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Predicting the syngas hydrogen composition by using a dual stage equilibrium model

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ABSTRACT

This paper presents an analysis of hydrogen syngas composition obtained by biomass gasification when simulated by a dual stage equilibrium model. The numerical model takes advantage of the carbon boundary point (CBP) concept to study the hydrogen production at maximum energetic and exergetic efficiencies. The numerical simulation was carried out using three large biomass residues available in Portugal: coffee husks, pine residues and vine pruning wastes. It was concluded that the three biomass substrates showed similar trends at different operating conditions and the vine pruning wastes showed the best hydrogen outputs. The computed results were also compared with pilot scale experimental data obtained for coffee husk residues. The numerical results differ from experimental data, but in both cases the hydrogen composition has similar changes taking into consideration the effect of different operating conditions. It was concluded that the hydrogen molar composition increases steeply with a steam to biomass ratio (SBR) below the CBP and with a slow rate above the CBP, up to an asymptotic value. Similar behavior was found considering the temperature effect on hydrogen production. It was also found that energy efficiency first increases with the SBR up to a maximum value and then decreases.

1. Introduction

The European Parliament has set a mandatory target for all energy consumption in the European Union, that the minimum share for renewable energy should be 20% [1]. The conversion of biomass to energetic products is expected to contribute a significant portion to the renewable energy matrix. In Portugal, there is a high availability of biomass for such purposes. Large amounts of lignocellulosic residues such as coffee husks, pine residues and vine pruning wastes are produced as waste products by the commercial (food and beverage), agricultural and forestry industries [2].

A detailed study of the types and amounts of available biomass in Portugal was performed by Ferreira et al. [2]. It was reported that the potential energy derived from pruning residues from vineyards, fruit-trees and olives was 2190 GWh/year and from forestry residues it was 11,578 GWh/year. However, these biomass materials have not been adequately characterized and more significant data is needed to consider its use in advanced energy conversion technologies.

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There are several methods to convert biomass feedstocks to electricity production, but it is expected that biomass gasification will become the dominant technology in the future [3] even comparable to combustion. Additionally, hydrogen is expected to play a major role in future energy scenarios, namely, replacing fossil fuels to some degree and to offer an excellent solution as an energy source for the transportation sector [4]. In fact the use of hydrogen as an energy carrier has several advantages, namely [4]:

- Hydrogen has a high specific energy on a mass basis and is not detrimental to the environment.
- Hydrogen is a very flexible option, both as a direct fuel supply for different transport vehicles or generating electricity by using fuel cells.
- Hydrogen can be stored over long periods and safely transported in pipelines.
- Hydrogen can be obtained from fossil fuels as well as from renewable sources.

Most of the traditional technologies for hydrogen production are fossil-fuel based, with 80–85% of total world production being derived from natural gas via steam-methane reforming [5], which is a very energy intensive process and releases large amounts of carbon dioxide and other greenhouse gases. In spite of this, hydrogen can also be obtained by more environmentally friendly processes such as biomass gasification [6]. Indeed, it is expected that in a not too distant future biomass gasification could be the most efficient and economical route for hydrogen production [7].

Over the past few years, research and development have made significant advances in the gasification of biomass [8]. It has been demonstrated that biomass gasification in a fluidized bed with pure steam has can potentially generate a 60% by volume H_2 rich gas (dry basis). This percentage can even be higher when the steam gasification is coupled with a CO_2 sorbent in the gasifier bed. The gasification mechanisms are very complex and the variables that have been shown to have significant effects on the outcomes are the gasifying medium, operating temperature and pressure, SBR, moisture content and equivalence ratio, among others [8].

Considering the gasifying medium, air gasification has an advantage that is an exothermic process, but also has inherent disadvantages of producing a low heating value gas (LHV 5.6/MJ/Nm^3), small amounts of hydrogen and considerable unwanted products. The use of oxygen streams with high purities, up to 40% (v/v) for example, generate a higher LHV but also imply higher production costs and lead to poor hydrogen content. Indeed, most of the time, steam gasification is the primary solution selected for commercial and research options to evaluate the hydrogen production possibilities concerning the biomass gasification.

A full factorial procedure of physical experiments to evaluate the effects of all variables and interactions would be expensive to gather and, therefore, simulating gasification with numerical models offers a practical alternative. Two methods for approaching gasification simulation are thermodynamic and kinetic models [9]. The thermodynamic equilibrium approach is very useful for determining design conditions by way of parametric evaluations. This is because thermodynamic methods provide the equilibrium composition of syngas at various conditions. Additionally, the thermodynamic models are also easy to implement and to converge. Unfortunately, it is often assumed that the system is steady-state but to estimate the syngas composition or other operating parameter at any point of space and time it is necessary to use a kinetic approach (which includes reaction kinetics and transfer phenomena).

The assumptions related to the equilibrium model are easily obtained when a bubbling fluidized bed is considered, as follows in this paper.

Several equilibrium models have been used to predict syngas composition from different biomass substrates [10–13]. A recent approach for modeling the gasification of biomass using thermodynamic methods considered the CBP, which means that at a particular reaction stage there is no carbon formation and gasification is fully achieved. Below the CBP, unconverted carbon still remains and both the gas and solid phases coexist. Above the CBP, only gas species are found. Thus, below the CBP there is a heterogeneous equilibrium stage and above it is a homogeneous equilibrium stage. Below the CBP, the relevant chemical reactions are the exothermic methane formation, endothermic water-gas and Boudouard reactions. The homogeneous equilibrium stage includes the water-gas shift and methane formation reactions. The CBP method is advantageous because both energetic and exergetic efficiencies are targeted [14–16]. Karamarkovic and Karamarkovic [17] developed an equilibrium model using the concept of CBP method for a parametric study. Gasification conditions were optimized by evaluating the effect of pressure, moisture content and heat addition on the exergetic and energy efficiencies. In this study, air was the

Table 1 – Ultimate and proximate analysis of coffee husks, pine residues and vine pruning waste.

Biomass properties	Coffee husks	Pine residues	Vineyard residues
Ultimate analysis (%)			
N	5.2	0.1	2.6
C	40.1	51.5	41.3
H	5.6	6.5	5.5
O	49.1	41.9	50.6
Proximate analysis (%) [19,20]			
Ash	2.5	0.41	3.1
Volatile Matter	83.2	73.6	83.6
Fixed carbon	14.3	15.6	13.3
Empirical formula	$CH_{1.676}O_{0.918}N_{0.111}$	$CH_{1.510}O_{0.610}N_{0.002}$	$CH_{1.598}O_{0.919}N_{0.054}$