

SUSTAINABLE CLAY BRICK PRODUCTION

Fritz MÖDINGER

ZIEGELEI GASSER MATTONI GmbH / S.r.l.

Schabs 104 (Sciaves 104) 39040 Natz - Schabs (Naz /Sciaves) (BZ) – Italy

(T: +39-0472-412033; F: +39-0472-412433; fritz.moedinger@gmx.net)

Giovanni D'ANNA

ANDIL – ASSOLATERIZI National Association for brick and tile producers

Via A. Torlonia, 15 - 00161 Roma – Italy

(T: +39-06-44236926; F: +39-06-44237930; andil@laterizio.it)

ABSTRACT

The search for alternatives to the classical, mainly fossil, energy sources within a high energy consumption process as brick making can certainly be very rewarding.

Within this framework the production of biogas by anaerobic digestion of locally available biomasses has been integrated in a brickyard. Experimental tests have been carried with different biomasses, mainly with fruit processing wastes and kitchen residues.

The generation of biogas from biomasses within a brickyard permits a considerable reduction of fossil fuels consumption and allows a profitable use of all fermentation wastes, both liquid and solid. The fermentation wastes, about 3% in weight of the total dry substance fed to the plant, can be used as pore forming agent without any major influences on the quality or chemical composition of the green or fired bricks. On the contrary, it appears from the tests that the organic sludge tends to increase plasticity of the feedstock on extrusion.

The investment for the biogas plant itself and the ancillary equipment is rapidly amortized: gate fees for the disposal of waste and missed purchase of primary fuels and last not least the considerable image gain. In certain countries, like for example in Italy, the substitution of renewable fuels is further financially incentivated by the government. CO₂ emission certificates trade can also generate a considerable additional income.

INTRODUCTION

Sustainable production of goods is to become a guiding principle for industry. It is about integrating economic, environmental and social values and the degree of sustainability of a production process can be easily measured by three indicators:

- Energy consumption;
- Emissions;
- Raw materials.

Energies derived from fossil fuels can be substituted with renewable energies. In the Gasser brickyard the fossil fuels traditionally used have been substituted completely with renewable fuels such as biogas and animal rendering fat thus reducing greenhouse gas (GHG) emissions voluntarily anticipating expected regulations and generating revenue, by selling emission credits. The clean flue gases by the combustion of renewable fuels permit to heat up the dryer directly with flue gases from the firing zone of the tunnel kiln hence reducing the overall energy consumption by 30%.

Emissions due to the combustion of fossil fuels have been reduced to zero. Most interesting is the reduction of emissions into air of the brickyard:

		Biogas	Rendering fat	Low SO₂ boiler fuel
Toxicity equivalent	NTEQ/Nm ³	0.0001	0.001	0.0024
SO ₂	mg/Nm ³	<0.11	<1.00	54
Cl	mg/Nm ³	0.1	0.5	19
CO ₂	t/a	<5000.00	<10.00	<3500.00

Table 1: *emissions into air: comparison biogas, rendering fat and fossil fuels*

The utilization of selected production wastes in substitution of raw materials reduces the environmental impact due to extraction of otherwise used raw materials by up to 20% and permits lowering of the firing temperatures.

PROCESS

In order to recover energy from biomass a number of processes can be applied that depend on the C/N ratio and humidity content.

- Thermo-chemical conversion processes such as direct combustion, pyrolysis or gasification are most suitable for cellulose and wood rich wastes featuring a C/N ratio greater than 30 and a humidity content inferior to 30. Most appropriate for a thermo-chemical conversion process is hence wood, its by-products and lignocellulose products such as grass, straw, hay and some production wastes such as shells, nuts, and similar.
- Biomasses with a C/N ratio inferior to 30 and featuring a dry substance percentage inferior to 30, like for example leaves, stems, etc. present themselves to be used in a biochemical conversion process in which energy is obtained by means of enzymes, fungus and microorganism that can be present in the biomass at given environmental conditions.
- Anaerobic digestion, a biochemical conversion process in a reducing, oxygen poor, environment, causes the breakdown by microorganism of complex organic substances such as lipids, proteins and glycosides that are contained in both vegetal and animal biomass. It is a biological stabilization process aiming to reduce the C/N ratio by ways of digestion of the organic matter that allows the production of energy.

The process takes place under anaerobic conditions; it can exist only in the absence of oxygen, bacteria flora. Depending on process temperature the different bacteria families are:

- Psychrophile, < 25°C
- Mesophile, > 25°C and < 45°C
- Thermophile, > 45°C.

These bacteria families are already present in the original biomass and flourish in a closed environment transforming the organic matter mainly in CH₄ and CO₂, using enzymes as a biocatalyzer.

Anaerobic digestion takes place in bioreactors (digesters) built to guarantee the optimum environmental conditions hence effectively avoiding contact between the liquefied biomass and atmospheric oxygen.

Biogas is known in nature and can be, for example, found in the alimentary canal of ruminants. There, under optimal process conditions, a series of symbiotically one to each

other adopted fermentation processes take place: a large variation of micro organisms are responsible for the decomposition of the organic content that have been taken up as food by the animals. The microorganisms principal role is to break down the organic fibers and nutrients in order to make them digestible by the animal. The bacteria active in the process draw their fodder from these substrates and decompose them catabolically under given conditions.

Bacteria family	Substrate (H release)	CH₄ source
Methanobacterium (omelianskii)	<i>H₂</i>	<i>CO₂</i>
Methanosaracina barkeri	<i>H₂; CO, Methanol, Acetate</i>	<i>CO₂; CO</i>
Methanobacterium formicium	<i>H₂; CO; Formiate</i>	<i>CO₂</i>
Methanococcus vanniellii	<i>H₂; Formiate</i>	<i>CO₂</i>
Methanobacterium ruminantium		
Methanobacterium suboxydans	<i>Butryate, Valerate, Capronate</i>	<i>CO₂</i>
Methanobacterium söhngeni	<i>Acetate, Butryate</i>	<i>CH₄ – group</i>
Methanosaracina methanica	<i>Acetate, Methanol, Butryate</i>	<i>CH₃ – group</i>
Methanococcus mazei	<i>Acetate, Butryate</i>	<i>CH₃ - group</i>

Table 2: *Methanforming bacteria stems*

From a biotechnological point of view these processes can take either be divided into parallel or sequenced processes. The most important process steps are:

1. Enzymatic hydrolysis of polymeric plant parts:
 - Polysaccharides to monomeric sugars
 - Proteins to amino acids and eventually peptides
 - Lipids to fatty acids and glycerin;
2. Anaerobic decomposition of sugars to biogen acids by heterofermentative acidifiers.

The types of microorganisms in these biotechnological processes are manifold and relative between them. In almost all cases the optimal bacteria cultures select themselves from the not sterile substrate.

The type and activity level of the bacteria can be influenced by:

- Optimal temperature;
- Optimal pH value;
- Optimal substrate.

As the bacteria tend not to proliferate very well under anaerobic conditions and like to settle on “internal” surfaces, the count of active bacteria is reduced by substrate withdrawal. It is hence necessary to feed back bacteria rich sludge to the process.

As these basic biological processes are superimposing each other and are influenced by external factors, they can be controlled and optimized in an industrial process only when they are separated.

The process takes place in three steps:

1. Hydrolization of cellulose, proteins, sugars and amino acids (starches need to be hydrolyzed at higher temperatures and hence can not be mixed to the standard flow).
2. Acidification by formation of simple organic acids (such as acetic acid) and alcohols (such as ethylic alcohol).

3. Methanization of the product of the second step. Methanisation of the now available organic acids by methanogen bacteria, that transfer their reduction equivalents to the carboxyl group or the methyl groups of the organic acids. In this phase a number of methano-bacteria are involved that will metabolize the CO_2 and the acids and alcohols into methane gas:

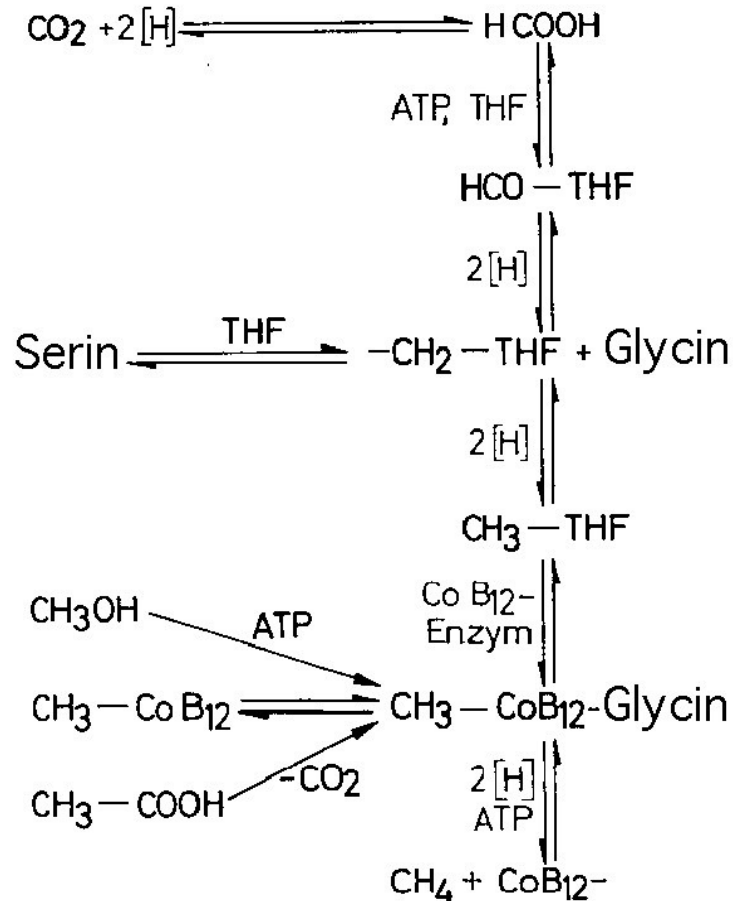


Figure 1: *Probable methane generation (Barker; H.A.:Biochem J 105 (1968)1)*

Separation of the single phases of the process, hydrolysis, acidification and methane metabolization in different treatment vessels and reactors, allows an easier control of the pH values and reduces the risk of over-acidification by formation of free acids. Over-acidification leads to much longer times of residence of the biomass in the fermenters and hence to larger and more difficult to control plants.

The cascade fermentation Gasser biogas plant features separation of the different phases of the process:

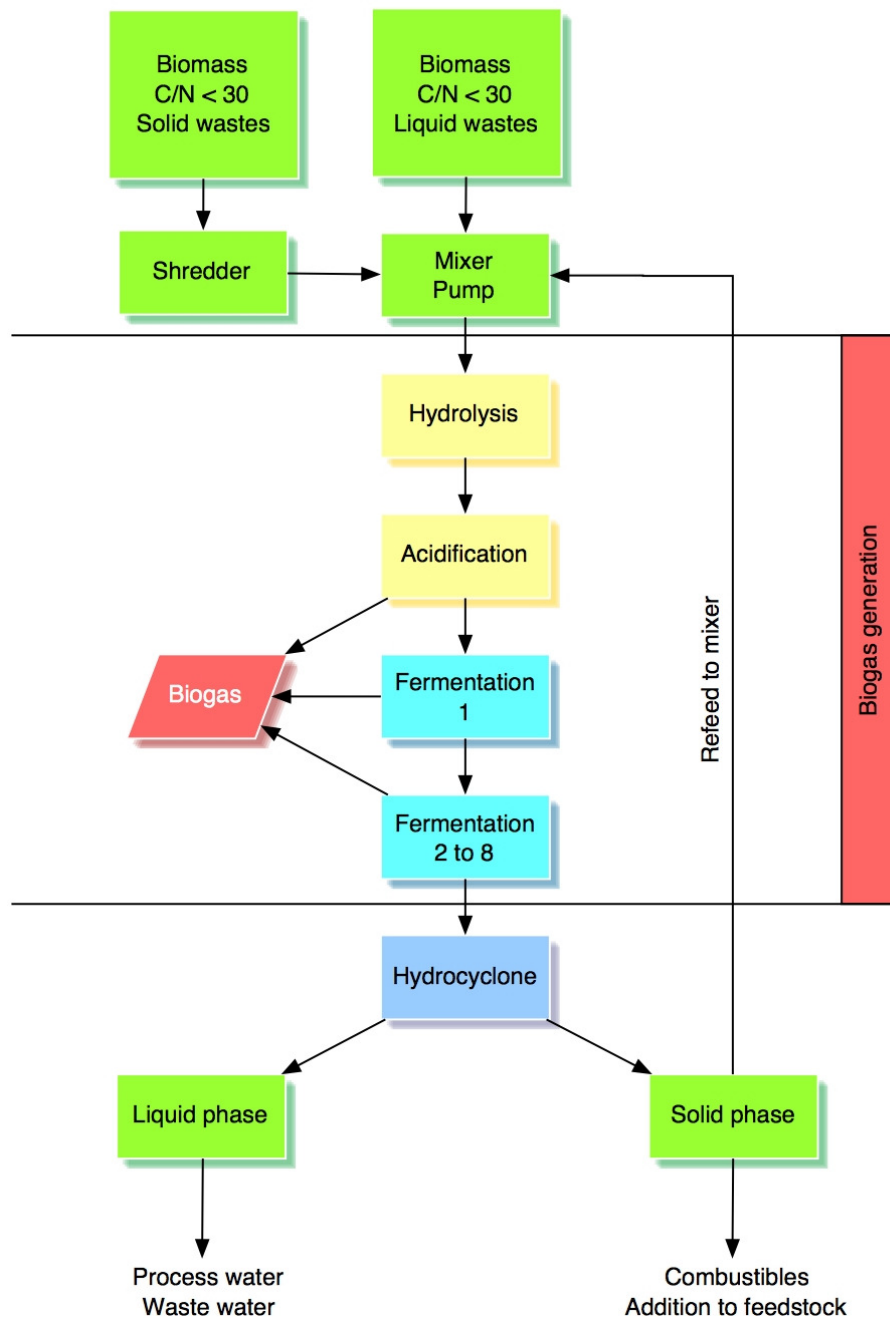
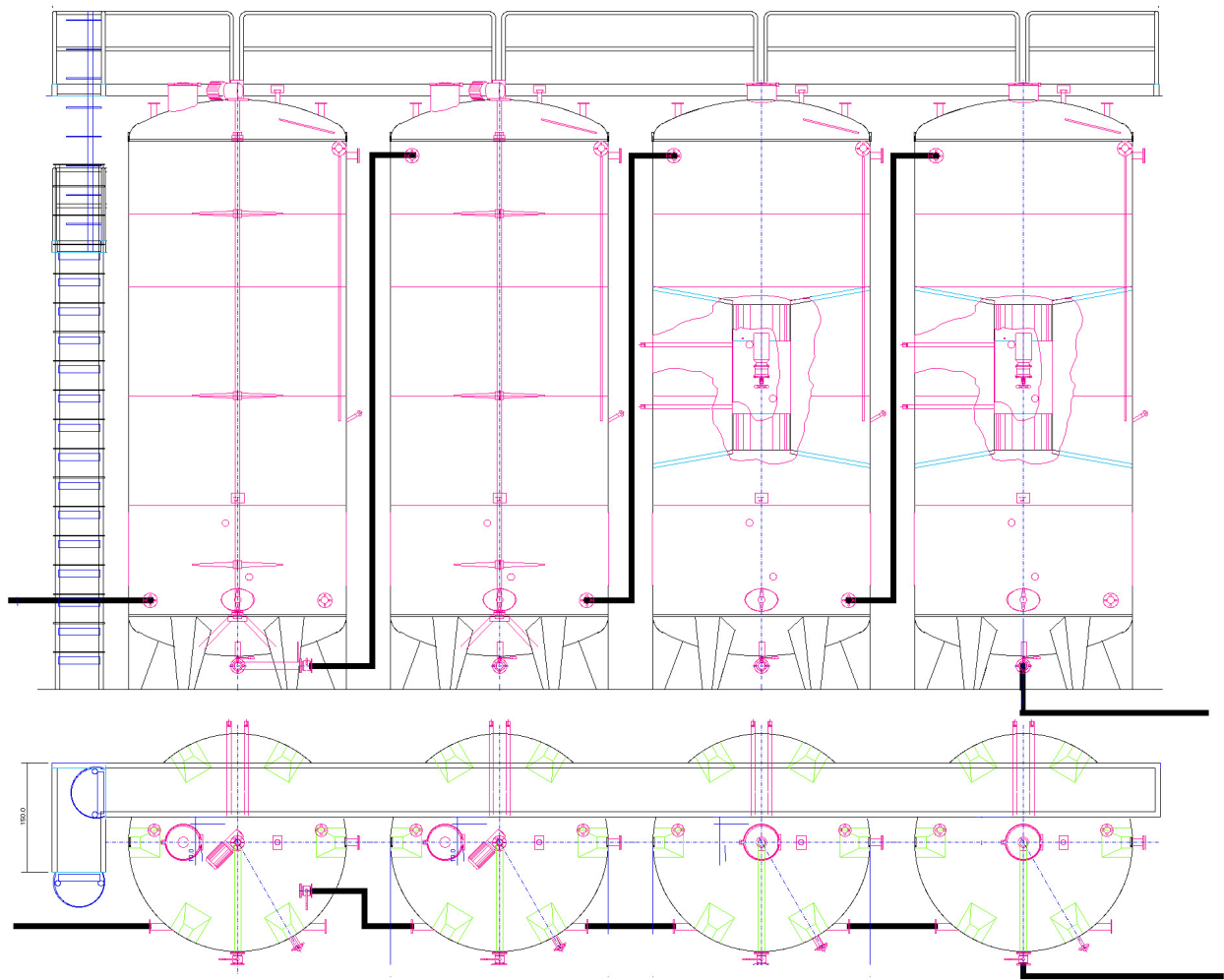


Figure 2: *process overview*

THE TECHNOLOGY

Currently a pilot plant is in operation. It consists of a number of fermenters that are set up in cascade fashion. Not shown in the above drawing are the loading station, pumps and a hydro cyclone at the end of the process.



Drawing 1: *Pilot plant*

The plant can either be adapted to liquid, oily or solid wastes. The below table gives an overview over the different plant concepts, they differ mainly in the pre-treatment phase of the process, over the concept:

	Starch	Fruit		Waste	Oil, Fat, Blood
		Solid	Liquid		
<i>Product Waste</i>	<i>Potato, Corn</i>	<i>Fruit marl</i>	<i>Processing wastes</i>	<i>Household</i>	<i>Frying oil, palm oil</i>
<i>Pre – feeding treatment</i>	<i>Mincing Steam > 100 °C</i>	<i>Mincing</i>	<i>None</i>	<i>Mincing Steam > 75°C</i>	<i>Soapification</i>

Table 3: *Pre – treatment*

The above is not a complete guide but rather a general overview.



Figure 3: *Pilot plant*

The products and by-products of the process are:

- Biogas;
- Process or waste water (in case of multiple cascade fermenter water sufficiently clean to be used as process water);
- Combustibles, organic sludge part of it recycled in the plant itself and part available as an addition to the feedstock.

The obtained biogas features a methane (CH_4) content of between 50-70% in volume, carbon dioxide (CO_2) of between 25-45%, nitrogen oxide 2-5%, hydrogen 0.5-3% and hydrogen sulphide 0.05-0.15%. Considering the calorific value of the sole methane, for biogas one would obtain a calorific value of between 4,500 e 6,000 kcal/Nm³.

Various substrates lead to different leads of biogas.

BIOGAS IN THE PRODUCTION OF FIRED CLAY BRICKS

Biogas is mainly used to drive engines or turbines used to generate electric energy, most of the times incorporating waste heat recovery processes.

Integrating a biogas production process in a brick plant will deliver best environmental and financial results.

The advantage of such a closed system where all products of the anaerobic digestion process find an use are:

- The biogas is used directly on site to fire kiln substituting totally or in part the hence used fuels. Low temperature waste heat can be recovered and used to heat up the fermenters;
- Direct use of the biogas does not require to build pressurized storage or transport vessels;
- The solid waste, bio sludge, can be incorporated into the feedstock itself as a pore former. A small quantity of energy is recovered by combustion of organic not digested parts during firing of the bricks. It appears from the tests that the organic sludge tends to increase plasticity of the feedstock on extrusion.

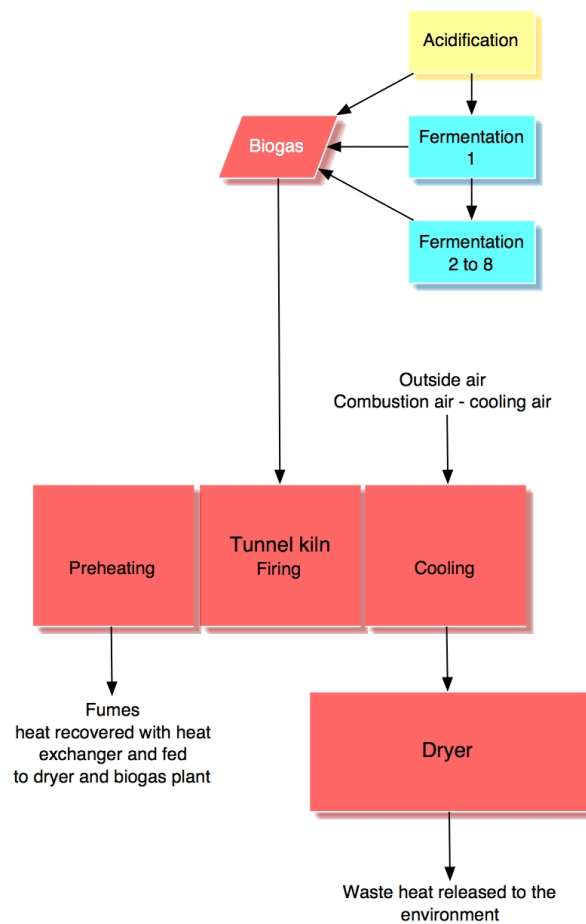


Figure 4: *Utilization of biogas in the brickyard*

From an environmental point of view the principal advantages are avoided consumption of scarce primary fuels, avoided pollution due to the use of renewable fuels and the avoided disposal of organic wastes in landfills hence reducing overall waste flows considerably. The avoided pollution can be summarized in about 40 to 50 TEP for every 1.000 metric tons of brick produced hence determining a reduction in the CO₂ emissions of about 100 to 200 metric tons for every 1.000 metric tons of brick produced (depending on the primary fuel that is to be substituted by biogas).

The investment for the biogas plant itself and the ancillary equipment is rapidly amortized: gate fees for the disposal of waste and missed purchase of primary fuels and last not least the considerable image gain. In certain countries, like for example in Italy, the substitution of

renewable fuels is further financially incentivated by the government. CO₂ emission certificates trade can also generate a considerable additional income.

Choice of the biomasses

The biomasses to be fermented have to be carefully chosen so that the utilization of the residues as pore forming agent is not hindered or impaired.

Gas yield and quality

Various biomasses have been laboratory and / or pilot plant tested in order to value quality and yield of biogas by mesophilic fermentation.

The results of the tests are:

Biomass	Gas yield, m³/kg DS
<i>Kitchen wastes</i>	<i>0.7–1.3</i>
<i>Biodegradable packaging</i>	<i>0.64</i>
<i>Packaged food production wastes</i>	<i>0.32–0.8</i>
<i>Slaughterhouse wastes</i>	<i>0.34–0.71</i>
<i>Organic based oils and greases including lubricant oils</i>	<i>> 0.5</i>
<i>Fishing wastes</i>	<i>≅ 0.5</i>
<i>Differentiated waste collection</i>	<i>0.40–0.58</i>
<i>Potato wastes</i>	<i>≅ 0.48</i>
<i>Wastes from the production of drugs</i>	<i>0.2–0.75</i>
<i>Potato distillation residues</i>	<i>≅ 0.46</i>
<i>Beer production residues</i>	<i>0.42–0.5</i>
<i>Fruit distillation residues</i>	<i>0.45</i>
<i>Green waste</i>	<i>0.35–0.46</i>
<i>Sewage sludge</i>	<i>0.39–0.41</i>
<i>Manure</i>	<i>0.22–0.55</i>
<i>Paper and cardboard production wastes</i>	<i>0.2–0.3</i>

Table 4: *gas yield from various biomasses*

The tests carried out in the pilot plant usually have resulted in yields that have been found to be between 50 and 88% of the laboratory results.

The chemical composition of the biogas during the tests with the various substrates resulted in:

Substance	Concentration, %
<i>Methane</i>	<i>40-75%</i>
<i>CO₂</i>	<i>25-55%</i>
<i>Water vapor</i>	<i>0-10%</i>
<i>Nitrogen</i>	<i>0-5%</i>
<i>Oxygen</i>	<i>0-2%</i>
<i>Hydrogen</i>	<i>0-1%</i>
<i>Ammonia</i>	<i>0-1%</i>
<i>Hydrogen sulphide</i>	<i>0-1%</i>

Table 5: *chemical composition of biogas*

The obtained biogas does have the following characteristics:

- Density 1.2 kg/Nm³
- Lower calorific value 3,400 – 6,400 kcal/Nm³
- Ignition temperature 650 °C – 750 °C
- Ignition concentration 6 – 12 % vol.
- Liter equivalent fuel oil / Nm³ biogas 0.60 – 0.56 l/Nm³
- Smell depends on substrate – none in case of organics

Use of solid fermentation wastes

A further advantage of the generation of biogas from biomasses within a brick yard results in the total usability of the fermentation waste. The fermentation wastes, about 3% in weight of the total dry substance (DS) fed to the plant, can be used as pore forming agent without any major influences on the quality or chemical composition of the green or fired bricks.

The following tests have been made by adding a 10 to 12 % in volume of fermentation waste to the standard feedstock of the Gasser brickyard:

Solid characterization			Production	20% Fermentation wastes
Aluminum oxide	Al ₂ O ₃	% DS	15.2	11.8
Sulphur trioxide	SO ₃	% DS	0.9	0.7
Antimony oxide	Sb ₂ O ₃	mg/kg DS	<1.2	5.2
Barium oxide	BaO	mg/kg DS	550	480
Boron oxide	B ₂ O ₃	mg/kg DS	195	300
Calcium oxide	CaO	% DS	12.3	9.2
Iron oxide	Fe ₂ O ₃	% DS	7.5	5.8
Phosphoros oxide	P ₂ O ₅	% DS	0.54	0.47
Magnesium oxide	MgO	% DS	3.5	2.5
Manganese oxide	MnO	% DS	0.11	0.09
Lead oxide	PbO	mg/kg DS	75	380
Potassium oxide	K ₂ O	% DS	2.7	2.3
Silicium	SiO ₂	% DS	49.5	39.7
Sodium oxide	Na ₂ O	% DS	1.9	1
Titanium oxide	TiO ₂	mg/kg DS	10,000	7,600
Zinc oxide	ZnO	mg/kg DS	210	165
Zirconium oxide	ZrO ₂	mg/kg DS	370	270
Chlorides	Cl	mg/kg DS	<50	<50
Arsenic	As	mg/kg DS	20	20
Cadmium	Cd	mg/kg DS	<1	<1
Chrome	Cr	mg/kg DS	160	115
Mercury	Hg	mg/kg DS	1	2
Nickel	Ni	mg/kg DS	100.3	74
Copper	Cu	mg/kg DS	41	41
Selenium	Se	mg/kg DS	<2	<2

Table 6: chemical composition of bricks

Leaching characterization			Production	20% Fermentation wastes
<i>Fluorides</i>	<i>F</i>	<i>mg/l</i>	<i>1.5</i>	<i>1.1</i>
<i>Chlorides</i>	<i>Cl</i>	<i>mg/l</i>	<i>13</i>	<i>3</i>
<i>Nitrates</i>	<i>NO₃</i>	<i>mg/l</i>	<i><1</i>	<i><1</i>
<i>Sulphates</i>	<i>SO₄</i>	<i>mg/l</i>	<i>155</i>	<i>93</i>
<i>Arsenic</i>	<i>As</i>	<i>µg/l</i>	<i>7</i>	<i>6</i>
<i>Barium</i>	<i>Ba</i>	<i>µg/l</i>	<i>6</i>	<i>4</i>
<i>Beryllium</i>	<i>Be</i>	<i>µg/l</i>	<i><0.5</i>	<i><0.5</i>
<i>Cadmium</i>	<i>Cd</i>	<i>µg/l</i>	<i><0.5</i>	<i><0.5</i>
<i>Cobalt</i>	<i>Co</i>	<i>µg/l</i>	<i><1</i>	<i><1</i>
<input type="checkbox"/> <i>Chrome</i>	<i>Cr</i>	<i>µg/l</i>	<i>290</i>	<i>185</i>
<i>Mercury</i>	<i>Hg</i>	<i>µg/l</i>	<i><0.1</i>	<i><0.1</i>
<i>Nickel</i>	<i>Ni</i>	<i>µg/l</i>	<i><1</i>	<i><1</i>
<i>Lead</i>	<i>Pb</i>	<i>µg/l</i>	<i><1</i>	<i><1</i>
<i>Copper</i>	<i>Cu</i>	<i>µg/l</i>	<i><1</i>	<i><1</i>
<i>Selenium</i>	<i>Se</i>	<i>µg/l</i>	<i><3</i>	<i>4</i>
<i>Vanadium</i>	<i>V</i>	<i>µg/l</i>	<i>89</i>	<i>64</i>
<i>Zinc</i>	<i>Zn</i>	<i>µg/l</i>	<i>2</i>	<i>2</i>

Table 7: chemical composition of brick's leaching

The tests and trials carried out clearly show that a brick yard can be run on renewable fuels.