POTENTIAL FOR HYDROGEN PRODUCTION FROM BIOMASS RESIDUES IN THE VALENCIAN COMMUNITY

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ABSTRACT

The production of hydrogen from renewable sources is essential to develop the future hydrogen economy. Biomass is an abundant, clean and renewable energy source and it can be important in the production of hydrogen. The Valencian Community due to its great agricultural and forestry activities, generates an important quantity of biomass residues that can be used for energy generation, approximately 778 kt of wet biomass residues per year. This great quantity of biomass can be transformed into a hydrogen-rich gas by different thermochemical conversion processes. In this article the potential of production of hydrogen-rich gas is analyzed, considering several factors affecting the conversion yield of these processes. As a result of this analysis it could be possible to produce 1271 MNm^3 of H_2 per year considering the total biomass residues of the community and selecting the gasification processes.

Keywords: *Hydrogen, Biomass, Gasification*.

1. INTRODUCTION

The constant growth on the energy demand and the concern of the society for the climatic change caused in great measure by the consumption of fossil fuels, makes necessary to look for environmentally friendly energy sources that can be developed in a sustainable way. The hydrogen is called to be the fuel of the future and it can be obtained from renewable energy sources. At the moment, most of the hydrogen production is obtained from natural gas based on the steam methane reforming (SMR) process that has important CO_2 emissions, for each kilogram of H_2 produced by this process it is emitted 13.7 kg of equivalent CO_2 [1]. Another method for production of H_2 at competitive prices is coal gasification, but this method would emit approximately double CO_2 than the SMR process. Biomass is a renewable energy source that, due to its chemical composition can be used for hydrogen production by thermochemical conversion processes like pyrolysis and gasification. In the article it will be compared the steam gasification and air gasification of biomass for hydrogen generation.

The use of biomass instead of fossil fuels for hydrogen generation would contribute to reduce the atmospheric emissions, for its well-known cycle of carbon where CO_2 emissions are considered null when is taken in account the gases absorbed in the process of photosynthesis of the plants. The biomass in the Valencian Community (C.V) is an abundant energy resource, and its use to generate hydrogen could help to a quicker and sustainable local transition toward an economy based on this fuel, besides to an increase of the percentage of contribution of the renewable energy sources in the primary energy consumption.

There are several technologies for hydrogen production from biomass, they can be divided into two main categories: biological and thermochemical processes. The first category includes: Direct biophotolysis, indirect biophotolysis, biological water-gas shift reaction, photo-fermentation and dark-fermentation. The themochemical processes are pyrolysis and gasification.

The pyrolysis of biomass takes place by heating it at high temperatures, about 650-800 K, at 0.1-0.5 MPa in absence of air. It can be classified in slow and fast pyrolysis, the main product of the slow one is charcoal so it is not suitable for hydrogen production. The fast pyrolysis is the process where the biomass is heated quickly in absence of air, to form gas, liquids and solids.

Studies about the pyrolysis of the biomass have been carried out by Demirbaş [2],[3] using diverse catalysts and different types of biomass, using Na_2CO_3 he obtains 62.9 % of gas volume of hydrogen-rich gas from olive-husk, for tea waste 59.7 % and for cotton cocoon shell 50.9 %, also Chen et al. made an analysis of catalytic effect in pyrolysis, achieving hydrogen yields of 49.5 % of gas volume for rice straw and 51.4 % for sawdust using Cr_2O_3 as catalyst [4].

Biomass gasification is the incomplete combustion of biomass and is carried out at high temperatures, approximately 1273 K, with a partial oxidation of the biomass producing different gases like H_2, CO, CO_2, CH_4, C_mH_n and charcoal. This mixture is call syngas and can be reformed in a water shift reaction process to transform the CO into H_2, increasing the hydrogen yield.

Currently, biomass gasification is considered as one of the most promising thermochemical technologies [5]. Coal gasification is a proven technology, with large-scale processes currently in place for the production of H_2 for use in the chemical industry (primarily for ammonia production). Thermal, steam and partial oxidation gasification technologies are being developed around the world [6].

In general the hydrogen is considered as a highly dangerous fuel, but it has been used in the industry for many years, the high flammability of the hydrogen makes it risky if it accumulates and mixes with air could, but as it is the lightest element a ventilated space will disperse the fuel very quickly avoiding any dangerous situation. It is true that the use of hydrogen can be dangerous, but not more than the use of petroleum or other gaseous fuels [7] if it is handled with care.

The gasification of biomass to produce hydrogen could be dangerous, if very high temperature and pressure are reached an explosive mixture could be formed in the reactor [8], but separating the hydrogen for safety and practical purposes this technology wouldn't represent a big risk and could contribute to reduce the risk of hydrogen transportation by producing the hydrogen on-site, which would reduce the use of long distance transport (pipeline or road) and the potential risks associated to these operations[9].

2. BIOMASS GASIFICATION PROCESS

The gasification process is carried out in the presence of oxygen, and the yield is affected by operation parameters like temperature, gasification agent, residence time, etc.

Different types of biomass gasifiers have been used for the production of hydrogen, obtaining diverse yields depending on the operation parameters and the type of reactor, as shown in Table 1 for steam gasification. The use of catalyst can increase the yield of hydrogen, Wei et al. showed that in steam gasification dolomite can increase hydrogen yield reaching 45 % mol of the product gas for legume straw and pine sawdust while the production of tar is reduced [10].

Table 1. Hydrogen production yields via steam gasification.

Reactor Type	Feedstock	Hydrogen (% vol)	Reference
Downdraft	Sawdust	35.39 at 870 ºC	[11]
Fluidized bed	Sawdust	57.4 at 850 ºC	[12]

Another gasification process is the gasification in supercritical water that is carried out when the moisture of the biomass is higher than 35 % or when water is added to the process; this process can have a gasification yield of 100 %, as well as a high volumetric rate of hydrogen of around 50 % [13], [14].

3. BIOMASS RESOURCES

In the C.V a great quantity of biomass waste is generated by different industrial and agricultural activities, citric fruits, olive tree, almond, grape and cereals. The main crops of the community generate 609 kt of residues per year and represents 78 % of the total biomass generated in the C.V. The biomass generated consist of agricultural and forestry residues, waste from the production of olive-oil, and the residues of gardening activities, all these biomass consist mainly in woody biomass that represents the 75 % of the total biomass, followed by the straw of cereals with 20 % and of the remains of the production of olive-oil with 5 % and are shown in Table 2.

Table 2. Total Biomass waste in the C.V [15]

	Agricultural biomass	Forestry	Olive-oil residue	Gardening	TOTAL (t/year)
Total (t/year)	609102	111350	37523	20192	778169
% Total	78	14	5	3	100
Composition					
% Straw	25	0	0	30	156739
% Woody	75	100	0	70	583906
% Other	0	0	100	0	37523

To make the analysis of the potential of production of hydrogen it was considered that the composition of the biomass was homogeneous according to the type of residue, to calculate the potential of the woody biomass it was considered the composition of sawdust, for the straw of cereals it was considered the composition of rice straw and the remaining biomass is olive-oil residue; in Table 3 is shown an average composition of each one of the residues that were considered representative of each type of biomass.

Table 3. Biomass composition [16]

Biomass Type	Ultimate Analysis (wt %) daf[a]					Proximate Analysis (wt %)				LHV (MJ/Kg)
	C	H	N	S	O	Moisture	Ash	Volatile matter	Fixed Carbon	
Rice Straw	44.2	6.2	0.8	-	48.8	9.96	15.23	69.11	5.70	14.93
Sawdust	52.22	5.55	1.57	0.068	40.6	12.27	0.83	70.55	16.35	17.77
Olive-oil residue	49.08	5.59	1.14	-	44.19	8.83	5.12	68.75	17.3	16.19

[a] Dry ash free biomass

4. ANALYSIS AND RESULTS

The yield of hydrogen from biomass varies according to the technology used, the operating parameters, and the composition of fuel used. To do the forecast of H_2 potential, the gasification process was considered the technology of hydrogen production for this analysis. To analyze the potential of the residues of the C.V, it was supposed a yield for each residue type according to the gasification reactions described below. It was compared the potential of hydrogen production of air gasification and steam gasification.

In general the biomass gasification reaction can be written:

$$nC_xH_yO_z + mH_2O + wO_2 \rightarrow x_1CO + x_2H_2 + x_3CO_2 + x_4CH_4 + x_5H_2O + x_6O_2 \tag{1}$$

If is considered that the fractions of CO_2, O_2 and H_2O formed in the gasification are mainly the products of the combustion to get the necessary energy to perform the gasification and cover the energy losses included in the efficiency of the gasification reactor, and also that the CH_4 production is negligible, the reaction to obtain hydrogen from biomass can be reduced to:

$$nC_xH_yO_z + mH_2O \rightarrow x_1CO + x_2H_2 \tag{2}$$

which is the general equation for biomass gasification and could be followed by the shift reaction:

$$x_1CO + x_3H_2O \rightarrow x_4CO_2 + x_5H_2 \tag{3}$$

these general equations are similar to those proposed by Turn et. al. in [12], to obtain the theoretical hydrogen production.

The energetic efficiency of a gasification process, generally known as the cold-gas efficiency [5], can be determined as:

Cold gas efficiency (%) = LHVgas / LHVbiomass (4)

where LHV_{gas} and $LHV_{biomass}$ are the net heats of combustion (lower heating values) of gas and biomass, respectively.

The energetic efficiency for the gasification process can be considered as 79 % get from the performance data of a gasifier published by Alfonso et. al. [17] for a real bubbling fluid bed gasification plant showed in Figure 1.

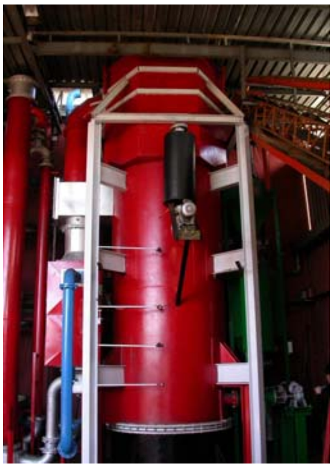

Figure 1. Bubbling fluid bed gasifier (courtesy of EQTEC Iberia, S.L. and Energía Natural de Móra, S.L.).

The energy efficiencies were evaluated with the LHV of the components, for H_2 it was 120 MJ/kg and for CO 10.1 MJ/kg. The theoretical value of hydrogen is obtained considering only the total hydrogen present in the chemical composition of wet biomass (including moisture). The yields of H_2 are expressed in grams of hydrogen per kilogram of wet biomass with the weight percentage of moisture and ash indicated in Table 3 for each kind of fuel.

For the theoretical potential production of hydrogen with the air gasification process based on the general equation for biomass gasification (2) and according to the percentage of C, H, and O present in the composition of the biomass showed in Table 3, the chemical reactions for hydrogen production from rice straw air gasification can be as follows:

$$CH_{1.7}O_{0.8} + 0.2H_2O \rightarrow CO + 1.05H_2 \tag{5}$$

from sawdust:

$$CH_{1.3}O_{0.6} + 0.18H_2O \rightarrow CO + 0.83H_2 \tag{6}$$

and from olive-oil residues:

$$CH_{1.4}O_{0.7} + 0.14H_2O \rightarrow CO + 0.84H_2 \tag{7}$$

Following these reactions and considering air gasification, the hydrogen production is shown in Table 4. For each kind of residue it was obtained the quantity of hydrogen and CO produced according to the reactions described before, for straw material it was used equation (5), for woody biomass equation (6) and for olive-oil residues equation (7).

Table 4. Potential of hydrogen from Biomass air gasification

	Straw[a]	Woody[b]	Olive-oil residue
Total Biomass available (kt/year)	156	583	37.52
H_2 Theoretical (g/Kg biomass)	59.28	62.99	58.77
CO Theoretical (g/Kg biomass)	790.45	1 062.53	979.43
H_2 Production (MNm^3)	103	409	24
H_2 Energy production (TJ)	1 115	4 413	264.61
Biomass energy (TJ)	2 340	10 373	607.46
H_2 + CO Energy (TJ)	2 366	10 680	635.8
Gasification Energy (TJ)	457	2289	132
Biomass to Hydrogen Efficiency	0.47	0.42	0.43
Process Efficiency	0.79	0.81	0.82

[a] For straw residues production it was considered the production from rice straw

[b] For woody biomass it was taken the sawdust reaction

The water gas shift reaction in this process was not considered for H_2 production therefore CO remains present in the gas. The energy that could be produced only from hydrogen would reach 5 793 TJ. The total Primary energy consumed in the C.V is 512 437 TJ [18], the energy content in the generated hydrogen is equal to 1.13 % of the primary energy consumption in the C.V and adding the energy from the CO it reaches the 2.67 % of the energy. Substituting the equal energy from the use of automotive fuels by the hydrogen produced energy, could be avoid 397.110 kt of CO_2 per year, considering an emission factor of 68.544 t CO_2 per terajoule consumed.

In this process a mixture of explosive gases is formed and the presence of air as gasification agent could make the gas reach its flammability limits, therefore monitoring the gases concentration becomes necessary to control the oxidant – gas relation, and so reduce the risk of an accident.

To obtain the theoretical production of hydrogen by the steam gasification of wet biomass it was used the general equation for biomass gasification (2) and according to the percentage of C, H and O of the biomass composition included in Table 3. After gasification of the biomass it was considered the water gas shift reaction based on equation (3), where the CO reacts with water molecules to produce more hydrogen. The reactions that would be carried out by the steam gasification process and shift reaction for the different biomass feedstock are included in equations 8, 9 y 10.

from rice straw:

$$CH_{1.7}O_{0.8} + 1.2H_2O \rightarrow 2.05H_2 + CO_2 \tag{8}$$

from sawdust:

$$CH_{1.3}O_{0.6} + 1.4H_2O \rightarrow 2.05H_2 + CO_2 \tag{9}$$

and from olive-oil residues:

$$CH_{1.4}O_{0.7} + 1.3H_2O \rightarrow 2H_2 + CO_2 \tag{10}$$

The production of hydrogen by steam gasification is given in Table 5. To obtain the theoretical efficiency of the process it was also added the necessary energy for steam production besides the gasification energy. The energy of steam production is calculated considering the energy necessary to vaporize water to 200 ºC and perform the complete gasification and the shift reaction of the CO formed.

Table 5. Potential of hydrogen from Biomass steam gasification

	Straw[a]	Woody[b]	Olive-oil residue
H_2 Total (g/Kg biomass)	115.74	155.58	139.91
H_2 production (MNm^3)	201	1010	58
H_2 Energy production (TJ)	2 177	10 901	630
Steam energy (TJ)	262.91	1 600	90.09
Gasification Energy (TJ)	457	2 289	132
Biomass energy (TJ)	2 340	10 373	607.4
Biomass to hydrogen efficiency	0.62	0.67	0.67

[a] For straw residues production it was considered the production from rice straw

[b] For woody biomass it was taken the sawdust reaction

The quantity of hydrogen generated in total by all the wet biomass residues would be 1 271 MNm^3 of hydrogen per year and it is equal to 13 708 terajoules per year.

The production of hydrogen starting from biomass according with the established yield would be approximately equal to 2.68 % of the primary energy consumed in the C.V. This energy would save 939.65 kt of CO_2 per year if is substituted the equal amount of energy from the use of automotive fuels.

In case of steam gasification, the presence air could be limited so the risk of reaching the flammability limits could be lower than the air gasification, so the process could be considered safer than air gasification process, however the risk exists and hydrogen concentration in the produced gas is higher, so safety measures should be taken.

5. CONCLUSIONS

The technologies of pyrolysis and gasification of biomass can be used for the production of H_2 in a sustainable way, giving an energy use of the biomass residues generated in the C.V. Of these two technologies, the gasification technology is more suitable for gas production, although both of them are still in process of improvement and investigation.

In accordance with the reactions for the calculation of the potential of hydrogen production, it would be possible to generate 1 271 MNm^3 of hydrogen per year by steam gasification; this is equal to 13 708 terajoules per year. This quantity of hydrogen would represent 2.68 % of the primary energy consumed in the C.V. This energy would save 939.65 kt of CO_2 per year if is substituted an equal amount of energy from the use of automotive fuels.

In case of air gasification, if is considered only the energy of the produced hydrogen to get the energy efficiency, it will be lower than that from the steam gasification process, but if the energy from the CO is added, the efficiency it higher than the steam gasification efficiency.

Although the energy efficiency of the steam gasification process is lower than that of air gasification considering the hydrogen-rich gas energy, the amount of energy compared with the energy of the hydrogen-rich gas of the air gasification process is greater.

Although the production of hydrogen is possible with the current technology, the yields reported will be lower and the later processes of purification of the resulting gas to obtain high purity hydrogen will decrease the energy efficiencies of the process.

To consider the establishment of a hydrogen production plant from biomass, safety measures should be taken due to the hydrogen explosiveness, but this kind of plants with a distributed production scheme could present lower risks than a big centralized plant for hydrogen production, reducing the transport distance between production plant and consumer in a hydrogen based economy.

To be able to carry out a better analysis of the potential of hydrogen production, gasification studies should be made according to the type of biomass present in the C.V since the yield varies depending on the composition of the fuel used, gasification agent, among other factors.

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