

# Assessment of gasification models for a BIGCC cycle using sugarcane bagasse and straw

*Andressa Lodi de Brito<sup>a</sup>, Antonio Garrido Gallego<sup>b</sup>, Marcelo Modesto<sup>c</sup>*

<sup>a</sup> *Universidade Federal do ABC, Santo André, Brazil, dessalodi@hotmail.com*

<sup>b</sup> *Universidade Federal do ABC, Santo André, Brazil, a.gallego@ufabc.edu.br*

<sup>c</sup> *Universidade Federal do ABC, Santo André, Brazil, marcelo.modesto@ufabc.edu.br*

## Abstract:

Once again Brazil faces the possibility of an electricity shortage in the near future. The low level of rain and the consequent reduction of hydroelectric reservoirs led to the dispatch of thermal plants based on natural gas and/or fuel oil. The higher operation costs of the thermal plants in comparison to the hydroelectricity leads to the electricity supply scenario which is pushing the electricity prices up in the near future.

A possible alternative to increase the electricity supply is the maximization of the electricity surplus in sugarcane mills. Back in 1970's and 1980's, cogeneration plants in sugarcane mills were primarily designed to consume all bagasse, and produce steam and electricity to the process. The plants used medium pressure steam boilers (21 bar and 300°C) and backpressure steam turbines.

Most recently, the economic value of by-products (bagasse, molasses, etc.) has increased, and the possibility of selling electricity led to the grid drove the sugarcane industry to search for more advanced cogeneration systems, based mainly on higher steam parameters (40-100 bar and 400-500°C). Another alternative to generate electricity is using gasification of bagasse and straw in a BIGCC (Biomass Integrated Gasification Combined Cycle).

In order to foresee a potential to electricity production in a BIGCC, an adequate simulation of the gasifier behavior must be done. A good gasification model needs to foresee the syngas composition and LHV considering the moisture of biomass and different compositions.

In this paper, an initial comparison between three different gasification models is performed. The models are based in a chemical equilibrium using the minimization of Gibbs free energy and using some empirical equations in order to predict the fractions of methane and unconverted carbon and adjust the model with the characteristics of the gasification process. The models were validated with data from other papers, and the best result was used to verify the influence of the moisture and type of biomass on the behavior of the process.

## Keywords:

Gasification models, sugarcane bagasse, cogeneration, thermodynamic analysis.

## 1. Introduction

One possible definition for gasification is a thermochemical process in which a solid/liquid fuel is converted due to the addition of heat in a sub-oxidizing atmosphere, into a mixture of gases (produced gas) with low calorific value, composed mainly by H<sub>2</sub> and CO.

The gasification technology has been object of study of many researchers, especially those involved in promoting large-scale electricity generation in sugarcane mills. Most recently, many works have been published in the field of gasification modeling by chemical equilibrium and its analysis [1], [2]. A non-stoichiometric model, which uses empirical relations in order to come closer to real operation of gasification of biomass, based on the operation of a circulating fluidized bed gasifier, were proposed by [1].

Gasification and combustion processes for CHO systems are analyzed based on first and second law of thermodynamics, following a stoichiometric approach [3], [4]. These studies have provided a fairly comparison between gasification and combustion, showing main irreversibility associated with each process, and the advantages of one and another. The aim of this paper is to develop a gasification model to show the behavior of the gasification process of sugarcane bagasse and straw

with different proportion and to perform an assessment of main parameters that has influence in the syngas production.

## 2. Gasification Models

The thermodynamic modeling of gasification process allows seeking the behavior of thermochemical conversion of lignocellulosic materials and optimizing the design and operations of gasifier.

There are three main models used to study the gasification process:

**Chemical equilibrium model:** the syngas composition is determined with constant temperature by the equilibrium reactions using the principles of mass conservation and minimizing the free Gibbs energy.

**Non-kinetic model:** the calculus is done for each gasification steps, separately.

**Steady flow models:** the reactor is divided in infinitesimal parts that integrate to obtain the syngas composition.

Several studies assessed the potential of gasification process in sugarcane plants, [5-10]. In these studies, the combination of gasification of sugarcane bagasse in a BIGCC (Biomass Integrated Gasification Combined Cycle) leads the sugarcane plants to increase the electricity generation potential until seven times than current configuration.

However, the previous studies do not worry to assess the performance of gasification process in different operation conditions. In order to assess these aspects it is necessary to develop a model that represents the gasification process and allows assess different operation parameters. According to [11], for chemical process involving biomass occurring between 800-900°C (pyrolysis and gasification), kinetic models are recommended.

The chemical kinetic models consist of a mechanism of heat and mass transfer that, through velocity of chemical reactions, determine the syngas composition in time function.

However, given the complexity of reaction, number of components and phase inside of the reactor, those models become very expensive to perform the analysis of the main parameters involved. Souza-Santos [12] and Corella and Sanz [13] show some of those models.

Thus, according to Li et al [1] chemical equilibrium models are a cheaper alternative than other models, and used in this assess. It is possible to use empirical correlations to correct the results of chemical equilibrium and approximate of experimental results. This kind of model is adopted in this study.

### 2.1- Chemical Equilibrium Model

The approach used to model the gasification process was developed through the chemical equilibrium concept, described by Smith et al [14]. The main hypothesis consist of:

- The system is in equilibrium;
- Uniform pressure and temperature;
- N phases with uniform compositions;
- System reversible heat exchange with the environment;

Using several concepts of First and Second Law of Thermodynamics it is possible to define the equation (1) that represents the condition of the isolated system to chemical equilibrium conditions based in Gibbs function.

$$dG_{\text{system}} + SdT_{\text{system}} + VdP_{\text{system}} \leq 0 \quad (1)$$

Equation (1) shows that any irreversible process occurs spontaneously since the value of Gibbs functions decreases, with constant temperature and pressure. Still, for a given temperature and pressure, an equilibrium state is defined as the Gibbs function is minimal (2).

$$(dG_{\text{system}})_{T,P} = 0 \quad (2)$$

Starting with chemical equilibrium model, there are two main approaches: stoichiometric and non-stoichiometric approaches. In this paper, the non-stoichiometric approach was used.

## 2.2- Non-stoichiometric model

For this model, are known only the components of syngas produced in gasification process and the Lagrange multipliers, as described by Jarungthammachote and Dutta [15]. This model is also known as “minimization method of Gibbs free energy”. The Gibbs free energy to a thermodynamic system with temperature T and pressure P is defined by (3).

$$(G^t)_{T,P} = \sum_{i=1}^N n_i \mu_i = G(n_1, n_2, n_3, \dots, n_N) \quad (3)$$

Where  $n_i$  is the moles number of species i, N is the total number of species in the system and  $\mu_i$  is the chemical potential of specie i, described by (4)

$$\mu_i = \sum_{i=1}^N n_i \mu_i = \left( \frac{\partial G^t}{\partial n_i} \right)_{T,P,n} \quad (4)$$

In order to minimize the Gibbs free energy value with specific temperature and pressure, they will be calculated using the Lagrange multipliers method. Firstly, must be performed a mass balance of elements of system by (5)

$$\sum_{i=1}^N a_{ij} n_i = A_j \quad j = 1, 2, 3, \dots, k \quad (5)$$

Where  $a_{ij}$  is the atom number of j element in each molecule of specie I,  $A_j$  is the atom total number of j element in the system and k is total element number of system.

Multiplying (5) by Lagrange multipliers ( $\lambda_j$ ), the result is:

$$\lambda_j \left( \sum_{i=1}^N a_{ij} n_i - A_j \right) = 0 \quad (6)$$

The sum of term in is:

$$\sum_f \left[ \lambda_j \left( \sum_{i=1}^N a_{ij} n_i - A_j \right) \right] = 0 \quad (7)$$

Adding (7) in (3), we have the L function:

$$L = G^t + \sum_f \left[ \lambda_j \left( \sum_{i=1}^N a_{ij} n_i - A_j \right) \right] \quad (8)$$

Thus, the minimal value of  $G^t$  found when the partial derivate of L in relation of a  $n_i$  is equal to zero. Deriving (8) and simplifying:

$$\mu_i + \sum_{j=1}^k a_{ij} \lambda_j = 0 \quad \text{com } i = 1, 2, 3, \dots, N \quad (9)$$

The chemical potential to gaseous reaction in reference state to 1 bar is:

$$\mu_i = G_i^o + RT \ln \left( \frac{f_i}{f_i^o} \right) \quad (10)$$

Where  $f_i$  is fugacity of specie I, and  $f_i^o$  is fugacity of specie I at the reference state. Fugacity is described by (11):

$$f_i = y_i \phi_i P \quad (11)$$

If the Gibbs free energy value is equal to zero at the reference state, the  $G_i^o$  will be equal to variation of formation energy of i species, as described in (12):

$$G_i^o = \Delta G_{f_i}^o \quad (12)$$

Considering  $y_i = \frac{n_i}{\sum n_i}$  and rearranging (10) and simplifying:



gasifier									
Biomass	Wood	Sawing wood	Rubber wood	Wood	Wood	Wood	Wood	Wood	Wood

The comparison of the results is shown in tables 2 to 5.

Table 2. Results of the models using data from Zainal et al [20].

	Zainal et al [20]	Zevallos [22]	Developed Models						
			Error (%)	M1	Error (%)	M2	Error (%)	M3	Error (%)
H <sub>2</sub> (%)	15.23	18.78	23.31	15.772	3.56	13.35	-12.35	13.50	-11.37
CO (%)	23.04	15.88	-31.08	21.458	-6.87	20.80	-9.74	16.98	-26.31
CO <sub>2</sub> (%)	16.42	12.92	-21.32	10.263	-37.50	11.50	-29.96	14.15	-13.84
CH <sub>4</sub> (%)	1.58	2.00	26.84	0.005	-99.68	2.33	47.28	3.14	98.61
N <sub>2</sub> (%)	42.31	47.67	12.67	52.50	24.09	52.03	22.97	52.24	23.46
O <sub>2</sub> (%)	1.42	-	-	-	-	-	-	-	-
C (mols)	-	2.76	-	-	-	-	-	0.62	-
LHV (MJ/N.m <sup>3</sup> )	4.85	4.79	-1.24	3.74	-22.85	4.13	-14.89	3.78	-22.10
HHV (MJ/N.m <sup>3</sup> )	-	5.19	-	4.01	-	4.43	-	4.10	-
Equivalence ratio	-	-	-	0.4285	-	0.3891	-	-	-

Table 3. Results of the models using data from Altafini et al. [11].

	Altafini et al [11]	Zevallos [22]	Developed Models						
			Error (%)	M1	Error (%)	M2	Error (%)	M3	Error (%)
H <sub>2</sub> (%)	14.00	16.07	14.79	19.329	38.06	16.44	17.44	19.66	40.43
CO (%)	20.14	16.87	-16.24	27.933	38.69	28.18	39.92	21.01	4.32
CO <sub>2</sub> (%)	12.06	11.44	-5.14	6.365	-47.22	7.24	-39.99	12.85	6.56
CH <sub>4</sub> (%)	2.31	2.001	-13.38	0.011	-99.52	2.96	28.27	5.74	148.57
N <sub>2</sub> (%)	50.79	52.2	2.78	46.36	-8.72	45.18	-11.05	40.74	-19.79
O <sub>2</sub> (%)	-	-	-	-	-	-	-	-	-
C (mols)	-	1.42	-	-	-	-	-	0.62	-
LHV (MJ/N.m <sup>3</sup> )	-	4.46	-	5.06	-	5.77	-	5.58	-
HHV (MJ/N.m <sup>3</sup> )	5.04	4.80	-4.76	5.45	8.19	6.17	22.40	6.07	20.52
Equivalence ratio	-	-	-	0.3423	-	0.2981	-	0.16	-

Table 4. Results of the models using data from Jayah et al. [21]

	Jayah et al [21]	Zevallos [22]	Developed Models						
			Error (%)	M1	Error (%)	M2	Error (%)	M3	Error (%)
H <sub>2</sub> (%)	17.00	16.17	-4.88	16.626	-2.20	14.27	-16.07	14.85	-12.62
CO (%)	18.40	17.11	-7.01	23.294	26.60	22.89	24.39	19.15	4.06
CO <sub>2</sub> (%)	10.60	11.21	5.75	8.217	-22.48	9.25	-12.75	11.69	10.29

CH <sub>4</sub> (%)	1.30	2.0004	53.88	0.001	-99.92	2.40	84.69	3.38	160.15
N <sub>2</sub> (%)	52.70	52.23	1.01	51.86	-1.59	51.19	-2.89	50.93	-3.37
O <sub>2</sub> (%)	-	-	-	-	-	-	-	-	-
C (mols)	-	0.262	-	-	-	-	-	0.75	-
LHV (MJ/N.m <sup>3</sup> )	-	4.27	-	4.09	-	4.54	-	4.26	-
HHV (MJ/N.m <sup>3</sup> )	-	4.64	-	4.37	-	4.86	-	4.60	-
Equivalence ratio	-	-	-	0.4086	-	0.3680	-	0.29	-

Table 5. Results of the models using data from Wei [19]

	Wei	Zevallos[22]		Developed Models					
	Case 2	Error (%)	MI	Error (%)	M2	Error (%)	M3	Error (%)	
H <sub>2</sub> (%)	17.06	21.04	23.33	18.50	8.46	16.05	-5.90	17.69	3.70
CO (%)	22.02	15.27	-30.65	25.47	15.67	25.52	15.89	21.22	-3.66
CO <sub>2</sub> (%)	12.42	13.08	5.31	4.49	-63.89	4.89	-60.60	7.10	-42.81
CH <sub>4</sub> (%)	3.41	2.02	-40.76	0.10	-97.01	2.35	-31.06	3.23	-5.25
N <sub>2</sub> (%)	45.09	41.36	-8.27	51.44	14.08	51.18	13.52	50.76	12.57
O <sub>2</sub> (%)	-	-	-	-	-	-	-	-	-
C (mols)	-	7.23	-	-	-	-	-	0.82	-
LHV (MJ/N.m <sup>3</sup> )	5.21	5.68	9.02	4.82	-7.56	5.30	2	5.08	-2.55
HHV (MJ/N.m <sup>3</sup> )	-	-	-	5.15	-	5.67	-	5.50	-
Equivalence ratio	-	-	-	0.3801	-	0.3478	-	0.28	-

By the analysis of the tables, it can be seen that there are some different results, particularly to the amount of methane produced. That difference is due to the corrections that the authors chose depending on the type of equipment used.

After the selection of simulation model to the gasification process (Model 2) some simulations were performed with different quantify of sugarcane straw and bagasse. The Table 6 presents the elementary analysis of dry straw and bagasse and lower heating value [23].

In sugarcane plants, the boilers are fuelled with the mixture of straw and bagasse with the maximum of 15% of straw. An increase on the percentage of straw leads to several instabilities in combustion process, mainly due to a higher volatile presence in straw than bagasse. In the gasification process, this phenomenon has lower intensity than combustion, thus, the percentage of straw in the mixture simulated until 40% of straw.

The bagasse moisture has influence in gasification process. It's recommended that the moisture must be lower than 25%, according to Basu [24]. The straw moisture value is lower than 25%.

Table 6. Elementary analysis of sugarcane straw and bagasse – dry basis [23].

Parameters – (%) weight	Straw	Bagasse
Carbon	46.2	44.6
Hydrogen	6.2	5.8
Oxygen	43.0	44.5
Nitrogen	0.5	0.6
Sulfur	0.1	0.1

Chlorine	0.1	0.02
Ash	3.9	4.38
Higher heating value (MJ/kg)	17.4	18.1

Basu [24] highlights that “at low reaction temperatures, the reaction rate is very slow, so the residence time required for complete conversion is long. Therefore, kinetic modeling is more suitable and accurate at relatively low operating temperatures (< 800 °C) and for higher temperatures, where the reaction rate is faster, the equilibrium model may be of greater use”. Thus, the temperature of gasification operation for this model was chosen in 900°C.

Fixing the temperature of the gasification in 900°C and keeping the straw moisture in 13% (wet basis), several simulations were performed, varying the straw mass fraction (straw % column) and varying bagasse moisture from 50 to 13% (bagasse % column). Some results are shown at Tables 7 to 10. The column “Mixture moisture” represents the moisture of the mixture of straw and bagasse, which was calculated considering the mass percentage of each component in the mixture and the moisture of each component, as shows (14):

$$\text{Mixture moisture} = \text{Straw percentage} \times \text{Straw moisture} + \text{Bagasse percentage} \times \text{Bagasse moisture} \quad (14)$$

The column  $\eta$  represents the cold gas efficiency, that can be calculated according to (15):

$$\eta = \frac{\text{Available energy at the gas}}{\text{Fuel consumed energy}} \quad (15)$$

*Table 7. Results of simulations: temperature of gasification 900°C, straw moisture 13% (wet-basis) and straw percentage 40%.*

Straw [%]	Bagasse moisture [%]	Mixture moisture [%]	$\Phi$	$\eta$ [%]	Rel 1 [kg/kg]	Rel 2 [kg/kg]	Rel 3 [kg/kg]
40	50	35.2	0.7279	29.34	2.714	3.495	2.898
40	40	29.2	0.6031	42.79	2.965	3.253	2.745
40	30	23.2	0.4978	54.13	3.216	3.012	2.592
40	20	17.2	0.4076	63.83	3.468	2.770	2.439
40	15	14.2	0.3673	68.17	3.593	2.649	2.363
40	13	13	0.352	69.82	3.644	2.601	2.332

*Table 8. Results of simulations: temperature of gasification 900°C, straw moisture 13% and straw percentage 30%.*

Straw [%]	Bagasse moisture [%]	Mixture moisture [%]	$\Phi$	$\eta$ [%]	Rel 1 [kg/kg]	Rel 2 [kg/kg]	Rel 3 [kg/kg]
30	50	38.9	0.8214	19.24	2.588	3.638	2.987
30	40	31.9	0.6596	36.66	2.885	3.355	2.808
30	30	24.9	0.528	50.84	3.181	3.073	2.628
30	20	17.9	0.4187	62.59	3.478	2.790	2.449
30	15	14.4	0.3707	67.75	3.626	2.648	2.359
30	13	13	0.3526	69.70	3.685	2.591	2.323

Table 9. Results of simulations: temperature of gasification 900°C, straw moisture 13% and straw percentage 20%.

Straw [%]	Bagasse moisture [%]	Mixture moisture [%]	$\Phi$	$\eta$ [%]	Rel 1 [kg/kg]	Rel 2 [kg/kg]	Rel 3 [kg/kg]
20	50	42.6	0.9281	7.74	2.459	3.782	3.078
20	40	34.6	0.7216	29.97	2.802	3.458	2.871
20	30	26.6	0.5600	47.35	3.144	3.134	2.664
20	20	18.6	0.4301	61.32	3.487	2.810	2.458
20	15	14.6	0.3742	67.32	3.659	2.647	2.355
20	13	13.0	0.3533	69.57	3.727	2.582	2.314

Table 10. Results of simulations: temperature of gasification 900°C, straw moisture 13% and straw percentage 15%.

Straw [%]	Bagasse moisture [%]	Mixture moisture [%]	$\Phi$	$\eta$ [%]	Rel 1 [kg/kg]	Rel 2 [kg/kg]	Rel 3 [kg/kg]
15	50	44.45	0.9872	1.374	2.393	3.855	3.123
15	40	35.95	0.7548	26.39	2.759	3.510	2.903
15	30	27.45	0.5767	45.54	3.125	3.165	2.683
15	20	18.95	0.4359	60.67	3.492	2.820	2.463
15	15	14.7	0.3760	67.11	3.675	2.647	2.353
15	13	13.0	0.3536	69.51	3.748	2.578	2.309

According to the results, bagasse moisture higher than 20% is not recommended to any composition of mixture of straw and bagasse, due to the decrease of cold efficiency. This phenomena is promoted by the increase of water quantity in syngas and the increase of equivalence ratio, since it leads to a process with characteristic of combustion and not gasification, that is the objective of this study. It must be noticed, though, that usually, the sugarcane bagasse leaves the milling process with moisture of 40-50%. Thus, before gasification, bagasse needs to go through a drying process.

The increase of straw percentage in the mixture increases the ashes quantity in the mixture. According to Hassuani et al [23], the percentage of ashes in bagasse is higher than the one found in straw. However, in most cases the percentage of ashes in straw can be twice as higher than in bagasse. The ashes presence compromises the operation of equipment such as boilers and gasifiers.

The increase of straw percentage in the mixture decreases the syngas production, and this can be explained from the lower value of molar relation between oxygen per carbon in straw (0.68) than the one found in bagasse (0.748) and the higher value of molar relation between hydrogen per carbon in straw (1.61) than bagasse (1.561). Figure 1 shows the influence of bagasse moisture in gasification efficiency, ratio equivalent, ashes and syngas mass, considering temperature of gasification in 900°C and straw percentage 30%.



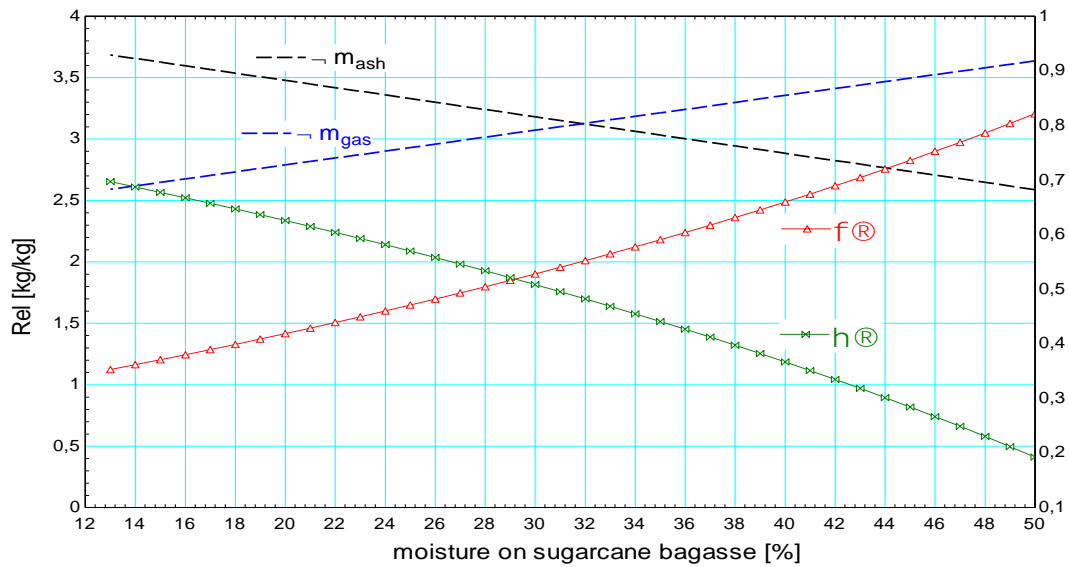


Fig. 1. Influence of bagasse moisture (wet-basis) using temperature of gasification 900°C and percentage of straw 30%

Moisture values lower than 20% represent cold efficiency values higher than 60%. Thus, in order to gasification process to occur in 900°C and moisture of 20%, the equivalence ratio must be 0.4187 (table 7).

Figure 2 shows the influence of equivalent ratio in molar fractions of syngas and temperature profile of gasification process (not included the nitrogen molar fraction).

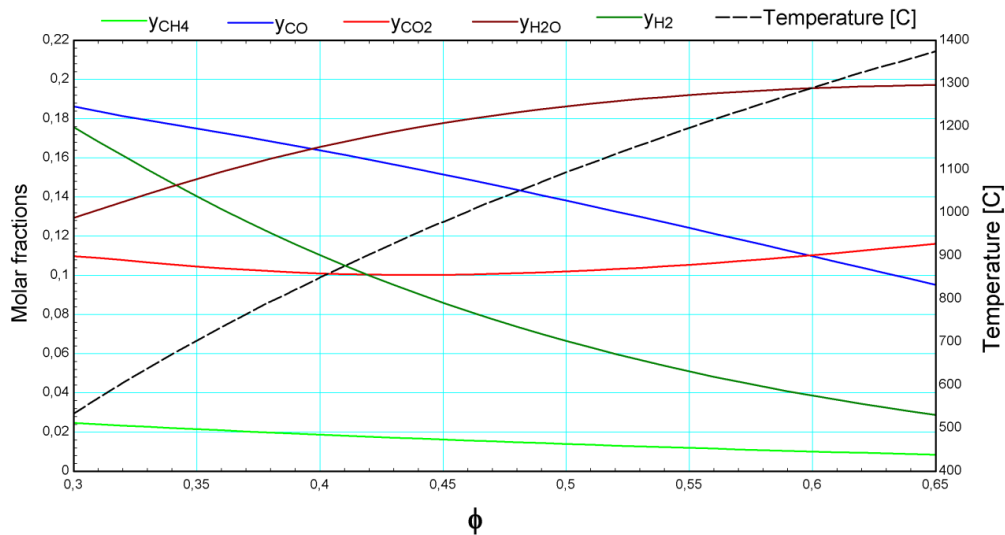


Fig. 2. Equivalence ratio influence in temperature and molar fraction of gases.

It is possible to observe an increase of water and carbon dioxide fractions with the increase of the equivalence ratio. Thus, since the objective is the gasification, it is necessary to operate with equivalence ratios that lead to the higher molar fractions of  $H_2$ ,  $CH_4$  and  $CO$  in desired temperature.

## 6. Conclusions

The modified equilibrium model (model 2), which contains the empirical equation to calculate the formation of methane, presented good results when compared with literature and experimental data. For that reason, this model was used in the analysis of the influence of the amount of straw and moisture on the results of the gasification process.

A limiter of the model was the determination of the methane fraction at the produced gas, since at most reactors, it did not reach the equilibrium condition. That is the reason for the use of the correlation presented by Li et al [18] for a specific type of reactor.

According to the results, the sugarcane bagasse moisture higher than 20% is not recommended to any composition of mixture of straw and bagasse, due to the decrease of cold efficiency promoted by the increase of water quantify in syngas and the increase of ratio equivalent, since it leads to a process with characteristic of combustion and not gasification, that is the objective of this study. In order to reduce the moisture of bagasse, it needs to go through a drying process before gasification.

At the most cases, the percentage of ashes in straw was higher than in bagasse, and that can be a problem, since the ashes presence compromises the operation of equipment such as boilers and gasifiers.

For the next study, it will be done a thermodynamic and exergetic analysis of the gasifier, using the results found so far.

## Nomenclature

$a$	number of atoms
$A$	total number of atoms in the system
$BIGCC$	Biomass Integrated Gasification Combined Cycle
$C$	Carbon
$CH_4$	Methane
$CHO$	Carbon Hydrogen Oxygen
$CO$	Carbon Monoxide
$dG$	variation of Gibbs free energy
$dP$	variation of the pressure, kPa
$dT$	variation of the temperature, °C
$f$	fugacity
$G^t$	total Gibbs free energy
$H_2$	Hydrogen
$HHV$	Higher heating value, MJ/(N m <sup>3</sup> )
$k$	Total number of elements in the system
$LHV$	Lower heating value, MJ/(N m <sup>3</sup> )
$M1$	Model 1
$M2$	Model 2
$M3$	Model 3
$n$	number of moles
$N$	number of phases
$N_2$	Nytrogen
$P$	Pressure, kPa
$R$	Universal gas constant, J/(mol K)
$Rel 1$	ratio of mass of ashes produced and the mass of biomass
$Rel 2$	ratio of mass of syngas produced and the mass of biomass
$Rel 3$	ratio of mass of syngas produced (dry basis) and the mass of biomass
$S$	Entropy, kJ/K
$T$	Temperature, °C
$V$	Volume, m <sup>3</sup>

$y$  molar fraction

### Greek symbols

$\eta$  cold efficiency

$\lambda$  Lagrange multipliers

$\mu$  chemical potential

$\phi$  equivalence ratio

### Subscripts and superscripts

$i$  specie

$j$  element

$^{\circ}$  reference state

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