# GREEN LABELED HYDROGEN FROM THE ORGANIC WASTE OF SÃO PAULO'S MARKETS AND STREET FAIRS

Uri Stiubiener [1,*], Gilberto Martins [1], and Adriano Gomes de Freitas[1]

[1]*Graduate Academic Program on Energy, The Federal University of ABC – UFABC , Santo André , SP, Brazil,*
*uri.s@ufabc.edu.br, gilberto.martins@ufabc.edu.br, adriano.gomes@ufabc.edu.br*

## ABSTRACT

Street markets of the city of São Paulo produce around 360 tons/day of vegetable solid waste (VSW) which is practically all food waste. The VSW collected by the city is currently sent to sanitary landfills. This study evaluates the potential for generating "green hydrogen" from this VSW. The treatment of VSW from street markets and supply centers can produce biogas through anaerobic digestion. This biogas can be purified into biomethane and then reformed into hydrogen. Hydrogen production from methane reforming is a well established process. Using biomethane will produce "*Green Labeled* $H_2$". Based on the projected population growth of the city, the estimated VSW production will reach 410 tons/day by 2043. In this scenario, all of the generated VSW is collected and used for this process. Plants around São Paulo have a potential to provide adequate treatment for this waste and produce 1,585 $t/year$ of "*Green Labeled* $H_2$" by 2043.

**Keywords:** Biobased products, Biomethane from organic waste, Energy transition, Sustainability, Waste valorization.

## Introduction

About a third of the food produced in the world is wasted and discarded as waste [1]. In addition to being a waste, this material ends up being a problem for cities and the health of the population when disposed of improperly. Street markets in the city of São Paulo produce around 360 t/day of VSW. The VSW collected is currently sent to sanitary landfills [2]. The treatment of the VSW can generate methane, by purifying the biogas produced via anaerobic digestion of these organic wastes.

Hydrogen gas ($H_2$) is seen as a vector for the energy transition, aiming at a new energy sustainability model to meet global demand as the concentration of greenhouse gases (GHG) in the atmosphere increases. A great growth of the world demand for this gas is expected to face global heating.

The colors assigned to o $H_2$ refer to the raw material from which it was produced and to the technology used. Fig.1 shows this color code.

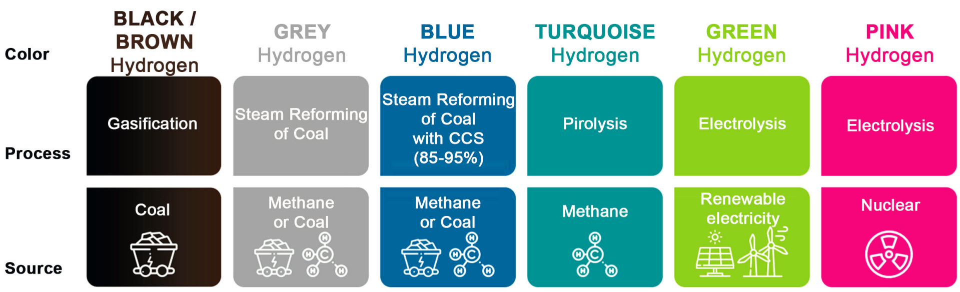


Figure 1: The $H_2$ color code. Source: IRENA, 2020

Several technologies are used to produce $H_2$. The currently most used technologies are natural gas steam reforming, with or without carbon capture and storage (CCS), resulting in the so-called gray and blue hydrogen; coal gasification (with or without CCS); biomass gasification; ethanol steam reforming, and water electrolysis.

In 2021, 98% of the global produced $H_2$ (94 million tons) was of fossil origin using conventional carbon-intensive production technologies. 75% of it was from Natural Gas Steam Reforming, and 23% was from Mineral Coal Steam Reforming [3]. Natural Gas is mainly methane ($CH_4$). $CH_4$ reforming, with or without carbon capture and storage (CCS), is the most currently used technology to produce $H_2$. It has the highest efficiency of 71-72% and the lowest cost, based on data from the Hydrogen Analysis Resource Center (HYARC) [4] (Fig.2).

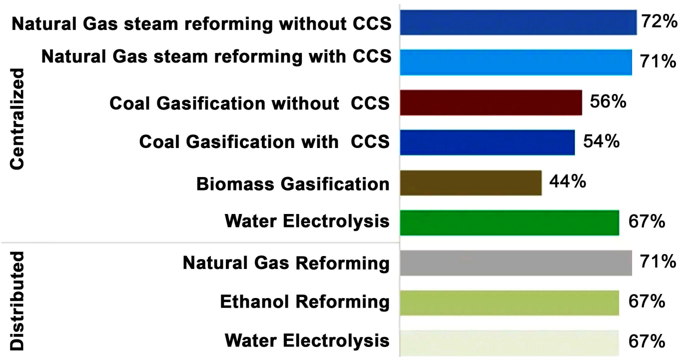


Figure 2: Efficiencies of the $H_2$ production processes. [4]

The carbon footprint of these production processes varies between 9 and 20 $kg\ CO_2/kg\ H_2$, depending on the fuel used and the efficiency of the applied technology [3]. Other, less used processes, are: reaction of simple exchange of acids with metals, reaction of hydrates with water, pyrolysis (thermal decomposition of hydrocarbons by the action of heat) etc.

This article analyzes the use of $CH_4$ produced from organic wastes, called biomethane, to produce hydrogen therefore classified as "Green Labeled $H_2$".

## Scope and methodology

The objective of this research was to evaluate the potential of $H_2$ production from VSW biogas plants to be installed in the city of São Paulo. To achieve this goal, the anaerobic digestion process was investigated to identify recent developments and new techniques to improve and optimize the efficiency of digesters [5]. The theoretical biogas production from the collected VSW was calculated, and the purification processes to obtain biomethane were evaluated. The following equations were used:

Eq.(1) The theoretical dry mass conversion rate to methane (TMCR) in $(Nm^3\ CH_4/kg)$ [6],

$$TMCR = \frac{22,4}{8} \times \frac{(4\times C)+(1\times H)-(2\times O)-(3\times N)-(2\times S)}{(12,017\times C)+(1,0079\times H)+(15,999\times O)+(14,0067\times N)+(32,065\times S)} \tag{1}$$

where $C, H, O, N\ and\ S$ are the molar fractions of these elements

Eq.(2) The maximum dry mass conversion rate (MMCR) in $(kg\ CH_4/kg\ of\ substrate)$,

$$MMCR = TMCR \times (1-\%A)\times\rho \tag{2}$$

where $\%A$ is the content of ash on dry basis and $\rho$ is the density of $CH_4$

Eq.(3) The expected $CH_4$ production (EMP) in $(kg\ CH_4/kg)$

$$EMP = EF \times MMCR \tag{3}$$

where $EF$ is an empirical efficiency factor

Eq.(4) Natural Gas reforming process

$$CH_4 + H_2O \longrightarrow 4H_2 + CO_2 \tag{4}$$

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## Results and discussion

### A. Material Characterization

VSW is a raw material with heterogeneous shape and dimensions . The apparent density of VSW is in the range of 200 to 600 $kg/m^3$. It contains, in average, 16% of contaminants witch should be removed for further biologic processing (plastics, metals and glass). The moist content is high, over 70% on wet basis. The immediate composition of this biomass is 90.8% volatile solids and 9.2% ash. A typical ultimate analysis is: 48%C; 6%H; 3%N, and 0.8%S. Its high heating value (HHV) is 20 $MJ/kg$ on dry basis. The low heating value (LHV) of VSW is only 5.5 $MJ/kg$ on a wet basis. Due to the high water content, thermochemical processes are not recommended.

### B. VSW treatment process

After a pre-treatment in which plastics, metals, and glasses are separated and removed, the organic material must be ground and diluted. The most suitable reactors for these flow rates are Continuous Flow Stirred Tank Reactors (CSTRs). These biodigesters without solids retention mechanisms, are considered the standard technology for wet anaerobic digestion of denser substrates, such as VSW [7].

Due to the large amount of fibers in VSW, a two-stage process was chosen. For the first stage, hydrolysis, the substrate diluted to 15% of total solids content will be placed in a reactor with vigorous mechanical agitation with a hydraulic retention time (HRT) of 5 days. This will allow better control of this step of the process. The reactor should be made of stainless steel, as a pH range of 5.2 to 6.3 is required for this phase at room temperature.

In this stage, complex molecular bonds such as carbohydrates, proteins, and fats are broken down by enzymes in a biochemical process by a specific group of bacteria into simple organic compounds (monomers) such as amino acids, fatty acids, and sugars. Insoluble organic matter is converted into soluble organic matter by the action of fermentative bacteria. Proteins, lipids, and carbohydrates (polymers) are converted into smaller molecules. This stage consumes water.

The hydrolyzed material then goes to the second stage in a CSTR, where the digestion process is completed. Acidogenesis, acetogenesis, and methanogenesis will convert the hydrolyzed materials to propanoic acid, butanoic acid, lactic acid, and alcohols, as well as $H_2$ and $CO_2$; then to ethanoic acid, $H_2$ and $CO_2$, and then, to acetic acid, $H_2$ and $CO_2$.

The temperature of the CSTR of 35-37°C is ideal for the methanogenic archaea to perform the final conversion of acetic acid, $H_2$ and $CO_2$ to biogas.

In addition to biogas, this process produces liquid and solid effluents called digestates. Digestates have low biochemical oxygen demand and can be used as fertilizers or sent to municipal wastewater treatment plants through the sanitary sewer network.

### C. Biogas production

VSW can be represented by the formula $C_{4,000}H_{6,000}O_{2,063}N_{0,214}S_{0,025}$ which allows the calculation of the theoretical dry mass conversion rate to methane. Eq.(1) results TMCR = 0.529 $Nm^3\ CH_4/kg$ in d.b. As ashes are 9.2% of the dry mass, and $\rho_{CH_4} = 0.717\ kg/Nm^3$, from Eq.(2) MMCR= 0.345 $kg\ CH_4/kg$. Although the MMCR gives an approximate idea of the expected production, gas production will be lower due to several factors, including: a fraction of biomass, 5 to 10%, is used by microorganisms to synthesize cellular material; part of the material is lost with the effluent; fibrous compounds are poorly degraded; limitations due to insufficient nutrients; part of the material may not be accessed by microorganisms. Using the empirical $EF = 0.725$ in Eq.(3), the expected gas production, EMP, is 0.250 $kg\ CH_4/kg\ VSW\ d.b.$. Fig.3 shows a schematic representation of the proposed process and a preliminary mass balance.

From the 360 t of VSW daily collected in the city of São Paulo, after separation and removal of plastics, metals ans glass, the remaining 300 t/d of wet material contains 86 t/d of solids. The expected production of the CSTR is a mix of gases containing 21.5 $t/d\ CH_4$ + 39.0 $t/d\ CO_2$, and 0.5 $t/d$ of other gases, totaling 61 $t/d$ of biogas.

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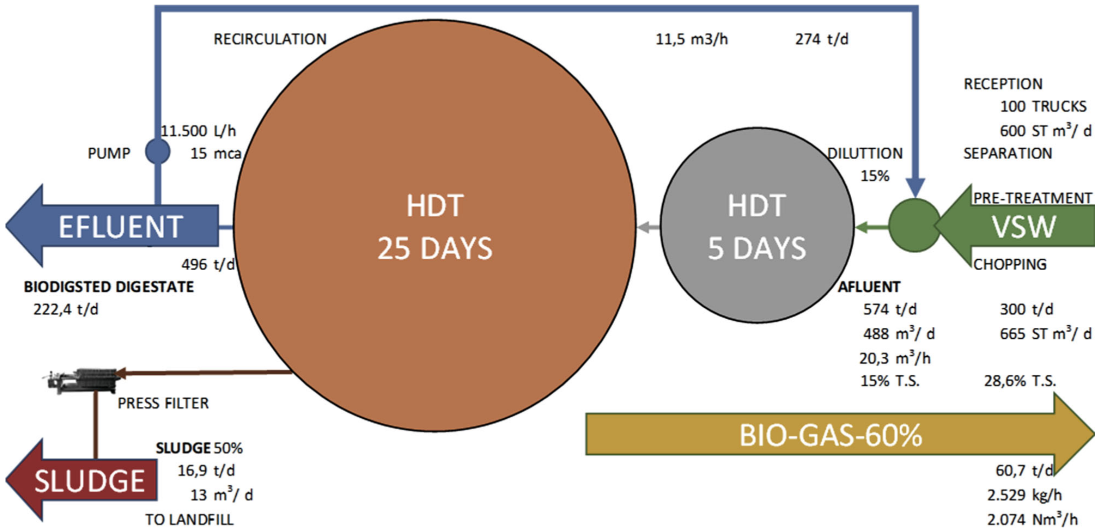


Figure 3: Process Diagram

Biogas is colorless, relatively odorless and flammable, which burns with a blue flame, composed of $CH_4$, $CO_2$ and other gases. This biogas has a typical molar composition of 60% methane and 40% carbon dioxide, and its HHV is 33.3 $MJ/kg$.

### D. Biomethane production

Biomethane is a gas consisting essentially of methane, derived from the upgrading of biogas [8]. It is defined as a gas resulting from the biological decomposition of organic products or residues, which has a $CH_4$ content greater than 90% and its HHV is 50 $MJ/kg$. The main characteristics of biomethane are summarized in the Resolution Nº 886, from 29/09/2022, of the National Agency of Petroleum, Natural Gas and Biofuels (ANP).

The biogas upgrading to biomethane, usually followed by compression of the purified gases to 20 $MPa$, can be by chemical methods or by physical methods, in which no chemical reactions occur. Chemical methods are: Absorption in potassium carbonate, calcium hydroxide, sodium hydroxide, among others. Physical methods are: Molecular sieves, Membrane separation, and Absorption in water scrubbing columns. Molecular sieves can result in further purification of biomethane, however, absorption by scrubbing with pressurized water resulted enough to produce biomethane within specifications and is a cheaper process [9].

### E. Hydrogen production

Natural Gas reforming is the same process of biomethane reforming. It is represented by the Eq.(4). This process has an efficiency of $\eta = 71\%$.

From the 21.5 $t/d$ $CH_4$ purified as biomethane from the biogas produced, 3.82 $t/d$ $Green\ Labeled\ H_2$ can be obtained. This production represents 1,390 $t/year$.

## Conclusion

$H_2$ obtained from $CH_4$ steam reforming should be designated as grey, blue, or turquoise. However, since the raw material is organic and renewable (biomethane), and if the power source is also renewable energy, it can be designated a as *Green* $H_2$ because the entire process uses only renewable feedstock and energy. Otherwise a new color should be assigned to this hydrogen. The fossil carbon footprint of this $H_2$ is as low as the $H_2$ produced by water electrolysis using renewable energy. If the process has CCS, then the carbon footprint may be negative.

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The $H_2$ and *Green* $H_2$ economy presents immense challenges. In the National Plan of Energy (PNE 2050), $H_2$ was included as a disruptive technology [10]. The Ten-Years Plan for Energy Expansion (PDE 2031) has an entire chapter dedicated exclusively to $H_2$, demonstrating the importance of this fuel for the country [11]. The Hydrogen Program (PNH2), a study conducted in cooperation with several ministries and with the technical support of EPE, was published in August 2021 [12].

Producing *Green* $H_2$ from waste is a great opportunity. Based on the projected population growth of the city of São Paulo, the estimated production of VSW will reach 410 tons/day by 2043 [13]. Assuming that all of the generated VSW is collected and used for this process, VSW biodigestion and $H_2$ plants around the city would be able to, in addition to providing adequate treatment for this waste, produce 1,585 $t/year$ of "Green Labeled $H_2$". Huge and the most populated cities, as São Paulo, have the opportunity to embrace policies to transform those VSW into Hydrogen all over the word.

The $CO_2$ captured from both the purification and reforming processes (Eq.(4)) can be used for filling fire extinguishers, beverage gasification, or other processes. Carbon capture can also be used to qualify for "carbon credits", which are tradable financial assets.

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