 0 \tag{22}$$

For:

$$A = dH_{H_2} - dH_{H_2O(g)} - 1{,}88dH_{N_2}$$

$$B = dH_{CO} + 2dH_{H_2O(g)} - dH_{CH_4} + 5{,}64dH_{N_2}$$

$$C = dH_{CO_2} + 2dH_{H_2O(g)} - dH_{CH_4} + 7{,}52dH_{N_2}$$

$$D = dH_{H_2O(g)} - dH_{H_2O(l)}$$

$$E = -1{,}44715dH_{H_2O(g)} - 2{,}892662dH_{N_2} - dH_{pneu}$$

Substituting Eq. (19) into Eq. (8):

$$x_1^2K_1 + x_2 + x_3 - 1 = 0 \tag{23}$$

Substituting Eq. (20) into Eq. (9):

$$-K_2(x_1x_2) + (w - 1{,}44715)K_2x_2 + 2K_2x_2^2 - x_1x_3 + 2K_2(x_2x_3) = 0 \tag{24}$$

Thus, it is possible to reduce the six equations and six unknowns system to a three equations system Eq. (22), Eq. (23) and Eq.(24), of which two are nonlinear equations and one linear equation with three unknowns. Therefore, the system is easily solved using the Newton-Raphson method or some mathematical software, for this work was used the *fsolve* function of Matlab. With the result, x_4, x_5, and m are calculated by equations Eq. (18), Eq.(19) and Eq.(21), respectively.

3.3 Model 2: Babu e Sheth (2005)

The equilibrium model proposed by Babu and Sheth (2005) to predict the performance of a downdraft gasifier is quite similar to the one of Zainal *et al.* (2001).

In order to assemble the system with which the composition of *syngas* will be calculated, it is used the balance for each component and the simplifications of x_4 and x_5 as a function of the other coefficients (x_1, x_2, x_4), along with the same equations for calculating the reaction constants. A difference in this model is that along with the water content per kmol of the tire (w), the oxygen fraction for the process (m) is an input data and so it is not calculated by the gas fractions as in the proposal of Zainal *et al.* (2001).

From the global gasification reaction (3), shown in the Zainal et al. (2001), the solution to the model proposed by Babu and Sheth follows the following steps:

1. Calculate the value of w using equation (4) according to the model of Zainal et al. (2001);
2. Specify the value of m, calculated according to the desired equivalence ratio (ER), as in Eq. (25);

$$ER = \frac{n_{real}O_2}{nesteqO2} \tag{25}$$

3. Assume a temperature T_2;
4. Calculate K_1 and K_2 using equations (16) and (17) according to the model of Zainal et al. (2001);

5. Calculate x1, x2, and x3 by the system of equations: (21), (23) and (24);
6. Replace the values calculated in 5 in equations (19) and (20), determining x_5 and x_4, respectively;
7. Calculate the new value of T_2 using equation (10);
8. Repeat steps 4-7 through an interactive process until the value of T_2 is constant.

3.4 Model 3: Jarungthammachote e Dutta (2007)

Similar to the model proposed by Babu and Sheth (2005), the model proposed by Jarungthammachote and Dutta (2007) can predict the reaction temperature from the amount of oxygen. In Zainal *et al.* (2001), the amount of oxygen is defined in terms of some components of the *syngas*.

For the same tire composition used in previous models, in the model proposed by Jarungthammachote and Dutta (2007), the typical chemical formula of the material, based on a single carbon, must be expressed in terms of CHON, in this case as $CH_{1,1057}O_{0,0915}N_{0,0035}$. It should be noted that different from Zainal *et al.*'s proposal, this author considers in this empirical equation the nitrogen content.

The overall gasification reaction of the tire can be written as:

$$CH_{1,1057}O_{0,0915}N_{0,0035} + wH_2O + mO_2 + 3{,}76mN_2 \\ = n_{H_2}H_2 + n_{CO}CO + n_{CO_2}CO_2 + n_{H_2O}H_2O + n_{CH_4}CH_4 + (0{,}00175 + 3{,}76m)N_2 \tag{26}$$

Through components mass balance equations and their relations with the equilibrium constant of the reactions, a system of five equations is assembled so that the five unknowns ($n_{H_2}, n_{CO}, n_{CO_2}, n_{H_2O}, n_{CH_4}$) can be determined.

The equilibrium constant for the methane formation reaction is calculated as:

$$K_1 = \prod_i (y_i)^{v_i} \left(\frac{P}{P_o}\right)^{\sum_i v_i} = \frac{n_{CH_4} n_{total}}{(n_{H_2})^2} \tag{27}$$

The equilibrium constant for the shift reaction is calculated as:

$$K_2 = \prod_i (y_i)^{v_i} \left(\frac{P}{P_o}\right)^{\sum_i v_i} = \frac{n_{CO_2} n_{H_2}}{n_{CO} n_{H_2O}} \tag{28}$$

For y being the molar fraction and ν the stoichiometric number.

For the calculation of the equilibrium constants of equation (15), the standard Gibbs energy of formation must be calculated by the following polynomial:

$$\Delta\bar{g}^0_{f,T} = \bar{h}^0_f - a'T\ln(T) - b'T^2 - \left(\frac{c'}{2}\right)T^3 - \left(\frac{d'}{3}\right)T^4 + \left(\frac{e'}{2T}\right) + f' + g'T \tag{29}$$

The coefficients a' – g' and the *syngas* formation are given in Table 2.

Table 2 Standard enthalpy values $\bar{h}^0_f$(kJ/mol) and coefficients for the empirical equation $\Delta\bar{g}^0_{f,T}$ (kJ/mol)

	$\bar{h}^0_f$	a'	b'	c'	d'	e'	f'	g'
CO	-110,5	$5{,}619.10^{-3}$	$-1{,}19.10^{-5}$	$6{,}383.10^{-9}$	$-1{,}846.10^{-12}$	$-4{,}891.10^{2}$	$8{,}684.10^{-1}$	$-6{,}131.10^{-2}$
CO_2	-393,5	$-1{,}949.10^{-2}$	$3.122.10^{-5}$	$-2{,}448.10^{-8}$	$6{,}946.10^{-12}$	$-4{,}891.10^{2}$	5,270	$-1{,}207.10^{-1}$
H_2O	-241,8	$-8{,}95.10^{-3}$	$-3{,}672.10^{-6}$	$5{,}209.10^{-9}$	$-1{,}478.10^{-12}$	0	2,868	$-1{,}722.10^{-2}$
CH_4	-74,8	$-4{,}620.10^{-2}$	$1{,}13.10^{-5}$	$1{,}319.10^{-8}$	$-6{,}647.10^{-12}$	$-4{,}891.10^{2}$	$1{,}411.10^{1}$	$-2{,}234.10^{-1}$

The calculation of the standard Gibbs energy of reaction is given by:

$$\Delta G^0_T = \sum_i v_i \Delta\bar{g}^0_{f,T,i} \tag{30}$$

Thus, the equilibrium constants of the equations can be calculated by equation (15). The energy balance is used to recalculate the gasification temperature and it is mathematically given by:

$$\sum_{j=reagentes} h^0_{f,j} = \sum_{i=produtos} n_i\,(h^0_{f,i} + \Delta\bar{h}^0_{T,i}) \tag{31}$$

The enthalpy variation between the reference state (298 K) and any temperature is calculated by:

$$\Delta\bar{h}^0_{T,i} = \int_{298}^{T} \bar{C}_p\,(T)\,dT \tag{32}$$

$$\bar{C}_p(T) = a + bT + cT^2 + dT^3 \tag{33}$$

$$\int_{298}^{T} \bar{C}_p\,(T)\,dT = aT + bT^2 + cT^3 + dT^4 \tag{34}$$

The specific heat coefficients at constant pressure are shown in Table 3.

Table 3 Coefficients for the specific heat at constant pressure for the gaseous species in the *syngas*

Compound	***a***	***b***	***c***	***d***	**Temperature**
H_2	29,11	$-0{,}1916.10^{-2}$	$0{,}4003.10^{-5}$	$-0{,}8704.10^{-9}$	273-1800
CO	28,16	$0{,}1675.10^{-2}$	$0{,}5372.10^{-5}$	$-2{,}222.10^{-2}$	273-1800
CO_2	22,26	$5{,}981.10^{-2}$	$-3{,}501.10^{-5}$	$-7{,}469.10^{-9}$	273-1800
H_2O	32,24	$0{,}1923.10^{-2}$	$1{,}055.10^{-5}$	$-3{,}595.10^{-9}$	273-1800
CH_4	19,89	$5{,}204.10^{-2}$	$1{,}269.10^{-5}$	$-11{,}01.10^{-9}$	273-1500
N_2	28,9	$-0{,}1571.10^{-2}$	$0{,}8081.10^{-5}$	$-2{,}873.10^{-9}$	273-1800

Thus, Eq. (31) can be rewritten as:

$$\sum_{j=reagentes} h^0_{f,j} = \sum_{i=produtos} n_i\,(h^0_{f,i}) + [\sum_i (n_i a_i)T + \sum_i (n_i b_i)\,T^2 + \sum_i (n_i c_i)\,T^3 + \sum_i (n_i d_i)\,T^4] \tag{35}$$

The solution for the proposed model follows the following steps:

1. Calculate the value of w using equation (4) according to the model of Zainal *et al.* (2001);
2. Specify the value of m, calculated according to the desired equivalence ratio (ER) (25);
3. Assume a temperature T_2;
4. Calculate K_1 and K_2 using equation (15);
5. Calculate the five unknowns n_i through the system composed of equations (5), (6), (7), (27) and (28).
6. Calculate the new value of T_2 using equation (34);
7. Repeat steps 4-6 as an interactive process until the value of T_2 is constant.

3.5 Model 4: Mendiburu *et al.* (2014)

The model of Mendiburu et al. (2014) considers the chemical formula of the material expressed in terms of all components, CHONS. Therefore, the tire formula used is given by $CH_{1,1057}O_{0,0915}N_{0,0035}S_{0,0066}$.

Thus, the overall gasification reaction can be written as:

$$\begin{aligned} CH_{1,1057}O_{0,0915}N_{0,0035}S_{0,0066} + wH_2O + n_{ar}O_2 + 3{,}76n_{ar}N_2 \\ = n_{H_2}H_2 + n_{CO}CO + n_{CO_2}CO_2 + n_{H_2O}H_2O + n_{CH_4}CH_4 + 0{,}0066SO_2 + (0{,}00175 + 3{,}76m)N_2 \end{aligned} \tag{36}$$

For this model, the amount of water per kmol of waste tire, given by w, can be calculated according to the moisture content (MC%) and ash content (A%), according to Eq. (37):

$$w = \frac{(MM_{pneu})(1 + \frac{A}{100 - A})}{(MM_{H2O}\left(\frac{100}{MC} - \frac{A}{100 - A} - 1\right)} \tag{37}$$

The mass balance applied to Eq. (36) leads to the following equations:

$$1 - n_{CO} - n_{CO_2} - n_{CH_4} = 0 \tag{38}$$

$$1{,}1057 + 2w - 2n_{H_2} - 2n_{H_2O} - 4n_{CH_4} = 0 \tag{39}$$

$$0{,}0783 + w + 2n_{ar} - n_{CO} - 2n_{CO_2} - n_{H_2O} = 0 \tag{40}$$

The equilibrium constant for the methane formation reaction and the equilibrium constant for the shift reaction are related to the gas compositions by Eq. (27) and (28). However, for Eq. (27), the total number of moles of *syngas* is expressed by algebraic manipulation of Eq. (38) - (40), resulting in Eq. (41):

$$n_{total} = 1 + \frac{1{,}1057}{2} + w + 0{,}066 + \frac{0{,}0035}{2} + 3{,}76n_{ar} - 2n_{CH_4} \tag{41}$$

Therefore, for this model, Eq. (41) must be substituted in Eq. (27), resulting in Eq. (42):

$$K_1 = \prod_i (y_i)^{v_i} \left(\frac{P}{P_o ntotal}\right)^{\Sigma_i v_i} = \frac{n_{CH_4}(1 + \frac{1{,}1057}{2} + w + 0{,}066 + \frac{0{,}0035}{2} + 3{,}76n_{ar} - 2n_{CH_4})}{(n_{H_2})^2} \tag{42}$$

According to Mendiburu *et al.* (2014), the Gibbs energy of formation, $\bar{g}_T^0$,, and the total enthalpy, $\bar{h}_T^0$,, must be calculated by sixth-degree polynomials, based on coefficients obtained by the thermodynamic tables of NIST-JANAF. However, once contacting the author to address some doubts, he advised to use the NASA-Glenn polynomials and coefficients to be more accurate and thus, show better results as he noticed on his latest studies.

Thus, with NASA-Glenn coefficients, the polynomials used were:

$$C_p = R\,(a_1T^{-2} + a_2T^{-1} + a_3 + a_4T + a_5T^2 + a_6T^3 + a_7T)\ [J/mol\ K] \tag{43}$$

$$\bar{h}_T^0 = RT(-a_1T^{-2} + a_2T^{-1}ln(T) + a_3 + a_4\frac{T}{2} + a_5\frac{T^2}{3} + a_6\frac{T^3}{4} + a_7\frac{T^4}{5} + \frac{b_1}{T})\ [J/mol] \tag{44}$$

$$\bar{s} = -a_1\frac{T^{-2}}{2} - a_2T^{-1} + a_3ln(T) + a_4T + a_5\frac{T^2}{2} + a_6\frac{T^3}{3} + a_7\frac{T^4}{4} + b_2\ [J/molK] \tag{45}$$

Eq. (44) and Eq. (45) were used in Eq. (46) to obtain equilibrium constants by Eq. (15).

$$G = \bar{h}_T^0 - Ts \tag{46}$$

Eq. (43) is used for the energy balance, with which it will be possible to calculate the gasification temperature T_2, and it can be simplified as in Eq. (47).

$$\sum_{j=reagentes} h_{f,j}^0 = \sum_{i=produtos} n_i(h_{f,i}^0) + R[\sum_i (n_i a_1)T^{-2} + \sum_i (n_i a_2)T^{-1} + \sum_i (n_i a_3) + \sum_i (n_i a_4)T + \sum_i (n_i a_5)T^2 + \sum_i (n_i a_6)T^3 + \sum_i (n_i a_7)T] \tag{47}$$

The solution for the proposed model goes with the following steps:

1. Calculate the value of w using equation (37);
2. Specify the value of n_{ar}, calculated according to the desired equivalence ratio (ER), as in Eq. (25);
3. Assume a temperature T_2;
4. Calculate K_1 and K_2 using equation (15);
5. Calculate the five unknowns n_i through the system composed of equations Eq.(38), Eq.(39), Eq.(40), Eq.(42) and Eq.(28).
6. Calculate the new value of T_2 using equation (47);
7. Repeat steps 4-6 as an iterative process until the value of T_2 is constant.

4. RESULTS

The results obtained with each equilibrium model are shown below.

4.1 Model 1: Zainal et al. (2001)

Figure 1 shows the effect of the variation of the operating temperature in the reactor bed on the composition of the gas produced. It can be seen from Figure 1 that the amount of the inert nitrogen increases with increasing temperature, this factor may also be related to the increase in the supply of the oxidizing agent (air). The share of carbon dioxide (CO 2) in the gas composition also increases with increasing temperature and as a result, the carbon monoxide (CO) fraction decreases, as expected. Decrease composition profiles are also observed for hydrogen gas (H2).

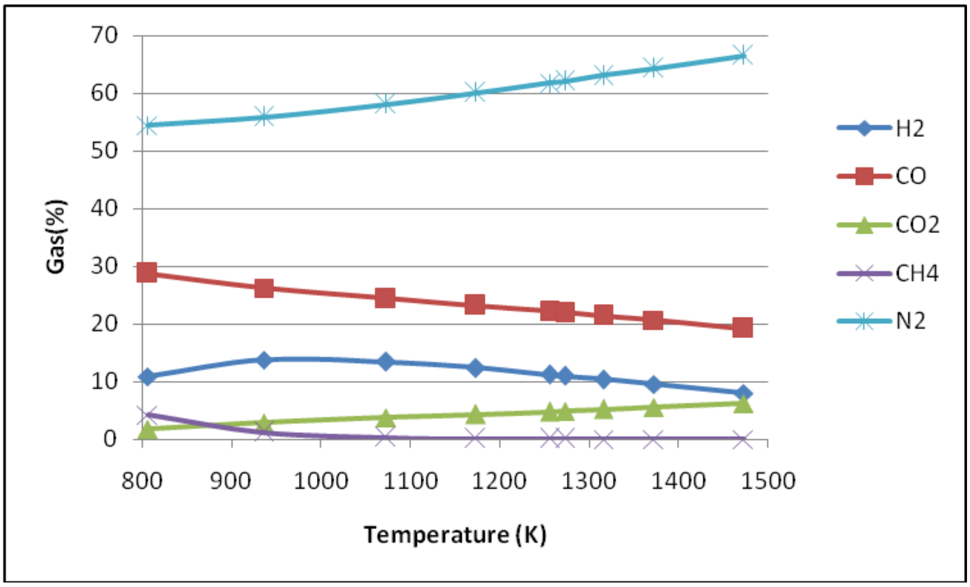

Figure 1 – Effect of temperature variation on *syngas* composition

Figure 2 shows the behavior of the low heat value (LHV) of the gas with the variation of the operating temperature in the gasifier. It is possible to observe that the lower calorific value of the *syngas* decreases with increasing temperature.

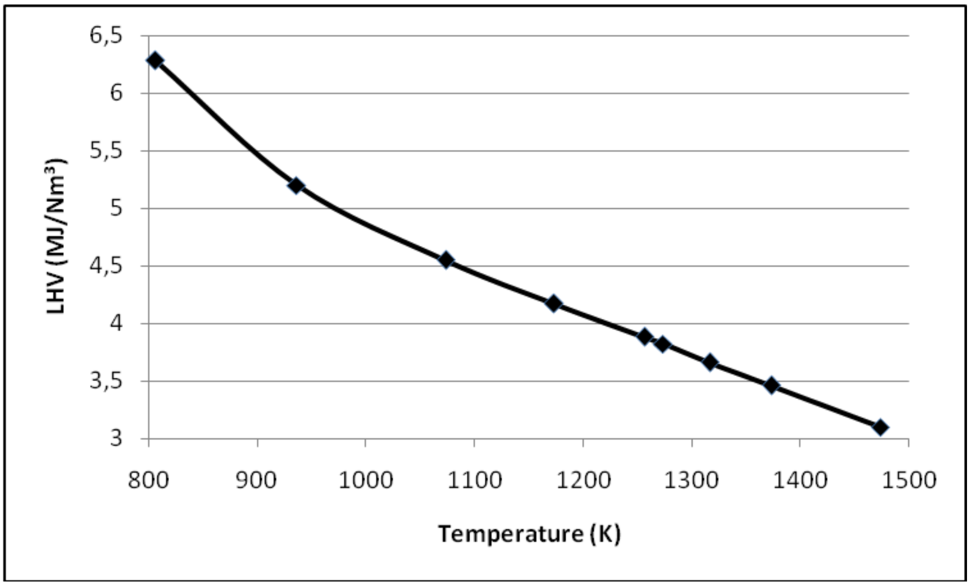

Figure 2 Behavior of calorific value with reaction temperature variation

The relation of the equivalence ratio with the temperature and the low heat value (LHV) of the gas is observed in Figure 3 and Figure 4. In the model of Zainal et al. (2001), the equivalence ratio is calculated as a function of the components of the gas produced, which are obtained with the temperature, which is an input data in the model, so with the increase in temperature an slightly linear increase in the equivalence ratio can be observed. In Figure 4 a decrease on the LHV of the gas can be observed with the increase in ER due to the increase of the amount of nitrogen in the *syngas*.

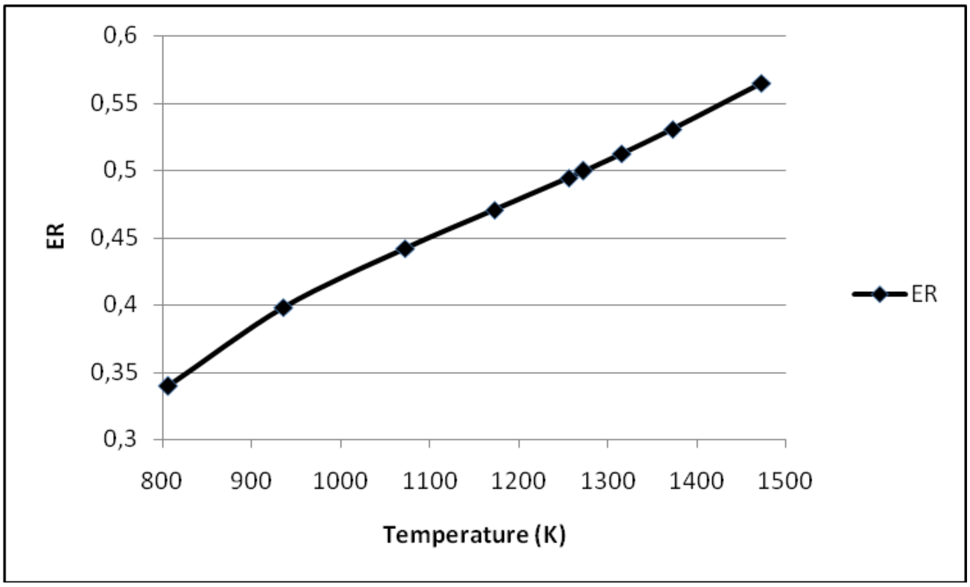

Figure 3 Behavior of the equivalence ratio (ER) with the reaction temperature variation

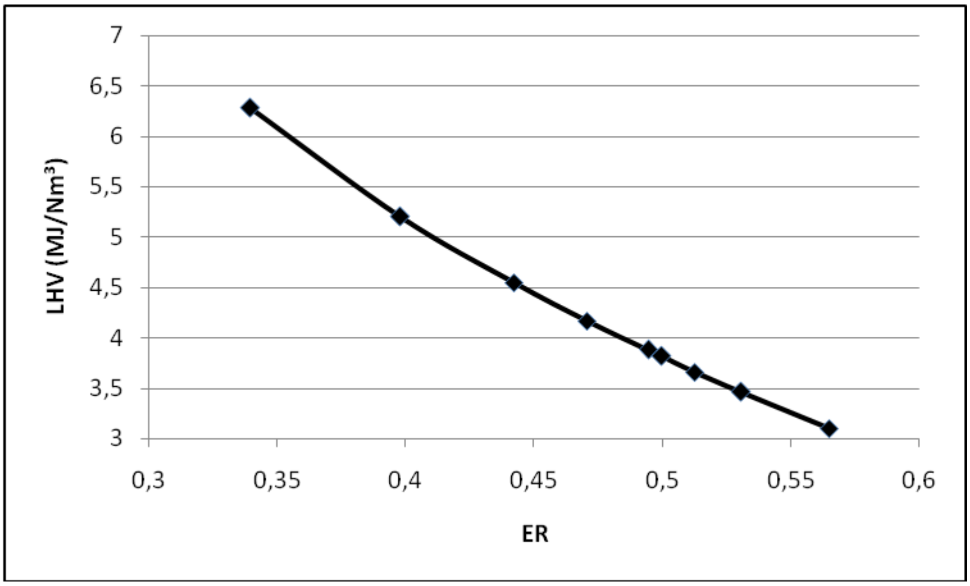

Figure 4 Behavior of *syngas* LHV with the equivalence ratio variation

4.2 Model 2: Babu and Sheth (2005)

For this model, two ER values (0.35 and 0.5) were specified so that the amount of oxygen required for the process (m) was determined.

Assuming an initial temperature for each ER value, and doing the whole iterative procedure, the reaction temperatures were found. For the equivalence ratio of 0.35, the reaction temperature has the value of 806 K. On the other hand, for the equivalence ratio of 0.5, the reaction temperature has the value of 1316 K.

Figure 5 shows the composition of the syngas for each temperature and equivalence ratio.

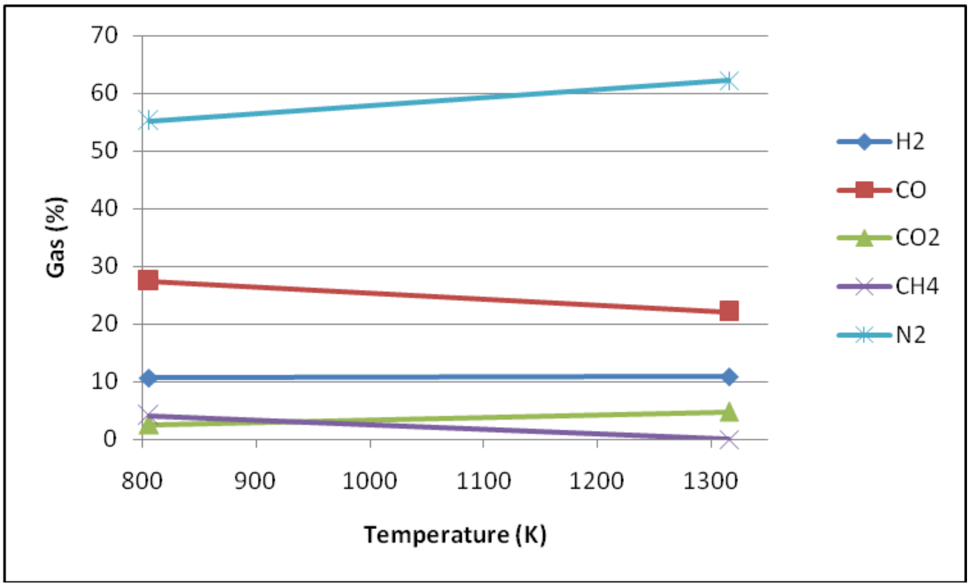

Figure 5 *Syngas* composition of the syngas for temperatures 806 K and 1316 K

Figure 6 shows the behavior of the lower heat value (LHV) of the gas for each temperature and equivalence ratio.

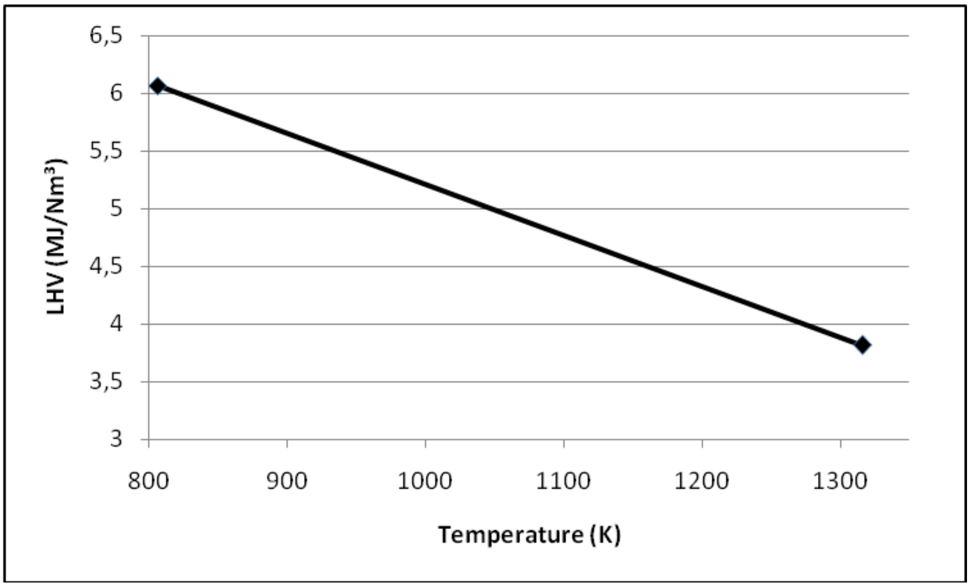

Figure 6 *Syngas* LHV for the temperatures 806 K and 1316 K

4.3 Model 3: Jarungthammachote e Dutta (2007)

The same equivalence ratio specification for calculating the amount of oxygen required in the process, which was made in the previous item was repeated in this item.

The model of Jarungthammachote and Dutta (2007) is also developed by iterative process to determine reaction temperature, as well as the model of Babu and Sheth (2005). Temperatures of 752 K and 1256 K were found for ER of 0.35 and 0.5, respectively.

Figure 7 shows the variation of the syngas composition for both conditions.

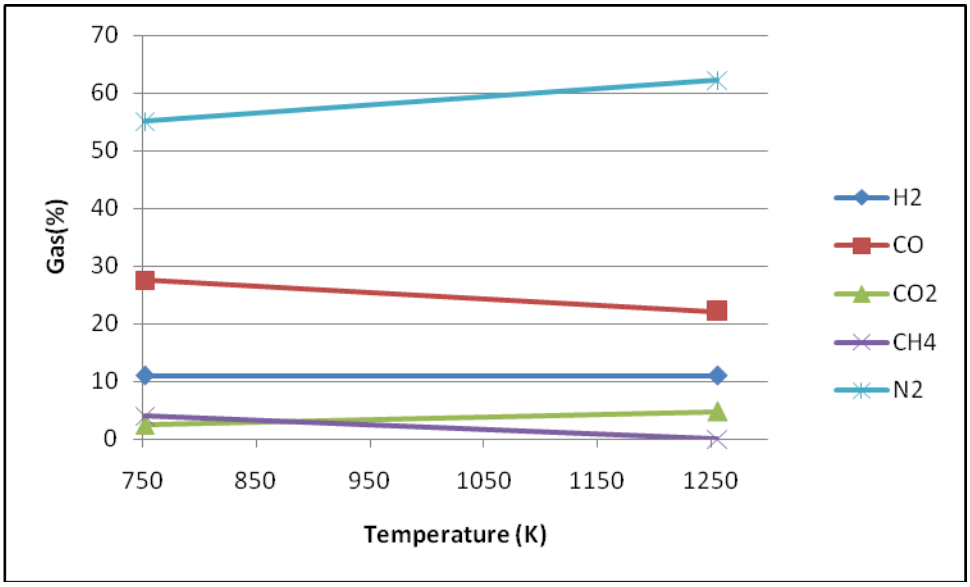

Figure 7 *Syngas* composition for temperatures 752 K and 1256 K

Figure 8 shows the behavior of the lower heat value (LHV) of the gas for each temperature, corresponding to each equivalence ratio.

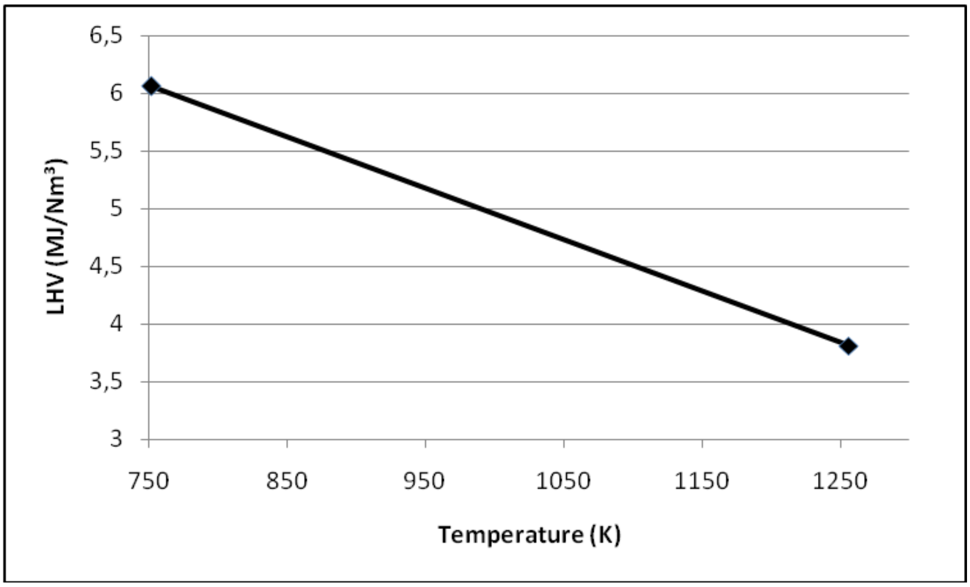

Figure 8 Variation of *syngas* LHV for temperatures 752 K and 1256 K

4.4 Model 4: Model 4: Mendiburu *et al.* (2014)

The the temperatures of 936 K and 1316 K. were obtained. for the model of Mendiburu *et al.* (2014). *Syngas* composition and the variation of the LHV are shown in Figure 9 and Figure 10, respectively.

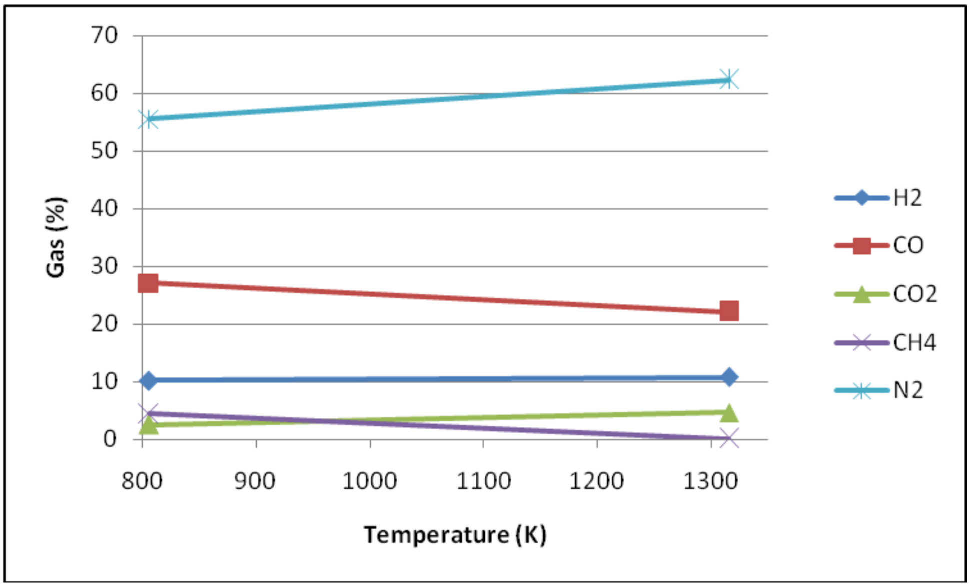

Figure 9 *Syngas* composition for temperatures 936 K and 1316 K

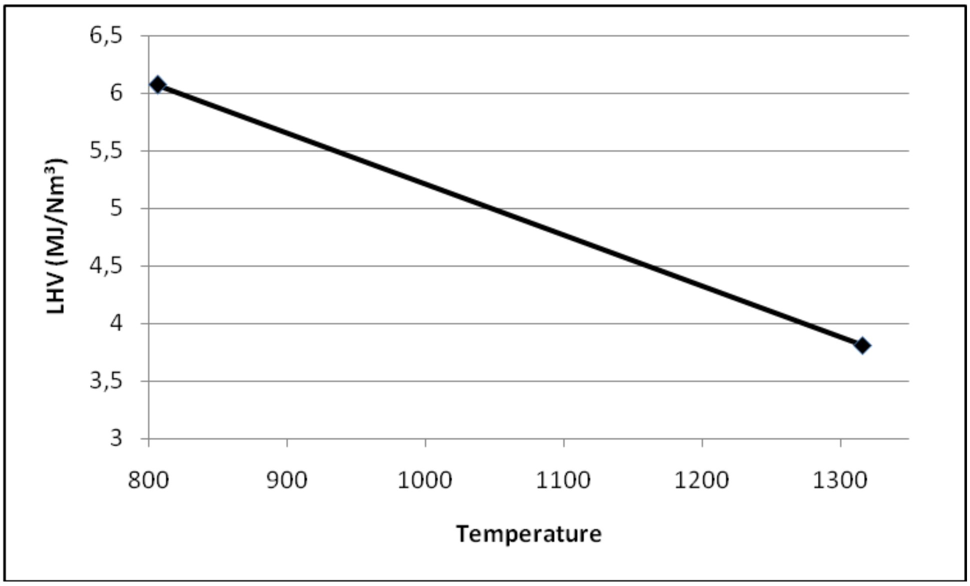

Figure 10 *Syngas* LHV variation for temperatures 936 K and 1316 K

4.5 Comparisons between models results

In Table 4 and Table 5 is shown a comparison between the compositions obtained with the models for different equivalence ratio conditions.

Table 4 Data obtained with the models for equivalence ratio of 0.35

	Model 1	Model 2	Model 3	Model 4
Temperature (K)	806	806	752	806
ER	0,3394	0,35	0,35	0,35
H2 (%)	10,89	10,68	13,6	10,16
CO (%)	28,71	27,46	29,59	27,14
CO_2 (%)	1,77	2,54	0,99	2,56
CH_4 (%)	4,19	4,11	2,39	4,38
N_2 (%)	54,44	55,22	53,44	55,54
LHV (MJ/Nm^3)	6,28	6,07	6,04	6,07

Table 4 Data obtained with the models for equivalence ratio of 0.5

	Model 1	**Model 2**	**Model 3**	**Model 4**
Temperature (K)	1316	1316	1256	1316
ER	0,51	0,5	0,5	0,5
H_2 (%)	10,38	10,86	10,96	10,79
CO (%)	21,41	22,12	22,04	22,08
CO_2 (%)	5,15	4,74	4,80	4,62
CH_4 (%)	0,03	0,03	0,01	0,06
N_2 (%)	63,03	62,24	62,18	62,27
LHV(MJ/Nm^3)	3,67	3,81	3,81	3,8106

5. CONCLUSION

The results obtained with the four models converge considerably to similar results, so there is an agreement between them. It was not found experimental results for gasification of waste tires in fixed bed reactors on the literature, thus, it was not possible to validate results with those obtained with the models.

This work aimed the study of waste tire gasification *syngas* production, a combustible gas that can be used in several types of equipment, from boilers and incinerators to gas turbines and internal combustion engines. The benefits that thermochemical processes of energy conversion can offer to the problem of waste tire disposal are numerous and they were a decisive factor for the choice of biomass for this study. It is expected that the more studies are developed on this theme, the closer will be the definitive solution to this environmental liability, the waste tire.

The disposal of used tires incorrectly has been a problem in the current environmental and energy scenario. Classified as hazardous waste and difficult disposal due to its biological and chemical resistance, waste tires have been an object of study by several researchers for the main thermochemical processes of energy conversion such as pyrolysis and gasification in order to reduce the impact caused and to develop products of relevant added energy value.

The prediction of the *syngas* chemical composition and the optimum reaction temperature based on the four models applied in this work, showed that the syngas with higher calorific value is the one produced with equivalence ratio of 0.35 and the temperature of 533 ° C, and this calorific value is almost twice the one obtained for a process at 1043 ºC and an equivalence ratio of 0.5, obtained with Mendiburu *et al.* (2014) model. The composition is given by 10.16% H_2, 27.14% CO, 2.56% CO_2, 4.38% CH_4, 55.54% N_2 and LHV of 6.085 MJ/Nm^3 was used on the next works.

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8 REFERENCES

ABDUL-RAOUF, M. E, *et al.*Thermochemical recycling of mixture of scrap tires and waste lubricating oil into high caloric value products. **Energy Conversion and Management**, v. 51, n. 6, p. 1304–1310, 2010.

BABU, B. V.; CHAURASIA, A. S. Pyrolysis of biomass: Improved models for simultaneous kinetics and transport of heat, mass, and momentum. **Energy Conversion and Management**, v. 45, p. 1297–1327, 2004.

BABU, B. V.; SHETH, P. N. Modeling, and simulation of biomass gasifier: In: ChemCon’04 Mumbai. **Biochemical Engineering**. Pilani, India. 2005.

BASU, P. **Biomass Gasification, and Pyrolysis: Practical Design and Theory**, Academic Press, 2010.

BASU, P. Combustion, and gasification in fluidized beds. Boca Raton: CRC Press, 2006. ISBN 0-849-33396-2.

CHANNIWALA SA, PARIKH PP. **A unified correlation for estimating HHV of solid, liquid and gaseous fuels**. **Fuel** 2002; 81:1051e63.

COUSINS, W. J. (1978), “A Theoretical Study of Wood Gasification Processes”, **New Zeland Journal of Science**, vol. 21, pp. 175-183.

FRIGO, S., et al. Liquid fuel production from waste tire pyrolysis and its utilization in a Diesel engine. **Fuel**, v. 116, p. 399–408, 2014.

JANAJREH I., RAZA S.S., VALMUNDSSON A.S., Plasma gasification process: modeling, simulation, and comparison with conventional air gasification, **Energy Convers. Manage**. 65 (2013) 801–809.

JARUNGTHAMMACHOTE, S.; DUTTA, A. Thermodynamic equilibrium model and second law analysis of a downdraft waste gasifier. **Energy**, v. 32, n. 9, p. 1660–1669, 2007.

KARATAS H., OLGUN H., AKGUN F., Experimental results of gasification of the waste tire with air in a bubbling fluidized bed gasifier, **Fuel** 105 (2013) 566–571

KUZNETSOV V.A., KUMKOVA I.I., LERNER A.S., POPOV V.E., **Equilibrium analysis of hydrogen production using the steam-plasma gasification process of the used car tires**, J. Phys.: Conf. Ser. 406 (2012) 012023.

LI, X. **Biomass gasification in a circulating fluidized bed.** Tese (Doutorado) - Department of Chemical and Biological Engineering. University of British Columbia, Vancouver, 2002.

MENDIBURU A Z. A, CARVALHO Jr J A., CORONADO C J.R. Thermochemical equilibrium modeling of biomass downdraft gasifier: Stoichiometric models. **Energy** 66 (2014) 189e201

PIATKOWSKI N., STEINFELD A., Solar gasification of carbonaceous waste feedstocks in a packed-bed reactor-dynamic modeling and experimental validation, **AIChE J.** 57 (12) (2011) 3522–3533

RECICLANIP. Entidades Internacionais, 2015.

RODRIGUES R., **Modelagem e simulação de um gaseificador em leito fixo para o tratamento térmico de resíduos sólidos da indústria calçadista**. Dissertação de mestrado, UFRGS, Rio Grande do Sul, Brasil, 2008

WORLD TIRES, Industry Study 3105. The Freedonia Group; 2014.

ZAINAL, Z. A., ALI, R., LEAN, C. H., SEETHARAMU, K. N. (2001), "Prediction of Performance of a Downdraft Gasifiers Using Equilibrium Modeling for Different Biomass Materials", **Energy Conversion and Management**, vol. 42, pp.1499–1515.

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