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A Numerical Algorithm for Solving a Specific Chemical Equilibrium Problem

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ABSTRACT

This article discusses a mathematical model for the thermochemical processes in a downdraft biomass gasifier. The model combines the chemical equilibrium and the thermodynamic equilibrium of the global reaction, predicting the final composition of the producer gas as well as its reaction temperature. Once the composition of the producer gas is obtained, a range of parameters can be derived, such as the cold gas efficiency of the gasifier, the amount of dissociated water in the process and the heating value and engine fuel quality of the gas.

KEYWORDS: mathematical model, thermodynamic equilibrium.

1. Introduction

Gasification of biomass provides clean and combustible gas with sufficient energy, which can be used for electricity generation, engine applications etc. However, the successful design and operation of gasifiers are not simple. There are no neat rules as the thermodynamics of gasifier operation are not well understood. In this paper, a preliminary study of the operation and the performance of downdraft biomass gasifier using a wood combustion is done.

In a reversible chemical reaction at a given time under specified conditions of temperature and pressure the state of dynamic equilibrium is determined, characterized by an unchanging composition over time.

A steady state is established when the speeds at which the performance of the two opposing reactions are equal and simultaneous.

For reversible chemical reaction of the form:

$$\sum_{i=1} \nu_i A_i \leftrightarrow \sum_{i=1} \nu' A'_i \ , \tag{1}$$

The direct reaction rate is:

$$v_1 = k_1 \prod_{i=1}^{n} C_{A_i}^{\nu_i} \ , \tag{2}$$

The reverse reaction rate is:

$$v_2 = k_2 \prod_{i=1}^{n} C_{A_i}^{\nu_i} \ , \tag{3}$$

In these conditions, in a steady state we can write

$$k_1 \prod_{i=1}^{n} C_{A_i,ech}^{\nu_i} = k_2 \prod_{i=1}^{n} C_{A'_i,ech}^{\nu'_i} \ , \tag{4}$$

thus

$$K_c = \frac{k_1}{k_2} = \frac{\prod_{i=1}^{n} C_{A'_i,ech}^{\nu'_i}}{\prod_{i=1}^{n} C_{A_i,ech}^{\nu_i}} \tag{5}$$

where: k1 and k2 is the rate constant for the reaction of one mole of reactant (s) and the reaction product, Kc, the equilibrium constant of reaction being expressed in units of molar concentrations.

The chemical reaction resulting in a liquid solution is the following relationship linking the equilibrium constant values expressed by the thermodynamic activity, K, Kn being the number of moles by molar fraction molar concentrations Kx and Kc:

Equation (4) defines the mass action law (Guldenbeg and Waage), which establishes the interdependence between the equilibrium concentrations of substances participating in the reaction temperature and time pressure (for gaseous systems containing chemicals).

The equilibrium constant depends on temperature, pressure and concentration of reactants and products at equilibrium response.

According to Le Chatelier's principle, the principle of chemical equilibrium movement, if one of the factors influence changes in the chemical

balance, the system moves to a new position of equilibrium in the sense that opposes change products. That means increasing a reactant concentration, the addition of the chemical system moving balance, for purposes of consumption so the result is a direct response.

The decrease in the concentration of reaction product by removing it from the system displaces the equilibrium in the sense of training, so the result is the direct reaction.

In this paper, we study the influence of concentration on the chemistry by doing the following reactionof the form:

$$\begin{aligned} &CH_xO_yN_z + m_wH_2O + x_g\left(O_2 + 3.76N_2\right) \quad , \\ &\rightarrow x_1CO + x_2H_2 + x_3CO_2 + x_4H_2O + x_5CH_4 + \\ &+\left(\frac{z}{2} + x_g 3.76\right)N_2 \end{aligned} \tag{6}$$

From the global reaction there results a system of six equations with six variables x_1, x_2, x_3, x_4, x_5, which represent five species of products and oxygen content for the reactions.

Six equations are required based on atomic balance (Carbon balance, Hydrogen and Oxygen balance):

$$x_1 + x_3 + x_5 = 1, \tag{7}$$

and

$$x + 2m_w = 2x_2 + 2x_4 + 4x_5, \tag{8}$$

and respectively

$$y + m_w + 2x_g = x_1 + 2x_3 + x_4, \tag{9}$$

The equilibrium constants in function of the molar composition can be written as follows:

$$K_1 = \frac{P_{CO_2} \cdot P_{H_2}}{P_{CO} \cdot P_{H_2O}} = \frac{n_{CO_2} \cdot n_{H_2}}{n_{CO} \cdot n_{H_2O}} = \frac{x_3 x_2}{x_1 x_4}, \tag{10}$$

and

$$K_2 = \frac{P_{CH_4}}{\left(P_{H_2}\right)^2} = \frac{n_{CH_4} \cdot n_{tot}}{n_{H_2}^2} = \frac{x_5}{x_2^2} n_{tot}, \tag{11}$$

2. Description of the Gasification Process

In the current study, a tar-free biomass gasification process by air is modelled. This concept was considered on wood sawdust under autothermic conditions [3].

The elemental composition structure has the main configuration given in Table 1 [3].

In order to overcome the prediction of the exit temperature a properly-developed model was considered relying on an algorithm used by Chen [2-3].

Table 1. *The main composition elemental structure (in percents)*

C	46,2
H	5,1
O	35,4
N	1,4
(ash)	1,3
Moisture	10,4%

The aim is to calculate the composition of the product gas entering the gasification zone in terms of CO, H_2, CO_2, H_2O, CH_4 and N_2.

At the same time it was considered an optimization evaluation in order to succeed in getting a superior efficiency.

3. Results

The algebraic method is one of the most used procedures to resolve systems of nonlinear equation in Matlab.

In this way, the algorithm has some elementary parts:

1. The model requests the elemental composition and the work temperature
2. the software computes the enthalpy variations in order to succeed in reaching the process temperature
3. in the third stage, the program succeed in building the linear equation system and obtains the syngas composition found on the basis dry syngas.
4. evaluate the process temperature and compute the evolution sense of the chemical reaction
5. using the energy balance the next step temperature variation could be found

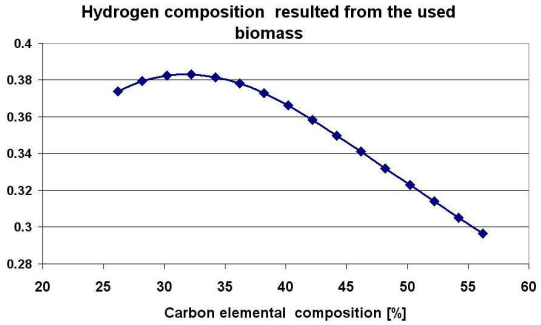

Fig 1. *Hydrogen resulted composition from the used biomass*

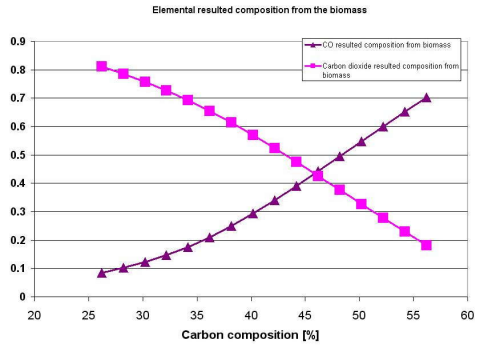

Fig 2. *Carbon monoxide and carbon dioxide resulted composition from the used biomass.*

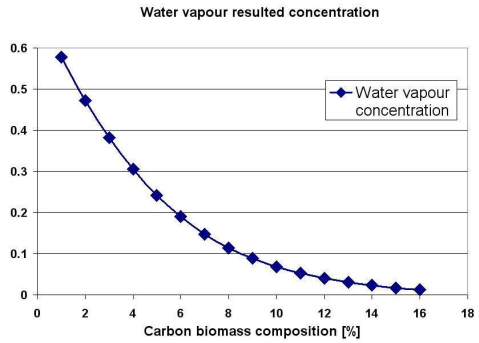

Fig 3. *Water vapour resulted composition from the used biomass.*

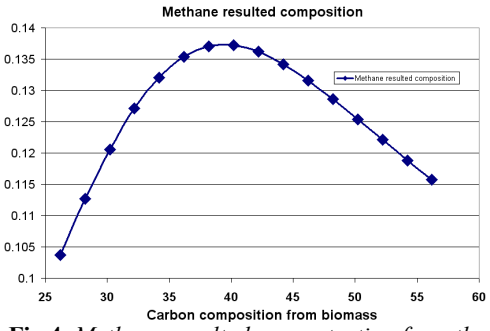

Fig 4. *Methane resulted concentration form the used biomass.*

Our study is only a preliminary debate with a view to succeding in analyzing the carbon composition variant influence on the elemental composition in terms of CO, H_2, CO_2, H_2O, CH_4 and N_2. At the same time, a preliminary software validation is made.

4. Simulations Results and Discussions

In many similar papers three of the parameters are studied (air inlet temperature, chip size and moisture content). In this way, they are operating parameters over which the user has control and the remaining two parameters (heat loss and throat angle) are functions of the gasifier design.

At the same time, the influence of the burned chips should be included in a coherent study. Thus gasifiers with shorter reactor lengths need small chips. With the same environmental conditions, larger chips also undergo the same fast conversion but because of their size, complete conversion may not be possible.

Larger chips undergo the remaining slow conversion and thus need a longer reactor length prior to leaving the gasification zone. As a result of faster char conversion, smaller chips increase the conversion efficiency compared to larger chips.

Generally speaking, the sizes of chips used in the gasifier varied from 1 to5 cm. But, in general, 5 cm chips are preferred due to their lower preparation cost, which is significant for the commercial gasifiers.

5. Conclusions

The goal of the study was to demonstrate the concept of a biomass air gasification process to produce fuel gas having a higher heating value with less tar formation. The experiments were conducted to investigate the impacts of parameter variation such as carbon composition influence composition in terms of CO, H_2, CO_2, H_2O, CH_4 and N_2. At the same time, is made a preliminary validation of the considered software model

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Un algoritm numeric pentru rezolvarea unei probleme de echilibru chimic

Rezumat

Acest articol prezintă un model matematic pentru procesele termochimice într-un gazeificator de biomasă. Modelul combină echilibrul chimic şi echilibru termodinamic de reacție, estimează compoziția finală produsa a gazelor, precum şi temperatura de reacție. Odată ce conținutul de gaze produse este obținut, o serie de parametri pot fi calculați, cum ar fi eficiența gaz rece de gazeificare, cantitatea de apă disociata în procesul de încălzire.