



Ecological and Exergetic Analysis of Hydrogen Production in a Sugar-Ethanol Plant

MSc. thesis

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ABSTRACT

This work aims an ecological and exergetic analysis of the hydrogen production by steam reforming of part of the ethanol produced in a sugar-ethanol plant. The Pioneiros Distillery, located in São Paulo, is used as model for this study.

Three cases are described. In case 1 the plant produces energy only for domestic needs. A part of bagasse is not burned and it is stored. In Case 2, all available bagasse is used for production of steam. Part of the steam is used in the production process meeting the demand of the plant and the rest of steam is converted into electrical energy that can be sold at concessionaires. In Case 2 it is produced more energy than in Case 1. Case 3 includes the production of hydrogen by steam reforming of a part of the produced ethanol. Steam and energy for steam reforming is generated from combustion of bagasse.

An exergetic analysis is performed. The exergy flows associated with the sugar-ethanol plant are calculated locating and quantifying the losses and irreversibility.

The ecological impact of use of the bagasse as fuel to generate thermal and electrical energy for the ethanol reformer was studied. The main pollutants that damage the atmosphere, namely: CO, CO₂, NO_x and PM have been taking into account. Carbon Dioxide emissions were calculated taking into account the carbon cycle (considering the absorption of carbon dioxide by the sugarcane during its growth), resulting in negative balance emissions, i.e., carbon dioxide was absorbed in higher amounts than emitted.

The thermodynamics (η_{system}) and ecological (ϵ) efficiencies of Steam reforming of ethanol were calculated. The thermodynamic efficiency was 56% and the ecological efficiency was 80%. When the carbon cycle is taking into account the ecological efficiency is 90%.

The incorporation of an ethanol reformer in a sugar-ethanol plant for hydrogen production is a very interesting option where environmental benefits are obtained. Problems related with the storage of bagasse are avoided because all the bagasse is burned for the production of steam and energy to the reformer. The amount of hydrogen that can be produced in Pioneiros Distillery could supply fuel for 68 buses with a range from 200 to 300 km per day.

SAMMANFATTNING

Arbetet omfattar en ekologiskt och exergetic analys av vätgasproduktion genom ångreformerings av en del av etanol som produceras i en socker-etanolfabrik. Pioneiros Destilleriet, som ligger i São Paulo, används som modell för denna studie.

Tre fall beskrivs. I fall 1 producerar anläggning energi endast för att täcka egna behov. En del av bagass bränns inte i panna och den måste lagras. I fall 2, används all tillgänglig bagass för produktion av ånga. En del av ångan används i process för framställning av etanol och socker och resten av ånga används för framställning av elektricitet som kan säljas vidare. I fall 3 produceras det mer energi än i fall 1. Fall 3 omfattar produktion av vätgas genom ångreformerings av en del av den producerade etanolen. Ånga och energi till reformer produceras genom förbränning av bagass.

En exergetic analys genomförs över processen av vätgasframställning. Exergiförluster och irreversibilitet lokaliseras och kvantifieras.

De ekologiska effekterna av förbränning av bagass för framställning av ånga och energi till etanolreformerings studerades. Man tog hänsyn till utsläpp av kolmonoxid (CO), koldioxid (CO₂), kväveoxider (NO_x) och partiklar (PM). Koldioxidutsläppen beräknades med hänsyn till kolcykeln (sockerrör under sin tillväxt absorberar koldioxid). Det visade sig att större mängd koldioxid absorberas under sockerrörs tillväxt än den släpps ut vid förbränning.

Den termodynamiska (η_{system}) och ekologiska (ϵ) effektivitet på ångreformerings av etanol beräknades. Den termodynamiska effektiviteten var 56 %. Den ekologiska effektiviteten var 80 %. När man tar hänsyn till kolets kretslopp, blir den ekologiska effektiviteten 90 %.

Resultaten visar att införande av ångreformerings av etanol i en anläggning för produktion av etanol och socker är mycket ett intressant och fördelaktigt alternativ, inte minst när det gäller miljön. Problem relaterade till lagring av bagass undviks eftersom all bagass bränns för produktion av ånga och energi till ångreformerings. Mängden vätgas som kan produceras i Pioneiros Destilleriet skulle kunna driva 68 bussar som kör 200 till 300 km per dag.

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OBJECTIVES

This work aims an ecological and exergetic analysis of the hydrogen production by steam reforming of part of the ethanol produced in a sugar-ethanol plant

The plant will be evaluated under the thermodynamic viewpoint, using the First and Second Laws of Thermodynamics. An exergetic analysis will be performed. The exergy flows associated with the sugar-ethanol plant will be calculated locating and quantifying the losses and irreversibility. The exergetic efficiency will be calculated.

The capacity of hydrogen production from available residual bagasse will be evaluated.

The incorporation of hydrogen production in a sugar-ethanol plant will be discussed taking into account the exergetic and ecological analysis. The pollutant emissions (CO₂ equivalent emissions) produced by the combustion of sugarcane bagasse will be characterized.

This work is performed in cooperation with Justo Roberts. Both Tulio Colombaroli and Justo Roberts use the Pioneiros Distillery in São Paulo as model for the analysis of production of hydrogen in the plant. This work focuses on exergetic and environmental aspects related with the incorporation of the hydrogen production. The work of Justo Roberts focuses on technical aspects.

1. INTRODUCTION

The use of fossil fuels is the main source of energy currently. Oil and coal fuels are still the most used around the world. But over the years these fuels are becoming increasingly scarce.

In the search for renewable fuels the ethanol has emerged as a fuel with great potential, because it has advantages in relation to other fuels. Ethanol is a renewable fuel. Ethanol burning occurs more cleanly than gasoline, producing less hydrocarbons and carbon monoxide.

Brazil stands out as a major producer of ethanol. Few regions of the world have so good combination of soil, climate, available land and labor costs for the cultivation of sugar cane like Brazil has. The sugar-alcohol industry in Brazil has great technology in the production of sugar and ethanol and also in the cultivation of sugar cane.

Hydrogen is another fuel that has gained prominence among researchers around the world in recent years. Hydrogen is mainly used in fuel cells. A great advantage of this fuel is that it can be obtained by numerous different sources, non-renewable sources (fossil fuels) like renewable sources such as biomass and ethanol.

The incorporation of hydrogen production from ethanol appears as good alternative, since the feedstock (ethanol) is produced in the own plant. Also the thermal and electrical energy required for ethanol reforming may be provided by using the resultant bagasse from sugar and ethanol production processes.

2. ETHANOL

Ethanol, also called ethyl alcohol, is an organic substance mainly obtained from fermentation of biomass: sugars (sugar cane juice, fruit juice and sugar beet), starch (corn, rice, wheat and potatoes) or cellulose (wood and paper).

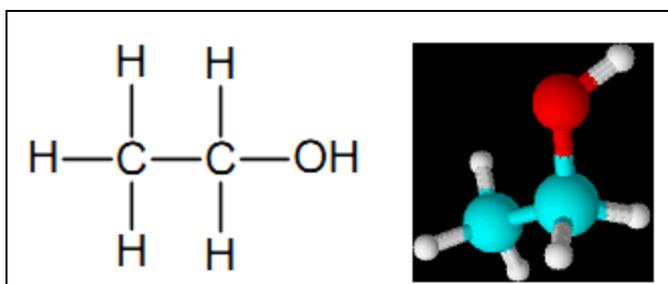


Figure 1– Structural formula and 3D model of an ethanol molecule

Under normal temperature and pressure, ethanol is a colorless substance, volatile, flammable and water soluble. Its molecular formula is C_2H_5OH . Figure 1 shows the structural formula and 3D model of a

molecule of ethanol, the white spheres represent hydrogen atoms; the blue spheres represent carbon atoms and the red sphere the oxygen atom (Silva, 2010).

2.1 USE OF ETHANOL

Ethanol is widely used in various areas of the economy, especially in the perfume industry and in fermentation processes for the production of alcoholic beverages.

2.1.1 Ethanol as fuel

The use of ethanol as fuel has reached a great highlight since it can be used as fuel in internal combustion engines. Ethanol can be blended with gasoline. Today is mandatory the addition of 25% ethanol to gasoline in Brazil. This fact has contributed to decrease the Brazilian oil dependency. The use of ethanol increased significantly with the introduction of flex fuel vehicles in 2003. (FECOMBUSTIVEIS, 2011)

2.1.2 Feedstock for Hydrogen Production

Alcohols can be used as an excellent feedstock for the production of hydrogen, due the decomposition in the presence of water vapor with the production of a mixture rich in hydrogen.

Methanol was an alcohol widely studied as source of hydrogen. However, methanol has high toxicity. Methanol is today produced from fossil fuel. Ethanol is a renewable. It does not present problems of toxicity and it is not harmful to the environment. Ethanol can be an excellent choice for applications in fuel cells.

2.2 HISTORY OF ETHANOL PRODUCTION IN BRAZIL

Although Brazil is a major producer of cane sugar since colonial times, its use was exclusively for the production of sugar. This scenario has changed from the 70's, with the decrease in price of the sugar and the explosion of the oil crisis in 1973 when oil prices increased by more than 300 %.

As most of the fuel used in Brazil was coming from oil and the fact that the country imported most of the oil, the government predicted a risk in the supply and decided to take precautions. It was created the National Alcohol Program intended to replace part of the gasoline with ethanol. That would reduce the dependence on oil and it would also help the sugar producers.

2.2.1 PROALCOOL (National Alcohol Program)

PROALCOOL was a support program to increase the production of ethanol from sugar cane including economic incentives to producers of sugar. In addition to restoring the supply of fuel, another

objective of this program was the modernization of the sugar-alcohol industry from the plantation of cane until the ethanol production.

The Alcohol Program can be divided in two phases: the objective during the first phase was to increase the percentage of ethanol in gasoline to 20 percent. The second phase was characterized by the production of hydrated ethanol (96 % ethanol and 4% water) for direct consumption in vehicles designed for the exclusive use of ethanol. In this second phase the National Council on Alcohol - CNAL and National Executive Committee of Alcohol – CENAL were founded.

PROALCOOL achieved great results surpassing in 15% the original target of 10.7 billion liters/year fixed by the government in the period 1986-87. During this period the ethanol production reached 12.3 billion liters. The proportion of alcohol-fueled cars produced in the country increased from 0.46% in 1979 to 26.8% in 1980 and 76.1% in 1986.

2.2.2 Flex-fuel vehicles (flex)

In 1985, Brazil’s ethanol program began to experience problems. The use of ethanol as fuel was always linked to oil and sugar prices. There was a resistance from automakers to produce pure ethanol-powered vehicles. The interest in ethanol decreased.

Then in 2003, with the emergence of dual-fuel cars there was renewed interest in ethanol. These also called flex-fuel vehicles (flexible-fuel) have the ability to work with more than one fuel. These cars gave the option to the consumer to choose the fuel in the car. The hydrated alcohol forgotten for some years gained market again. The auto industry pushed by environmental concerns became interested in these types of cars. Investments in this type of vehicle led to the development of engine technology and the popularization of flex vehicles mainly in Brazil and the USA. In Europe, Sweden has been prominent in the usage of ethanol as fuel, mainly in buses. Sweden has the largest ethanol bus fleet in the world, with over 600 buses running in the country, mainly in Stockholm. (Green Car Congress, 2011)

In Brazil there are a growing number of these types of vehicles, according to the National Association of Automobile Manufacturers (ANFAVEA, 2011). Sales of flex-fuel vehicles accounted for 86.4% of car sales in 2010. The Table 2.1 shows these results:

Table 2.1 – Vehicle registration (passenger cars and light commercials) by fuel type -locally-manufactured and imported.

Share (%)	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YEAR
Gasoline	9.1	8.1	7.7	8.6	8.9	8.2	7.8	8.4	8.8	8.5	8.1	9.1	8.4
Ethanol	0	0	0	0	0	0	0	0	0	0	0	0	0
Flex Fuel	85.3	87.2	87.9	86.6	85.4	86.2	87	86.8	86	85.9	86.6	85.6	86.4
Diesel	5.6	4.7	4.5	4.8	5.6	5.6	5.2	4.8	5.2	5.6	5.3	5.3	5.2

2.2.3 Analysis of ethanol production in Brazil

Ethanol production in Brazil has been influenced by fluctuating sugar prices and especially the oil price. The adoption of PROALCOOL in the 70s and its end in the 90s played a major role in ethanol production. Moreover, the recovery of oil prices and increased national oil production have led to the decreased of alcohol production. The insertion of flexible-fuel vehicles on the market led to the boom in ethanol production. Figure 2 shows the ethanol production in Brazil from 74/75 to 2010/2011 (UNICA, 2010).

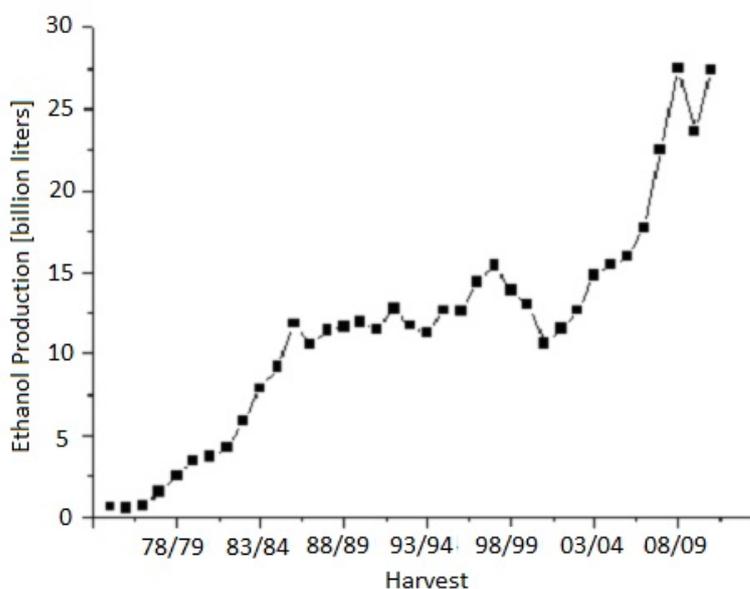


Figure 2 – Ethanol production in Brazil from 74/75 to 2010/2011

2.3 SUGARCANE

Ethanol can be obtained from various sources such as sugar cane, corn, sugar beets and potatoes. But the use of sugar cane for this purpose has many advantages. The sugar cane is one of the few plants that store their carbohydrates as sugar (sucrose) instead of starch. This fact has a great advantage, because starch has to be converted first to sugar and then to ethanol.

The sugarcane also presents a high productivity that can reach 80 to 90 t / ha. As comparison the productivity of the corn is 8 to 9 t / ha. This high productivity of sugarcane is due to the high rate of photosynthesis per unit area of land, influenced by leaf area index (LAI). (Pellegrini, 2009)

Moreover, it can be noted in Table 2.2 some advantages of sugarcane over other primary sources (corn, wheat and sugar beet), such as higher productivity (liters / hectare), higher energy balance, i.e. a greater amount of energy contained in ethanol (Souza, 2010).

Table 2.2 – Comparison of Cane Sugar, Corn, Wheat and Beet

Feedstock	Sugarcane	Corn	Wheat	Beet
Country	Brazil	USA	UE	EU
Productivity	7000	3800	2500	5500
Energy balance	9.3	1.4	2.0	2.0
GHG emission reduction	90%	35%	34%	45%
Cost of ethanol production	22	40	68	68

2.5 ENVIRONMENTAL IMPACTS

The use of ethanol as fuel involved several environmental benefits.

The use of ethanol as fuel contributes to the reduction in greenhouse gas emissions and also it improves the local air quality. Most of carbon dioxide emitted by burning ethanol is reabsorbed during the growth of sugarcane. Combustion of ethanol is associated with lower emissions of carbon dioxide and monoxide as well as lower emission of other gases harmful to the environment, in comparison to combustion of fossil fuels.

The waste from sugarcane industry (bagasse) can be used for cogeneration of heat and power. The combustion of bagasse supplies heat and electricity for alcohol production. Other byproducts as vinasse can be used as fertilizer. (Silva, 2010)

Figure 3 shows the situation with biofuels in road transport in the world (WEC/ENERDATA, 2011):



Figure 3 – Share (%) of Biofuels in Road Transport 2008

2.6 COOPERATION BETWEEN BRAZIL AND SWEDEN

There is already strong relationship between the two countries since a large portion of ethanol used in the Swedish vehicles is coming from Brazil. Swedish companies have research centers in Brazil. The governments are studying the possibility of the intensification of these relationships promoting the common interests of both countries. Brazil has a leading position in the world as exporter of ethanol (UNICA, 2011). Scania has introduced bioethanol buses in Sao Paulo as result as the demonstration activities of the European project BEST - Bioethanol for Sustainable Transport (Ethanol summit, 2011). Recently, the Swedish company Scania and Brazilian VSE (Valley Energy Solutions) signed an agreement for the development of ethanol engines in Brazil.

3. SUGAR-ALCOHOL PLANT

3.1 THE PRODUCTIVE PROCESS IN SUGAR AND ALCOHOL MILLS

The production of sugar and ethanol includes several stages such as harvesting, handling of raw material extraction milling, electricity generation, processing of mixed juice, fermentation, distillation of ethanol, and dehydration. The mixed juice goes through different processes for the production of sugar and ethanol. The overall scheme of production of sugar and ethanol from sugar cane is shown in Figure 4 (Neto, 2002).

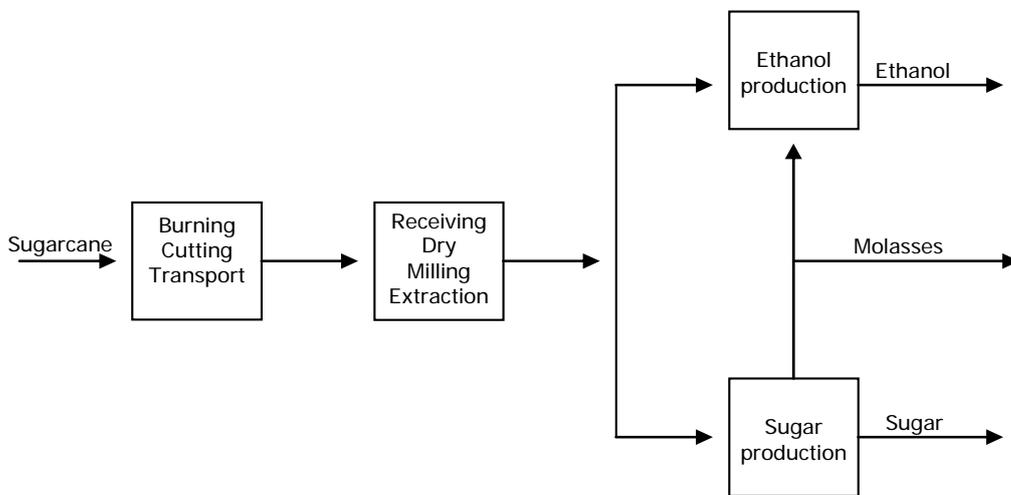


Figure 4 – General flowchart of a sugar-ethanol plant.

3.1.1 Sugar Production

The production of sugar includes a three step juice treatment: Evaporation and concentration, Cooking and Drying. Figure 5 shows the juice treatment for sugar production (Neto, 2002).

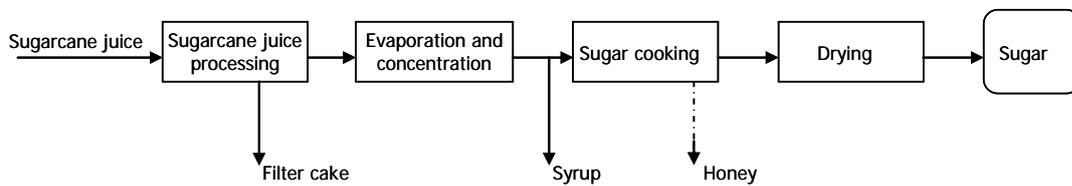


Figure 5 –Detailed flowchart of sugar production.

3.1.1.1 Evaporation and Concentration

The juice from the sugar cane crush has to be purified and it undergoes an evaporation procedure. The concentration procedure includes removal of water and production of sucrose crystals. During this stage the juice is concentrated and the solution reaches 60 to 70 ° Brix (Pellegrini, 2009).

* brix: percentage by weight of soluble solids contained in a solution

3.1.1.2 Cooking

The syrup is boiled for crystal formation. The sugar crystals are allowed to grow in a crystallizer. The sucrose crystals are separated in centrifugals (Pellegrini, 2009). The cooking is certainly one of the most critical steps in the production of sugar, both in terms of product quality and energy consumption. Although there is a tendency towards automatization of this operation, it still depends critically on the ability of operators. (Neto, 2002).

The process is completed by washing with water or steam. The removed honey is collected in a tank and returns to the cookers for recovery of dissolved sugar still present (Pellegrini, 2009).

3.1.1.3 Drying

The sugar from the centrifuges has high moisture content. The sugar is dried and then stored (Neto, 2002).

3.1.2 Ethanol Production

In the process for production of ethanol (figure 6), the treated juice is sent to the preparation wort tank where fermentation and distillation take place (Neto, 2002).

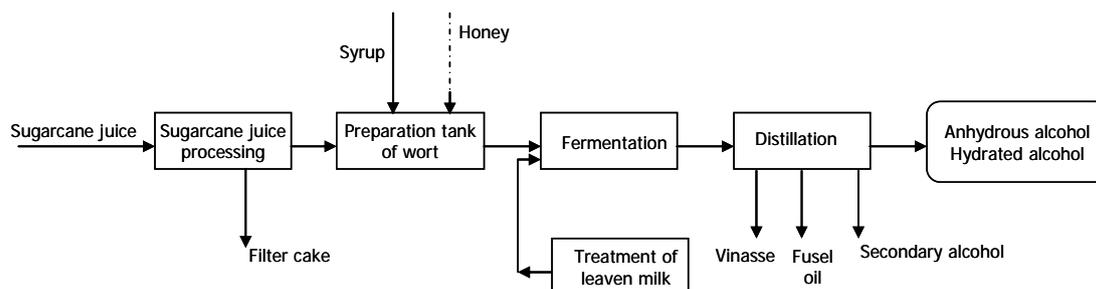


Figure 6 – Detailed flowchart of processes for production of alcohol.

3.1.2.1 Wort Preparation

The wort preparation is a process where syrup and honey are added to the treated juice. Then the wort is fermented.

3.1.2.2 Fermentation

The sugars are converted to ethanol by a process that consists of adding the microorganism *Saccharomyces cerevesae*. This microorganism produces the zimase enzyme that acts as a catalyst transforming the sugars into ethanol. During the reaction, carbon dioxide is produced. During fermentation is produced heat and by-products such as higher alcohols, glycerol, aldehydes, etc.

The fermented wort is then centrifuged and separated in wine and yeast cream. The wine goes to distillation and the yeast cream is diluted in water and treated with sulfuric acid, returning to the process.

3.1.2.3 Distillation

The wine pass through a sequence of distillation columns depending on the type of alcohol and quality desired. Most of the water is removed by distillation. It is obtained ethanol 96° GL (hydrated ethanol, water-ethanol azeotrope with 96 % v/v ethanol and 4 % v/v water), secondary alcohol with 92 ° GL and byproducts like the vinasse, phlegm and fusel oil.

By the addition of small amount of benzene as entrainer, all the water can be extracted and anhydrous ethanol is obtained.

4. STUDY OF SUGAR-ALCOHOL PLANT

The bagasse is burned directly in the boiler producing steam at 2.5 MPa and 300 ° C (high pressure steam). This steam is distributed to the mechanical drives (grinders, rotary blades, grinders, pumps and others) and to the turbines for electricity production.

The exhaust steam leaves the turbine at a pressure of 245 kPa. The steam at low pressure is then used in the production process of sugar and alcohol and to drive devices with low energy needs. The turbines chosen in the process are backpressure turbines. The steam is leaving the turbines with considerable energy potential that allows its use for other purposes. This type of turbine is used in cogeneration systems. Figure 7 shows an example of a topping cycle cogeneration:

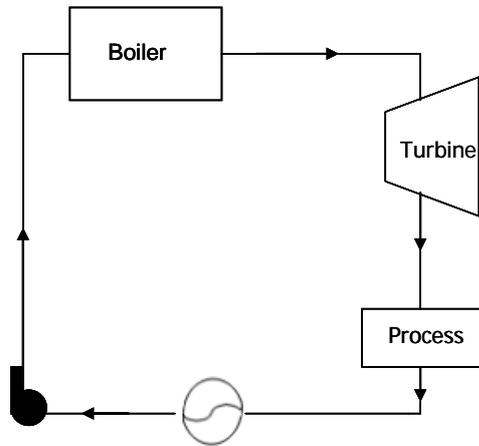


Figure 7 - Topping cycle cogeneration

4.1 COGENERATION SYSTEM

The proposed cogeneration system is based on the “Destilaria Pioneiros” plant and it is presented below in Figure 8 (Fiomari, 2004).

The steam leaving the boiler (Point 1) enters the steam turbine generator (Point 3) for production of electricity and the steam turbines for mechanical drives (Points 7, 9, 11, 13, 15, 17 and 19).

It is necessary to activate two turbines for the preparation of the sugarcane before crushing: Turbine Chopper (Point 9) and Turbine Grinder (Point 11). The extraction of the juice is made with the other three turbines (Turbine Milling 1^a/2^a, Turbine Milling 3^a/4^a and Turbine Milling 5^a/6^a) through double activation, i.e. each turbine drives two mills that are composed of four rolls each one. The remainder of the steam is consumed by the turbine destined to move a boiler feedwater pump.

Leaving the turbine generator, a small portion of exhaust vapor (Point 5) is used to heat the deaerator for removal of oxygen and other dissolved gases from the feedwater to the boiler. The rest of the exhaust steam from turbine generator joins the exhaust steam from other steam turbine for mechanical drives, and then continue to the desuperheater where the superheated steam is cooled to a temperature close to its saturation temperature, by spraying water (Point 23).

The steam returns to the thermal deaerator (Point 24). The water is then pumped to the boilers (Point 25).

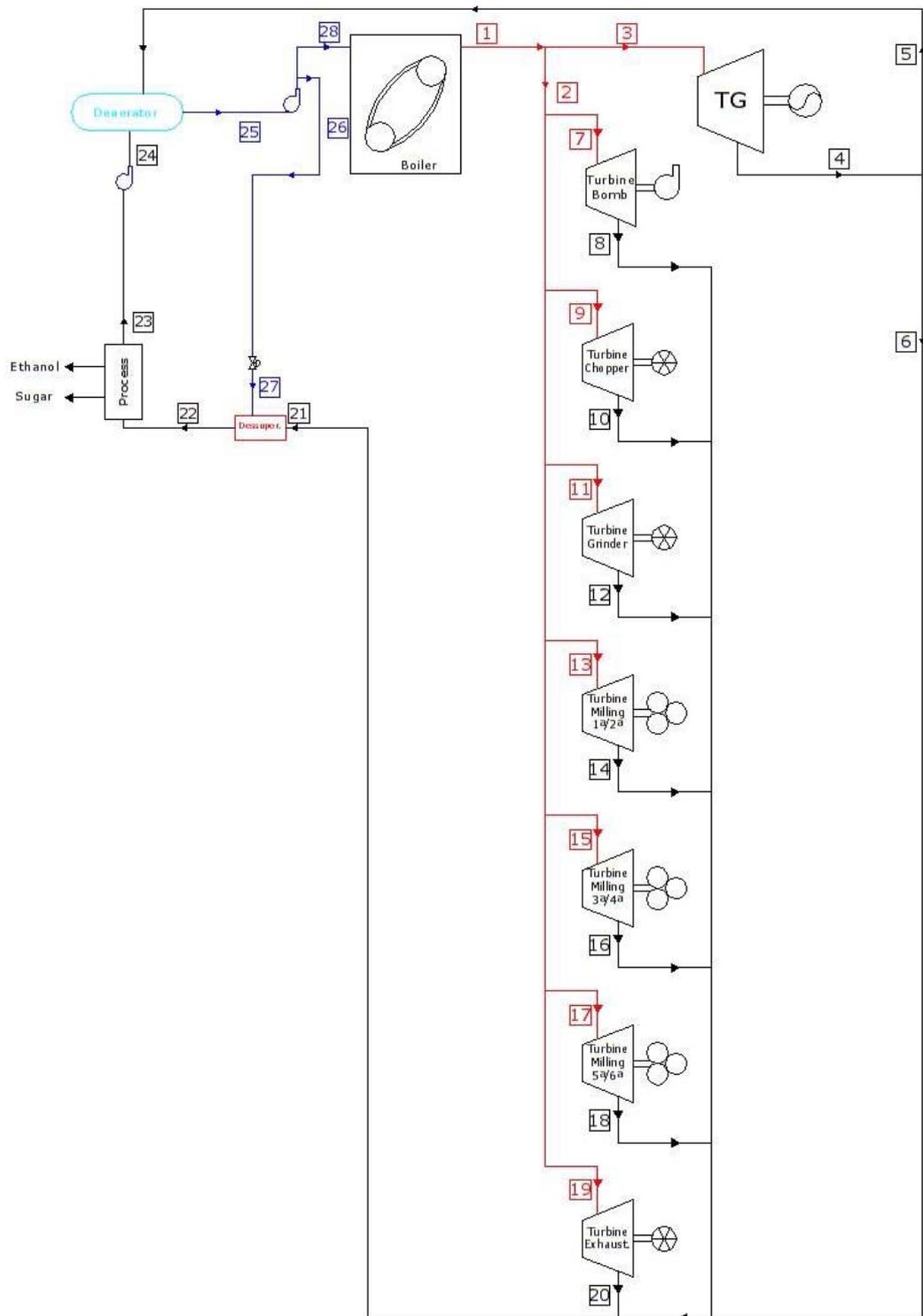


Figure 8 – Cogeneration System of the sugar-ethanol plant.

4.2 CASES

The expectations to 2005/2006 harvest provided in table 4.1 (Fiomari, 2004) have been used for the calculation presented in this study.

Table 4.1 - Expectations for the 2005/2006 harvest “Destilaria Pioneiros”

Cane crushed (t)	1 300 000
Sugar (t)	95 000
Anhydrous alcohol (L)	52 100 000
Hydrated alcohol (L)	714 000

The operating parameters with the days of harvest, effective hours of grinding and milling hourly planned for the 2005/2006 harvest as well as industrial and agricultural efficiencies are given by Table 4.2 (Fiomari, 2004):

Table 4.2 - Operating Parameters to 2005/2006 harvest of “Destilaria Pioneiros”

Parameters	Values	Units
Days of harvest	215	Days
Effective hours of crushing	4 695.60	Hours
Grinding Hours	276.85	t _{sugarcane} /h
Agricultural Efficiency	94.30	%
Industrial efficiency	89.60	%

The crushed sugarcane generates a considerable amount of sugar cane bagasse. The characteristics of the produced bagasse are given in Table 4.3 (Fiomari, 2004):

Table 4.3 - Expectations for the 2005/2006 harvest Distillery Pioneiros

Parameters	Values	Units
Sugarcane fiber content	13.50	%
Bagasse fiber content	47.40	%
LHV bagasse	7 736.00	kJ/kg
Relation bagasse-steam	0.52	kg _{bagasse} /kg _{steam}

Considering the current situation and the emergence of new technologies, three different cases for the use of bagasse are presented

- Case 1: The plant produces energy through the turbine generator only to supply the required internal needs. Thus there is an excess of bagasse, which is not burned in the boiler.
Context: In Brazil there is still no defined policy on the sale of electricity to concessionaires. Although many plants have the potential to produce excess energy, a small number of plants does it.
- Case 2: Use of all the bagasse to produce electricity to be sold to the concessionaires.
Context: Since the adoption of a concrete policy on the sale of electric energy to concessionaires, the plants can increase the economical efficiency by selling power.
- Case 3: Incorporation of hydrogen production by the addition of a steam reformer of ethanol. In this case, part of the thermal and electrical energy generated at the plant will be used in the production of hydrogen.
Context: The production of hydrogen in the plant is very interesting since it can be obtained from the alcohol. Combustion of sugarcane bagasse would provide the required energy for the reformer.

4.2.1 Case 1: Sugar-alcohol Plant. Production of power only for domestic needs

This case is common to many plants currently; the surplus of bagasse is not used, because the plant is not considering selling electricity. The generation of excess steam can cause higher maintenance expenses. Flows of bagasse in this case are described in Table 4.4 (Fiomari 2004).

Table 4.4 - Flows of total bagasse and steam generated, 2005/2006 harvest, Case 1

Bagasse in the boiler	70.50	$t_{\text{bagasse}}/\text{h}$
Total bagasse produced	78.90	$t_{\text{bagasse}}/\text{h}$
Residual bagasse	8.40	$t_{\text{bagasse}}/\text{h}$
Bagasse total residual of the harvest	39 443.04	t_{bagasse}
Total steam generated	135.70	$t_{\text{steam}}/\text{h}$

For Case 1 the Turbine Generator operates below the nominal conditions and the generated power is used to attend the process demand of electricity (Fiomari 2004)

Table 4.5 – Thermodynamic parameters, 2005/2006 harvest, Case 1

Points	m (t/h)	P (kPa)	T (°C)	h (kJ/kg)	s (kJ/kg.K)
1	135.7	2,156	300	3 019.6	6.728
2	78.7	2,156	300	3 019.6	6.728
3	57.0	2,156	300	3 019.6	6.728
4	57.0	245	161	2 788.4	7.234
5	2.9	245	161	2 788.4	7.234
6	54.1	245	161	2 788.4	7.234
7	7.1	2 156	300	3 019.6	6.728
8	7.1	245	215	2 899.0	7.474
9	13.4	2,156	290	2 996.1	6.686
10	13.4	245	165	2 796.90	7.253
11	13.4	2,156	290	2 996.1	6.686
12	13.4	245	165	2 796.9	7.253
13	13.7	2,156	290	2 996.1	6.686
14	13.7	245	174	2 816.1	7.297
15	13.2	2 156	290	2 996.16	6.686
16	13.2	245	174	2 816.1	7.297
17	13.2	2 156	290	2 996.1	6.686
18	13.2	245	174	2 816.1	7.297
19	4.7	2 156	300	3 019.6	6.728
20	4.7	245	185	2 838.1	7.345
21	132.8	245	169	2 806.2	2.274
22	137.0	245	135	2 733.6	7.104
23	137.0	245	100	419.2	1.307
24	137.0	490	100	419.8	1.307
25	139.9	245	105	440.3	1.363
26	139.9	3 920	105	446.4	1.369
27	4.200	3 920	105	446.4	1.369
28	4.2	245	105	443.7	1.372
29	135.7	3 920	105	446.4	1.369

Mass flow (m), pressure (P), Temperature (T), enthalpy (h), Entropy (s) are calculated in the different places of the process (table 4.5) using the total generated steam and the thermodynamic tables.

4.2.2 Case 2: Sugar-alcohol Plant with excess electric power generation

In this case, the flow of bagasse used in the boiler is increased in order to produce surplus electricity (Fiomari, 2004). All the bagasse is utilized and no storage of bagasse is necessary. This is an advantage because the storage of bagasse is a problem in many plants. The values of total flows of bagasse and generated steam are presented in Table 4.6:

Table 4.6 - Data from the grinding, 2005/2006 harvest, Case 2

Bagasse in the boiler	78.90	$t_{\text{bagasse}}/\text{h}$
Total produced bagasse	78.90	$t_{\text{bagasse}}/\text{h}$
Residual bagasse	0.00	$t_{\text{bagasse}}/\text{h}$
Bagasse total residual of the harvest	0.00	t_{bagasse}
Total generated steam	167.87	$t_{\text{steam}}/\text{h}$

The generated electricity surplus can be sold to concessionaires. There is also excess of steam exhaust that can be used, if necessary, to increase production or for other purposes that require high temperature.

The thermodynamic parameters of Case 2 are shown in Table 4.7.

Table 4.7 - Thermodynamic parameters, 2005/2006 harvest, Case 2

Points	m (t/h)	P(kPa)	T(°C)	h(kJ/kg)	s(kJ/kg.K)
1	167.9	2 156	300	3 019.6	6.728
2	78.7	2 156	300	3 019.6	6.728
3	89.2	2 156	300	3 019.6	6.728
4	89.2	245	161	2 788.4	7.799
5	35.1	245	161	2 788.4	7.234
6	54.1	245	161	2 788.4	7.234
7	7.1	2 156	300	3 019.6	6.728
8	7.1	245	215	2 899.0	7.474
9	13.4	2 156	290	2 996.1	6.686
10	13.4	245	165	2 796.9	7.253
11	13.4	2 156	290	2 996.1	6.686
12	13.4	245	165	2 796.9	7.253
13	13.7	2 156	290	2 996.1	6.686
14	13.7	245	174	2 816.1	7.297
15	13.2	2 156	290	2 996.1	6.686
16	13.2	245	174	2 816.1	7.297
17	13.2	2 156	290	2 996.1	6.686
18	13.2	245	174	2 816.1	7.297
19	4.7	2 156	300	3 019.6	6.728
20	4.7	245	185	2 838.1	7.345
21	132.8	245	169	2 806.2	2.274
22	137.0	245	135	2 733.6	7.104
23	137.0	245	100	419.2	1.307
24	137.0	490	100.100	419.8	1.307
25	172.1	245	105	440.3	1.363
26	172.1	3 920	105.800	446.4	1.369
27	4.2	3 920	105.800	446.4	1.369
28	4.2	245	105.800	443.7	1.372
29	167.9	3 920	105.800	446.4	1.369

4.1.3 Case 3: Sugar-alcohol Plant including hydrogen production

In the Case 3 the hydrogen production by steam reforming of ethanol is discussed. Hydrogen widely used in petrochemical industry has also great potential as fuel. It is already used in fuel cells. Reforming of ethanol in sugar-alcohol plants is interesting, because anhydrous ethanol is produced in the plant and the heat necessary to maintain the thermal conditions of the reformer can be obtained by the use of sugarcane bagasse. In the Chapter 5 the production of hydrogen by ethanol reforming is evaluated.

5 HYDROGEN

5.1 INTRODUCTION

Hydrogen has the highest energy content per unit mass (LHV = 119.95 kJ/kg). Usually hydrogen is found in nature combined with other elements, such as oxygen, nitrogen and carbon. Hydrogen can be obtained from various raw materials, using various technologies. (Silva et al., 2009).

5.2 APPLICATIONS

5.2.1 Petrochemical

The major applications for hydrogen are in the petrochemical industry where hydrogen is used in hydrotreating process to remove contaminants from oil. The heavy hydrocarbons are broken down into light hydrocarbons by hydrocracking.

5.2.2 Fuel Cells

Hydrogen can also be used as fuel in fuel cells to obtain energy. Fuel cells are electrochemical devices that convert chemical energy into electrical and thermal energy. They operate similar to a battery, using a fuel (hydrogen or hydrogen-rich gases) and an oxidant (air, oxygen). There are several types of fuel cells that operate at different temperatures and are made from different types of materials.

The use of fuel cells in vehicles is a reality and all the major automakers already have prototype hydrogen-powered systems. The environmental advantage of using hydrogen as fuel is that hydrogen emits only water vapor. Hydrogen can also store up much energy than natural gas.

5.2.2.1 Program CUTE (“Clean Urban Transport for Europe”)

Recently the European Union launched a program called CUTE (Clean Urban Transport for Europe). During the project 27 buses were operated in nine European cities including Stockholm (Haraldsson et al, 2005). The buses were based on a conventional urban buses Mercedes-Benz Citaro low-floor, with a length of 12 meters, as shown in Figure 9 (Platinum Today, 2011):

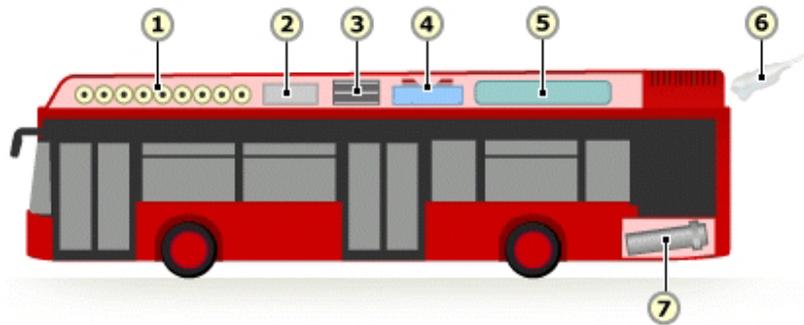


Figure 9 – Schematic of the Mercedes-Benz Citaro Fuel Cell Bus.

1. Cylinders hold hydrogen sourced from natural gas
2. Fuel cell supply unit – the cells have a gross power of 250 kW
3. Fuel cell stacks
4. Fuel cell cooling units
5. Air conditioning unit
6. Water vapor from exhausts is the buses' only emissions
7. Electric motor, can give a top speed of 80kph

5.3 OBTAINING HYDROGEN

Hydrogen can be produced from various sources such as water, coal, natural gas, petroleum as well as renewable resources such as sunlight, wind and biomass. The methods of production include principally electrolytic (thermolysis and electrolysis of water) and thermochemical (catalytic reforming, gasification and pyrolysis) processes. Table 5.1 shows the main sources and their methods of obtaining hydrogen for:

Table 5.1 Sources and methods for obtaining hydrogen

Sources	Methods of Obtaining
Water	Electrolysis or thermolysis of water (steam electrolysis)
Petroleum, Coal and Natural Gas.	Catalytic reforming or gasification followed by purification
Biomass	Gasification or catalytic reforming, followed by purification.

5.3.1 Electrolytic process

The electrolytic processes are basically processes of water decomposition into hydrogen and oxygen. The energy required to release hydrogen is supplied by heat or electricity. Energy Electrolysis by electricity or water electrolysis is accomplished by breaking chemical bonds between atoms of hydrogen and oxygen by applying an electrical current. The thermal electrolysis is also called thermolysis and involves the decomposition of water by high temperatures and pressures.

These methods are promising and have great potential. The decomposition of water does not generate pollutants. Despite these advantages, the use of electricity or high temperatures and pressures for the decomposition of water increases the cost of the process.

5.3.2 Thermochemical processes

Hydrogen obtaining by thermochemical process involves chemical reactions (in the presence of catalysts) and heat. The raw material includes fossil fuel (natural gas, gasoline) and renewable fuel (biomass, ethanol). The processes can be divided into thermochemical gasification and pyrolysis and catalytic reforming.

Gasification refers to the use of solid feedstock and heat to obtain synthesis gas while the pyrolysis involves decomposition of solid feedstock by heat into solid, liquid and gaseous products.

The catalytic reforming steam or just steam reforming is the most frequently used process for production of hydrogen on industrial scale. This process occurs in two stages: the first occurs at high temperatures ("Steam Reforming Reactions" - (SRR)) and the second step takes place at low temperatures ("Water Gas Shift Reactions" - (WGSR)). (Silva, 2010)

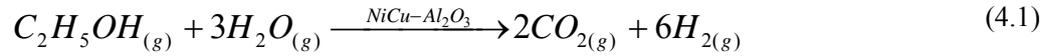
The first step, "SRR", includes the catalytic conversion of fuel / water vapor in a gaseous product that include hydrogen (H_2), carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4).

The low temperature step, "WGSR" includes the removal of CO and, consequently, the additional production of hydrogen through catalytic reactions. This step is necessary in order to decrease the amount of CO present in the products of the steam reforming and partial oxidation.

The use of fossil fuels as oil and natural gas for production of hydrogen by steam reforming has lower costs compared to the use of other sources. However the use of fossil fuels involves harmful impact on the environment. A large number of pollutants are emitted in these processes, besides the fact that fossil fuels are not renewable sources of energy. The use of biomass for hydrogen production is given a great emphasis currently. Biomass is a renewable source. The emissions of carbon dioxide during hydrogen production are compensated by the absorption of carbon dioxide during the growth of the biomass.

5.3.2.1 Steam Reforming from ethanol

The reforming reaction of ethanol can occur in presence of catalysts supported on alumina and Ni_2Cu at temperatures of 773 - 923 K and pressures close to 101.325 Pa (Brown, 2001). During steam reforming of ethanol six moles of hydrogen are produced from 1 mol of ethanol (equation 4.1).



The main components of the reformer studied in this work are as follows:

- Dosing pump: fuel feeding (water and ethanol)
- Vaporizer: Provides a mixture of vaporized fuel and air
- Catalytic Reactor for Reform at high temperatures (Steam Reforming Reactions- SRR)
- Catalytic Reactor for water exchange "shift reactor (Water Gas Shift Reactions - WGSR)

A schematic of the Reformer is presented in Figure 10 (Silva, 2010):

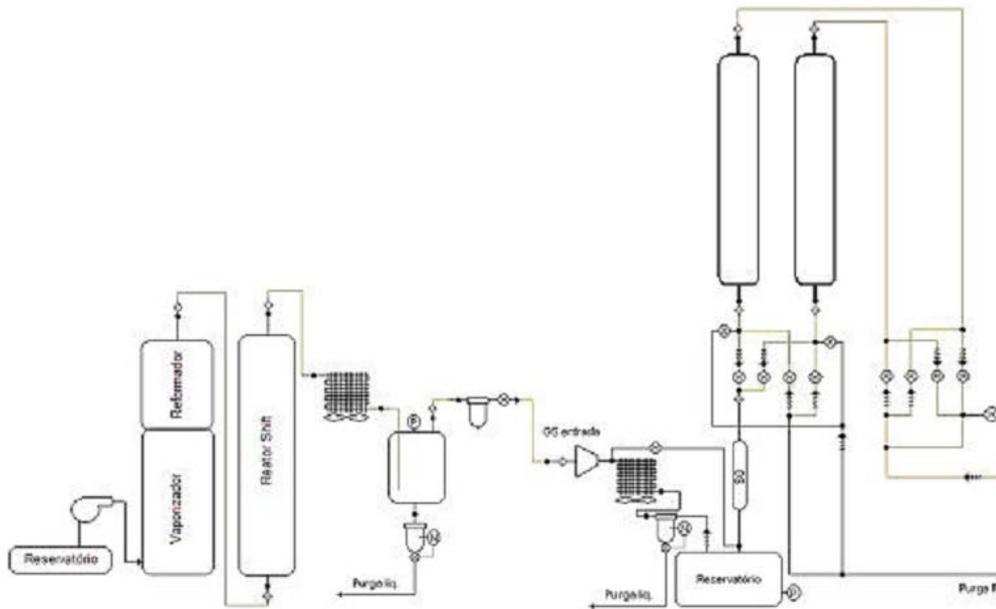


Figure 10 - Schematic of steam Reformer used for analysis.

The studied reformer has a capacity for 1 Nm³/h, consuming 0.79 L of anhydrous ethanol and 0.40 kg of water. In order to operate effectively, it is necessary 1.90 kWh of electricity and 1.23 kilos of sugar cane bagasse per hour, which represents 2.64 kW of thermal power (Silva, 2010)

6 EXERGETIC ANALYSIS

6.1 INTRODUCTION

The energy analyses, based on the first law of thermodynamics, have been constituted one of the most used tools for evaluating the efficiency of energy systems. However, this type of analysis does not consider the losses and the energy that can not be used.

The exergy analysis evaluates the system using the First and Second Law of Thermodynamics. The useful energy in the system is evaluated. The exergetic analysis in co-generation plants are used in order to achieve greater efficiency in combustion processes.

6.2 SECOND LAW OF THERMOYNAMICS

While the first law of thermodynamics deals with energy conservation, the Second Law of Thermodynamics describes the flow of energy in nature in irreversible processes. The energy flow in such processes is always in a particular direction, toward a more uniform distribution of the energy. i.e., the heat can not flow spontaneously from a colder body to a hotter body (Branco, 2005).

Thus, the Second Law states if a process is possible to take place in practice. The essence the second principle is the directional nature of the transfer of heat and power quality (ability to produce work). When the energy is transformed from one to another form, the quality of this energy is degraded.

6.3 GENERAL ASPECTS OF ANALYSIS BY THE FIRST LAW OF THERMODINAMICS

The first law analysis of a system is based on conservation of energy and mass. The equations for a control volume on permanent regime, in general, do not take into account the variations in kinetic and potential energy (Branco, 2005):

$$\sum \dot{m}_e - \sum \dot{m}_l = 0 \tag{6.1}$$

$$\sum \dot{Q}_{cv} - W_{cv} + \sum \dot{m}_e h_{ent} - \sum \dot{m}_l h_{out} = 0 \tag{6.2}$$

where:

\dot{m}_e - Mass flow entering the control volume (kg/s);

\dot{m}_l - Mass flow leaving the control volume (kg / s);

h_{ent} - Specific enthalpy at the entrance of the control volume (kJ/kg);

h_{out} - Specific enthalpy at the outlet of the control volume (kJ/kg);

\dot{Q}_{cv} - Heat transfer rate to the control volume (kW);

W_{cv} - Power refers to control volume (kW).

Equation 6.1 indicates that amount of mass entering the control volume is equal the amount of mass leaving the control volume.

Equation 6.2 states that the energy entering the control volume is equal to the energy leaving the control volume. The variations in kinetic and potential energy are not taken into account.

6.4. GENERAL ASPECTS OF ANALYSIS BY THE SECOND LAW OF THERMODYNAMICS

The irreversibilities in a process are quantified by the Second Law of Thermodynamics, through the property called entropy. In a control volume, the equation of entropy is defined as (Branco, 2005):

$$\dot{S}_{gen} = \frac{dS}{dt} - \sum_{i=0}^n \frac{\dot{Q}_i}{T_i} - \sum_{in} \dot{m}s + \sum_{out} \dot{m}s \geq 0 \quad (6.3)$$

Where:

\dot{S}_{gen} - the rate of generation of entropy in the control volume (kW/K);

$\frac{dS}{dt}$ - change of entropy rate (kW/K);

$\sum_{i=0}^n \frac{\dot{Q}_i}{T_i}$ - the rate of entropy due to the flow of heat (kW/K);

$\sum \dot{m}s$ - the rate of entropy due to the flow of mass into and out of the control volume (kW/K).

The entropy balance equation can be used to predict whether any process that involves interactions of energy, may occur, or even if the directions of heat transfer processes are possible. You can also say that the Second Law governs the limits of conversion between different forms of energy.

The energetic analysis of the first law of thermodynamics (energy balance), does not take into account the quality of energy and the irreversibility of the process.

6.5 EXERGY

According to the First Law of Thermodynamics, the energy cannot be destroyed (conservation of energy). But when the energy is transformed from one to another form, the quality of this energy is degraded. A portion of this energy is not available to do work.

Rant introduced the term Anergy to denote the energy that cannot be used (Rant, 1956). Thus, energy can be described as the sum of the energy available to do work (exergy) and the portion of energy that cannot be used (anergy), as summarized in Equation 6.4:

$$\text{Energy} = \text{Exergy} + \text{Anergy} \quad (6.4)$$

To calculate the exergy of a system, it is necessary to define a reference state for evaluating the maximum work possible to be produced.

Thus, exergy can also be defined as a measure of the degree of separation between the system and its environment or reference state. This measure means the maximum work that can be obtained from the system in its interaction with the environment until equilibrium.

5.6 METHODOLOGY OF EXERGY ANALYSIS IN A SUGAR-ALCOHOL

Exergy is the maximum amount of work available by bringing the system into mechanical, thermal and chemical thermodynamic equilibrium. This state is called a dead state (reference state) and is designated by the index 0. The work is maximum when $h_{out}=h_0$, $s_{out}=s_0$, $T_{out}=T_0$, $Z_{out}=Z_0$. Thus the flow of exergy, the specific exergy (ex) (maximum reversible work per unit mass, without heat transfer) can be defined by Equation 6.5:

$$ex = \left(h - T_0 \cdot s + \frac{V^2}{2} + g \cdot Z \right) - (h_0 - T_0 \cdot s_0 + g \cdot Z_0) \quad (6.5)$$

Ignoring the variations in kinetic and potential energy, we have then the equations for the specific input (Equation 6.6) and output (Equation 6.7) of exergy:

$$ex_{in} = (h_{in} - h_0) - T_0 (s_{in} - s_0) \quad (6.6)$$

$$ex_{out} = (h_{out} - h_0) - T_0 (s_{out} - s_0) \quad (6.7)$$

The temperature and pressure as well as the enthalpy and entropy considered for the reference state were presented in the Table 6.1:

Table 6.1 - Conditions Temperature (T_0) and pressure (P_0) for the reference state;

T_0 -Temperature	P_0 -Pressure	H_0 - Enthalpy	S_0 -Entropy
298.15 °K (25 °C)	0.10 MPa	104.93 (kJ/kg)	0.37 (kJ/kg.K)

6.7 CALCULATION OF EFFICIENCIES BY THE FIRST AND SECOND LAW OF THERMODYNAMICS

The thermodynamic efficiency based on the first law (η_I) relates the work done in the control volume with the work produced in a theoretical isentropic process. The thermodynamic efficiency for pumps is the inverse relation of the efficiency for turbines. Equations 6.8 and 6.9 show the efficiency based on the first law for turbines and pumps, respectively:

$$\eta_{I(turbine)} = \frac{\dot{W}_{cv}}{m \cdot \Delta h_{iso}} \quad (6.8)$$

$$\eta_{I(pump)} = \frac{m \cdot \Delta h_{iso}}{\dot{W}_{cv}} \quad (6.9)$$

To measure the performance of a device, the efficiency is defined based on the second law of thermodynamics (η_{II}), as the ratio of actual thermal efficiency to maximum possible (reversible) thermal efficiency (Eq. 6.10).

$$\eta_{II} = \frac{\dot{W}_{cv}}{m \cdot (ex_{in} - ex_{out})} \quad (6.10)$$

For the specific case of a boiler, assuming that the flow of steam that comes out is equal to the flow of water entering, you have the efficiencies by Equations 6.11 and 6.12:

$$\eta_{I(boiler)} = \frac{m_{steam} \cdot (h_{steam} - h_{water})}{m_{bag} \cdot LHV_{bag}} \quad (6.11)$$

$$\eta_{II(boiler)} = \frac{m_{steam} \cdot (ex_{steam} - ex_{water})}{m_{bag} \cdot ex_{bag}} \quad (6.12)$$

Equation 6.13 calculates the specific exergy of bagasse. It takes into account the correlation between chemical exergy and lower heating value of fuel (Szargut, 1988).

$$ex_{bag} = \beta \cdot (LHV_{bag} + L_{water}) + ex_{water} Z_{water} \quad (6.13)$$

β is a function of mass fractions of chemical components of bagasse (%) and is given by relation (Equation 6.14):

$$\beta = \frac{1.0412 + 0.2160 \cdot \left(\frac{Z_{H_2}}{Z_C} \right) - 0.2499 \cdot \left(\frac{Z_{O_2}}{Z_C} \right) \left[1 + 0.7884 \cdot \frac{Z_{H_2}}{Z_C} \right] - 0.0450 \cdot \frac{Z_{N_2}}{Z_C}}{1 - 0.3035 \cdot \frac{Z_{O_2}}{Z_C}} \quad (6.14)$$

Where,

$L_{water} = 2442$ (kJ / kg); Latent heat of water vaporization

$ex_{water} = 50$ (kJ / kg); specific exergy of water

Z_{water} : weight fraction of water in wet bagasse (%);

Z_i : weight fraction of chemical element i (%);

The elemental analysis of bagasse is given in Table 6.2 (Silva, 2010):

Table 6.2. Elemental analysis of sugarcane bagasse.

Carbon mass fraction	Z_C	44.80%
Hydrogen mass fraction	Z_{H_2}	0.054%
Oxygen mass fraction	Z_{O_2}	39.55%
Nitrogen mass fraction	Z_{N_2}	0.38 %

6.8 QUANTIFICATION OF IRREVERSIBILITIES AND QUALITATIVE LOSSES OF THE COMPONENTS

An important parameter to be observed in the exergetic analysis is the irreversibility in each device, and consequently in the whole system. The irreversibility shows the amount of exergy that is destroyed at each device cycle. The exergy analysis indicates the effectiveness of equipment.

For a process in Steady State, the exergy variation or irreversibility generation is shown by Equation 6.15:

$$I_{cv} = \sum \dot{Q}_j \left(1 - \frac{T_0}{T_j} \right) - \dot{W}_{cv} + \sum \dot{m}_{in} (ex_{in}) - \sum \dot{m}_{out} (ex_{out}) \quad 6.15$$

7. ECOLOGICAL ANALYSIS

7.1 INTRODUCTION

Several methods evaluate the environmental impacts of a process. In this study the environmental impact will be evaluated by the concentrations of carbon monoxide, carbon dioxide, sulfur dioxide, nitrogen oxides and particulate matter in the gases emitted to the atmosphere. These gases are products of the fuel combustion. In Table 7.1 the origin and health risks of pollutants gases are shown (Saldiva, 1991; Villela, 2007).

Tabela 7.1 – The origin and health risks of emitted gases.

POLLUTANTS	ORIGIN	RISKS TO HEALTH
Carbon monoxide (CO)	Incomplete Combustion	Carbon monoxide inhibits the blood's ability to carry oxygen to body tissues
Oxides of Nitrogen (NOx)	Combustion due to chemical reaction of oxygen with nitrogen from the air or with the nitrogen in the fuel	High levels may be fatal, while lower levels affect the delicate structure of lung tissue
Sulfur Oxides (SOx)	Mainly in combustion of fossil-fuel	SOx irritates mucous membranes and respiratory tract.
Particulate Matter (MP)	Natural activities and combustion processes. Coal power plants generate large emissions of PM	Inhaled particulate matter affects lungs, causing coughing, asthma, difficulty breathing, bronchitis

7.2 CALCULATION OF CARBON DIOXIDE EQUIVALENT [(CO₂)_e]

Equivalent Carbon Dioxide (CO₂)_e is a measure used to compare emissions of various greenhouse gases based on the global warming potential. It describes the amount of CO₂ that would have the same global warming potential than the referred greenhouse gas. Carbon dioxide equivalent is the result of multiplying the tons of emitted greenhouse gases (GHGs) by their global warming potential (GWP). For example, the global warming potential of methane is 21 times greater than the potential of CO₂ (IPAM, 2011).

The calculation of carbon dioxide equivalent [(CO₂)_e] is done by considering the concentrations of CO₂, SO₂, NO_x, PM in the emitted gas when 1 kg of fuel (sugarcane bagasse in this work) is burned. Equation 7.1 shows the calculation of carbon dioxide equivalent (Cardu and Baica, 1999).

$$(CO_2)_e = CO_2 + 80(SO_2) + 50(NO_x) + 67(PM) \quad (7.1)$$

Where:

(SO₂)_e = 80 * (SO₂) = sulfur dioxide equivalent

(NO_x)_e = 50 * (NO_x) = nitrogen oxide equivalent

(PM)_e = 67 * (PM) = particulate material equivalent

7.3 CALCULATING THE POLLUTION INDICATOR (Π_g)

The Pollution Indicator is used to quantify the environmental impact caused by burning fuel. The pollution indicator is defined as the ratio of the amount of emitted carbon dioxide equivalent to the lower heating value (LHV) of fuel (Silva, 2010), as described in Equation 7.2:

$$\Pi_g = \frac{(CO_2)_e}{LHV} \quad (7.2)$$

Where:

(CO₂)_e - Carbon dioxide equivalent [kg / kg_{comb}]

LHV - Lower Heating Value of fuel [MJ / kg_{comb}]

Π_g - Pollution indicator [kg / MJ]

7.4 ECOLOGICAL EFFICIENCY

The ecological efficiency calculates the environmental impact of thermochemical processes by comparing the theoretically integrated pollutant emissions (CO₂ equivalent emissions) to the existing air quality patterns. (Equation 7.3).

$$\varepsilon = \left[\frac{0,204 \times \eta_{sistema} \times \ln(135 - \Pi_g)}{\eta_{sistema} + \Pi_g} \right]^{0,5} \quad (7.3)$$

Where:

ε - Ecological efficiency [-]

η_{system} - Thermodynamic efficiency of the reforming process [-]

Π_g - Pollution indicator [kg / MJ]

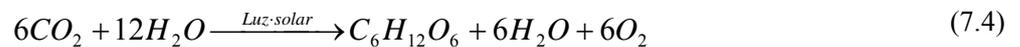
Table 7.2 shows reference values for [(CO₂)_e], Pollution indicator (Π_g) and ecological efficiency ε for some fuels (Villela et al, 2007)

Table 7.2 - Environmental characteristics for reference fuels

Fuel	S (%)	(CO ₂) _e (kg/kg _{fuel})	LHV (MJ/kg)	Π_g (kg/MJ)	ε (-)
Hydrogen	0	0	119.95	0	1
Sulfur	100	1 400	9.270	134	0

7.5 CARBON CYCLE

Biomass absorbs carbon dioxide during growing because the plant performs photosynthesis (Equation 7.4).



The amount of 173 kilos of carbon dioxide (CO₂) are emitted during the production of 1000 L ethanol taking into account the use of fertilizers and pesticides as well as the emission caused by the machinery and equipment (Silveira et al. 2009). It is estimated that 12 tons of cane sugar are necessary to produce 1000L ethanol. During the growth of sugar cane, 7 464 kg CO₂ are absorbed. In harvesting and transport, 2 940 kg CO₂ are emitted. The production of alcohol emits 3140 kg CO₂. Figure 11 shows the

carbon cycle and the amount of CO₂ emitted and absorbed during the production of 1000 L ethanol (Silveira et al., 2009)



Figure 11 - Cycle of CO₂ from the planting of sugarcane to ethanol manufacturing

So, the total amount of 6253 kg CO₂ is emitted to produce 100 L ethanol and 7464 kg CO₂ are absorbed during the growth of the sugarcane. The balance shows that 1211 kilos of carbon dioxide are absorbed in the all process. This value will be used for calculation concerning ecological analysis in Chapter 8.

7.6 ANALYSIS OF PROPOSED SYSTEM

The proposed system includes the ethanol reformer for hydrogen production using sugarcane bagasse to produce the required heat in the process (Figure 12).

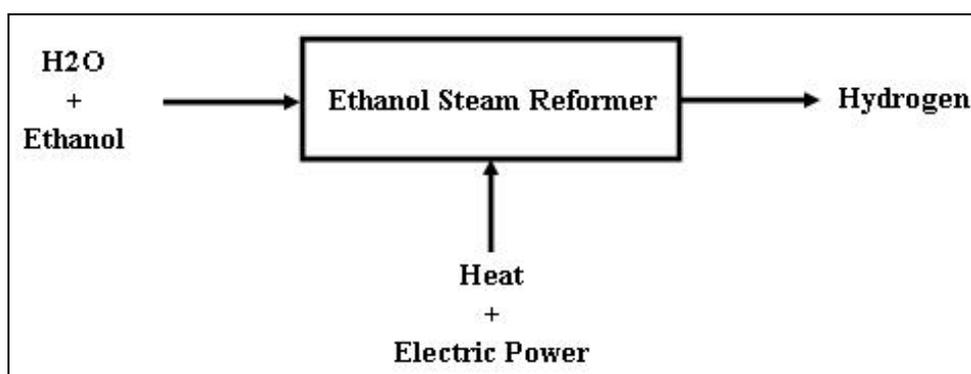


Figure 12 - Flowchart of the Reformer of ethanol

The composition of bagasse (dry basis) is given in Table 7.3 (Sales 2007):

Table 7.3 Ultimate and proximate analysis of sugarcane bagasse

Biomass	Ultimate analysis (%)							Proximate analysis		LHV (MJ/kg)
	C	H	O	N	S	Ash	Volatiles	Ash	Fixed Carbon	
Bagasse	44.8	5.35	39.55	0.38	0.01	9.79	73.78	11.27	14.95	7.32

The amount of carbon dioxide emitted by sugarcane bagasse is calculated by Equation 7.5:

$$a_1C + b_1H + c_1O + d_1N + e_1S + 3,83(\alpha O_2 + \alpha 3,76N_2) \rightarrow \quad (7.5)$$

$$w_1CO_2 + y_1H_2O + 3,83(1 - \alpha)O_2 + 3,83\alpha 3,76N_2$$

Where:

$\alpha = 1.3$ (assuming 30% excess air in the combustion of bagasse)

a_1, b_1, c_1, d_1, e_1 - values of the elemental components of bagasse.

7.6.1 Calculation of CO₂ emissions in the combustion process of sugarcane bagasse

CO₂ emissions resulting from the combustion of 1 kg fuel can be calculated according to Equation 7.6 (Villela, 2007):

$$M = \frac{(w_1 \times 44 \times 1)CO_2}{N} \quad (7.6)$$

Where:

M_{CO_2} - CO₂ Emissions [kgCO₂/kgcomb]

N- Molar Mass of fuel (bagasse) [kg / kmol]

The Molar Mass of bagasse (N) can be calculated by:

$$N = (a_1 12) + (b_1 1) + (c_1 16) + (d_1 14) + (e_1 32) \quad (7.7)$$

7.6.2 Emissions of the system steam reforming of ethanol

In order to calculate the Equivalent Carbon Dioxide (CO₂) from the combustion of bagasse sugarcane, the emission factors for NO_x, SO₂ and PM presented in Table 7.4 has been used (Lora, 2004).

Table 7.4 - Emission Factors for NO_x, SO₂ and PM in the combustion of bagasse sugarcane

Components	Combustion of Bagasse
SO ₂ (kgSO ₂ /kgComb)	0
NO _x (kgNO _x /kgComb)	0.0012
MP(kgMP/kgComb)	0.0071

8. RESULTS and DISCUSSIONS

8.1 EXERGY ANALYSIS

The equations mentioned in Chapter 6- and the values quoted in Chapter 4 are utilized in order to perform the exergy analysis. The evaluated cases vary only in relation to excess bagasse, therefore it will be only presented separately the values that differed significantly in the system as irreversibilities and power generation.

8.1.1 Thermodynamic Efficiencies of Thermal System Components Presented

The efficiencies of the First Law of Thermodynamics or isentropic efficiency (η_I) and the Second Law of Thermodynamics efficiency or exergetic efficiency (η_{II}) were calculated from the values obtained in Tables 4.5 and the equations of the Item 4.8. Table 8.1 shows the results.

Table 8.1 - Efficiency thermodynamics of turbine calculated by the First and Second law of Thermodynamics

System Points	Turbines	η_I (%)	η_{II} (%)
3-4	Turbo Generator	52.97	60.5
7-8	Hydraulic pump	27.62	35.1
9-10	Chopper	46.35	54.1
11-12	Grinder	46.35	54.1
13-14	Milling 1 ^a /2 ^a	41.88	49.7
15-16	Milling 3 ^a /4 ^a	41.88	49.7
17-18	Milling 5 ^a /6 ^a	41.88	49.7
19-20	Turbine Exhaust.	41.59	49.7

8.1.2 Power generation in each equipment

The power generated in each equipment was calculated by the difference between the incoming and outgoing energy flow. The system point refers to the Figure 8. The results are presented in Table 8.2.

Table 8.2 - Power generation in each equipment

System Points	Turbines	W_{shaft} (kW)
7-8	Hydraulic pump	237.68
9-10	Chopper	741.30
11-12	Grinder	741.30
13-14	Milling 1 ^a /2 ^a	684.81
15-16	Milling 3 ^a /4 ^a	659.82
17-18	Milling 5 ^a /6 ^a	659.82
19-20	Turbine Exhaust.	236.96
Electromechanical Total Power		3 961.69

The generated power in cases 1 and 2 were different, since in case 2 all available bagasse was used for production of surplus energy. It was considered a power generation efficiency of 95% at the generator. Table 8.3 shows the power generated in cases 1 and 2.

Table 8.3 - Power generation in case 1 and 2

	Case 1	Case 2
Electric power generated (kW)	3 477	5 440

8.1.3 Irreversibilities in each equipment

The irreversibilities of each equipment in the system were calculated from the Equation 6.15. Table 8.4 shows the amount of irreversibility in turbines and pumps of the system.

Table 8.4 – Irreversibility in the equipment

System Points	Turbines	Irreversibilities (kW)
7-8	Hydraulic pump	438.66
9-10	Chopper	629.25
11-12	Grinder	629.25
13-14	Milling 1 ^a /2 ^a	693.26
15-16	Milling 3 ^a /4 ^a	667.96
17-18	Milling 5 ^a /6 ^a	667.96
19-20	Turbine Exhaust.	240.17

There is also a difference between the irreversibilities generated in the Turbine Generator for cases 1 and 2. The amount of irreversibility is higher in case 2 than in case 1, due the use of all available bagasse and produced steam for energy production. Table 8.5 shows the amount of irreversibility in turbine generator for cases 1 and 2.

Table 8.5 –Irreversibility in Turbine Generator for cases 1 and 2

	Case 1	Case 2
Turbine Generator (kW)	2 388.68	3 736.91

8.1.4 Production of Hydrogen (Case 3)

The purpose is to evaluate the amount of hydrogen that can be produced according to the available energy (thermal and electric) provided by the combustion of bagasse.

In order to calculate the total consumption of bagasse, for the production of 1Nm³/h Hydrogen, the following parameters were utilized (Silva, 2010):

- Electrical need: 1.9 kWh

Using the ratio 2.13 t_{steam}/t_{bagasse} on Boiler and 129, 75 kWh/t bagasse on Turbo Generator, the consumption of bagasse is 14.64 kg_{bagasse} / h.

- Thermal need: 1.23 kg_{bagasse}/h (SILVA, 2010)

Table 8.6 shows the amount of consumed bagasse calculated taking into account the parameters of the thermal system of "Pioneiros Distillery", and the surplus of 15.1 tons of bagasse (Case 1).

Table 8.6 - Consumed bagasse in Pioneiros Distillery

Fractions of bagasse	ton/h	Consumed portion of the surplus (%)
Electrical Energy	13.93	92.25
Thermal Energy	1.17	7.75
Surplus Bagasse	15.10	100

The maximum amount of produced hydrogen will be 951.24 Nm³/h. A volume of 757.28 liters of ethanol is needed to produce this amount of hydrogen. This amount of hydrogen could supply 68 buses with a range of 200 to 300 km daily. (Halmeman 2008)

6.9 % of anhydrous ethanol generated in the plant will be used in the reformer for the production of this amount of hydrogen.

8.2 ECOLOGICAL ANALYSIS

8.2.1 Emissions of the steam reforming of ethanol

Taking into account a stoichiometric combustion of sugarcane bagasse, a stoichiometric ratio of water/ethanol in steam reforming of ethanol (Equation 8.1) and considering the CO₂ cycle (Figure 11), the emissions shown in Table 8.7 are calculated:



Table 8.7 - Results of emissions to CO₂, SO₂, NO_x and Particulate Matter

Components	Combustion of Sugar Cane Bagasse		Steam reforming to ethanol	
	With Cycle	Without Cycle	With Cycle	Without Cycle
CO ₂ (kg _{CO2} /kg _{Comb})	1.83360	0.39926	0	-1,43433
SO ₂ (kg _{SO2} /kg _{Comb})		0		0
NO _x (kg _{NOX} /kg _{Comb})		0.0012		0.0012
MP(kg _{MP} /kg _{Comb})		0.0071		0.0071

8.2.2 Ecological Efficiency of the steam reforming of ethanol

In order to determine the ecological efficiency of the steam reforming of ethanol, the carbon dioxide equivalent [(CO₂)_e] and the pollution indicator (Πg) are calculated (table 8.8) considering the emission of NO_x, SO₂ and PM (Table 7.4) suggested by (Lora, 2004) and taking into account the LHV of sugarcane bagasse as 7.32 MJ / kg.

Table 8.8 - Values of carbon equivalent [(CO₂) e] and pollution indicator (Πg)

(CO ₂)e[kg/kgcomb]		Πg [kg/MJ]	
Without Cycle	With Cycle	Without Cycle	With Cycle
2.36930	0.93496	0.324	0.12773

Evaluating the hydrogen production process by steam reforming represented schematically in Figure 12, the expression to calculate the system thermodynamic efficiency (η_{sistema}) is defined as (Silva, 2010):

$$\eta_{\text{sistema}} = \frac{E_{H_2}}{(E_{\text{bagaço}} + E_{\text{etanol}})} \quad (8.2)$$

Where:

$$E_{H_2} = m_{H_2} \times \text{LHV}_{H_2}$$

$$E_{\text{bagaço}} = m_{\text{bagaço}} \times \text{LHV}_{\text{bagaço}}$$

$$E_{\text{etanol}} = m_{\text{etanol}} \times \text{LHV}_{\text{etanol}}$$

$$\text{LHV}_{H_2} = 119.95 \text{ MJ/kg}$$

$$\text{LHV}_{\text{etanol}} = 28.3 \text{ MJ/kg}$$

$$\text{LHV}_{\text{bagaço}} = 7.32 \text{ MJ/kg}$$

Table 8.9 shows the ecological and thermodynamic efficiencies of the system:

Table 8.9 - Thermodynamics (η_{system}) and Ecological (ϵ) Efficiencies of Process Steam reforming of ethanol

η_{system} (%)	ϵ [%]	
	Without Cycle	With Cycle
55.78%	79.56%	90.23%

9. CONCLUSIONS

The exergetic analysis shows that changes in the configuration of the systems generate only local changes, principally at points where the turbo generator is located.

More energy is produced in Case 2 than in Case 1. Thus the amount of irreversibility is higher in case 2 than in case 1. In Case 3, the surplus bagasse is burned to supply with energy an ethanol reformer for hydrogen production.

The ecological impact of using bagasse, as fuel to generate thermal and electrical energy for the ethanol reformer, was studied. The main pollutants that damage the atmosphere, namely: CO, CO₂, NO_x and PM have been taking into account. The emissions of these pollutants were much lower than those emitted by fossil fuels. Carbon Dioxide emissions were calculated taking into account the carbon cycle (considering the absorption of carbon dioxide by the sugarcane during its growth), resulting in negative balance emissions, i.e., carbon dioxide was absorbed in higher amounts than emitted.

The thermodynamics (η_{system}) and ecological (ϵ) efficiencies of steam reforming of ethanol were calculated. The thermodynamic efficiency was 56% and the ecological efficiency was 80%. When the carbon cycle is taking into account the ecological efficiency is 90%.

The results show that the incorporation of an ethanol reformer in a sugar-alcohol plant can bring many environmental benefits. The amount of hydrogen produced in the system could supply fuel for 68 buses with a range from 200 to 300 km per day. That means that enough amount of hydrogen to supply a larger number of vehicles and thus reduce pollution in cities could be produced at the sugar ethanol plants if a small part of the produced ethanol is used for hydrogen production by steam reforming.

The incorporation of an ethanol reformer in a sugar-ethanol plant for hydrogen production is a very interesting option where environmental benefits are obtained. Problems related with the storage of bagasse are avoided because all the bagasse is burned for the production of steam and energy to the reformer.

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