Chapter 12

Generation of Biohydrogen by Anaerobic Fermentation of Organics Wastes in Colombia

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Additional information is available at the end of the chapter

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1. Introduction

1.1. The trouble of organics solids wastes

In the protection of environment, the adequate handling of solids wastes occupy a main place, the integral handling of wastes is a term applied to all activities associated with the wastes management in the society. The main aim is the administration of wastes associated with the environment and public health. The handling of solid wastes is one of the main environmental problems in the cities due to its generations increase simultaneously with the growth of the cities, its industrialization and the increase of population. In addition, the actual life style carries out a high demand of consumption of goods that generally are thrown out in a short time; this generates more production of wastes and therefor having to search for solutions to the final disposition.

A solution for the trouble of the urban solids wastes is the implementation of process of reusing and giving value to the different materials that form what is known as "garbage", with the purpose of obtaining products or sub products that can be to introduce into new economic cycles. The maximization of reusing and giving value to solids wastes carry out benefits as: less consumption of natural sources, reduction of energy consumption, less environmental pollution, better use of the location where the garbage is placed and economic benefits from recovered materials. So the changes of consumption patron and the sustainable production are essential for the reduction of wastes production.

Is very difficult to stop the production of solids wastes, the idea is consider the solids wastes as a source of material reusable, raw matter, organics nutrients, biofuels and energetics fuel. The set of process to recover and treatment the wastes are known as valorization of solids wastes. This production of wastes is due to origin, social context and production activities [1]. During the valorization and reusing of wastes, is necessary take account aspect as recollection and transport, with this is possible to obtain highs benefices by the transformation. Additionally is necessary to include applications of new concepts related to the financial services, decentralized management, community contribution and the options of transformation, valorization and incorporation to economic cycles [2].

1.2. Source of wastes

At the whole world, the solids wastes from different sources are generating negative environmental impact to the nature, the biodiversity and life in the planet. This is caused by the inappropriate disposition of wastes, the increase of population, the processes of industrial transformation, agroindustrial and life habits of people [3]. At the present time, one characteristic of the society is the increase unbridled of the production and accumulation of solids wastes, which are generated without a solution to its final disposition. In the most of cases, this produced an inappropriate final disposition, an increase in the environment deterioration (air, surface water and groundwater, soil, landscape), problems in the public health and personal security [2].

The characteristics of solids wastes changed in function of the main activity (industry, trade, tourism and others), the habits of the population, type of fed, consumption models, environment conditions and others. The solids wastes can be classified according to: the source (domestic activities, institutional, commercial, industry, farming, municipal services and construction); the constitution (recyclable material and non-recyclable) and grade of danger (commons and dangerous).

The present chapter shows the energetic potential of the solid organic wastes generated in Colombia and its capacity to produce biohydrogen by anaerobic fermentation; additionally is presented a research carried out at the Laboratory of Agricultural Mechanization of the National University of Colombia in Medellín between the years 2009 and 2012, which main aim was determinate the initial feasibility to generate biohydrogen from urban organics wastes and to establish some conditions to operate a bioreactor type batch.

2. Generation of solids wastes in Colombia

The quantity of wastes produced depend of factors as: the number of inhabitant in the city, urbanization rate, consumption habits, cultural practices to handle of wastes, the income, the application of technology and industrial development. According to the information reported by the "Superintendencia de Servicios Públicos Domiciliarios" by 2008, see [4], in Colombia were generated daily 25.079 tons of urban solids wastes, 10 million of tons/year, which 77% were domestics (19.310,8 ton); 15% Industrials (3.761,9) and 8% others (2.006,3 ton). In the

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country, the management of wastes is focused to the final disposal in landfill; only 2,4% is dedicated to recycle and valorization [1].

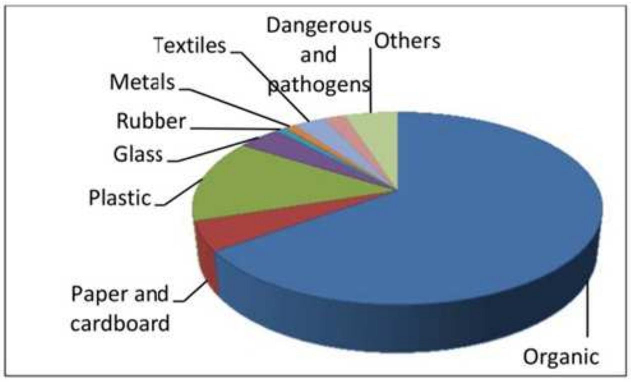
Disposing of wastes	tons/day	Participation (%)	Municipalities
Landfill	22.204	88,5	653
Open dumpsite	2.185	8,7	297
Treatment facility	615	2,4	98
Buried	75	0,3	19
Discharged into rivers		<0,1	10
Incineration		<0,1	11
Total	25.076	100	1.088

Source: [4].

Table 1. Disposing of wastes in Colombia

In the country, the solid wastes are mainly composed of organic material (65%), followed by the plastics (14%), paper and cardboard (5%), glass (4%), other components with minor participation.

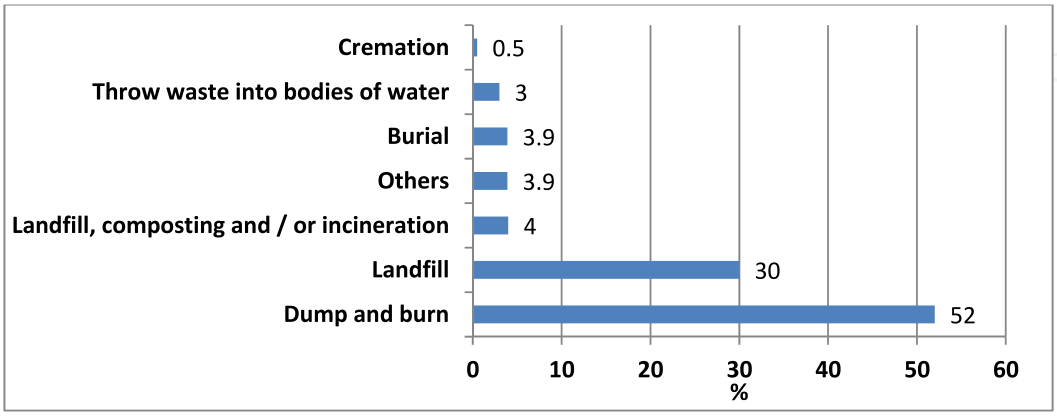
Type of waste	Percentage %
Organic	65
Paper and cardboard	5
Plastic	14
Glass	4
Rubber	1
Metals	1
Textiles	3
Dangerous and pathogens	2
Others	5



Source: [2].

Table 2. Composition of solids wastes in Colombia

In Colombia the major quantity of solid wastes generated are collected and treated by municipal companies (waste from domestic activities, commercials and industrials); however in some regions the problem of wastes solids is very important as the final disposition is made with little control, generating environmental pollution. The production of wastes (kg/habitant/day) is approximately 0,5 kg/habitant/day, oscillating between 1 kg/habitant/day for the big cities until 0,2 kg/habitant/day in the small towns [5]. The "Superintendencia de Servicios Públicos Domiciliarios" published by 2002 a study about the final disposition of the solids wastes in 1.086 cities. The technologies more frequent are: dumpsite and open incineration (52%), then landfill (30 %), and finally the use of composting, incineration and others (18%), [6].



Source: [6].

Figure 1. Final disposition of solids wastes in Colombian for 1.086 municipalities, 2002.

There are two options to solve the problems generated by urban solid wastes which can be applied simultaneously to reach an optimum result:

- The first option according to the National Politics of Solid Wastes is give priority to integral management of solids wastes, focusing the operations management in the reuse and valorization of different materials that integrate the urban solid wastes.
- The second option is to take the wastes and give them an adequate final disposal in landfill operated technically.

The biomass in Colombia has calorific values between 4,384 kcal / kg for stems of coffee and 1,800 kcal / kg for banana rachis [7]. These values are comparable with reports from other countries as China where biomass from agricultural and forest activities have values between 3,827 to 4,784 kcal / kg [8]. In Argentina the lignocellulose biomass has values between 3,000 – 3,500 Kcal / kg and the municipal wastes between 2,000 and 2,500 Kcal / kg [9].

2.1. Colombian normativity about solid wastes

The Colombian normativity related to management of organics solids wastes began with the code of renewable natural sources (decree 2811 of 1974) and were implemented the followed norms:

- Decree 2104 of 1983: management of solids wastes.
- Resolution 2309 of 1986: special solids wastes.
- Law 142 of 1994: Law of public services.

- Decree 605 of 1996: Indications for an adequate cleaning service, from the generation, storage, collection, transport, to final disposition.
- Committee Technical ICONTEC 000019 about environmental management of solids wastes.
- Decree 1716 of August 2002 of "Ministerio de Desarrollo Económico" (In English: Economic Development Ministry) by mean the law 142 of 1994, law 632 of 2000 and the law 689 of 2001, related to the cleaning public service, the law 2811 of 1974 and the law 99 of 1993. The article 8 related to the program for the integral management of solids wastes, which should be realized by the cities in a maximum time of 2 years [10].

2.2. Organic solids wastes and its energetic potential in Colombia

The increase of energy demand in recent decades driven in particular by developed countries and countries with economic growth as Colombia, is leading to rapid depletion of nonrenewable energy resources, increasing pollution and global warming. The alternatives energetics sources emerge as a great option to reduce the adverse effects of this development. The biomass is considered as the alternative energetic source the most potential, according to reports from the World Energy Council [11] it is estimated that energy from biomass will account for 25,4% of global consumption by 2030 and 80% by 2080. Biomass is very varied due to its production and origin, a particular type are the wastes of natural processes, industrial or agroindustrial. It is estimated that Colombia has an energy potential from residual biomass of 449.485 TJ / year, also has a land area of 114,174,800 hectares, of which 44,77% are engaged to agricultural activities, this places to sector as the main source of wastes (with an energy potential of 331.645 TJ / year, mainly from annual and permanent crops). At the second place are the wastes from livestock activities (with an energy potential of 117.747 TJ / year), then the urban organic wastes (wastes from food and homes with an energy potential of 91 TJ / year) and finally the wastes from agroindustrial activities [12].

Among the methods to profit energetically the residual biomass, the anaerobic fermentation is a way of great interest, with this bioprocess is possible to generate a gas with high energy characteristics such as hydrogen and sludge that could be employed as fertilizer on crop. The generation of biohydrogen by anaerobic fermentation of wastes has generated great interest in the last decades. Hydrogen is a promising option as energy source [13, 14], it is a clean renewable resource because its combustion produces only water as emissions, in addition has the highest energy content per unit mass, with a value of 122 kJ / g [13]. The biological production of hydrogen can be seen as a promising option [15], two types of bacteria are involved in the process: acidogenic bacteria which initially to reduce the substrate in H_2 (biohydrogen), acetic acid and CO_2 and the methanogenic bacteria that converted these elements in methane gas. If the purpose is to produce biohydrogen, favorable conditions for the growth of the first type of bacteria (acidogenic) should be provided, inhibiting or eliminating the population of methanogenic bacteria [16]. Currently there are two methods to inhibit this type of bacteria: thermal shock and acidification [17, 18].

The residual biomass in Colombia has a high potential as alternative energetic source, only in wastes of sugar cane, rice husk, coco fiber, coffee pulp, oil palm, bean seed and barley, the potential is 12.000 MW/year approximately. The wastes are produced in different regions of the country and during all year. The country has a potential for generation of biomass of 331’638.720 ton/year, if all agricultural and urban wastes were treated by fermentation anaerobic, could be generated 28’825.609 m^3 of biohydrogen, this might give a energetic potential of 144 GW, upper value to country potential in wind energy (21 GW), tidal energetic potential (30 GW with two coasts) and geothermic energetic potential (1 GW).

In Colombia this quantity of biohydrogen could replace all diesel requested by the diesel electrical plants installed in the country. This has a great important especially in regions without connection to national electrical grid. In the country approximately the 66% of the territory are not connection to national electrical grid, this is 1,4 millions of people, namely the 4% of the population. The country has an installed electric capacity at the region without connection to national electrical grid of 102 MW of which 97 MW are produced by diesel plants, this quantity could be generated, using only the 40% of the urban organic wastes generated at the country. Colombia produces 250.000 tons/year of banana wastes with a potential to generated 100.000 m^3 of biohydrogen by anaerobic fermentation, this represent 500 MW of energy per year, quantity enough to supply the electric energy demand of 200.000 people during a year.

3. Generation of biohydrogen in Colombia

A research in order to determine the initial feasibility to generate biohydrogen from urban organics wastes and then established some conditions to operate a batch bioreactor was developed in Colombia. This section presents the results of this research and analysis the potential use of urban wastes as sources to generate hydrogen.

3.1. Localization

The research was performance between the years 2009 and 2012, at the Laboratory of Agricultural Mechanization of the National University of Colombia in Medellín, localized in 6°13′55″N and 75°34′05″W, with average annual temperature of 24°C, relative humidity of 88% and average annual precipitation of 1571mm.

3.2. Methods

Two stages were established to develop the research, the first had five phases.

3.2.1. First stage

Phase 1. Identification of organic wastes generated at the Central Wholesaler of Antioquia

The Central Wholesaler of Antioquia is the main company dedicated to trade food in the city of Medellín (fruits, vegetable and some grains). At the first phase historical information related to organic wastes production during two year was supplied by Central Wholesaler of Antioquia and was made a photographic register of solids wastes generated. The photographs were taken twice per day at the morning and afternoon.

Phase 2. Selection of wastes with greater production

According to the information collected and the photographic register from the first phase, the wastes with greater production were selected to be introduced into a batch bioreactor.

Phase 3. Elemental Composition and chemical composition analysis

The quantity of volatile solids, total solids and elemental composition on both wet and dry basis (coal, nitrogen and hydrogen) were obtained for each wastes. Were taken samples of 5 grams and the analysis method applied was the Wendee method (the analysis was made at the chemical analysis laboratory of National University in Medellin). With that information was calculated the quantity of wastes to use. Six samples of 3 grams in each wastes were taken in order to obtain the elemental analysis, in this case the method applied was burn of sample and the equipment employed was an elemental analyzer CE – 440 (Figure 2a). The samples were triturated with a precision crusher – IKA WERNE with sieve of 0,5 mm (Figure 2b) and then were dried in a lyophilizer LABCONCO Freezone 12L (Figure 2c). In order to determine the quantity of wastes and water to be employed, 6 grams of volatile solids per liter-day were used as organics load [19], additionally was employed a concentration on volatile solids of 5% [20].

Figure 2. Elemental analyzer CE – 440 (a), Crusher MF Basic- IKA WERKE (b), Lyophilizer LABCONCO - Freezone 12L (c).

Phase 4. Installation of bioreactor

A batch bioreactor of 2000 liters was installed, the wastes were triturated to facilitate its access into bioreactor and its process by the bacteria. The quantity of gas generated was registered with a gas flow meter Metrex G 2,5 with accurate of 0,040 m^3/h; maximum pressure of 40 kPa, additionally was employed a gel of silica to remove the wet of gas. The load of bioreactor was made during four days, each day was used the same quantity until to complete the total load.

Phase 5. Principal variables to register

The relativity humidity and environment temperature were registered daily, was used a thermohygrometer with rank in temperature until 120°C and 100% in relativity humidity (Figure 4). The pH into the bioreactor was registered daily too, in this case was employed a digital pH-meter Hanna Instruments, with accurate of ± 0,2 (reference temperature of 20°C).

Figure 3. Installation of bioreactor and equipment to trituration

Figure 4. Thermohygrometer and pH-meter

The organics load was determined at the beginning and end of bioprocess; in this case the total suspended solids (TSS), total solids (TS), volatile fatty acids (VFAs), chemical oxygen demand (COD) and biochemical oxygen demand (BOD) were determined. The analytics method employed were Standard Method by water and residual water of the APHA-AWWA-WPCF, edition 19 of 1995.

The production of gas was registered daily, samples were collected in Tedlar bags (with capacity of 1 liter, Figure 5) and then were analyzed in a chromatographic gas (Perkin Elmer) to establish its composition (percentage of CO_2, O_2, H_2, CH_4 and N_2). During the tests, the wastes were subjected to an acid pretreatment to eliminate the methanogenic bacteria, after several days, agricultural lime was added to increase the pH until to obtain a value most adequate to the acidogenic bacteria.

3.2.2. Second stage

With the information from the first stage was elaborated an experiment with three treatments and three repetitions, were used three bioreactors of 2000 liters each them. The treatments were integrated by three values of duration to acid pretreatment (3, 7 and 10 days) and three values of pH to operation of the bioprocess (4,5 – 5,0; 5,1 – 5,5 and 5,6 – 6,0). The materials used were wastes of different fruits and vegetal from Central Wholesaler of Antioquia. The wastes were

Figure 5. Gas flow meter and Tedlar bag

triturated and mixed with water in a relation of 1:2,5. In each test were taken samples of wastes and sludge to determinate the organic load, in addition was recorded daily the pH and the gas production. When the pretreatment of acidification ended, agricultural lime was added like at the first stage. The methodology employed to obtain the quantity of gas generated was the same of the first stage, was used a gas flow meter Metrex G2,5 with accurate of 0,040 m^3/h and maximum pressure of 40 kPa. Samples of gas were collected in Tedlar bags and then were analyzed in a chromatographic gas (Perkin Elmer) to determinate its composition.

The organics load of wastes was obtained at the beginning and end of bioprocess; this included the total suspended solids (TSS), total solids (TS), volatile fatty acids (VFAs), chemical oxygen demand (COD) and biochemical oxygen demand (BOD). The analytic method employed was the Standard Method by water and residual water like the first stage. Was calculated the production of gas (liters/day), hydrogen percentage (% de H_2) and yield of biohydrogen (liters of H_2/day).

3.3. Results

3.3.1. First stage

First and second phase: The quantity and percentage of wastes generated at the Central Wholesaler of Antioquia during the year 2011 are show at the Table 3 and Figure 6. The highest production of wastes was associated to cabbage and lettuce leaves then wastes of citrics (orange and lemon) and finally wastes of mango, guava and others tropical fruits. The Figure 7 shows some pictures of wastes in the storage containers at the Central Wholesaler of Antioquia. With the information of production were selected wastes of cabbage and lettuce leaves, orange, mango, papaya and guava to be employed at the bioprocess.

Third phase: The elemental analysis of wastes selected is show at the Table 4. To orange wastes, the relation C/N obtained was less than values reported in others research. In the others cases the results were close to values reported for wastes with similar characteristics. A relation C/N close to 30 is considered appropriate to growth of anaerobic bacteria [22].

Organic wastes	Volumen average month (m^3)
Lettuce and cabbage leaves	360
Orange and lemon	38
Pimento, cucumber	26
Mango	23
Tomato	23
Papaya and guava	22
Total	492
Source: [21].	

Table 3. Organics wastes generated at the Central Wholesaler of Antioquia

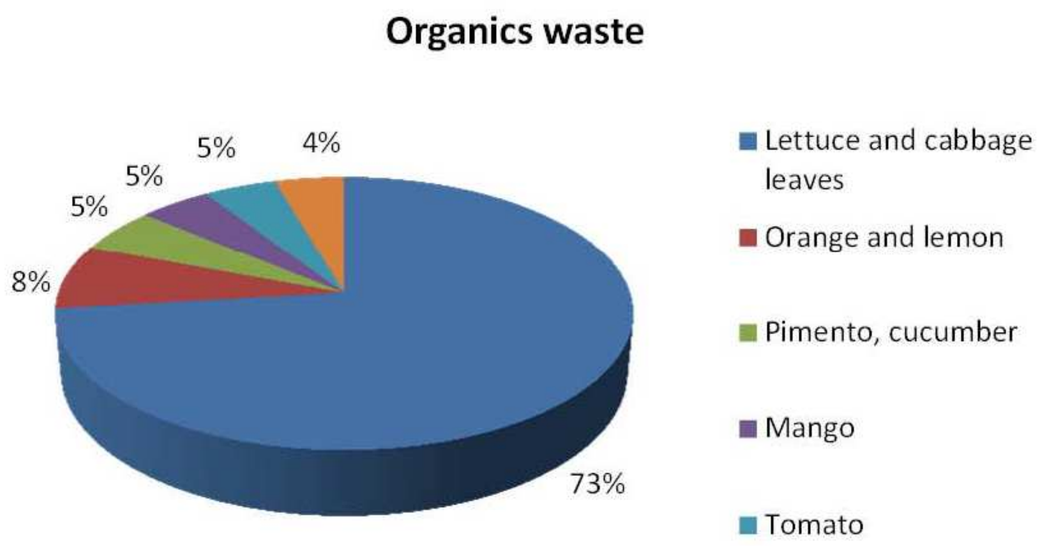


Figure 6. Percentage of wastes generated at the Central Wholesaler of Antioquia, year 2011

Wastes	C	H	N	C/N	C/N (Literature)
Mango	37.6	6.0	1.5	25.9	34.8
Orange	40.6	5.5	1.3	31.5	75.6
Guava	40.9	5.7	1.4	29.2	34.8
Papaya	36.7	5.7	1.3	27.6	34.8
Lettuce and cabbage leaves	37.6	5.3	1.5	25.1	18.0

Table 4. Result of elemental analysis on dry basis (%), (Coil laboratory, National University of Colombia)

Figure 7. Pictures of wastes in the storage containers at the Central Wholesaler of Antioquia

The chemical composition analysis of wastes showed that the highest values of volatile solids were found in the tropical fruits (mango, orange, guava and papaya). The volatile solids are the proportion of the raw material that bacteria using to generate biogas and have an outstanding role during the anaerobic fermentation process.

Waste	ST (%)	SV (%ST)	SV (%)
Mango	97,4	15,1	14,71
Orange	96,6	14,3	13,81
Guava	96,7	15,3	14,79
Papaya	97,1	12,7	12,33
Lettuce and cabbage leaves	86,5	8	6,92

Table 5. Chemical composition analysis, (Chemical composition analysis laboratory, National University of Colombia)

In order to determinate the quantity of wastes to be used was obtained the density of each wastes, to this were taken samples and then were triturated, weighed and finally was calculated the volume to employ. The bioreactor was loaded with 422 kilograms of wastes and 1110 kilograms of water, this provided an average relation (wastes: water) of 1:2,5.

Wastes	Density (kg/l)	So (g SV)/l	Organic load (g SV)/day [19]	Wastes to use (l)	Wastes to use (kg)	Concentration of volatile solid (% SV)/day [20]	Relation (wastes: water)	Water to use (l)
Mango	0,8820	129,7	6,0	22	19	5	1 : 2.94	64
Orange	0,9639	133,1	6,0	22	21	5	1 : 2.76	61
Guava	1,1655	172,4	6,0	29	33	5	1 : 2.96	85
Papaya	1,1907	146,8	6,0	24	29	5	1 : 2.47	60
Lettuce and cabbage leaves	0,4579	31,7	6,0	5	2	5	1 : 1.38	7
Total				102	105			278
Total to 4 days				409	422			1110

Table 6. Quantity of wastes and water to the fermentation process

Fourth phase:

Each waste was triturated and mixed with water during three minutes until to reach an average size of 2 centimeters. In order to reduce the quantity of methanogenic bacteria, the wastes were submitted to acidic conditions during three months with a value of pH close to 3,5. Afterwards was added during three days agricultural lime until to reach a pH of 6,2; in that moment the production of biohydrogen started. The quantity of agricultural lime added was 7 kilograms (Figure 9).

Figure 8. Bioreactor used by the first stage and wastes triturated

Fifth phase:

The organics load showed an important reduction during the process, the total suspend solids were reduced in 83%, the chemical oxygen demand was reduced in 65% and the biochemical

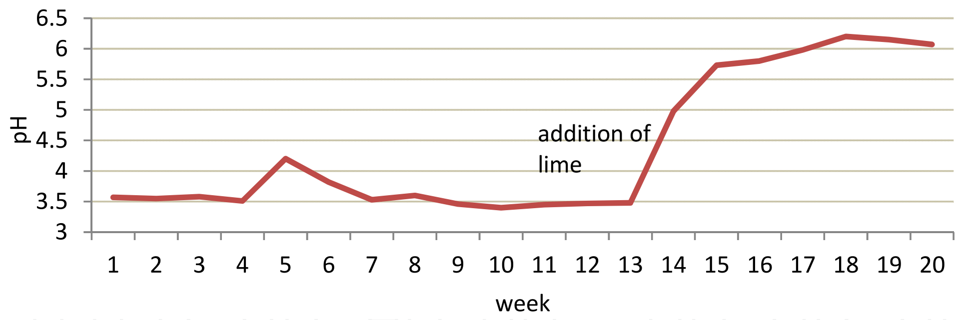


Figure 9. Behavior of pH during the first stage

oxygen demand was reduced in 63,6%. The environment temperature was between 21,8 y 31 °C, this mean that the biohydrogen production was developed under mesophilic conditions. The average relative humidity was between 38 y 73%.

Analysis	Beginning	End
SST (mg/l)	1920	325
STV(mg/l)	54815	8296
ST(mg/l)	62395	9893
COD(mg/lO_2)	54000	19133
BOD(mg/lO_2)	37633	13713

Table 7. Organic load of wastes at the first stage (Laboratory of Sanitary Engineering, National University of Colombia)

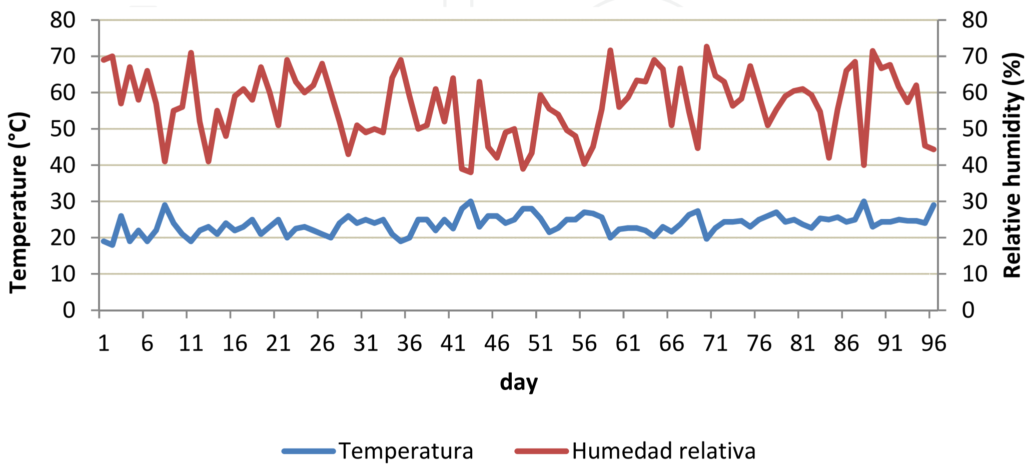


Figure 10. Behavior of temperature and relative humidity average

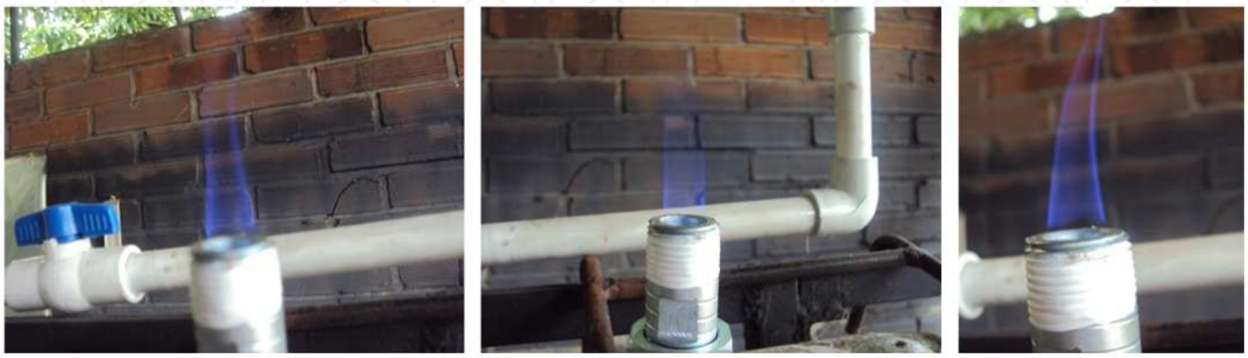
The gas production started three days after application of agricultural lime and continued for 22 days more. The hydrogen (biohydrogen) percentage found in gas ranged between 6,37 y 17,26; with a percentage of hydrogen less than 13,3; there was carbon dioxide and nitrogen in the biogas, however when the percentage of hydrogen was greater than 13,3; the gas composition was only hydrogen and carbon dioxide. The greater value of methane was 1,25% and less was 0%, this mean that the pretreatment to reduce the methanogenic bacteria was satisfactory.

Sample	CO_2 (%)	H_2 (%)	N_2 (%)	O_2 (%)	CH_4 (%)
1	31,79	6,72	48,19	13,06	0
2	70,99	13,31	2,63	0,42	1,25
3	75,67	17,26	0,65	0,096	0,73
4	80,98	13,51	ND	ND	0,6
5	32,80	6,37	48,13	13,16	0,24

ND: not detected

Table 8. Composition of gas generated (Coil laboratory, National University of Colombia)

The total production of hydrogen was 177 liters in 22 days, with a maximum value of 14,5 liters, an average of 7,4 liters of H_2/day and maximum yield of 83 liters of H_2/m^3 of bioreactor. The maximum value of generation of hydrogen was registered 7 days after from started the gas production and the maximum rate of hydrogen generation was obtained between first and seventh days. The Figure 12 shows a several pictures of biohydrogen generated, the color blue is from silica gel used to remove the wet of the gas. The quantity of organic load removed was 26.400 mg/liter of O_2, (COD).



Source: Information personal from research

Figure 11. Pictures of biohydrogen generated

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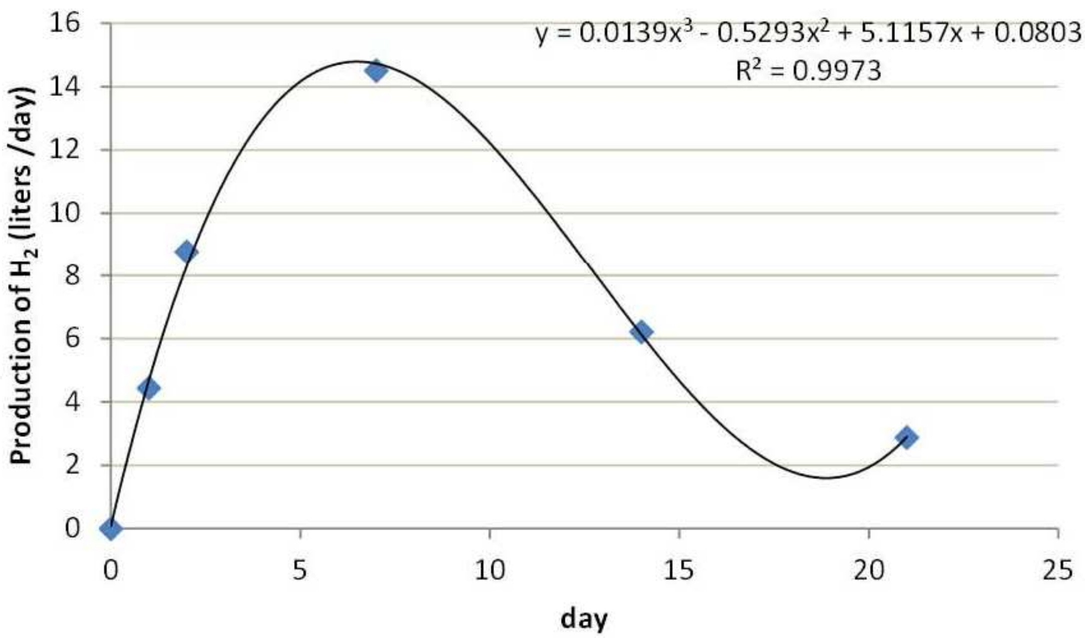

Figure 12. Production daily of hydrogen

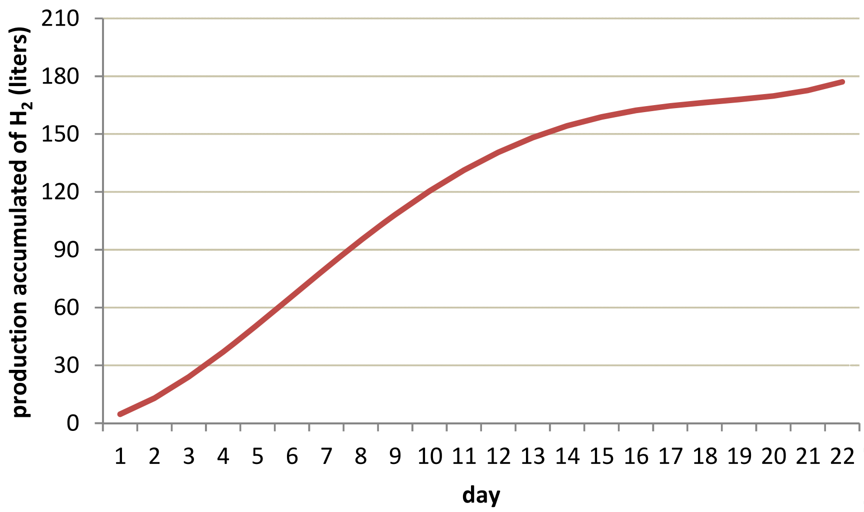

Figure 13. Production accumulated of hydrogen

3.3.2. Second stage

Installation of bioreactors and wastes to use

At the second stage were used the same wastes of first stage, but additionally were employed wastes of tomato, onion, garlic and husk of cape gooseberry (Table 10). The wastes were triturated and mixed with water during three minutes, the relation of wastes: water was 1:2,5 like at first stage. The quantity of wastes employed in each treatment was similar to quantity used at first stage. The volume of work in each bioreactor was 70% and 30% was dedicated to storage the gas generated.

Figure 14. Set of bioreactors employed at the second stage

Repetition	Wastes	Quantity of wastes (kg)		
		T1	T2	T3
1	Lettuce and cabbage leaves, tomato, onion, garlic, pimento, orange, lemon, mango, guava and papaya	506	514	453
2	Lettuce and cabbage leaves, tomato, onion, garlic and husk of cape gooseberry	450	450	450
3	Lettuce and cabbage leaves, orange, mango, guava and papaya	500	500	400
Average		485,3	488	434,3

Table 9. Wastes used in each repetition

The highest values of chemical oxygen demand (COD) were obtained in the treatment 2 during the repetition 1 and the treatments 1 and 3 of the repetition 3 respectively, namely in these cases there were more quantity of food available to the microorganisms.

Analysis	Repetition 1			Repetition 2	Repetition 3		
	T1	T2	T3	T1, T2 y T3	T1	T2	T3
ST (mg/l)	5322	8198	4700	11280	16290	9830	10500
COD (mg/ lO_2)	8667	18000	8000	12000	27140	17940	23340
BOD (mg/lO_2)	7617	10983	6200	5840	24415	3775	14455

Table 10. Organic composition of wastes employed

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Behavior of pH during the pretreatment and operation of bioreactors

Due to type of wastes employed in the repetition 2, was necessary to add muriatic acid into all bioreactors to achieve the pH of acidification, but there were not response (pH between 3,5 and 4,5). However, during the repetitions 1 and 3, in all treatments was used wastes of orange and lemon, this allowed to apply the pretreatment of acidification, afterwards was added agricultural lime and was reached a pH between 5 and 6, values adequate to generate biohydrogen.

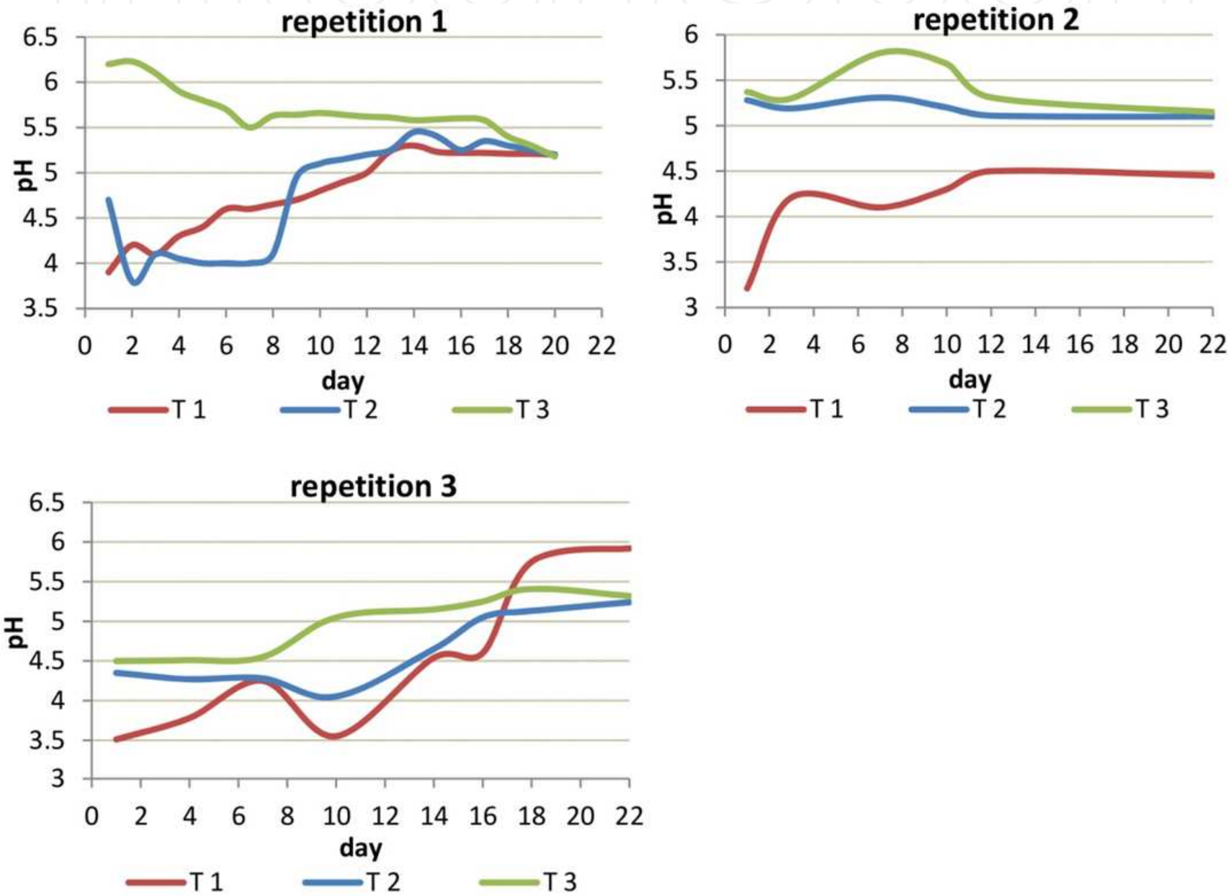

Figure 15. Behavior of pH in each treatment and repetition

Production of biohydrogen

The gas generated in all treatments was compound of hydrogen, carbon dioxide, nitrogen and oxygen. The greater value of methane was 3,7% and the less was 0%, in many times the methane was not detected (ND), this mean that the pretreatment to reduce the methanogenic bacteria was satisfactory. The percentage of hydrogen in gas was between 5 and 18,08; this was the highest value in the research and was obtained in the treatment 3 during the repetition 3 when the wastes used were Lettuce and cabbage leaves, orange, lemon and papaya. In the repetition 2 in all treatments, there were not generation of hydrogen (NG). The oxygen content in some repetitions show maybe that some air entered to bioreactor when the samples were taken.

Treatment	Sample	CO_2 (%)	H_2 (%)	N_2 (%)	O_2 (%)	CH_4 (%)
1	1	35,1	6,7	53,9	3,0	1,4
	2	16,2	6,4	64,8	13,6	ND
	3	18,2	0,02	67,2	13,9	0,8
2	1	40,0	10,5	45,7	0,9	0,8
	2	46,5	7,5	43,7	1,8	ND
	3	34,1	0,02	54,3	7,0	3,7
3	1	40,2	7,7	45,0	2,5	0,4
	2	43,9	7,0	47,0	2,1	ND
	3	4,0	0,02	77,3	18,1	ND

Table 11. Composition of gas generated, first repetition

Treatment	Sample	CO_2 (%)	H_2 (%)	N_2 (%)	O_2 (%)	CH_4 (%)
1	1	NG	NG	NG	NG	NG
	2	NG	NG	NG	NG	NG
	3	NG	NG	NG	NG	NG
2	1	11,4	5,5	41	13,4	0,2
	2	37,8	5,5	36,2	5,4	0,5
	3	20,1	5,7	43,5	12	3,3
3	1	NG	NG	NG	NG	NG
	2	NG	NG	NG	NG	NG
	3	NG	NG	NG	NG	NG

Table 12. Composition of gas generated, second repetition

Treatment	Sample	CO_2 (%)	H_2 (%)	N_2 (%)	O_2 (%)	CH_4 (%)
1	1	29,08	7,5	50,3	3,0	0,2
	2	23,88	6,5	41,7	10,3	2,6
	3	42,14	8,2	36,1	7,1	1,4
2	1	28	7,0	52,2	4,4	0,1
	2	45,29	5,8	38,1	3,0	0,1
	3	40,69	5,3	40,8	3,2	0,1
3	1	8,96	18,0	51,3	12,1	0,2
	2	43,32	6,3	36,5	7,1	0,7
	3	52,85	5,0	30,5	5,1	0,3

ND: not detected
NG: not generated

Table 13. Composition of gas generated, third repetition

The maximum production of biohydrogen per day obtained at the first stage was 15 liters, however at the second stage the maximum production was 38 liters, this mean that the production was duplicated during the second stage. In the repetition 3, in the treatment 3 were generated 32 liters of biohydrogen, meanwhile in the treatment 1 were generated 15 liters. The wastes employed in both treatments were Lettuce and cabbage leaves, orange, lemon and tropical fruits as mango, guava and papaya, the initial pH was lesser to 4,5 during 7 and 8 days, and the pH of bioreactors operation was between 5 and 5,5.

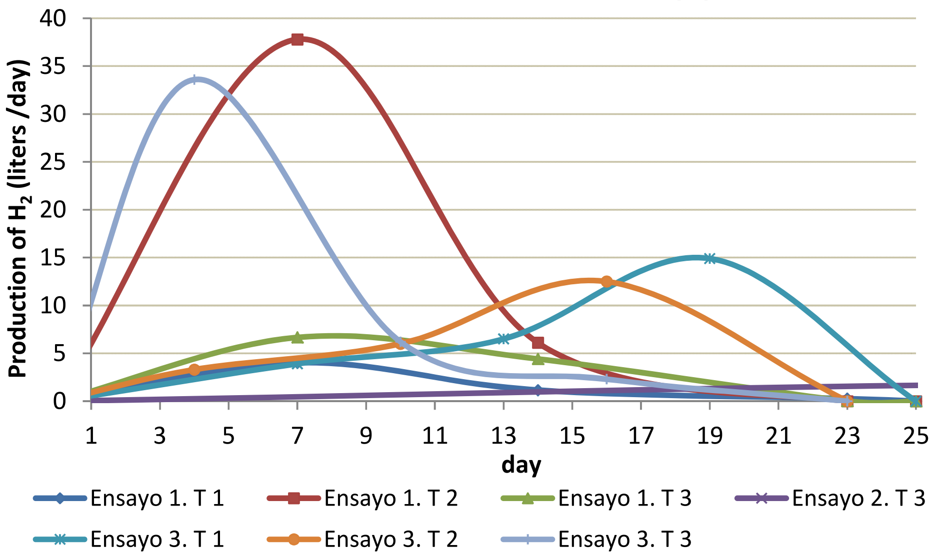

Figure 16. Production of hydrogen

The greater accumulated production was reached in the treatment 2 and the repetition 1, followed by the treatment 3 in the repetition 3. In both cases were used vegetal wastes and tropical fruits in same proportions in addition, initially the wastes were subjected to acid conditions with a pH less to 4,0 during 8 days and a pH for operation of bioreactor between 5 and 5,5. Under those conditions the hydrogen content into gas ranged between 7,5 and 10,5%. The total production of hydrogen in the treatment 2 and the repetition 1 was 317,8 liters in 22 days, with 14,44 liters of H_2/day (twice the result from the first stage), and maximum yield of 159 liters of H_2/m^3 of bioreactor. Other outstanding result was reached when were employed the same wastes, at beginning were applied acid conditions during 7 days under a pH less to 4,5; and then was used a pH for the operation of bioreactor between 5 and 5,5. In this case the percentage of hydrogen into gas ranged between 5 and 18,08% (the last value was the maximum content reached in the research). The production of hydrogen was 231,1 liters of H_2 in 22 days with 10,5 liters of H_2/day (duplicated the value reached from the first stage) and a maximum yield of 115,6 liters of H_2/m^3 of bioreactor.

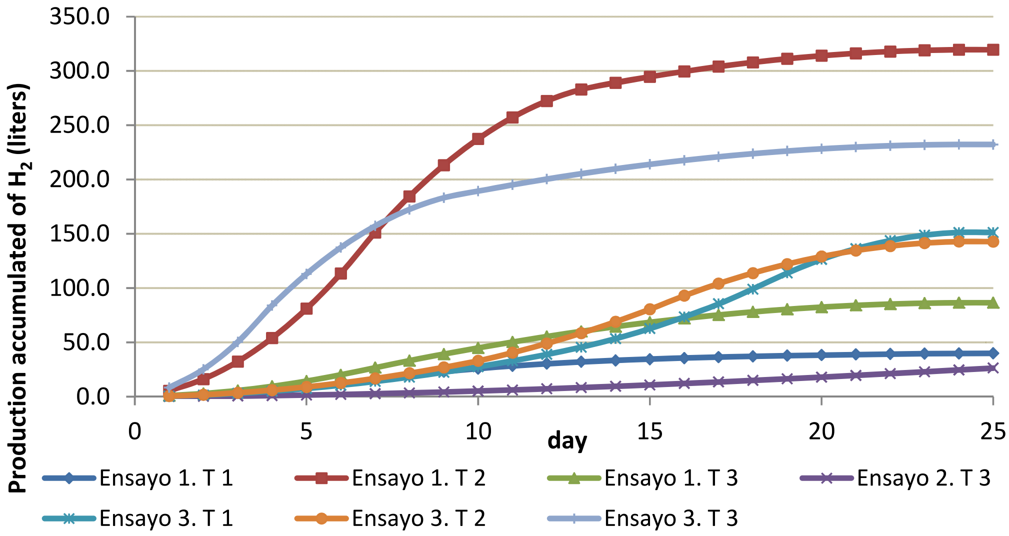

Figure 17. Production accumulated of hydrogen

4. Final analysis

Two treatments showed the highest production of biohydrogen, the treatment 2 in the repetition 1 and the treatment 3 in the repetition 3, the maximum value was obtained with the treatment 2 in the repetition 1 in which were used wastes from lettuce and cabbage leaves, tomato, onion, garlic, pimento, orange, lemon, mango, guava and papaya. The acid conditions were implemented 8 days with value of pH near to 4, the operation of bioreactor was between 5 and 5,5. In the treatment 3 in the repetition 3 were used the same wastes, the acid condition was applied during 7 days with value of pH near to 4,5; the pH of bioreactor operation was between 5 and 5,5. Although was generated more quantity of hydrogen in the treatment 2 during the repetition 1, was in the treatment 3 in the repetition 3 where was obtained the greater hydrogen content in the gas (18,04%) and greater rate of generation of hydrogen.

The maximum production of hydrogen was obtained at the second stage when the pretreatment of acidification was applied during 8 days with a value for the pH of 4, a pH of reactor operation between 5 and 5,5; and a value of chemical oxygen demand (COD) near to 20.000 mg/liter of O_2. At the first stage when was used a quantity of wastes from tropical fruits greater than wastes of lettuce and cabbage leaves, the chemical oxygen demand (COD) initial was 54.000 mg/liter of O_2, however the hydrogen production was significantly less respect to second stage. This indicates that a high value of chemical oxygen demand could inhibit the hydrogen generation; this result is according to reports of different authors [13, 23-29]. When were used vegetal wastes (without wastes of tropical fruits) as lettuce and cabbage leaves, tomato, onion, garlic and husk of cape gooseberry, there were no acid conditions at beginning the process and was necessary to add acid, however there was no response in the biosystems and the pH always was upper than 4,5. Under these conditions there was no production of hydrogen. In addition the chemical oxygen demand was low (12.000 mg/liter of O_2).

The results shows that is feasible to produce biohydrogen (hydrogen) when are employed organic wastes from the Central Wholesaler of Antioquia. The wastes should be submitted to a pretreatment acid with a pH between 3,5 y 4,0; during 7 days (or less), then the operation pH should be increased until a value between 5 and 5,5. The chemical oxygen demand (COD) should be between 20.000 and 54.000 mg/liter of O_2, this is possible to reach when in the bioprocess is employed a proportion similar of tropical fruit waste and vegetal waste.

5. Conclusions

- It was possible to generate hydrogen from organic wastes of Central Wholesaler of Antioquia and to improve the bioprocess.
- The chemical oxygen demand (COD) promoted the biohydrogen production, the best results were obtained to values between 20.000 and 54.000 mg/liter of O_2. These values were achieved with a heterogeneous mix of fruits and vegetal wastes.
- There was not generation of biohydrogen when the bioprocess started with a pH upper than 4. This ratifies that to generate biohydrogen by anaerobic fermentation is necessary to apply a pretreatment, in this research, a pretreatment under acid conditions (pH between 3,5 and 4,0) was successful.
- Colombia has a high potential to generate hydrogen by anaerobic fermentation due to organic wastes available, these wastes could generate until 28’825.609 m^3 of biohydrogen and supply an energetic potential of 144 GW, value upper than the installed potential (13,5 GW).
- The results show that is possible to produce biohydrogen by anaerobic fermentation of organic wastes and providing new sources energetic.

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