UNIVERSITY OF BERGAMO

School of Doctoral Studies

Doctoral Degree in ENGINEERING AND APPLIED SCIENCES

XXIX Cycle

MEASURING AND PROCESSING BIOGAS PRODUCED IN LABORATORY-SCALE BATCH REACTORS

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Doctoral Thesis

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Academic year 2015/16

ABSTRACT

In this work the upgrading of biogas into biomethane has been addressed by resorting to the use of the chemical capture of carbon dioxide. We started with the realization of a biodigestion systems used as source of biogas. With this system, we investigated either the production capacity of the different substrates and the main factors (temperature, pH and mixing of the substrate) which influence the biodigestion process. To make accurate measurements of the amount of biogas and biomethane produced, three types of different gas-meters, all based on the principle of liquid displacement, have been devised, assembled and compared. We have also evaluated three different types of gas flow calibrators, based on the principle of thermal mass flow sensing, constant differential pressure and mechanical displacement. At the end, we used the systems built to investigate the capture of carbon dioxide by ammonia in aqueous solution at room temperature and pressure where the volatilization of the ammonia has been limited by non-traditional methods.

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INTRODUCTION

THE ANTHROPIC CO_2 AND THE ROLE OF BIOGAS

Anthropogenic emissions of CO_2, the most important of the greenhouse gases, are mainly due to the consumption of fossil fuels from which nearly 80% of the energy used by the human society is derived. Since the beginning of the industrial era, the oceans have absorbed about half of these emissions, while the remainder went to increase the concentration of carbon dioxide in the atmosphere, which has now reached 400 ppm, a concentration nearly 50% higher than the maxima of the interglacial periods over the past ten million years. The problem is not just the atmospheric concentration of carbon dioxide, but rather the speed of its variation, which is taking place over decades, rather than over millennia or hundreds of millennia. This rapid change creates a dangerously unstable condition to which the biosphere, which adapts to climatic-atmospheric changes over geological times, responds with a mass extinction. In this respect, the earliest signs may come from the oceans whose pH is decreasing, endangering the crustacean fauna and its capability of permanently storing the atmospheric CO_2. Furthermore, due to the heating, the oceans may return, over a short time period, some of the CO_2 absorbed in the upper layers of its water, triggering an avalanche process between temperature rise and CO_2 release from the ocean surface.

The Kyoto Protocol sought to limit emissions, but it had in fact an effect opposite to the intentions as global emissions have also increased because the transfer of energy-intensive processes from developed to developing countries, which were not restricted by Kyoto, and are characterized by lower efficiencies and a higher content of carbon in the energy mix.

A contribution to the problem, relatively modest but exemplary, would have come from the DESERTEC project which planned to produce, by means of solar systems in the Algerian desert, a significant portion of the European electricity, which is mostly produced with fossils. But Europe would have been at the mercy of Algeria (or of terrorist attacks against the DESERTEC power lines); moreover, investing the financial resources required by DESERTEC in European renewables would have produced a bigger reduction in emissions.

An issue that increasingly engages the international research is the ***Carbon Capture and Sequestration*** (CCS) whose ultimate goal is not so much the reduction of anthropogenic emissions but rather the suppression of the excess CO_2 from the atmosphere. Lackner [I1] showed that the only reasonable way to permanently solve the problem is a chemical reaction involving atmospheric CO_2 and the abundant siliceous rocks. Essentially, we need to accelerate the natural (and slow) process of weathering, i.e. the meteoric degradation of siliceous rocks. A detailed proposal to that effect was put forward by House et al. [I2] which suggest using, on a very large scale, the electrochemical chlor-alkali process; the alkaline component placed in the oceans controls

the pH and captures the atmospheric CO_2 in the form of stable carbonates; the acid component is neutralized with siliceous rocks.

We have shown [I3] that the demand for electricity from the chlor-alkali process would entail, with the current mix of primary sources, additional emission almost equal to the amount of CO_2 sequestered. Furthermore, the estimated cost would be around € 100/t(CO_2), which is impossibly stiff.

On the other hand, thanks to advanced electrochemical technologies [I4], just a modest incentive would be needed to transfer chlorine factories from advanced countries to tropical areas where the sun power is readily available; it would result in an emission savings comparable to that provided by DESERTEC, with political and social advantages, and without negative strategic implications of this project. Our study indicates that a complete solution of the problem of greenhouse gas emissions into the atmosphere is still far away, but that many small useful projects are now within our reach. Perhaps, today the more important intervention is the partial replacement of fossil fuels with biofuels. Due to its origin, a biofuel does not involve an increase in atmospheric CO_2 since it contributes to the natural CO_2 exchanges between the atmosphere and biomass. Furthermore, a biofuel does not require major changes of the current productive structure, or development of new technologies for energy use and processing.

Within the biofuels, a special position is covered by biogas for the following reasons:

- biogas is produced by means of a natural process (anaerobic digestion) that is relatively easy to control;
- the operating cost of a biogas plant and the raw material (often a "waste" from other processes) is typically much smaller than the energy value of the product: this is not true, for example, in the case of ethanol produced with US maize ;
- biogas, unlike ethanol, is suitable for a distributed generation (with typical installations of less than one MW of electrical power), which reduces the biomass transportation costs and facilitates the re-use of the by-product (digestate);
- the production of biogas occurs at ambient temperature and pressure, and its treatment is easier compared to combustion gases that are at high temperature, and rich in chemically aggressive compounds;
- biogas can be burned directly to produce heat and electricity, or separated into its main components: CO_2 and CH_4. In turn, this CO_2 can be used or sequestered, further contributing to the reduction of atmospheric CO_2.

This thesis deals with the production and treatment of the biogas starting from the evaluation of the methanogenic power of different substrates in series of small laboratory reactors maintained at a controlled temperature. Although the commercial systems for biogas/biomethane measurement in the lab as a function of the reaction time are adequate (but expensive!), we chose to evaluate different, and partially new, techniques for measuring the small biogas/biomethane flows from our reactors. We

encountered and solved many problems, often unforeseen. This work has resulted in a manuscript submitted for publication in an international journal.

The next step consisted in the experimenting techniques designed to improve the efficiency of the anaerobic digestion process. The last experimental part of the thesis focused on the production of biomethane through capture of the biogas CO_2. Only chemical methods, utilizing the low-cost products, are valued because they are able to operate directly on the biogas produced by the digester and to seize "permanently" CO_2.

Chapter 1

BIOGAS AND BIOMETHANE

1.1 - THE BIOGAS RESOURCE

A central theme of the research focusing on mitigation of greenhouse effect is the capture and "seizure" of CO_2; in fact an important quantity of CO_2 is emitted by thermal power plants but the problem of the treatment of a high temperature gaseous flow rich in hazardous and / or corrosive substances has not yet been solved in an economically / technically satisfactory manner. Much less complex is the problem of removal of CO_2 from the biogas produced at room temperature by means of anaerobic digestion, a natural process that takes place under controlled conditions in small plants. Proceeding in this chapter, the basic information to understand most of the issues concerning the production and use of biogas will be given. In detail, the process of anaerobic digestion, from a microbiological point of view, will be initially described together with the main environmental factors to be considered in order to maximize the biogas production. Moreover the main analytical methods for process control and production estimation will be considered. Finally, after a description of the main components of biogas, a general overview about the state of the art of the techniques available for the upgrading of biogas into biomethane will be given.

1.2 - OVERVIEW OF ANAEROBIC DIGESTION PROCESS

1.2.1 - Degradation steps

The anaerobic degradation pathway of organic matter is a multi step process. This process is based on parallel and cross linked reactions and proceeds through four successive stages:

i) hydrolysis,
ii) acidogenesis,
iii) acetogenesis
iv) methanogenesis.

The anaerobic ecosystem is the result of complex interactions among microorganisms of several different species. The major functional groups of bacteria, according to their metabolic reactions, are:

i) fermentative bacteria,

ii) hydrogen-producing acetogenic bacteria,

iii) hydrogen-consuming acetogenic bacteria,

iv) carbon dioxide-reducing methanogens,

v) aceticlastic methanogens [A1].

A schematic of the reaction steps is given below (fig. 1.1)

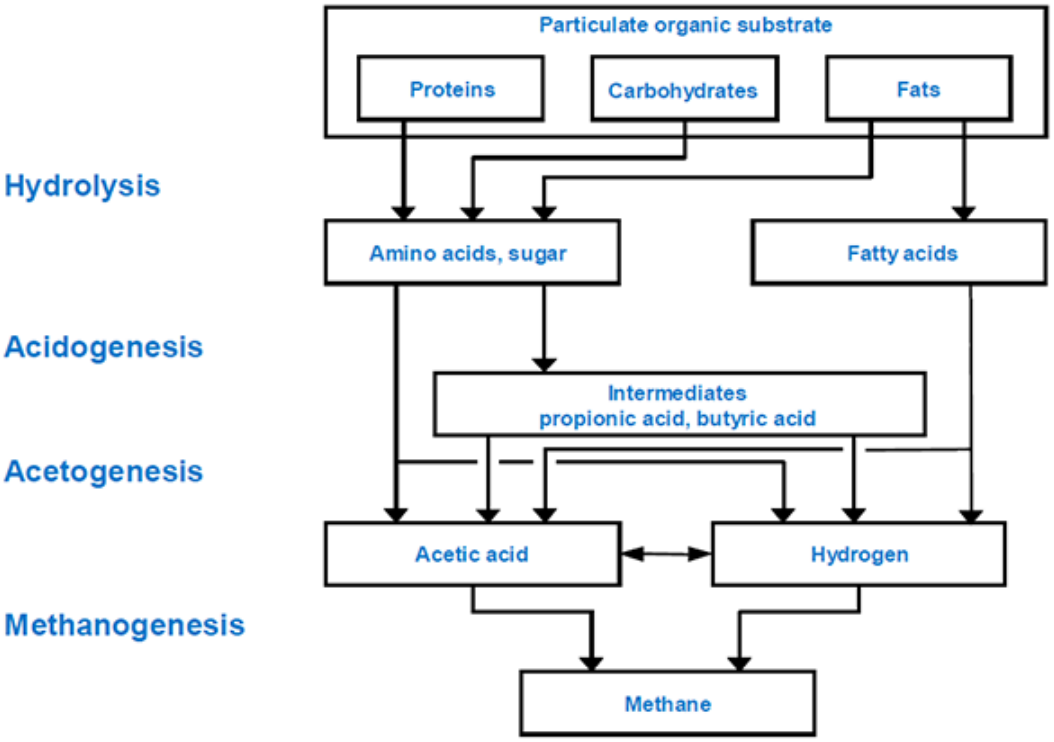

Figure 1.1: Degradation steps of anaerobic digestion process [A26]

The degradation process of anaerobic digestion consists of the following main steps:

1. Hydrolisys
2. Acidogenesis
3. Acetogenesis
4. Methanogenesis

Hydrolisys

In the anaerobic digestion, the term hydrolysis is used to describe degradation of a defined particulate or macromolecular substrate into its soluble monomers. For particulates, hydrolysis is merely a surface phenomenon while the process is molecular for smaller macromolecules (biopolymers). In detail, during

hydrolysis, bacteria transform the particulate organic substrate into liquefied monomers and polymers i.e. proteins; carbohydrates and fats are transformed to amino acids, monosaccharides and fatty acids respectively. Equation 1 shows an example of a hydrolysis reaction where organic waste is broken down into a simple sugar, in this case, glucose [A2].

$$C_6H_{10}O_4 + 2H_2O \rightarrow C_6H_{12}O_6 + 2H_2 \quad \text{(eq. 1)}$$

The hydrolisys process is performed by heterotrophic microorganisms that attached to particles, produce enzymes in the vicinity of the particle and benefit from soluble products released by the enzymatic reaction. Therefore, the microorganisms growing on the particle surface, rather than the enzyme produced, should be regarded as the effective catalyst [A3]. Products from hydrolysis are readily accessible for acidogenic bacteria.

The hydrolysis process is very sensitive to temperature and temperature fluctuations. Hydrolysis is generally considered to be the rate - limiting step during the anaerobic digestion of complex substrates. Investigations by Chandler et al. (1980) and Zeeman et al. (1996) [A1] showed that this happens not because of lack of enzyme activity but more due to the availability of free accessible surface area of the particles and the overall structure of the solid substrate.

Acidogenesis

In the second stage, acidogenic bacteria transform the products of the first reaction into short chain volatile acids, ketones, alcohols, hydrogen and carbon dioxide. The principal acidogenesis stage products are propionic acid (CH_3CH_2COOH), butyric acid ($CH_3CH_2CH_2COOH$), acetic acid (CH_3COOH), formic acid ($HCOOH$), lactic acid ($C_3H_6O_3$), ethanol (C_2H_5OH) and methanol (CH_3OH), among other.From these products, the hydrogen, carbon dioxide and acetic acid will skip the third stage (acetogenesis) and will be utilized directly by the methanogenic bacteria in the final stage.

Equations 2, 3 [A2] and 4 [A4] represent three typical acidogenesis reactions where glucose is converted to ethanol, propionate and acetic acid, respectively.

$$C_6H_{12}O_6 \leftrightarrow 2CH_3CH_2OH + 2CO_2 \quad \text{(eq. 2)}$$

$$C_6H_{12}O_6 + 2H_2 \leftrightarrow 2CH_3CH_2COOH + 2H_2O \quad \text{(eq. 3)}$$

$$C_6H_{12}O_6 \rightarrow 3CH_3COOH \quad \text{(eq. 4)}$$

Acetogenesis

In the third stage, known as acetogenesis, the rest of the acidogenesis products, i.e. the propionic acid, butyric acid and alcohols are transformed by acetogenic bacteria into hydrogen, carbon dioxide

and acetic acid. Hydrogen plays an important intermediary role in this process, as the reaction will only occur if the hydrogen partial pressure is low enough to thermodynamically allow the conversion of all these acids. Such lowering of the partial pressure is carried out by the hydrogen scavenging bacteria, thus the hydrogen concentration of a digester is an indicator of its health [A5]. Equation 5 represents the conversion of propionate to acetate, only achievable at low hydrogen pressure. Glucose (Equation 6) and ethanol (Equation 7) among others are also converted to acetate during the third stage of anaerobic fermentation [A2].

$$CH_3CH_2COO^- + 3H_2O \leftrightarrow CH_3COO^- + H^+ + HCO_3^- + 3H_2 \quad \text{(eq. 5)}$$

$$C_6H_{12}O_6 + 2H_2O \leftrightarrow 2CH_3COOH + 2CO_2 + 4H_2 \quad \text{(eq. 6)}$$

$$CH_3CH_2OH + 2H_2O \leftrightarrow CH_3COO^- + 2H_2 + H^+ \quad \text{(eq. 7)}$$

Methanogenesis

The fourth and final stage is called methanogenesis. During this stage, microorganisms convert the hydrogen and acetic acid formed by the acid formers to methane gas and carbon dioxide (Equations 8, 9 and 10) [A6]. The bacteria responsible for this conversion are called methanogens and are strictly anaerobes. Waste stabilization is accomplished when methane gas and carbon dioxide are produced.

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad \text{(eq. 8)}$$

$$2C_2H_5OH + CO_2 \rightarrow CH_4 + 2CH_3COOH \quad \text{(eq. 9)}$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad \text{(eq. 10)}$$

1.2.2 - Environmental factors

The successful operation of anaerobic reactor depends on maintaining the environmental factors close to the comfort of the microorganisms involved in the process. The main environmental factors to consider are temperature and pH of the substrate.

Temperature

Anaerobic processes, like other biological processes, operate in certain temperature ranges. Typically, as a general rule, it is possible to estimate that the rate of a biological reaction doubles for each 10°C rise in temperature up to an optimum value and then it declines rapidly. Particularly, on the basis of the temperature value, the digestion process can be defined psychrophilic, mesophilic or thermophilic. The influence of temperature on the growth rate of methanogens is described in the following figure (fig 1.2).

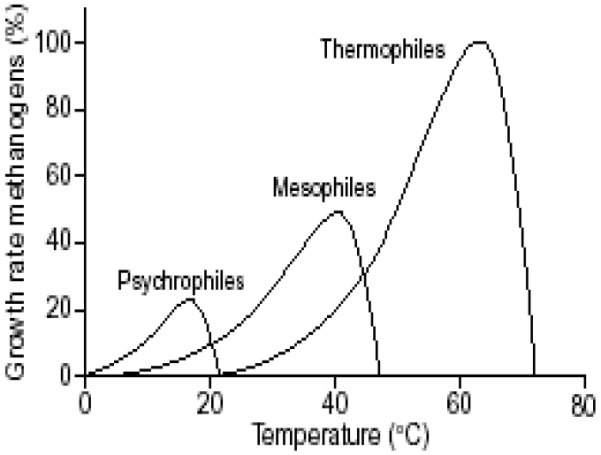

Figure 1.2: Temperature influence on the growth rate methanogens

Psychrophilic digestion

The anaerobic digester that operates at the psychrophilic temperature range (10-20 degree centigrade) is known as psychrophilic digestion. Typically, psychrophilic digestion is not considered attractive because of its low biological activity leading to low biogas production rates, although some research [A7-A8] presented that psychrophilic anaerobic digesters can successfully degrade organic matters for a reasonable biogas production.

Mesophilic digestion

The anaerobic digester that operates at the mesophilic temperature range (35-38 degree centigrade) is known as mesophilic digestion. Mesophilic anaerobic digestion is the most common system which has a more stable operation but a lower biogas production rate. Another disadvantage of mesophilic digestion is that it does not reduce enough the pathogen concentrations in order to produce a biosolids that contains no detectible levels of pathogens [A9].

Thermophilic Digestion

The anaerobic digester that operates at the higher thermophilic temperature range (50 to 65 degree centigrade) is known as thermophilic digestion. Interest in the thermophilic digestion is based on the fact that higher temperatures reduce pathogens and thermophilic temperatures provide more rapid reaction rates than mesophilic temperature. Indeed thermophilic digestion, when some time/temperature criteria are satisfied as that specified in the US EPA Part 503, can produced biosolids that contains no detectible levels of pathogens. Moreover, thermophilic anaerobic digestion in general are more efficient in biogas production but are also associated with higher maintenance costs.

The advantages of thermophilic digestion can be summarized in:

- Increased volatile solids reduction
- Faster reaction rates for shorter retention times
- Higher capacity for a given volume
- Increased pathogen destruction
- Improved dewaterability of the digested biosolids

Vice versa, the main disadvantages of thermophilic digestion are:

- Higher odor formation resulting from a higher volatile fatty acid (VFA) concentration
- Higher energy requirements for heating
- Increased sensitivity to thermal shock

pH

Two microbial domains exist in terms of optimal pH range namely acidogens and methanogens. The best pH range for acidogens is 5.5 – 6.5 and for methanogens is 7.8 – 8.2. The operating pH for combined cultures is 6.8 – 7.4 with neutral pH being the optimum value. Since methanogenesis is considered a rate limiting step, it is necessary to maintain within the reactor a pH close to the neutral value.

Low pH reduces the activity of methanogens causing an accumulation of VFA and H_2. At higher partial pressure of H_2, propionic acid degrading bacteria will be severely inhibited, thereby causing an excessive accumulation of higher molecular weight VFAs such as propionic and butyric acids so that the pH drops furtherly. If the situation is left uncorrected, the process may eventually fail. This condition is known as going "SOUR" or STUCK". In this case the remedial measures are the reduction of the loading rates and the supplement of chemicals to adjust the pH: alkaline chemicals such as $NaHCO_3$, NaOH, Na_2CO_3 , quick lime (CaO), slaked lime [$Ca(OH)_2$], limestone (or softening sludge) $CaCO_3$, and NH_3 can be used. The pH dependence of methanogens is shown in the next figure (fig. 1.3)

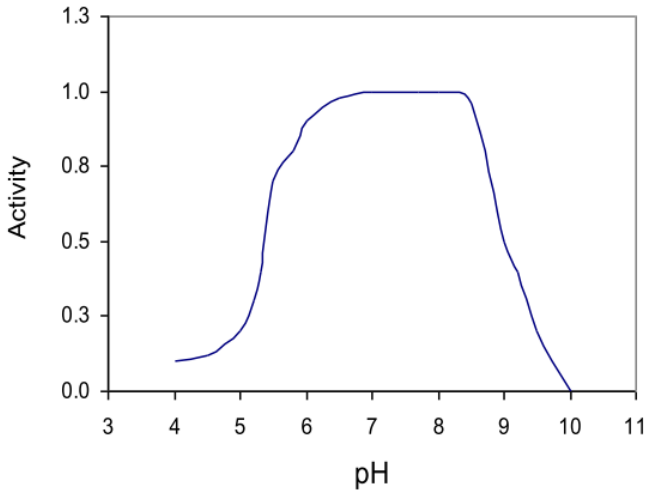

Figure 1.3: Relative activity of methanogens to pH

1.2.3 - Analytical methods

Following are reported the main chemical and physical analyzes useful to identify the main features of the feedstock.

Total solids (TS)

The total solids, also called dry matter (DM), represent the organic fraction and the inert fraction which constitute the total of the dry substance present in the sample. In other words, they allow to estimate the water content of the feedstock. The percentage of total solids (TS%) are determined as the ratio between the weight that the sample assumes after a drying process (12-24 hours in oven at 105 °C , until constant weight is reached) and the initial weight of the sample. On the basis of the percentage of the total solids content, the biodigestion process can be defined as: dry (TS > 20%), semi-dry (10% < TS < 20%) or wet (5% < TS < 10%).

Volatile solids (VS)

The volatile solids, also called organic dry matter (oDM), represents the amount of organic material in a sample. They are particularly important because represent the part of the sample which can be transformed into biogas, which yields depends in turn on the type of molecules that form it.

In general, this determination is carried out together with the TS determination described above.

Practically, after the sample is dried in a drying chamber at 105°C (for the TS determination), it's ignited for 1-2 hours, until constant weight is reached, in a muffle furnace at 550°C. The percentage of volatile solids (VS%) is calculated as the ratio between the result obtained by subtracting ash from the total solids and the initial weight of the sample. To limit the emission of unpleasant odors, very significant at this stage, a good procedure is to heat the sample on a electric cooker under a fume hood until the extinction of the visible smoke and only after putting it into the muffle furnace.

pH

The term pH mean "pondus Hydrogenium", i.e. literally hydrogen weight. Its value determines the acidity or basicity of an aqueous solution. Its unit is the negative logarithm of the concentration of hydronium (H^+) ions. The pH value can be determined in a liquid feedstock with a standard potentiometric electrode.

COD

The chemical oxygen demand (COD) is a parameter which indicates the total chemically oxidisable material in the sample and therefore is a parameter which indicates the energy content (or organic pollution) of a

feedstock. In this analysis, the sample is refluxed in a boiling mixture of sulphuric acid and potassium dichromate ($K_2Cr_2O_7$). In the next step, the remaining unreduced potassium dichromate is titrated with ferrous ammonium sulphate, which allows the determination of the equivalent oxygen consumed.

VFA

Volatile fatty acids (acetic acid, propionic acid, butyric acid, valeric acid,...) are intermediate metabolites of the anaerobic digestion process. Therefore, their accumulation can give direct feedback on the interactions of the different groups of micro-organisms in the reactor.

Alkalinity ratio

The Alkalinity ratio is a titration measurement with sulphuric acid, it determines the ratio of the intermediate alkalinity (IA) caused by the organic acids over the partial alkalinity (PA) due to the bicarbonates. In the English literature it is called the IA/PA ratio, however, also other terms are used like VFA/bicarbonate, VFA/ALK or Ripley ratio are in use. In German literature this parameter is called FOS/TAC

TKN

The nitrogen content of a feedstock can be determined approximated by the total Kjeldahl nitrogen (TKN) determination. In this analysis, organic nitrogen is converted to ammonium nitrogen by boiling the feedstock sample in the presence of sulphuric acid and a catalyst. After that, similar to the NH_4-N analysis, a base is added and ammonia is distilled from the alkaline solution to an acid solution (usually boric acid) where ammonia is quantitatively absorbed and then measured.

1.3 - BIOGAS COMPOSITION

Biogas consists mainly of methane and carbon dioxide, but it also contains several impurities. It has specific properties which are listed in Table 1.1

Detailed overview of biogas components

Depending on the production technology and the substrate used, biogas can have significantly different compositions that should be checked regularly on a long-term basis. The next table (Tab. 1.1) gives an overview of the typical gas components and their impacts on the gas quality.

Component	*Content*	*Effect*
CO_2	25–50% by vol.	– Lowers the calorific value – Increases the methane number and the anti-knock properties of engines – Causes corrosion (low concentrated carbon acid). if the gas is wet – Damages alkali fuel cells
H_2S	0–0.5% by vol.	– Corrosive effect in equipment and piping systems (stress corrosion); many manufacturers of engines therefore set an upper limit of 0.05 by vol.%; – SO_2 emissions after burners or H_2S emissions with imperfect combustion – upper limit 0.1 by vol.% – Spoils catalysts
NH_3	0–0.05% by vol.	– NO_x emissions after burners damage fuel cells – Increases the anti-knock properties of engines
Water vapour	1–5% by vol.	– Causes corrosion of equipment and piping systems – Condensates damage instruments and plants – Risk of freezing of piping systems and nozzles
Dust	>5 µm	– Blocks nozzles and fuel cells
N_2	0–5% by vol.	– Lowers the calorific value – Increases the anti-knock properties of engines
Siloxanes	0–50 mg m^{-3}	- Act like an abrasive and damages engines

Table 1.1: Typical components and impurities in biogas [A10].

Below are detailed all the substances that are present even in trace in biogas. [A10, A12, A13, A27].

Methane

The methane is present in the biogas in a variable amount from 30 to 70% vol. depending on many factors. It is by far the most desired component of the biogas, which become flammable when the content of this molecule is greater than 45%. The methane is obtained from the reactions of methanogenesis. These reactions produce methane starting from acetic acid or hydrogen, in turn freed, passing through intermediate compounds such as monosaccharides, amino acids and long chain fatty acids, supplied from the fermentation of carbohydrates, protein and lipid content in the substrate. The production of methane depends strongly on many operating parameters, such as the temperature or the pH in the digester, as well as from the quality of the substrate (the major productions are mainly obtained using lipid substrates or ethanol-rich materials), from its movement and physical pretreatment, as well as the water content.

Carbon dioxide

The biogas can contain a 15-50% vol. of carbon dioxide. It is one of the main products of anaerobic fermentation, produced in acidogenesis, acetogenesis and methanogenesis phases. It is proper to observe that, in some applications, the carbon dioxide is not a totally unwanted component, such as when the biogas is used on site to produce heat. In this case it's sufficient to adopt a combustion apparatus suitable for fuels with low calorific value. For more important applications, such as the injection into the natural gas grid or use in motor vehicles, it is however necessary to separate the carbon dioxide from the methane.

Water

The final product of digesters is biogas saturated with water vapor. The water comes from the substrate which, for practical reasons, it is often characterized by a certain fluidity.

Sulfur compounds

Sulfur compounds are present in the biogas in the form of sulfides, disulfides and mercaptans. However, the reducing atmosphere of digester causes that the sulfur is present mainly in the form of hydrogen sulphide (H_2S). It is formed by the bacterial decomposition of proteins containing sulfur. The content of sulfur in the exhaust gases depends on the process and the type of waste. Without a desulfurizing step, the concentration of H_2S would exceed 20000 ppm (0.2% by volume) [A12]. It is a compound harmful to the environment and for many technical applications, since it is highly corrosive. For these reasons it is one objective to keep the hydrogen sulfide content at the lowest level possible, since plant components downstream could be damaged by H_2S. For all the above reasons, the biogas is usually desulfurized while it still stays in the bioreactor by means, for example, of air injection into the digestion chamber.

Oxygen

Typically in biogas digesters molecular oxygen is virtually absent and, in the case, its presence is due to air infiltration caused by imperfect sealing of the gas pipes. The oxygen concentration, however, can rise if biological desulphurization methods, which provide for the introduction of air into the digestion chamber, are used.

Nitrogen

Because the nitrogen is not participating in the reactions and so it's not consumed, it can be present also in higher percentages of about 15% by vol. As in the case of oxygen, its presence is due to air infiltration caused by imperfect sealing of the gas pipes or biological desulphurization methods.

Hydrogen

The molecular hydrogen is present in traces, it develops as a byproduct of the phases of acidogenesis and acetogenesis, but is then consumed by other stages of the process.

Ammonia

The concentration of ammonia is usually very low, often lower than 100 ppm. It is formed as a byproduct of acidogenesis reactions. High concentrations can affect the burn behavior and the life of the engines [A10].

Carbon monoxide

Typically the amount of carbon monoxide is below the detection limit of 0.2% by vol.

Halogen compounds

In the biogas halogenated compounds are manifested mainly in the form of molecules containing chlorine or fluorine, such as carbon tetrachloride, chlorobenzene, chloroform, trifluoromethane. They are mostly present in landfill gas as a result of volatilization of the organic fraction of municipal waste, while they are rarely present in biogas from digesters. The combustion of these compounds cause the emission of dioxins and furans, which are a high environmental impact molecules. The total chlorine is detectable in the landfill biogas in amounts of about 20 to 200 mg/Nm3, in the gas from anaerobic digesters is instead almost absent (0 ÷ 5 mg/Nm3).

Siloxanes

Siloxanes are volatile organic compounds containing silicon and oxygen. They are found in higher concentrations in the biogas by the anaerobic digestion of sewage effluents, due to silicon compounds contained in urban exhaust because they are constituents of various detergents and cosmetics. For this reason the biogas from sewage wastewater show peak concentrations of 400 mg/Nm3, whereas the biogas from other substrates (agriculture or livestock) show instead lower contents, of the order of 30 ÷ 50 mg/Nm3 [A11].

Solids

Each of anaerobic digestion system provides biogas with suspended solid particulates also of large size (up to orders of magnitude of mm), also the biogas flow can be affected by the formation and entrainment of foams.

1.4 - BIOGAS PURIFICATION

The main purification technologies, divided according to pollutant that are capable of removing [A10, A12, A21, A27, A28] are described below.

1.4.1 - Carbon dioxide removal

Carbon dioxide, together with methane, is one of the main components of biogas, so the separation of the CO_2 allows the enrichment of biogas with methane. There are many different techniques to accomplish the

separation of CO_2 from biogas, they are based on different physical, chemical or thermodynamic principles [A23, A30].

1.4.1.1 - Absorption

The separation of CO_2 from the biogas flow is carried out by the contact with a liquid stream which can absorb it selectively; the contact occurs, by feeding the gas and liquid flow from below and from above of a column where devices, suitable to promote the transfer of matter from one phase, are placed.
The purified gas stream exits from the top of the column while the liquid solvents, rich in carbon dioxide, are removed from biogas flows from the bottom of it. So it is necessary to regenerate the solvent by the removal of CO_2 absorbed.
The absorption processes also are classified as a function of the solvent regeneration mode: the absorbate species can be released by

I) simple expansion of the solvent (flashing),
II) contact of the solvent with an inert gas stream (stripping),
III) heating the solvent (reboiling).

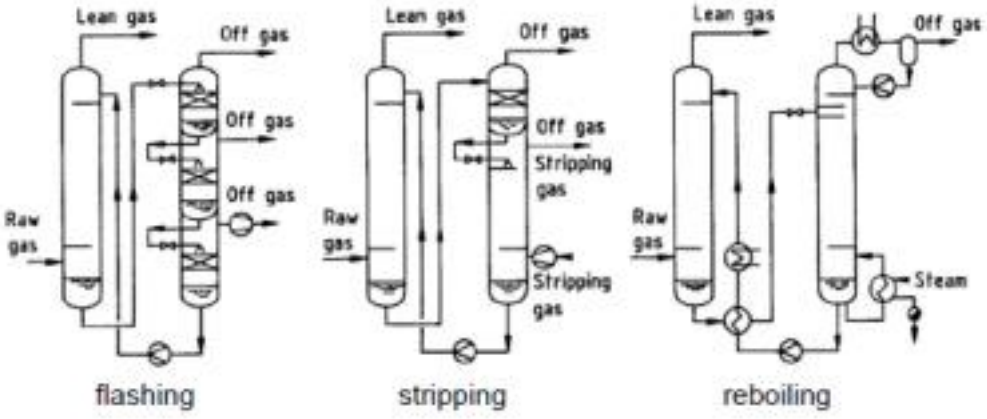

Figure 1.4: Regeneration modes [A27]

The absorption can be pushed by physical or chemical mechanisms.
The physisorption is caused by physical interactions (Van der Waals forces) between the molecules of the species that absorbs and those of the solvent. It establishes a linear relationship between the partial pressure of the species to be absorbed in the gas phase and its amount dissolved in the solvent. Linearity can be tested in a large operating range.
By assuming the thermodynamic equilibrium for the solvent on the bottom of the column, it is possible to absorb a considerable quantity of the species to be separated with relatively little solvent only if its partial

pressure in the gas is high (this is the case of CO_2 in the biogas). The pressure, in fact, has a strong effect on the equilibrium.

On the contrary, chemisorption is characterized by the formation of chemical bonds between the molecules of the species that absorb and those of a compound that are already dissolved in solvent. Typically, compound which trigger reactions with very favorite chemical balance are used, they virtually proceed until empty reagent is obtained. On the bottom of the column a good quantity of the substance to be absorbed can be removed, even if it has a modest partial pressure, with moderate amounts of solvent.

The Increase of the partial pressure of the gas to remove the solvent is rapidly saturated. In this case the pressure has little effect on the absorption pressure.

It is possible to adopt mixed systems, which combine the advantages of the physical and chemical absorption using physical solvents that dissolve chemical sorbents. This allows to expand the scope of application and to facilitate an easy regeneration of the solvent.

Absorption with water washing

The absorption system with water scrubbing is a purely physical method to separate the carbon dioxide from the biogas stream. The CO_2 is located in the biogas in high percentages (up to about 50%) and the physical absorption offer, as already mentioned, good removal efficiencies in this operating condition.

It is carried out in normal packed columns. By feeding the biogas flow to the column (pre-compressed at 4 to 12 bar) acid gases such as carbon dioxide and hydrogen sulphide are removed simultaneously due to the difference between the bonding forces of CO_2 and H_2S (polar) and CH_4 (non-polar).

The apparatus design of the gas washing is made on the basis of solubility of the gases to be considered, it also depends on temperature, pressure, and acidity.

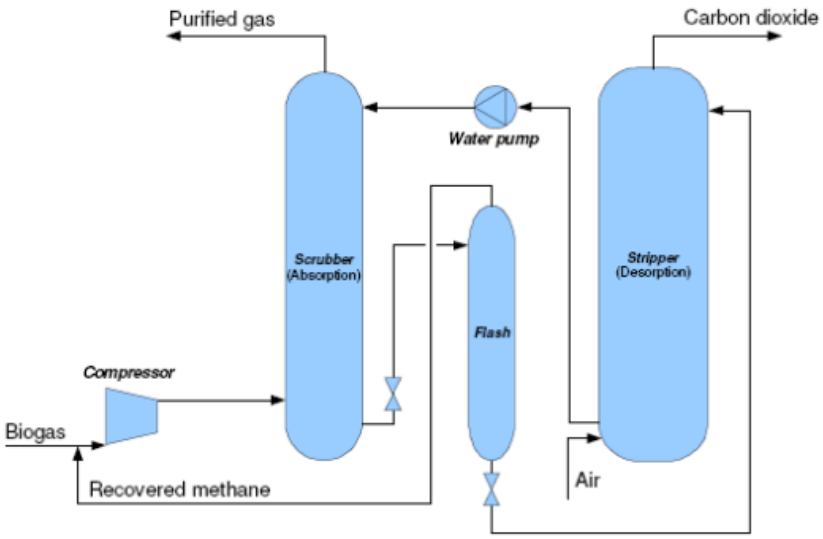

Figure 1.5: Water washing with regeneration [A25]

The regeneration is made by expanding the solvent (flashing), generally in atmospheric pressure.

It is possible to apply sub-atmospheric pressures to facilitate the desorption, high temperatures and possibly stripping air. Depending on the technical requirements and the design choices, it is possible to subtract from the biogas also hydrogen sulphide in addiction to the carbon dioxide.

In this case, during regeneration both components are released in the flash chamber. Consequently, further treatments are necessary to avoid placing the hydrogen sulfide into the environment. The alternative is the separation of H_2S before the enrichment of biogas by absorption; in this way the corrosion problems on the system is avoided and it's possible to release directly into environment the desorbed gas from the solvent.

If there of large amounts of water are available, as in the plants purification of sewage sludge, it's possible to opt for a single system column regeneration. In this way the water used for the absorption is lost and the carbon dioxide contained will be dispersed in the environment. It is therefore appropriate that the concentration of other dissolved contaminants (H_2S) is sufficiently low, so it does not require a step of post-treatment. Another advantage of this technique is the use of absorbent fluid practically "pure", i.e. not contaminated departing with the species which must retain, offering the best potential for absorption.

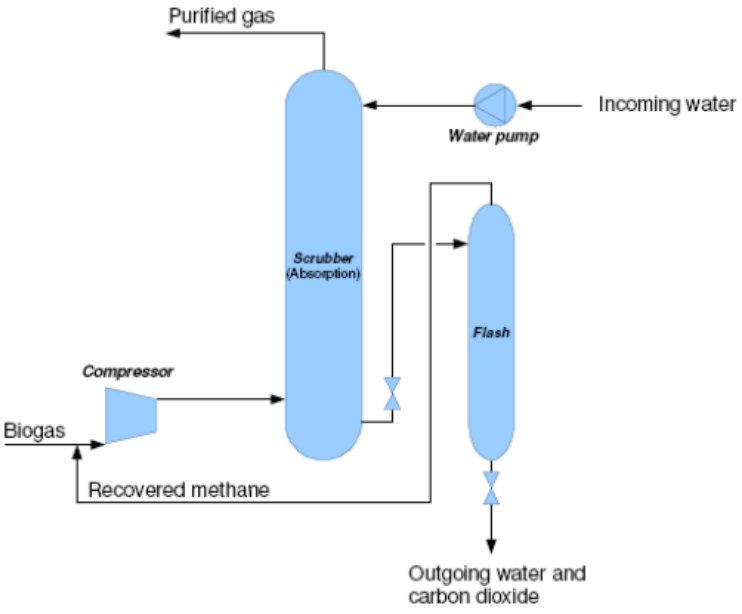

Figure 1.6: water washing without regeneration [A25]

In any case, the absorption column is frequently subject to clogging by fouling, it is therefore necessary to adopt equipped columns with automatic cleaning systems.

It is possible to increase the removal efficiency by adopting a system of absorption of physical-chemical mixture, using calcium hydroxide solutions Ca(OH)2. CO_2 and H_2S react with it by forming CaCO3 and CaS, precipitates insoluble.

Other fluids

There are fluids for physical absorption in which the carbon dioxide (and hydrogen sulphide) is more soluble than in water.

The Selexol process uses mixtures of dimethyl ether and polyethylene glycol, which is not toxic and not-corrosive. It operates by the absorption at pressures of 20 to 30 bar. The regeneration is problematic in the presence of sulfur compounds, as it is not possible to desorb them at atmospheric pressure. It is therefore preferable to perform a preliminary desulfurization.

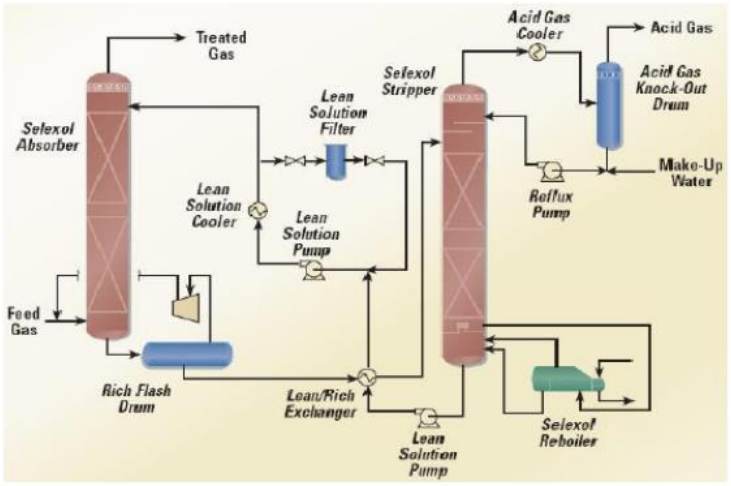

Figure 1.7: Selexol process [A31]

The Rectisol process instead uses methanol; the washing is carried out at high pressure (50 bar) and at low temperature, it can operate selectively by separating carbon dioxide and hydrogen sulphide in different flows. However, it is suitable for currents of already poor biogas CO_2.

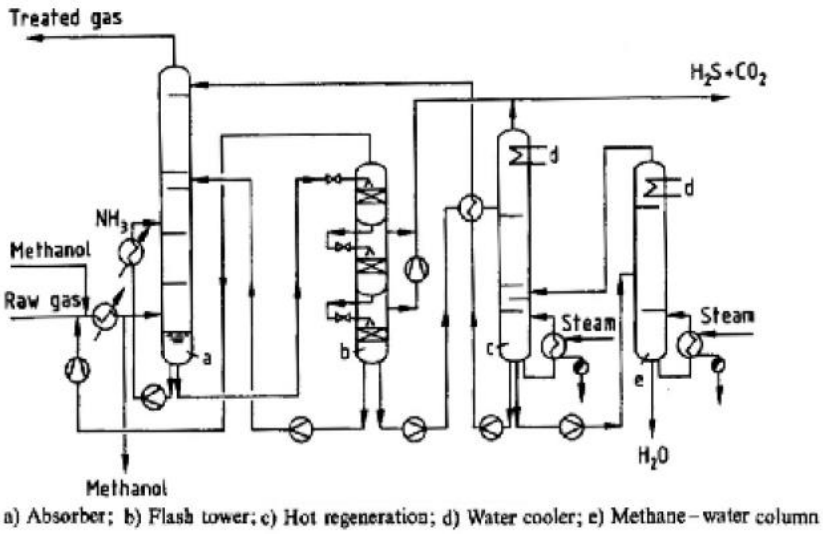

Figure 1.8: Rectisol process [A27]

It is also useful to mention the Purisol, Sulfinol and Sepasolv processes, that little differ from those that are dealt with.

Processes of chemical absorption

Chemical absorbents can ensure greater removal efficiencies and selectivity; the gas absorption acids is carried out with alkaline solvents, at low pressures and temperatures of 40 ÷ 70 ° C. As solvents are mainly used ethanol-amines, such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), methyldiethanolamine and (MDEA) or potassium carbonate solutions. Currently, the technology considered the most convenient and reliable is the separation of CO_2 with MEA. If should also be removed hydrogen sulphide, instead, it is preferred use MDEA.

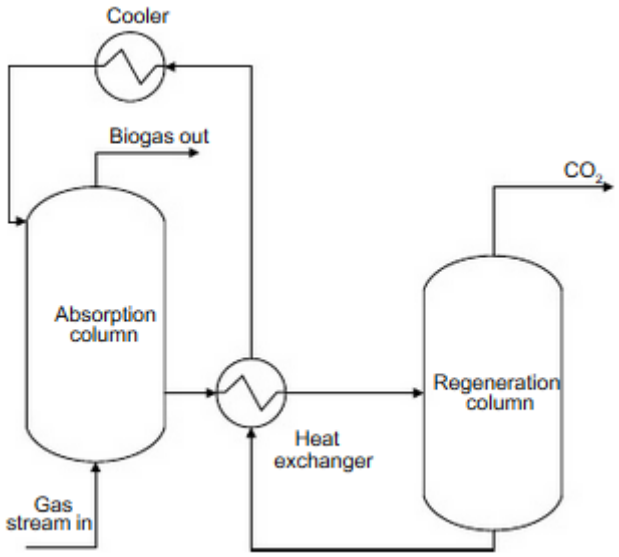

Figure 1.9: Chemisorption: principle of operation [A28]

The power of absorption of the amines may be limited by the presence of impurities in the biogas, such as particulates, sulfur oxides and nitrogen and oxygen, that degrade quickly. In the presence of these compounds is therefore required their preliminary removal. If this purification is problematic or uneconomical, may be convenient to choose different technologies for the enrichment of biogas. After the chemical absorption, regeneration must force the reverse chemical reaction to take place with introduction of heat and a strong low blood pressure, with a considerable energy demand. Not in all cases it is convenient to regenerate on site solvents and, if necessary, they can be replaced.

There are other reagents that can be used similarly to those already set, among them can be mentioned ammonia (NH_3) and potassium carbonate (K_2CO_3).

1.4.1.2 – Adsorption

It is possible to separate the carbon dioxide from biogas by its adsorption on beds of active carbon or molecular sieves. The gaseous stream is contacted with a solid on which, due to the different chemical affinity of the species in the fluid phase with respect to the solid surface, takes place the selective deposition of one or more species. In the case of molecular sieves, the smaller molecules exceed the solid bed, while the larger adhere on it.

Zeolites or the CMS (coal molecular sieves) can be used as molecular sieves. The raw materials are natural or synthetic mineral aluminosilicate hydroxide containing metal ions; releasing water sites are created of the regular cavity and identical to each other, this is the premise to use them to selectively adsorb specific molecules. The CMS are obtained from finely crushed coal that are pre-oxidized with air and then mixed with pitch and extruded to obtain forms with high surface to volume ratios.

Unlike absorption, the adsorption can not be operated in stationary conditions. The difficulty of handling the solid phase makes in fact necessary to operate with fixed beds. On them the phenomenon of absorption continues with a progressive saturation of the sorbent; during the operation, the front of saturation moves from the inlet section to the outlet of the fluid stream.

After some time, the removal efficiency suffers a decline so that it's necessary to proceed to the regeneration of the solid bed. The regeneration can occur in two different modes:

i) decreasing the pressure (pressure swing adsorption, PSA)

ii) by increasing the temperature (Temperature swing adsorption, TSA).

The last method is used in the presence of strong interactions between adsorbed and the adsorbent, as in the case of the purification driven by micro-pollutants.

The PSA process is instead indicated for weak interactions, as in the case of the separation of carbon dioxide.

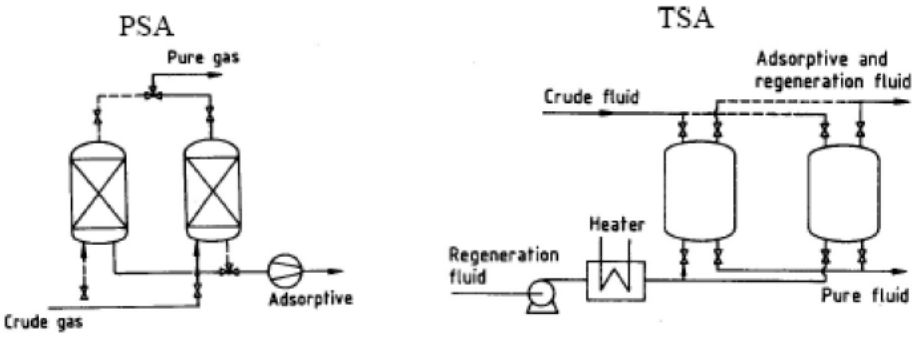

Figure 1.10: PSA and TSA: conceptual schemes [A27]

PSA process

In this case, the regeneration is carried out by depressurizing the bed; often a purge current is sent to the bed, after the depressurization, to complete the desorption. In order to ensure a continuous operation process, it is necessary to provide at least two beds that are alternately used by a suitable system of valves in conditions of adsorption and regeneration.

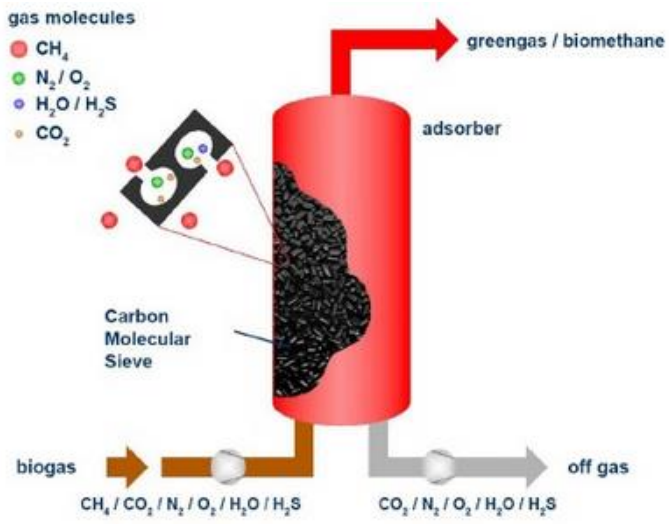

Figure 1.11: PSA with CMS principle of operation [A29]

For the use of this technique, the biogas must be the more dehydrated as possible, otherwise the solids will be damaged. Typically, it removes water biogas making condense on the heat exchangers. Substances adsorbents may have a useful life that is theoretically infinite, provided that harmful contaminants are absent in the biogas, such as the oils used in compressors.

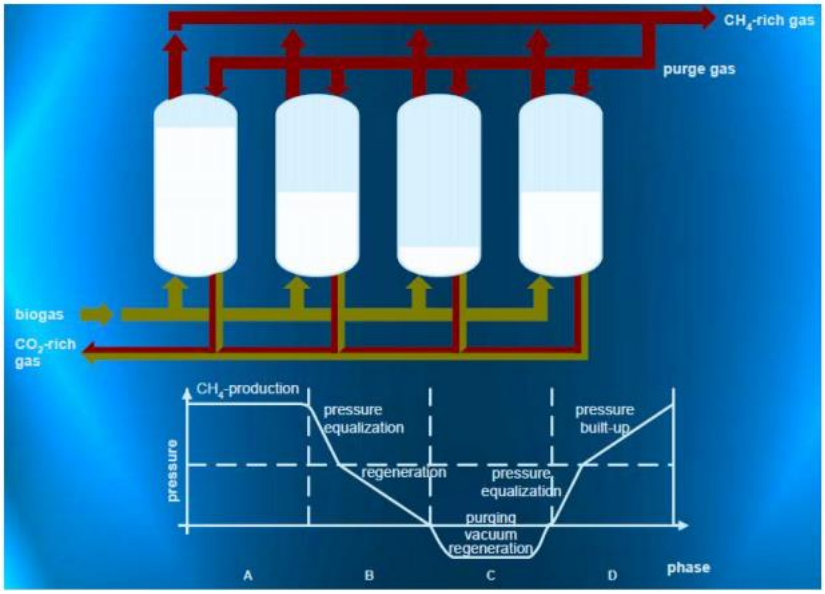

Figure 1.12: PSA process [A32]

Normally a PSA process is adopted in a 4-bed configuration: the first operates is the adsorption under pressure (10 ÷ 15 bar), the second is depressurized by emptying enriched biogas and partly by the CO_2 adsorbed, the third bed is purged at atmospheric pressure by the current outgoing from the second bed to complete the regeneration.

The fourth bed is pressurized using the current supplied from the first and the second bed. The operating phases of the various beds are cyclically rotated within time. This multi-bed configuration can be operated continuously and reduces the power to engage in compression.

Generally enrichments obtained are sufficient to meet the specifications on biogas for traction and no further treatments are needed for the abatement of CO_2.

However, if the starting biogas is rich in O_2 and N_2, it has also adsorption of methane, which is then recovered in the desorption; in this case it is required a two-stage process.

The amount of methane contained in the separated CO_2 makes necessary, to avoid the emission of CH_4 in the atmosphere, to burn it in the combustor for low-calorific gas, this requires the prior removal of hydrogen sulphide, which can be carried on a separate bed of active carbon.

VPSA process

A variant of the process is the"vacuum" version also known as "Vacuum pressure swing adsorption". It operates as the PSA system and with the same adsorbents. Biogas undergoes only a modest compression with the fan and does not need pretreatment or preliminary purifications (excluding drying and oils removal). Regeneration indeed is an "empty" process, adsorption and desorption takes place at approximately the same temperature. For these reasons, the VPSA system has greater construction cost and operation.

1.4.1.3 - Separation with semi-permeable membranes [A16-A19]

The use of a selective membrane allows to separate the components of a gaseous stream which present different permeability. These are porous membranes, in which the selectivity depends on the pore size and diffusive membranes, where the selectivity is determined by the speed of spreading.

For biogas purification are normally used diffusional membranes. Each gas has a different rate of diffusion in the solid of which the membrane is formed; materials used in the diffusion of methane is much slower compared to the CO_2 or the H_2S. The transport is then governed by the permeability of the component to be removed within the material of the membrane. For polymeric membranes of cellulose acetate the permeability to CO_2 and H_2S is greater by respectively 20 and 60 times compared to that of the CH_4.

The process can be accomplished in two ways: gas - gas or gas - liquid.

In the first case on both sides of the membrane there is a gaseous phase: biogas from one side and air on

the other. They are also called dry membranes. The process can be performed at a low (8 ÷ 10 bar) or high pressure (> 25 bar).

In the second case there is biogas on a face of the membrane and a liquid on the other one, the liquid (for example the amines) absorbs the gas that crossed the membrane. In this case it is not necessary that the membrane is selective, the process takes place approximately at atmospheric pressure.

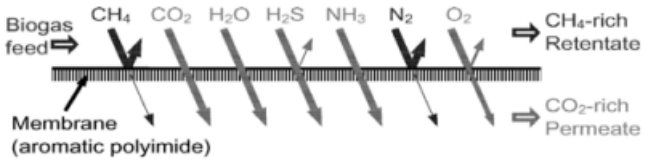

Figure 1.13: Operating principle of the semi-permeable membranes [A15]

The membranes do not tolerate the presence of water in the biogas; they can be used for the simultaneous removal of CO_2 and H_2S, except for manipulating the substances separately to avoid sulfur compounds into the atmosphere. The removing of hydrogen sulfide accomplished by these membrane systems is not enough to meet the specifications on biomethane traction.

The goodness of the process is strongly influenced by the temperature of the gas and the difference on the horseback pressure of the membrane, which may not be excessive to maintain an acceptable mechanical stress on it.

Methane losses can be significant if the process is very fast: it is impossible to achieve high removal efficiencies without high doses of CH_4 exceeding the membrane. It's possible to avoid this problem by adopting a plant configuration with multiple membranes connected in series. Otherwise methane contained in the CO_2 stream should be recovered if there are in the system thermal requirements that can be combusted on the site.

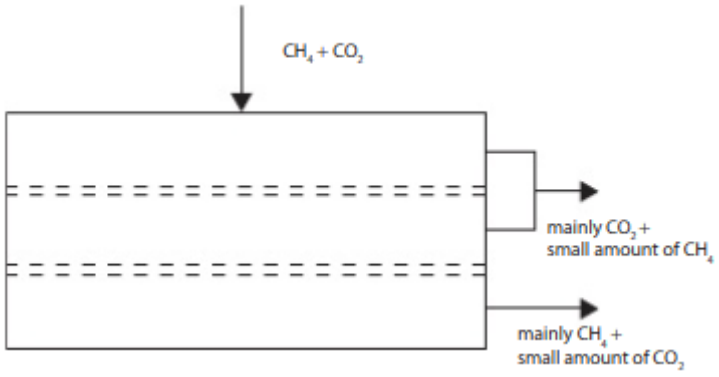

Figure 1.14: Membrane system with two indoor steps [A28]

1.4.1.4 - Cryogenic separation

The carbon dioxide is separated physically from the methane condensing it at cryogenic temperatures. It is a favorable method when the CO_2 initial concentration is high, as in the case of biogas, but it requires a strong spending energy and significant investment cost, justifiable only if the process fits itself synergistically in the upgrading chain.

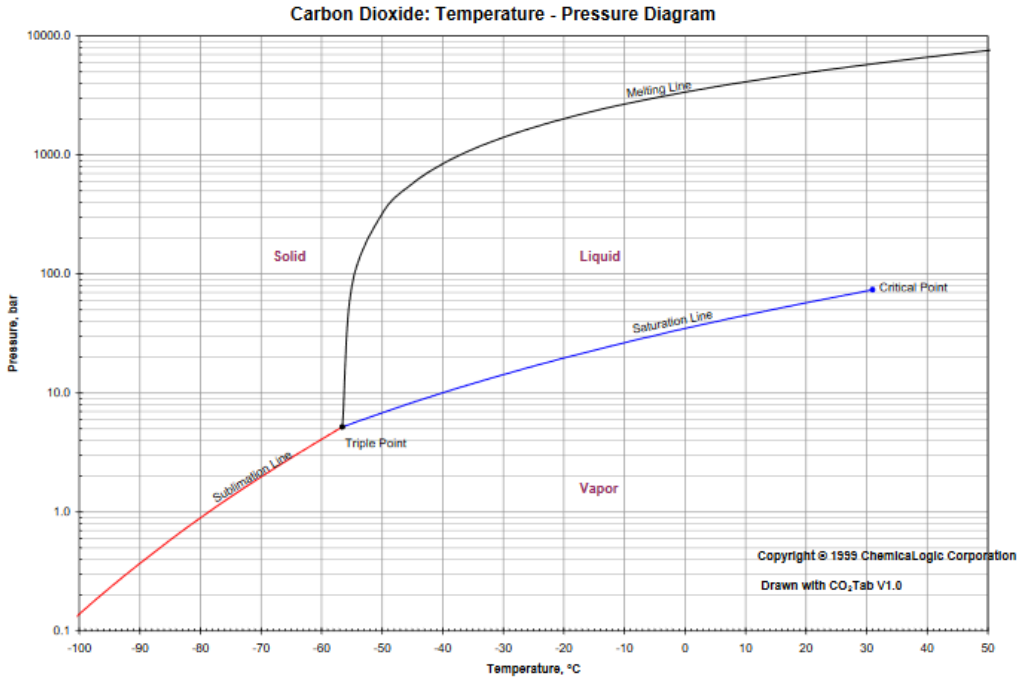

Figure 1.15: Semi-logarithmic phase diagram of carbon dioxide [A20]

In fig. 1.15, the temperatures at which the phase transition takes place, referred to the atmospheric pressure values, are of -161.4 ° C for the CH_4 and -78 ° C for the CO_2; at 50 bar instead the temperatures are -80 ° C and +15°C.

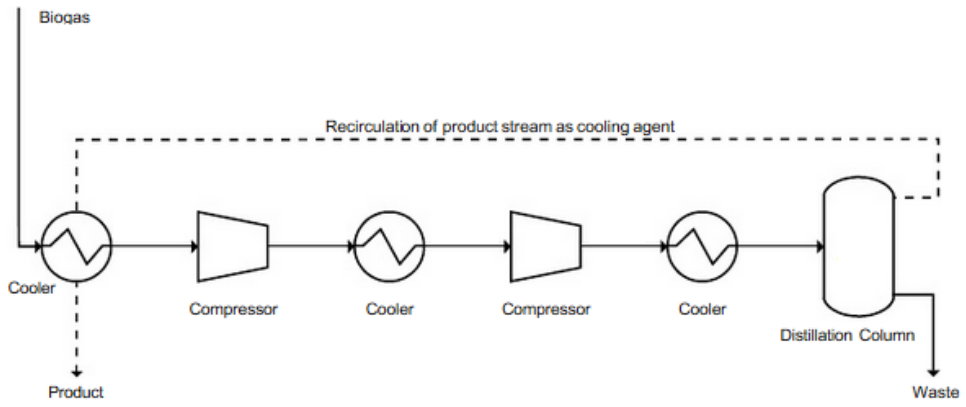

Figure 1.16: cryogenic separation: Example of process flow [A28]

Theoretically it is also possible to condense the sulfur compounds, given that hydrogen sulphide has the boiling point at -60 ° C and the carbonyl sulfide in -50 ° C (at atmospheric pressure). However it depends on design choices, in relation to the technical problems that would arise, especially in terms of corrosion on exchangers, pre-separation is sometimes done for sulfur compounds. Once the carbon dioxide is condensed, it is possible to condense also the methane; so it would remain only gaseous nitrogen (If present), which can be released into the atmosphere.

Compression and cooling can be realized in several steps. This technique provides the product as a pure liquid CO_2 and therefore salable. By further lowering the temperature (in excess of -161.4 ° C) you can push the process to the liquefaction of natural gas at atmospheric pressure. The production of liquid biomethane would give advantages in terms of storage volumes. The technology of liquefied biomethane (LBG) is gaining interest and we should deepen it. Applications already exist in Sweden and the USA, but the technology is not widely tested to date.

1.4.1.5 - Formation of carbonates [A14]

It is possible to react carbon dioxide with lime (CaO), producing calcium carbonate ($CaCO_3$).

$$CaO + CO_2 \rightarrow CaCO_3 \qquad \text{(eq. 11)}$$

It should be remembered that lime is produced by thermal decomposition of carbonate, releasing a molecule of CO_2 to the CaO molecule produced; this contributes the overall impact of the process environment.

1.4.2 - Removal of sulfur compounds

The methods of hydrogen sulfide removal are multiple and can be divided in substrate pretreatment interventions, in the gas flow or in upgrading process. As already discussed, some of the methods of removal of carbon dioxide are also able to separate the hydrogen sulphide.

The specifications on biomethane for traction are stringent, far more than those adopted on engines for stationary use, they imply the need to adopt different configurations compared to plants that use biogas for electricity production and cogeneration, so it is often necessary to have to support different desulphurization methods to obtain the required gas purity.

The methods involved in the digestion process consist in biological desulphurization and pretreatment of the substrate, the other methods are applied on biogas.

1.4.2.1 - Pretreatment of the substrate

In biogas plants for controlled anaerobic digestion, it is possible to add iron salts to cause the precipitation of insoluble sulfides by removing H_2S in the digester.

To apply this sulfur-fixing method is possible to use ferrous chloride ($FeCl_2$) or ferric ($FeCl_3$), which can be added in liquid form directly into the digester or in the substrate before its release. There is the precipitation of iron sulfides and elemental sulfur, which will remain all in the digestate. The typical reactions for this process are:

$$Fe^{2+} + S^{2-} \rightarrow FeS \qquad \text{(eq. 12)}$$

$$2\ FeCl_3 + 3\ H_2S \rightarrow 2\ FeS + S + 6\ HCl \qquad \text{(eq. 13)}$$

For this technique is necessary a tank for mixing the salts to the substrate together with a dosing pump, which result in lower costs investment. The costs of the chlorides which must be constantly added to the substrate are considerable, because large quantities of iron chloride are required for the decontamination of biogas.

The process is applied mainly to the digestion of sewage and is capable of reducing the concentration of H_2S in the biogas outlet of the digester to about 100 to 150 ppm, depending on the dosage of the added reagent. With respect to the stoichiometric, chloride overdose allows us to achieve the best results, although they are not satisfactory for the strict specifications on biomethane purity.

This method can only be used for a first partial desulfurization, which can be useful to avoid corrosion problems on the plant and to resize other desulfurization methods adopted.

1.4.2.2 - Biological desulphurization

There are the family of microorganisms of tiobacilli capable to degrade hydrogen sulphide. Many of them are autotrophic, using the CO_2 in the biogas as a source of carbon. They act producing elemental sulfur and sulfuric acid, which in turn gives rise to an immediate formation of sulfates.

$$2\ H_2S + O_2 \rightarrow 2\ S + 2\ H_2O \qquad \text{(eq. 14)}$$

$$2\ S + 2\ H_2O + 3\ O_2 \rightarrow 2\ H_2SO_4 \quad \text{(eq. 15)}$$

$$H_2S + 2\ O_2 \rightarrow H_2SO_4 \quad \text{(eq. 16)}$$

Typically 75% of removed H_2S is brought into sulfur, the rest into sulfates (salts of the sulfuric acid).

To perform these reactions, the microorganisms require nutrients such as carbon and salts inorganic nitrogen, phosphorus and potassium, which are normally found in the substrates in more than sufficient doses. The biological desulphurization process is aerobic, then the microorganisms require oxygen.

It is therefore necessary to insert air into the digester, in doses of 2 to 6%. To avoid any risk of explosion, the percentage of added air must not exceed the lower limit of flammability of biogas (approximately 12% by volume). Furthermore, the amount of air fed in must be kept low not to affect the anaerobic digestion mechanisms. The reactions take place at the interface between the gas and the substrate; the result of desulphurisation depends on the surface offered to microorganisms: 1 m^2 of the surface provides a good desulfurization at 20 ° C for 20 Nm^3 of daily biogas production.

The easiest method for inducing desulfurization is the introduction of air directly into the digestion chamber; the achievable results, with good control of temperatures and reaction times, consist of removals of 95% sulphide excess with a final concentrations of 50 ppm. An alternative configuration, adopted especially in small agricultural installations, is the use of separated bioreactors filled with plastic bodies to increase the useful surface of reaction.

Larger plants uses reactors like those equipped with the addition of a countercurrent liquid stream taken from the fermenting sludge or special solutions that facilitate the life and the multiplication of microorganisms. The addition of air takes place directly in the reactor at slightly higher doses than those mentioned for the treatment in the digester; in this way the digester is not polluted with oxygen, which would reduce the methane production rate. In this last type of filter (trickling filter) removal efficiencies of higher than 99% may be obtained but they are more complex and expensive than the simple air insufflation in the digesters.

A competitive alternative to the trickling filters is represented by bioscrubbers, these are reactors in two columns which operate a washing with an aqueous solution of caustic soda at 20% containing the necessary nutrients for microorganisms.

Biogas flows through a column, yielding H_2S by reacting with soda forming sodium sulfide or hydrosulfide:

$$2\ NaOH + H_2S \rightarrow Na_2S + 2\ H_2S \quad \text{(eq. 17)}$$

$$NaOH + H_2S \rightarrow NaHS + H_2O. \quad \text{(eq. 18)}$$

The air flows in the second column, here microorganisms regenerate the solution removing hydrogen sulfide from the caustic soda:

$$2\ NaHS + O_2 \rightarrow 2\ NaOH + 2\ S \qquad \text{(eq. 19)}$$

$$2\ NaHS + 4\ O_2 \rightarrow NaHSO_4. \qquad \text{(eq. 20)}$$

In this phase also sulfur and sodium bisulfate are issued. Elemental fixed sulfur collects on the bottom of the column. Biogas not overly contaminated arrives at concentrations of H2S of 75 ÷ 150 mg / Nm^3 [A21] (according to [A10] 50 -100 ppm starting from 3000-5000 ppm).

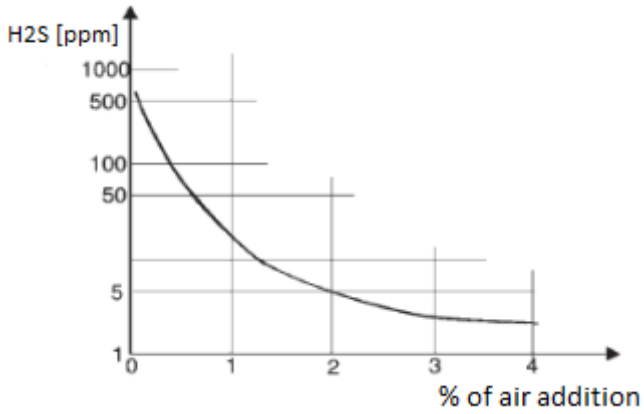

Figure 1.17: Correlation between quantity of air blown and % H_2S [A14]

The double column system is more expensive than the others aimed to the biological desulfurization. Also trickling filters and bioscrubber operate optimally at temperatures of 28 ÷ 32 °C, and then must be heated in the winter and cooled in summer, giving rise to an increase in the operating energy costs. Often in these reactors problems of corrosion are found, due to the low pH value; the problem can be solved by using antiacid materials or reducing the acidity by selecting microorganisms suitable to operate in this condition. A further advantage of these systems is the contextual abatement of the ammonia concentration.

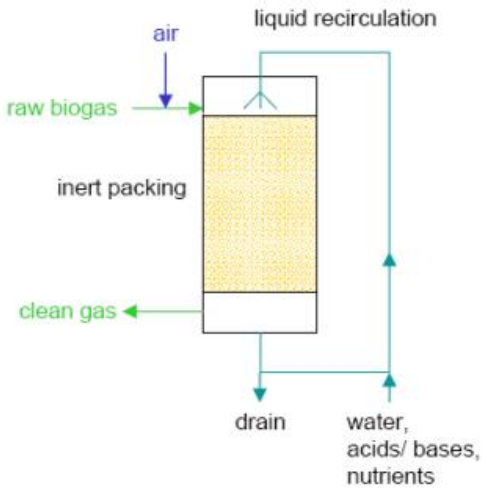

Figure 1.18: Trickling filter operating principle [A27]

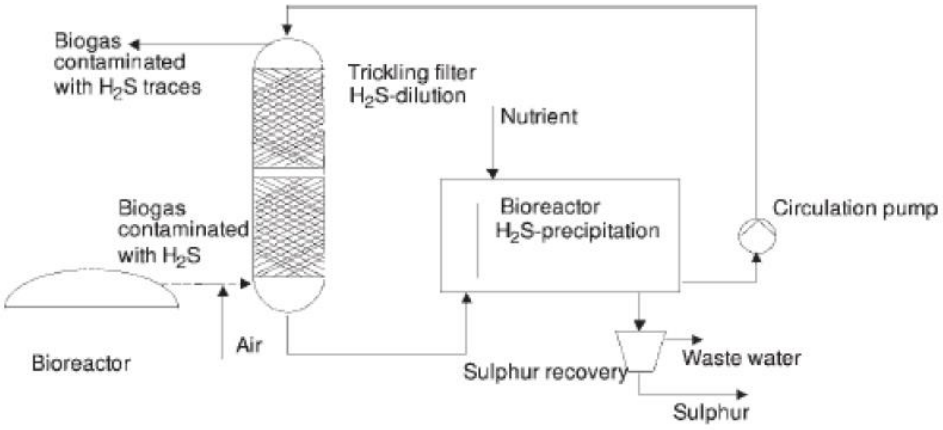

Figure 1.19: Trickling filter plant scheme [A14]

1.4.2.3 - Absorption

They are absorption processes that have already been analyzed for the CO_2 removal: many of them are particularly suitable for the simultaneous removal of both the species or may be used only for the removal of H_2S.

Physical absorption with water

The absorption by water washing, is a physical process aimed to the removal of both components; this configuration works under pressure and allows to reduce the volume of the column.

Unfortunately this system is characterized by a massive energy consumption.

You can choose among various types of systems for physical absorption, operating with different types of fluid.

Physical absorption with other fluids

In Selexol process it is not possible to desorb the sulfur compounds at atmospheric pressure, so vacuum regeneration is required.

The Rectisol process instead allows to separate selectively these two species. Other little different processes have been mentioned in the paragraph on the CO_2 removal.

Chemical absorption in sodium hydroxide solutions

As already explained for the removal of CO_2, you can create mixed systems of physico-chemical adsorption by adding suitable reagents to the water.

An aqueous solution of NaOH can be used to separate hydrogen sulphide from biogas. The two species react forming sulfide or hydrosulfide sodium, according to the same reactions that occur in bioscrubbers.

$$H_2S + 2\ NaOH \rightarrow Na_2S + H_2O \quad \text{(eq. 21)}$$

$$H_2S + NaOH \rightarrow NaHS + H_2O \quad \text{(eq. 22)}$$

The products are two-insoluble salts; unfortunately in this case the regeneration is not possible.

Chemical absorption in solutions of calcium hydroxide

Similarly to the use of sodium hydroxide, H_2S reacts with calcium hydroxide to give calcium sulfate.

$$Ca(OH)_2 + H_2S \rightarrow CaS + 2\ H_2O \quad \text{(eq. 23)}$$

Chemical absorption with amines

The most suitable fluid to a simultaneous slaughter of CO_2 and H_2S is the methyldiethanolamine. The other amines processes are recommended for the separation of carbon dioxide alone.

Chemical absorption in the ferric chelate solutions

In iron chelate solutions the $Fe3^+$ ions are reduced to $Fe2^+$ in a process in which hydrogen sulphide is oxidized to elemental sulfur.

$$H_2S_{(aq)} \leftrightarrow H^+ + HS^- \quad \text{(eq. 24)}$$

$$HS^- \leftrightarrow H^+ + S^{2-} \quad \text{(eq. 25)}$$

$$S^{2-} + 2\ Fe^{3+} \leftrightarrow S + 2\ Fe^{2+} \quad \text{(eq. 26)}$$

The plant consists of a tank containing a solution of iron ion (concentrations of 0.01 ÷ 0.05% by weight) in which the biogas is circulated with a minimal addition of air. If the biogas contains sufficient oxygen to regeneration of iron ions you can use a single reactor; if the presence of oxygen is not tolerated in the biogas, a second reactor is necessary wherein the solution is regenerated with air. The solids deposit on the bottom of the reactor and must be periodically removed.

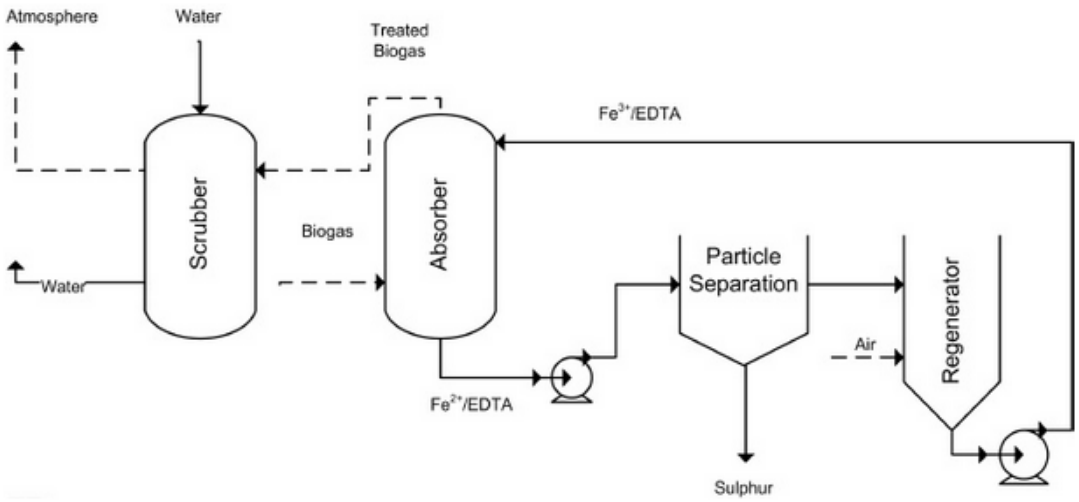

Figure 1.20: Chemisorption system of H_2S with iron-chelate, plant regeneration [A28]

The following reactions illustrate how the oxygenation regenerates the solution:

$$O_{2\,(aq)} + 2\,Fe^{2+} \leftrightarrow 2\,Fe^{3+} + 2\,OH^{-} \qquad \text{(eq. 27)}$$

Absorption in foams

The hydrogen sulfide can be removed by absorption of produced foams from surfactants. It is necessary to pass the biogas current through the foams. To ensure the contactament is necessary that the gas velocity is extremely low, for this reason, this method can be applied on only small scales. The adoption of this technology for large gas flow would require too large reactors.

1.4.2.4 - Adsorption

On impregnated activated carbon

The adsorption of H_2S on activated carbon is feasible and affordable if the biogas does not contain oxygen and if the initial concentration is high; in this case hydrogen sulphide adheres directly to the surface of activated carbon. The efficiencies of removals obtainable in this way are scarce. To improve the results, the

use of suitable activated carbon, impregnated by agents catalysts, promote the conversion of hydrogen sulfide to elemental sulfur. There are several catalysts suitable for this purpose, the most used is potassium iodide (KI), added to the charcoal in the proportion of 1 to 5% in weight. In the presence of oxygen and water, at a temperature and optimal pressure (50 ÷ 70 ° C; 7 ÷ 8 bar), so the following reaction is catalyzed:

$$2\ H_2S + O_2 \rightarrow 2\ S + 2\ H_2O. \qquad \text{(eq. 28)}$$

This catalyst has the advantage of preventing the formation of acid sulfuric, that would be counterproductive for the desulphurization.
Alternatively, you can use potassium carbonate (K_2CO_3) in dosages of 10 ÷ 20% in weight, at about 50 ° C potassium sulphate, is settles on the coals.

$$H_2S + 2\ O_2 + K_2CO_3 \rightarrow CO_2 + H_2O + K_2SO_4 \qquad \text{(eq. 29)}$$

Among others, a good impregnating is potassium permanganate ($KMnO_4$).
You can replace or regenerate on site the coals. For regeneration is needed a stream of high-temperature air or steam (at least 450 ° C) which contacts the bed of saturated adsorbent.
The adsorption on impregnated active carbon is the most commonly method used for the removal of sulfur compounds before removal of the carbon dioxide with the PSA process.

On molecular sieves

As already treated for the removal of the carbon dioxide, you can purify the methane on suitable molecular sieves that retain the larger CH_4 molecules. The disadvantage of this technique is represented by the loss of a 10% portion consisting of methane.

On iron oxides

In this process hydrogen sulphide is adsorbed on ferric hydroxide (Iron hydroxide (III), $Fe(OH)_3$) or of ferric oxide (iron oxide (III), Fe_2O_3). It is a dry desulphurisation system that provides the conversion of H_2S to sulfur ferric (iron sulfide (III)):

$$2\ Fe(OH)_3 + 3\ H_2S \rightarrow Fe_2S_3 + 6\ H_2O \qquad \text{(eq. 30)}$$

Or:

$$Fe_2O_3 + 3\ H_2S \rightarrow Fe_2S_3 + 3\ H_2O \qquad \text{(eq. 31)}$$

Small masses of these oxides / hydroxides are placed in tower containers which is flowed with the biogas. This takes place by introducing air into the biogas and inducing the reaction:

$$2\ Fe_2S_3 + 3\ O_2 + 6\ H_2O \rightarrow 4\ Fe(OH)_3 + 6\ S \qquad \text{(eq. 32)}$$

according to which, in addition to the starting reactant, elemental sulfur is produced. In the case of high flow rates (up to 200 m^3/h) it is appropriate to provide two beds to operate alternatively allowing either the regeneration or the continuous operation.

During regeneration the sulfur produced is deposited on the adsorbent and reduce its extent, therefore it is advisable oversize the load.

The adsorption reaction is slightly exothermic and proceeds for temperatures above 12 °C (optimal range of 25 ÷ 50 °C). The normally used as adsorbent materials are:

• fine wool of oxidized steel;

• wood chips artificially covered with rust;

• pellets in the "red mud", mining by-product of aluminum.

The used pellets are characterized by the highest possible ratio of surface to volume; therefore, 1 kg of this material is able to adsorb 500 g of H_2S.

The wood chips have a lower surface to volume ratio but are benefited with a much lower density: 1 kg of these adsorbs up to 200 g of H_2S. It is also a very cheap product.

1.4.2.5 - Reaction with zinc

In smaller agricultural plants, the biogas can be achieved with a low content of H_2S by flushing it on zinc oxide beds and causing the reaction:

$$ZnO + H_2S \rightarrow ZnS + H_2O \qquad \text{(eq. 33)}$$

The sulfur is trapped in the solid bed, which is generally constituted by replaceable cartridges. Carbonyl sulfide and mercaptans are simultaneously removed if brought to H_2S by hydration.

$$COS + H_2O \leftrightarrow CO_2 + H_2S \qquad \text{(eq. 34)}$$

With this method you can get off at concentrations of 1 mg/Nm^3.

1.4.2.6 - Reaction with alginates

There is the possibility of desulfurizing biogas with the reactors containing special algae, this method has never been put into practice for economical reasons, while the prospect of adding sodium alginate to the substrate seems much more promising. The sodium alginate is obtained from the cell wall of seaweed and it is a product that has already many industrial, food and pharmaceuticals uses. By adding the sodium alginate, the concentration of hydrogen sulphide falls below 20 mg/Nm^3 to the substrate in proportions of 1:10000. We can also observe an increased production of methane and a reduction of the formation of ammonia.

1.4.2.7 - Direct oxidation

When the concentration of H_2S is extremely high (i.e. greater than 15000 mg/Nm^3), the choice to do a direct catalytic oxidation in a Claus process becomes economically viable. It consists of a sulfur production, released in liquid form. The reaction requires a preheated stream of air and fuel.

1.4.3 - Removing the water

The biogas whether is produced from the controlled anaerobic digestion or by a landfill, is supplied with saturated water vapor. In order to avoid condensation, which could damage the treatment plant, it is often necessary to a first abatement of the water content to obtain biogas humidity less than 60%.
Biomethane for transport requires very low content of water, that makes necessary to boost furtherly the gas drying. In the upgrading chain may be present processes that require a minimum of gas humidity value and / or others for which it is required accurate dehumidification. For this reason, the devices for the reduction of the water content should be placed as appropriate depending on the system needs.

1.4.3.1 - Condensation

The most commonly used method to reduce the content of water vapor in the biogas is to cause its condensation and subtract subsequently the liquid phase.
The simplest method, frequently used in systems of agro and animal husbandry industries, is based on a first reduction of the gas dew-point temperature, It consists of gas circulation the in ducts placed underground.

The tubes are usually arranged horizontally with a slight inclination to allow the outflow of the liquid and tanks to allow its collection. This method is exploited in the warm seasons to lower soil temperature and prevent - in the cold months - extreme temperatures to which is connected the risk of solidification of the condense.

Alternatively you can condense water on cold exchangers. The source refrigerant can be ground water or special cooling machine. You can still use other cold fluids if available in the system.

The condensation water can be also induced by compression of the biogas and this possibility should be taken into special consideration since the biogas upgraded into biomethane necessarily involve its compression.

To achieve best results it is possible to perform the condensation into successive stages of cooling and compression.

1.4.3.2 - Absorption

For the very large plant it is convenient to have systems for absorption.

As absorbent liquids substances such as glycol or triethylene glycol are used. They consider other components of biogas as a long-chain hydrocarbons, mostly found in landfill gas.

Alternatively may be used solutions of hygroscopic salts such as LiCl (Lithium chloride), LiBr (lithium bromide), calcium chloride ($CaCl_2$) or sodium (NaCl); they need the periodic reintegration of salts.

The regeneration must take place at a high temperature. Two columns are necessary to perform their absorption and regeneration.

1.4.3.3 - Adsorption

Adsorption systems are normally adopted to purify biogas flows up to 100000 Nm^3/h. The adsorbents materials commonly used are alumina, silica gel, active charcoal or molecular sieves (zeolites). They are used in batch processes (Adsorption - regeneration) with fixed beds of PSA or TSA type.

The adsorption can be carried out under pressure (6 ÷ 10 bar) or at atmospheric pressure. In the first case, a share of gas compressed and purified is used for the regeneration, then recirculated it in the bed of adsorption; in the second case it is preferable to carry out a regeneration air to subatmospheric pressure, with the disadvantage of contaminating either the biogas with air in the initial stage of adsorption or the newly regenerated bed.

These methods are those that ensure compliance with the more stringent specifications; for an efficiency increase in adsorbent removal it is possible to recirculate an already dehydrated gas into the adsorbent bed.

The adsorption processes, present very high operating and investment costs, therefore they should be adopted only if essential to achieve very thorough dehumidification, such as required on biomethane for vehicle traction.

1.4.4 - Removal of oxygen and nitrogen

Generally biomethane not have particularly stringent specifications for these compounds, for which the removal can make only if necessary for achieve the desired methane enrichment. Oxygen and nitrogen can be easily separated from biogas in processes already present in the purification plant. For example, activated carbons, molecular sieves, elective membranes and adsorption with PSA are useful for this purpose.

1.4.5 - Ammonia removal

Ammonia can be found in substantial volumes of biogas; especially in the production from food waste, depending upon the stability of the fermentation process. With a proper operation of the plant, the content of ammonia can be reduced to a minimum value, however, it always requires a further reduction. It is carried out by removal systems dedicated to other pollutants that have good separation capacity also for ammonia. There is also a method to reduce the ammonia content in the substrate it is a process known by the trade name of ANAStrip (fig. 1.21). It allows for a desorption in a stripping column by means of a gas warm (maximum 80°C) and to a low pressure. The gas leaves the column enriched in ammonia and then it enters into a wash column in which ammonia is absorbed in an aqueous solution of calcium sulfate which reacts with it, forming ammonium sulphate and limestone.

$$CaSO_4 + 2\ NH_3 + CO_2 + H_2O \rightarrow\ CaCO_3 + (NH_4)_2SO_4 \qquad \text{(eq. 35)}$$

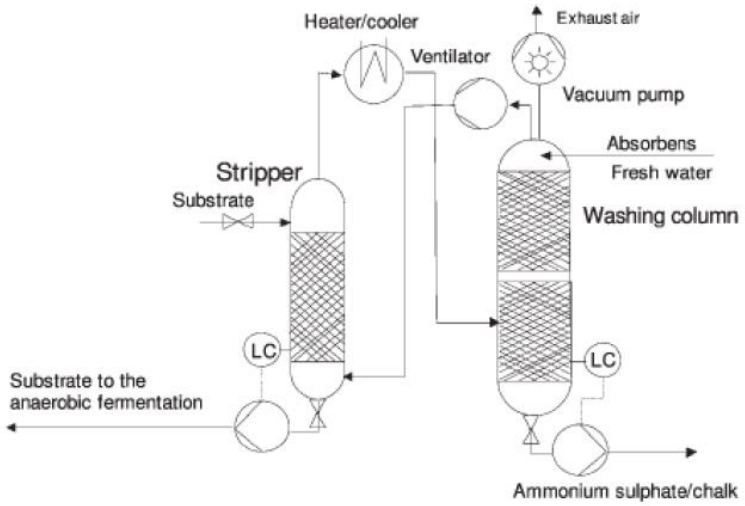

Figure 1.21: ANAStrip process [A27]

It is a method used mainly for conditioning the substrate characteristics in terms of pH and composition but it has as useful result the reduction of ammonia in the produced biogas.

1.4.6 - Removal of solid particulate

A first coarse filtration is generally made by cyclones or filters in gravel or sand, for large size solids removal and brought into suspension from biogas, fats and any foams. To perform this, it must follow successive stages of filtration to remove even the smaller particles. The Swedish specifications indicate the maximum diameter of the particles is 5 microns. The filtration can be obtained with different devices, typically mechanical. the positive contribution of the differents washing systems (Scrubbing) must not be overlooked because they are present in the system for other purposes (i.e. biogas dedusting).

1.4.7 - Removal of halogenated compounds

The removal of halogenated hydrocarbons is necessary to avoid the corrosivity problems linked to them and because, when burnt, they would result in highly polluting emissions.
By adsorption the halogenated hydrocarbons are retained by specifically activated carbon and agents based on molecular sieve. The coals are used in appropriate tubular reactors by alternately subjecting to regeneration and adsorption. Regeneration takes place at temperatures of about 200 °C and hydrocarbons halogenated are desorbed in the vapor phase and are removed with a stream of purge of inert gas. A good

abatement of these compounds, complement or alternative to these ones, is also obtained by other methods used for the desulfurization and CO_2 removal.

1.4.8 - Siloxanes removal

In some applications, e.g. in biomethane for traction, is required a very low concentration of siloxanes, (order of mg/Nm^3).
Several techniques are feasible for their removal, some of which conveniently integrated into the upgrading chain.

1.4.8.1 - Absorption

The absorption of the siloxanes is feasible in appropriate non-volatile mixtures of organic solvent, they are mainly hydrocarbons arranged in spray or packed columns. The liquids are regenerated at low pressures and high temperatures. The main disadvantage of this technology is constituted by the impossibility of achieving a complete removal, due to the fact that the more volatile siloxanes are easily stripped from the solvent by the biogas flow. The problem occurs because the process is purely physical: if the pollutant would bind chemically to the absorbent, fluid could easily be desorbed because it is converted into a low volatility compound.

1.4.8.2 - Adsorption

Siloxanes can be separated with high efficiency by using biogas adsorption on materials such as activated carbon, molecular sieves, pellet polymers and activated alumina. Many of these materials capable of removing the siloxanes and are also able to separate water and other micropollutants from biogas. For this reason, if you can remove the water with other cheaper techniques, it would be good to do it before using these materials to break down the siloxane content.
By drying the gas in advance you will get more removal efficiencies on siloxanes and it will not be necessary an excessive oversizing plant. However it remains the need to load doses of adsorbent greater than those theoretically predictable, since various other micropollutants can bind to the media adsorbents, shortening the life of the bed more than expected.

The activated carbons are hardly regenerable by siloxanes, consequently it is necessary their periodical replacement. This question is crucial in the cost of which thereby they are used in large plants.
Even the use of silica gel is expensive but the possibility of their use in the biogas drying makes them technically interesting.

1.4.8.3 - Cryogenic condensation

The condensation of the siloxane is a possible removing method but it becomes expensive if not integrated in systems where cryogenic techniques have already applied. In the case of biogas enrichment effected with cryogenic condensation of the CO_2, it is instead interesting to pursue this technique if the plant is provided for the methane condensation. At the temperatures at which carbon dioxide condenses, the removal efficiency of siloxanes is approximately 99.3%. On this basis, depending on the initial concentration. it may be necessary to intervene with additional techniques to break down more radically siloxanes. Knowing the average concentrations of this pollutant in the biogas, it is expected that after the condensation it is appropriate to have a further abatement system of siloxanes, preferably based on adsorption techniques.

1.4.8.4 - Chemical abatement

The chemical conversion of these compounds is possible by hydrolysis with acids or caustic catalysts, silicon bond - oxygen. Due to the high stability of these compounds, the reaction requires very low pH and / or high temperatures. The efficiencies obtained with this process are quite low, insufficient to bring gas to the desired conditions.

1.4.8.5 - Treatment peroxidative on the substrate

A recent study [A22] has highlighted the possibility, until not considered before, to make a first partial reduction of the siloxane content through a chemical pretreatment of the digestion substrate.
The process implies to perform perossidative reactions so as to convert siloxanes into lighter siliceous compounds and reduce its concentration in the biogas, reducing the volatility of these compounds prior to digestion. The experiments have demonstrated a 50% average reduction for the various types of siloxane and 85% for the D4 siloxane.

It is an interesting process to perform a preliminary reduction of pollutant, subtracting a good share of contaminant processes that refine the removal, to the benefit of obtainable purity.

1.4.8.6 - Biological treatment

Recent studies [A24] demonstrate the ability to perform a removal of the volatile siloxanes, based on the bacterial degradation. Biodegradation acts transforming the complex siloxane molecules into ortho silicic acid (Tetraidrossisilano) $Si(OH)_4$ and carbon dioxide, to form salts orthosilicates.
The treatment can be carried out by dosing of bacteria (Fusarium oxysporum and Arthrobacter) in trickling filters in which the reactions take place and which hold the products. If well developed, this technique can be valid to make a good abatement of these components pollutants, promising much lower operating costs than those presented by the classic technology active carbon.

Chapter 2

INSTRUMENTS DEVELOPED FOR THE BIOGAS PRODUCTION ASSESSMENT

2.1 - INTRODUCTION TO THE PROBLEM

In the process of anaerobic biodegradation, gas flow rate and total gas production of biogas and/or methane are important parameters for evaluating the performance of the overall process. In laboratory scale experiments, the bioreactor volume is usually quite small, often in the range from 1 to 50 liters [B1].

With these processing volumes, biogas production rates are quite small, particularly during the startup period, when biogas production is often below 0.1 lt/h [B2].

The commercially available gas flow meters are usually unable to accommodate such small rates and/or the wide range of their variations [B3-B8]; for this reason, several gas-measuring systems have been devised for the purpose of studying arrays of laboratory-scale anaerobic digestors [B9-B21].

At the beginning of the work, the simplest and most traditional gas meters, made by us in many exemplary for the first tests of anaerobic digestion with rows of small reactors, are the water displacement gasometers: the biogas feeds a sealed container (pressure cooker) filled with water by draining the liquid in a bottle that is weighed once or twice a day. In this system, both the measurement and the restoration of the displaced liquid are performed manually. The system depends critically on the cooker sealing and connections and it may cause harmful refluxes of liquids to and from the reactor due to changes in temperature and / or atmospheric pressure. This system operates at varying pressures dependent on the liquid level in the pressure cooker, it shows modest temporal resolution and its accurate calibration depends on the pressure and temperature data which should be recorded continuously.

Because of all these problems the indispensable study for developing an automatic and accurate biogas measuring systems was undertaken.

In this regard, most laboratory electronic gas meters are of a discrete type, namely they measures the time spent by the biogas to fill a known volume - typically less of at least four orders of magnitude to the volume produced by a batch. The "ideal" requirements of this class of meters are, in order of importance:

a. Maximum measurable flow rate of at least 3 times higher than the maximum expected by the biodigester; this flow rate depends substantially on the "known volume" and the speed of the transitions induced by the situation of "full".
b. Minimum flow rate substantially equal to zero; this requirement is achieved by a system without measurable loss in a day
c. Ability to work with almost constant differential pressure, namely in the order of centimeters of water; even if the pressure is not as important as the temperature in determining the rhythm of the digestion processes, small pressure fluctuations on large volumes of digesters cause significant changes on the response times measured as a result of operator intervention (pH shift, eating, ...)
d. Cheapness and ease of realization of controllers armies: the laboratory systems typically consist of many digesters in parallel in identical temperature conditions.

Hence**,** besides having a very high dynamic range, a good flow meter for anaerobic digesters should be able to work also with “small” differentials of pressures, should be insensitive to fluctuations of these differentials, should be accurate by design (with a gas volume, as determined before software corrections, little dependent upon flow rate), and should be able to completely forbid a flow in the reverse direction.

The last provision is very important when, for example, a CO_2-capturing liquid is in the biogas path which should not go back in the anaerobic digestor.

As aforementioned, a common method of biogas measurement and collection is by liquid displacement.

The volume of gas produced is determined by counting the number of cycles carried out by a movable volumetric cell in contact with a liquid that acts as gas barrier. Gasometers of this type are often used in labs since they are inexpensive, easy to set up and use, robust and capable of working for long periods without maintenance. Their interface with a data acquisition system is also simple. In this work, three types of different gas-meters, based upon the liquid displacement principle but with different mechanisms, electronic complexity, operating volumes and pressures, were made and tested in order to assess their merits and weaknesses. To this purpose, also three different types of gas flow calibrator, based on the principle of thermal mass flow sensor, constant differential pressure and mechanical displacement were used.

2.2 - DESCRIPTION OF THE DEVELOPED GAS METERS

Three types of gasometer based on the liquid displacement were developed during this project; they are called bell gas meter, drop gas meter and spoon gas meter respectively; they will be now described.

2.2.1 - The bell gas meter

2.2.1.1 – Concept and evolution of the bell gas meter

The bell gas meter was the first attempt to automate the measurement of the production of biogas / biomethane coming from cells of biodigestion. Conceptually, this is constituted by a vertically movable bell immersed in a liquid driven by the gas flow. Greatly simplifying the description of its functioning (for detailed description see the following section), when the gas is injected inside the bell, it begins to rise upwards. Once it reached a certain level, the gas flow is stopped and the discharge conduct is open.

The bell then, under the effect of its own weight, begins to fall causing the expulsion of the gas accumulated in its interior and the cycle restarts. This behavior (i.e. the system does not exploit the gas pressure at the inlet also to lower the bell) may result in a malfunction, and in fact, during the first experimental tests, it emerged that the gas meter could work sometimes only for a few hours after which crashed. The cause was due to the condensation droplets formed on the top of the bell that, when fall down, sooner or later, ends to hit the entrance of the discharge tube, clogging it. Unfortunately, the weight of the bell was not able to cause the expulsion of even a single drop of liquid from the discharge tube; the inlet tube which, was completely full of liquid during the startup, did not have this problem since the gas pressure at the inlet could purge it.

The first solution was to weigh down the bell by means of lead disks, made by melting some shotgun pellets. As molds were used, after several tests, commercial aluminum crucibles that have finally led to thin and homogeneous disks (fig. 2.1).

Figure 2.1: The aluminum crucibles and the 40 g lead disks created by melting

Such discs, applied to the mobile element, allowed the correct operation of the bell that could expel the occasional drop of liquid present in the emission conduit at the expense of a slight excess pressure due to the lead disk weight. However, the system employed three or four cycles to expel the drop; if in the meantime another drop of liquid fell within the conduit, the meter was again blocked.

At the end, a solution has been obtained by shaping the outlet pipe in a different way, in particular by moving the gas access in a lateral position, where it is virtually impossible to collect a drop of condensation (fig. 2.2)

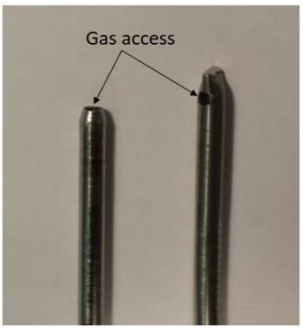

Figure 2.2: Outlet tube; initial version (left) and version with gas access in lateral position (right)

This ploy has allowed to solve the main system shutdown problems making it ready for field tests. A wider and more exhaustive description of the bell gas meter is shown in the following section.

2.2.1.2 - Detailed description of the bell gas meter

The bell gas meter comprises a container, a liquid with gas-barrier characteristics, a bell shaped volumetric cell, a pneumatically actuated valve, two photo-interrupters, placed on an infrared-transparent pipe and an interface to the control and the data acquisition system.

The container is partially filled with a displaceable liquid, the mobile bell is placed in the interior of the container, partly submerged by the liquid. The bell has a rod on its top, which is aimed to activate two optical switches placed above the container. The electronics, depending upon previous and current configuration of the optical switches, controls a pneumatically actuated valve that manages the flow of gas filling or emptying the bell. The container has three ports: the upper port is placed on the upper plate and the other two ports lies on the lower plate, which led the gas inside the bell (i.e. the inlet port) or outside the bell (i.e. the outlet port).

When the inlet port is connected to gas source, the bell is being filled with the gas and is pushed upwards. Simultaneously, by ascent of the bell, the gas located in the container\ outside the bell is forced through the upper port and outside the meter. This happens as long as the rod above the bell is placed below the upper photo-switch. When the beam of this switch is shut off, the pneumatic valve closes the inlet port and connects the outlet port to the upper port so that the bell, due to its weight, moves downwards decanting the gas to its exterior, but always inside the container. When the rod goes below the lower optical switch, the pneumatic valve is reset to its initial status, and a new cycle begins.

The two operational phases and the components of this first gas-measuring system are shown in the next figure (fig. 2.3):

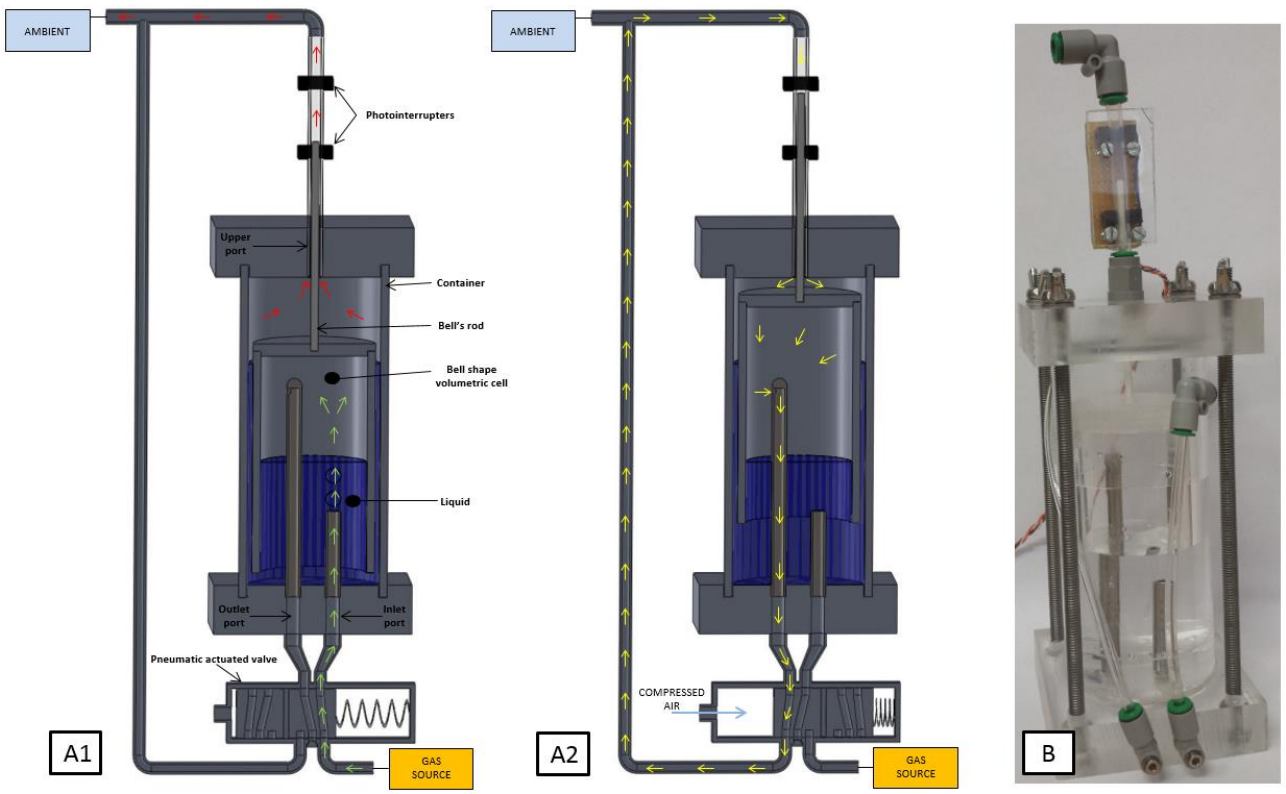

Figure 2.3: Bell gas meter A1: components display and work phase 1; A2: work phase 2; B: real device

Constructively, the container is obtained by assembling three mainly elements: an acrylic tube, 3 mm thick, 135 mm long, with outside diameter of 60 mm. Two acrylic square plates are attached at the two ends of the tube: the lower plate is permanently glued while the upper plate connects to the top of the tube trough a rubber gasket and four tensions screws, to allow inspection and cleaning. In the lower plate, two 5 mm channels have been carved for the gas inlet and outlet which ends with two vertical pipes that end within the bell. The inlet pipe is a 35 mm long stainless steel tube, 2 mm thick, 6 mm outside diameter ; its task is to carry the gas into the bell trough the blocking liquid. The outlet pipe is similar, but it is 85 mm long to stay above the liquid. Furthermore, this pipe is sealed on the and has a small hole at the top of its wall in order to avoid drops of dew entering this tube and blotting it. The upper plate has a threaded hole with a gas tight connector (Pneumax T010618) holding a clear tube housing a rod bonded above the bell, which activates the two optical switches. The bell is the movable element of the system, it performs a vertical translation with a stroke of about 25 mm. The bell is made of an acrylic tube 3 mm thick, 49.5 mm output diameter and 90 mm long sealed by means of a gas proof adhesive on the top by a 3 mm thick acrylic disk.

The rod at the top of the bell is 3 mm in diameter and 85 mm long, made of an opaque polymer. Special consideration must also be given to the liquid used in the gasometer which acts as a gas barrier (with minimal

biogas solubility) or as a biogas filter. In the former case, acidified water (addition of HCl to pH=3) may be used [B22, B23].

The gas meter we have made (see fig. 2.3 B) can measure flows up to 12 l/h; its resolution is about 55 ml and it works with a pressure differential of about 100 mm of water (981 Pa). Of course, the higher the pressure differential and the bigger the size of the bell, the larger is the range of flows that can be measured.

The two transmission IR optical switches are GP1S53VJ000F by Sharp; they have a 5 mm gap and their separation (25 mm) determines the bell's stroke. The pneumatic valve is a 5 ports, 2 state, mod 105.52.11.1 by Pneumax. The valve contains a suitably grooved piston with two stable positions, moved by compressed air in the 2.5 - 10 bar range. When no compressed air is applied, the piston is kept in its rest position (A1- Fig. 2.3) by a spring, the inlet port of the meter is connected to the gas source, the upper port is connected to the ambient (or to the collecting tank) while the outlet port is closed. When the compressed air is applied (A2 - Fig. 2.3), the piston compresses the spring in the second stable position, the outlet port of the meter is connected to its upper port and the inlet port is closed. The control electronics operates the pneumatic valve trough a solenoid valve (Pneumax N331.0B) on the compressed air path.

The control electronics consists of three elements: a SN74HC112 Texas Instruments dual J-K negative edge triggered flip-flop with clear and preset functions, a MN74HC04 Panasonic buffer inverter and a 2N2222A STMicroelectronics NPN switching transistor. The main feature of this flip flop, compared to the classic J-K flip flop, is the presence of two additional pins that can set or reset the outputs regardless of the levels of the other inputs. The output of the upper optical switch, responsible of the valve power on the signal, is sent from the meter to the preset pin of the flip-flop. Instead, the output of the lower optical switch goes to a buffer inverter whose output drives the reset pin; the clock pin is maintained permanently at the high level. The 5V output signal of the flip flop drives directly the 24V switching transistor by feeding the solenoid valve. The scheme and the real control circuit capable of driving four bell gas-meters is shown in the next figures (fig. 2.4 – 2.5)

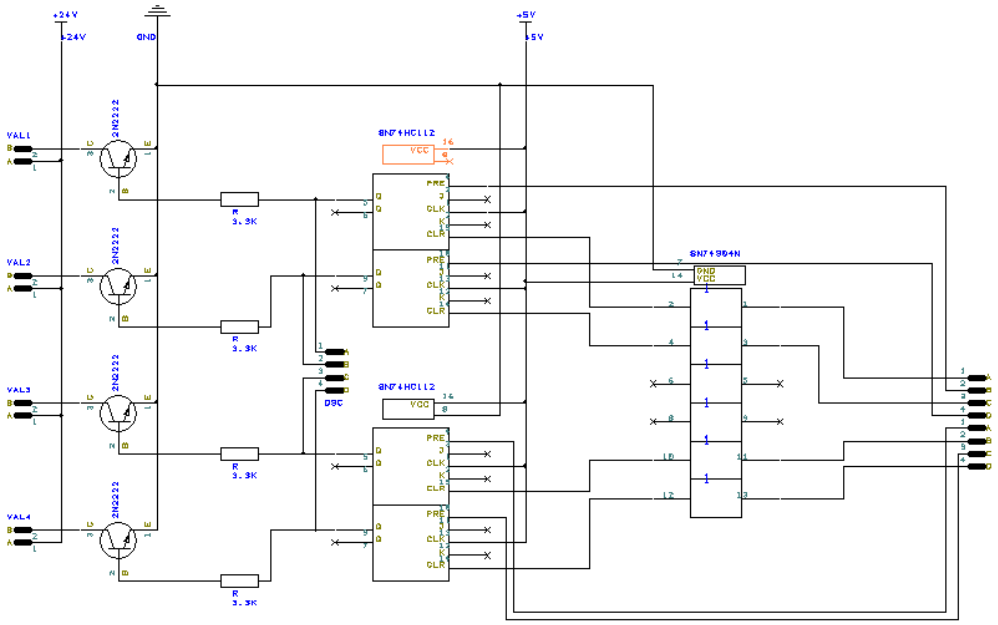

Figure 2.4: Control electronic circuit scheme that drives four bell gas-meters

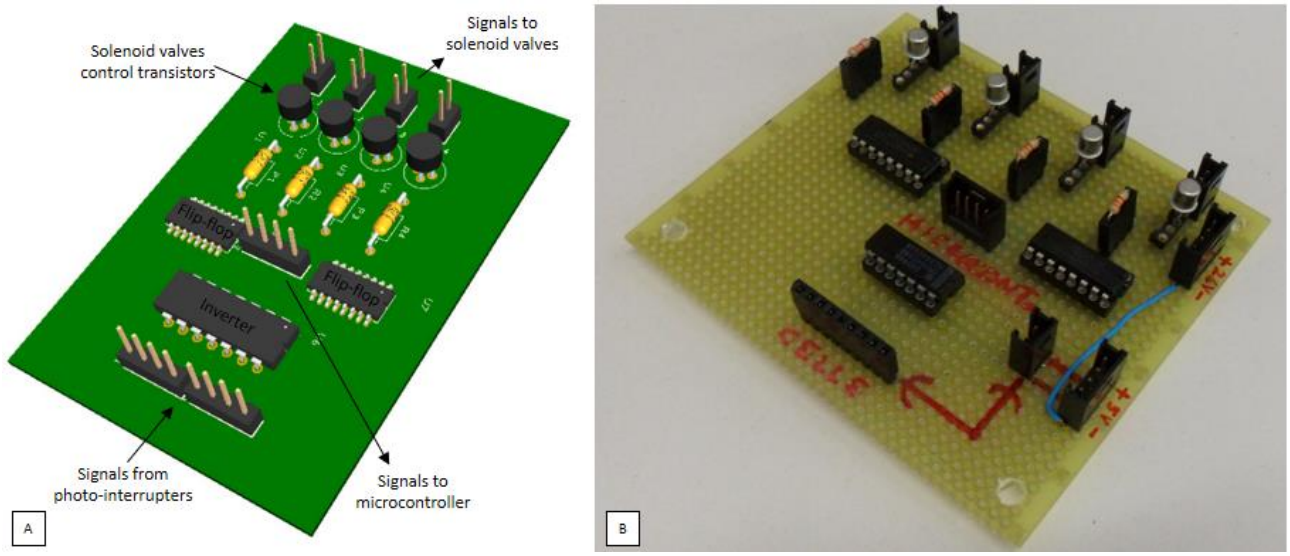

Figure 2.5: Bell gas-meter control circuit. A: Circuit prototype. B: Real circuit

The data acquisition, storage, display and computer communication are all performed by the Ethernet Rev. 2 Arduino board microcontroller with PoE module. The Ethernet Arduino microcontroller, like all the Arduino board, is an open-source hardware that is programmable with an open-source software named IDE (integrated development environment). This board provides a set of digital and analog I/O pins, an onboard microSD card reader and a Ethernet interface facility. Some digital I/O pins present on the microcontroller were used for the data acquisition; these pins have been directly linked to the output pins of the flip-flop .

In this way, the microcontroller receives a signal whenever the gas-meter has completed a cycle.

A microSD memory card, inserted into the onboard microSD reader, was used for the data storage. On this memory card we saved the number of the cycle and the time from the start up of the system. For computer

communication, a RJ-45 jack cable was used to connect the microcontroller's onboard Ethernet socket to the nearest router's Ethernet socket present in the laboratory. A simple website is then loaded on the microcontroller to which any laboratory computer can connect and download the data files. A LCD display was used for an immediate data visualization, it is connected to some others microcontroller's digital I/O pins and displays the total number of cycles performed by the gas-meter. For calculation of all the relevant parameters like gas flow, gas volume, etc. it is necessary a computer program to process the data file stored in the microSD memory card.

The final system described is shown in the next figure (fig. 2.6).

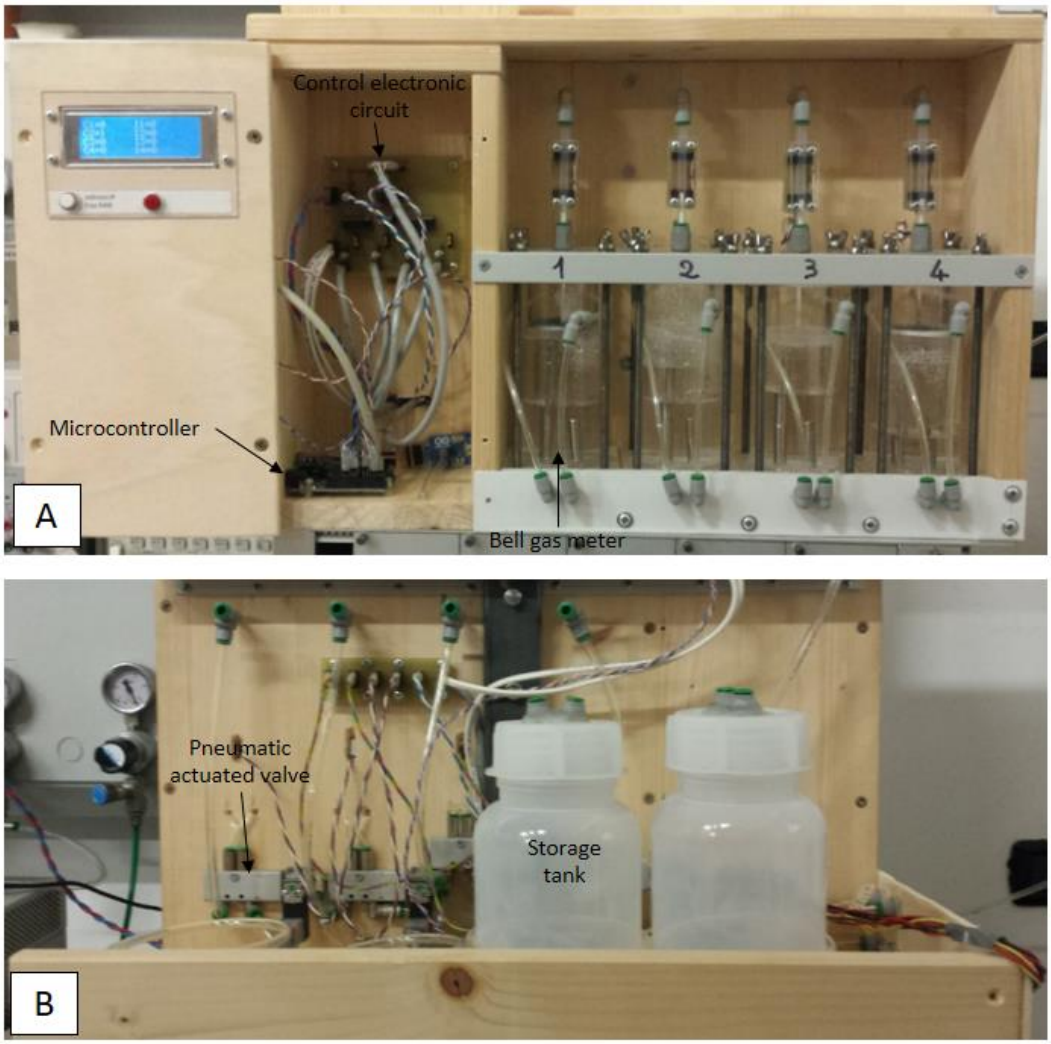

Figure 2.6: Four bell gas meter system. A: front view. B: rear view

2.2.1.3 – Last evolution of the bell gas meter

The bell gas meter described in the previous paragraph is a fully functional system. In fact, as will be better described in the next chapter, the device has been reproduced in an array of sixteen elements for measuring the biogas and, after upgrading the system, also the biomethane produced by eight cells of biodigestion, with volume of two liters, for more than two months without particular problems.

However, as it was described in the initial paragraph, this system is plagued by a potential underlying malfunction. In detail if, for any reason, a drop of liquid is able to enter into the conduit of the outlet port, then the system crashes. As already observed, this occurs because the bell falls only thanks to the effect of its own weight which, however, can not generate a pressure sufficient to expel this hypothetical drop of liquid. In principle, the possibility that a drop enters in outlet port is very remote; in fact, it has never occurred in the eight-cells system. The bell gas meter has however been used also to measure the biogas / biomethane produced from a digester with a volume of thirty liters, that is characterized by much greater flow rates. In this case, it happened for a few times that the gas meter it has be blocked due to the presence of a drop of liquid in the outlet port. It is useful to note that these unwanted arrests were always associated with peaks of the gas flow, likely caused by temporary blockage of the ducts due to the organic material coming from the biodigester. Although these events are sporadic and caused mostly by abnormalities in the digester, a major effort was made to resolve definitively the arrests of the bell gas meter. By analyzing the gas path in the system circuit, a solution that would allow to keep all the main components of the gas meter was found. This solution allows, through a simple change of the connections in the solenoid valve, to ensure that ,even in the descent phase of the bell, the gas pressure of the source can to push it down. In this way, the device has all the energy needed to eject this hypothetical drop of liquid from the outlet port.

Regarding the operation of the system, the first step is similar to that described in the previous configuration. Instead, when the inlet port is connected to gas source, the bell is being filled with the gas and is pushed upwards. Simultaneously, by ascent of the bell, the gas located in the container outside the mobile element is forced through the upper port and outside the meter. The second step has a rather important difference, in fact, when the rod above the bell shut off the beam of the upper photo-switch, simultaneously, the pneumatic valve closes the inlet port, connects the upper port to the gas source and the outlet port to the external environment. In this configuration, only the container outside the bell is connected to the gas source. So, unlike the previous configuration of the gas meter, it is precisely the gas pressure and not only the mere weight of the mobile element, which push the bell downwards. As a result of the descent of the bell, the gas contained inside it is pushed through the outlet port outside the meter.

Then, when the rod goes below the lower optical switch, the pneumatic valve is reset to its initial status, and a new cycle begins.

The new contact scheme of the evolved version of the bell gas meter is shown in the next figure (fig. 2.7):

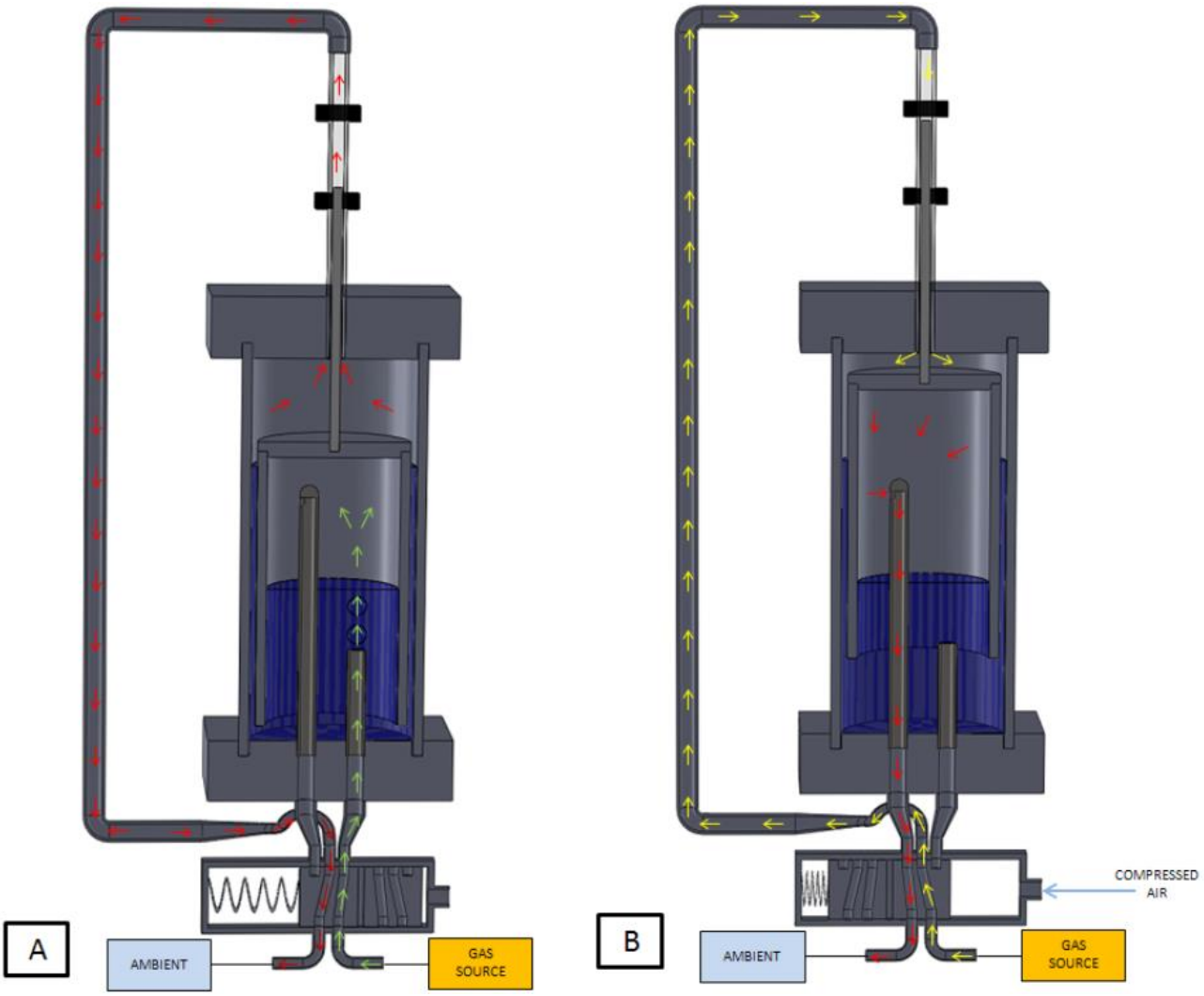

Figure 2.7: Modified bell gas meter. A: work phase 1. B: work phase 2

Focusing on the solenoid valve connections, when no compressed air is applied to the pneumatic actuated valve and the piston is in its rest position (A - fig. 2.7), the inlet port of the meter is connected to the gas source, the upper port is connected to the ambient (or to the collecting tank) while the outlet port is closed. When instead the compressed air is applied (B - fig. 2.7) and the piston is in its second stable position, the upper port of the meter is connected to the gas source, the outlet port of the meter is connected to the ambient and the inlet port is closed.

An interesting advantage of this latest model of the bell gas meter is that it allows to process the gas at its input continuously. Instead, in the previous version of the gas meter, during the descent phase of the bell, the gas flow was interrupted although for a short period, condition that does not occur in the new model. Clearly in this case the volume processed at each cycle is double as compared to the previous one, because

the external volume of the bell is also counted which, for the uniformity of the volume spaced by the mobile element, is filled with the same amount of gas that fills the interior of the bell.

2.2.2 - The drop gas meter

2.2.2.1 – Concept and evolution of the drop gas meter

The literature describes gas meters based on counting the bubbles of gas which rise along an inclined transparent tube filled by a liquid [B21]. However, to our knowledge, the mutual system consisting of a drop of liquid in a tube moved by the gas has never been presented. The great advantage of this type of gas meter consists in the fact that it is able to reduce drastically the pressure differentials between its input and its output. Conceptually, the drop gas meter is simply constituted by a tube inside which is placed a gas-tight drop which is moved by the gas flow. Greatly simplifying the description of its functioning (for detailed description, see the following section), when the gas enters from one side of the tube, the drop moves toward the opposite side, however, before that it comes out of the hose, the ends of the tube are inverted, so the input becomes the output and the output becomes the input and the drop moves back to the other end and a new cycle begins.

The first difficulty encountered was the choice of the drop material. The first liquid used was paraffin oil, however, it adhered excessively to the walls leading to the disappearance of the drop. Afterwards, the mercury has been used but, however, it tended to break up too easily. Finally, the right balance between cohesion and adhesion forces was found using water added with a small amount of acid (mainly used to reduce the permeability to carbon dioxide). Another issue to be addressed was the choice of pipe material. In fact, it would minimize the friction within the drop and should be equipped with a good infrared transparency, because two photointerrupters was entrusted with the task to indicate when the drop had reached the end of the tube. For this reason, the idea of using a PTFE tube had been discarded because of its excessive opacity. However after disappointing results with other materials, in which the drop remained intact only for relatively small flows, the choice about the tube material was reconsidered. In order to solve the problem of this excessive opacity two short sections of transparent tube (where the photointerrupters were accommodated) were added to end portions of the PTFE tube; however a satisfactory seal junction was never reached. So the decision was to apply the photointerrupters directly on the PTFE tube. In this regard, the current of the LED photointerrupters was increased almost to the maximum value granted by datasheet in order to compensate the opacity of the tube. This technique has brought the desired results because the devices were able to detect the passage of the drop.

Moreover, the use of ink to make the drop opaque to the infrared radiation was not necessary, whereas it was a mandatory with the use of transparent tubes. As regards the arrangement of the tube, at the beginning it was horizontally arranged in the shape of "U". However, in the area of the curve, the drop tended to shatter. To minimize the curvature, a circular arrangement was adopted and then moved on to a perfectly linear disposition of the tube. Some figures about the evolution of the drop gas meter are provided below (fig. 2.8).

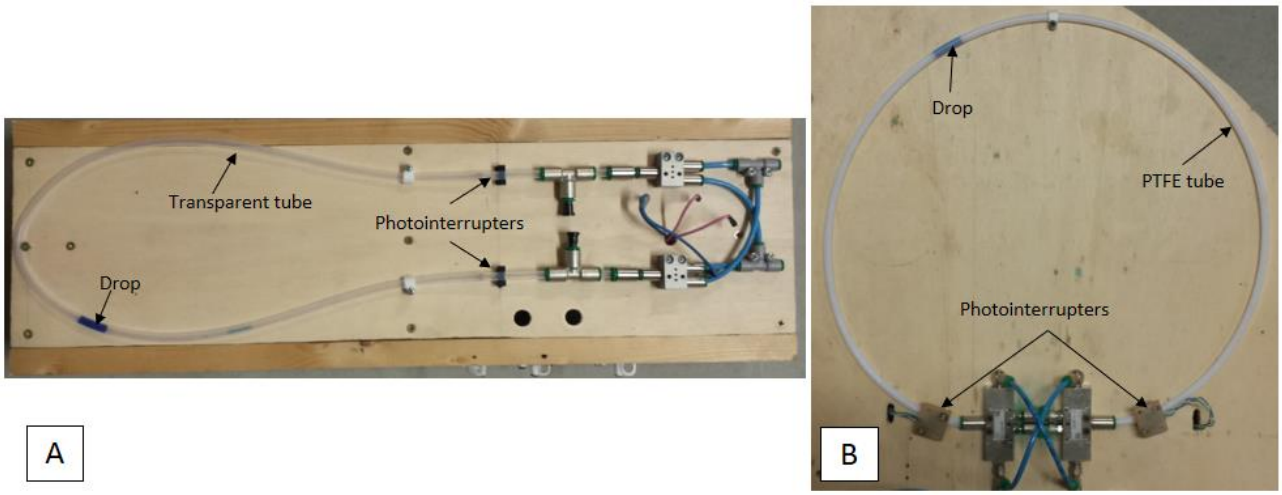

Figure 2.8: First prototypes of the drop gas meter. A: U shape tube. B: circular shape tube

2.2.2.2 - Detailed description of the drop gas meter

The drop gas meter is composed by a tube transparent to the infrared radiation, a drop of liquid with gas-barrier characteristics, a pneumatic actuated valve, two photo-interrupters and the electronics for control and data acquisition.

In the transparent tube is inserted a movable gas-tight drop that divides the tube into two zones with variable volume and without any gas transfer between them. The tube ends may be connected alternately at the gas source or at the external environment by means of a pneumatic valve. At the beginning and at the end of the tube are positioned two photo-interrupters. When the drop of liquid, moved by the gas pressure, interrupts the light beam of one photo-interrupter, it means that the drop is in the proximity of an end of the tube; so the electronics actuates the pneumatic valves which reverse the ends of the tube.

Therefore the tube inlet becomes the tube outlet and the end connected to the gas source become connected to the external environment, the tube outlet becomes the tube inlet and the end connected to the output environment become connected to the gas source; so that the gas pressure moves the drop in the opposite direction toward the other end of the pipe. When the drop reaches the other photo-interrupter, the electronic valve again reverse the ends of the tube and the system is ready for a new cycle.

The two operational phases and the components of this second gas-measuring system are shown in the next figure (fig. 2.9).

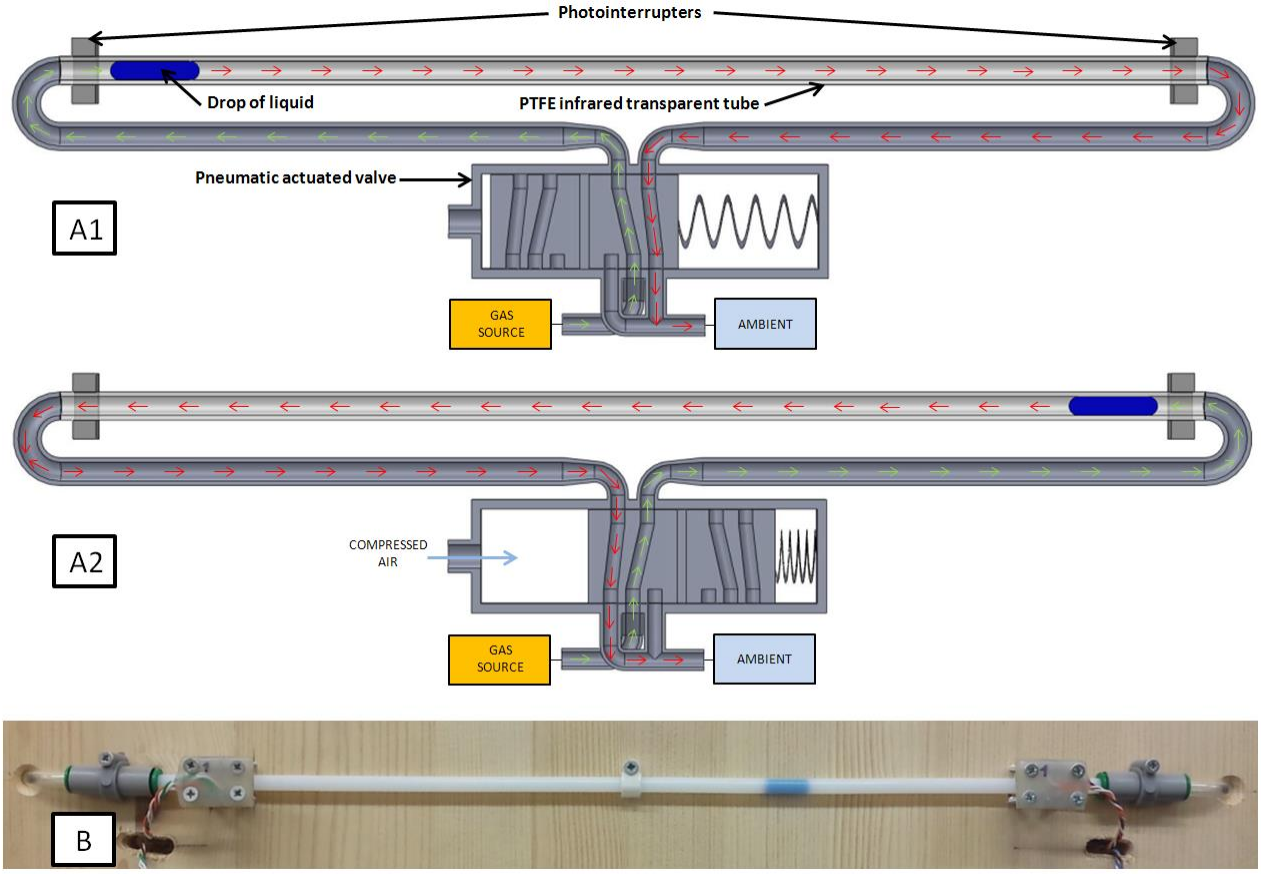

Figure 2.9: Drop gas meter. A1: components display and work phase 1. A2: work phase 2. B: real device

This device that we call drop gas meter is original, in the sense that, to our knowledge, it has not yet been described in patents or in the open literature or used in commercial devices. It works with small pressure differentials (in our case, of the order of 50 Pa) and has a high resolution (in our implementation few ml and it can be easily improved) but it has also an intrinsically low top flow rate (see below). It can be physically modelled with relative ease, but some parameters of the interaction between the drop and the inner tube are difficult to obtain. Since the geometry of the system adds additional complexity, we carried out many attempts to end up with the system described here, which represents its simplest from the conceptual point of view.

The hearth of the device is a liquid drop (in our case, colored water), which “wets” an inner tube and is moved by a pressure differential along it. The drop acts as a “gas plug”. Our tube is made of hydrophobic polytetrafluoroethylene (PTFE), to reduce the drop/wall friction, 1 mm thickness, 6 mm outside diameter and 350 mm long. We tried other plastic tubes (polyurethane, PVC, polyethylene) which had, as expected, inferior performances. The tube is kept straight and in the horizontal position by brackets; it is connected with less expensive and more flexible tubes pneumatic valve.

The drop fills a 25 mm long cylinder inside the PTFE tube; it is made of acidic water (pH= 3 by addition of HCl) to enhance the biogas barrier effect. It is not necessary to add a colorant to make the drop opaque to the infrared radiation; vice versa, a colorant is required by our optical switches when a more transparent material than PTFE is used. The optical switches are described before; they are placed on the PTFE tube at the distance of 320 mm, which, unless the drop thickness, is essentially the drop stroke .

Also the pneumatically actuated valve is the same as before. However, the valve output ports are connected at the two ends of the tube, while the central port, closed in the basic version of the previous meter, is connected to the gas source. The two side ports are connected to the external environment (biogas tank or ambient).

The control electronics of the meter has the task of drive the solenoid valves and hence the pneumatic actuated valves on the basis of the signals coming from the two optical switches. It is mainly composed of three elements: a SN74HC112 Texas Instruments dual J-K negative edge triggered flip-flop with clear and preset functions, a 2N2222A STMicroelectronics NPN switching transistor, these two components have already been described before. The output of the phototransistor at the right side optical switch is connected to a pull up resistor and to a flip-flop preset pin, which drives the valve power on through the 2N2222A. The output of the left sided optical switch goes to a pull up resistor and to the clear pin of the flip flop. When the drop is not at the left or right optical switches, they are conducting and then carry to ground (logic zero) the output connected to the pull up resistor. When the drop goes in, the output is pulled high by the pull up transistor and the preset or clear transition occurs. Note that, once a transition has been occurred, the drop has to move completely along the PTFE tube before the opposite transition is triggered. In other words, the system is simple and very stable as when the phototransistor is saturated, the flip flop receives a high signal, necessary to insert a pull-up resistor before the flip flop.

Then the output 5v signal of the flip flop is sent to the NPN transistor that provides directly to the solenoid valve the 24v working voltage.

The scheme and the real control circuit, capable of driving four drop gas-meters, is shown in the next figures (fig. 2.10 – 2.11)

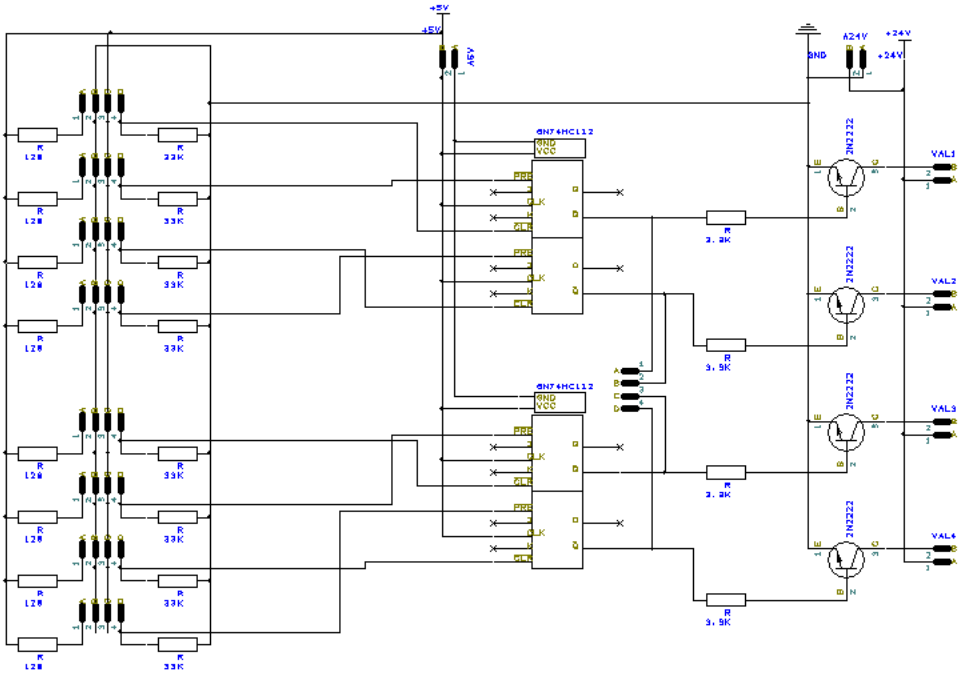

Figure 2.10: Control electronic circuit capable to drive four drop gas-meter

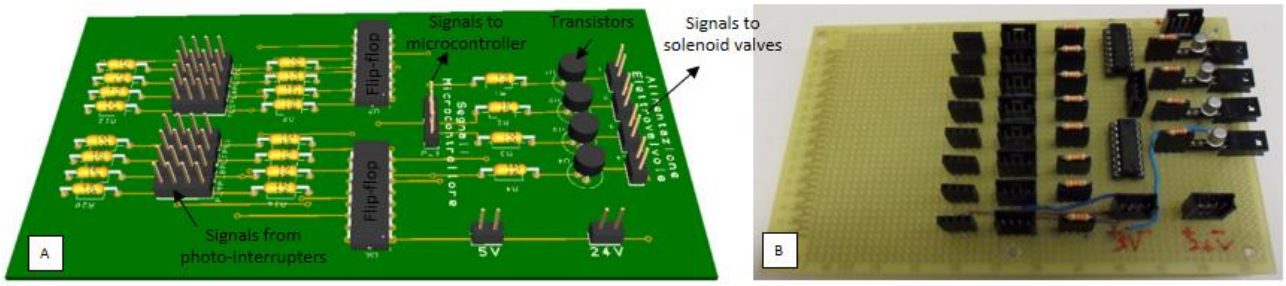

Figure 2.11: Drop gas-meter control circuit. A: Circuit prototype. B: Real circuit

Regarding the data acquisition, data memorization, data displaying and computer communication, all these functions are performed by the same Arduino board mentioned in the description of the bell gas meter. The final system described is shown in the next figure (fig. 2.12).

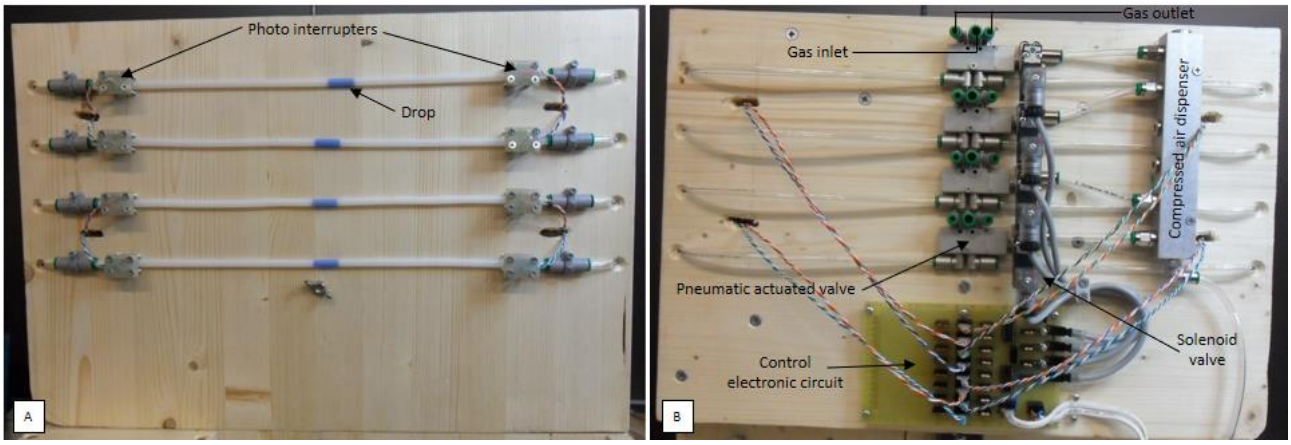

Figure 2.12: Four drop gas meter system. A: front view; B: rear view

2.2.2.3 – Last evolution of the drop gas meter

One of the tests that a gas meter must overcome in order to be approved for its use the on field is the behavior in case of external counterpressure. In fact, all the gas meters described in this chapter are designed to operate with a positive differential pressure: i.e. higher at their inlet and lower at their outlet.

In particular environmental conditions it can verify an increase of atmospheric pressure capable to overcome the pressure inside the biodigester. In the case of the drop gas meter, this condition would cause the backwash of the droplet into the digester and the only way to counteract the system stop, consequent to this phenomenon, is to use a non-return valve as specified in the dedicated paragraph (2.2.4).

However, in our experience, if the experiment lasts for several months, is possible that at the end some impurities coming from the digester or, depending on the position of non-return valve, some condensation salts coming from the biogas upgrading system (especially in the case of chemical capture) can reach the non-return valve compromising its operation and also the operability of the gas meter.

In this regard, one last important modification was added to the drop gas meter in order to make it immune to backpressure phenomena. This innovation consists of adding a pair of photo-interrupters, external to those necessary for the basic operation of the gas meter, which causes a reversal of the solenoid control logic. In other words, during the normal behavior of the gas meter, the drop moves always within the space of the two central photo-interrupters. When an external overpressure occurs, the drop exceeds the central photo-interrupter, which would have to reverse its motion, and interrupts the beam of an external photo-interrupter. When this happens, the solenoid control logic that allows the proper functioning of the system is reversed and the drop, despite the external pressure, moves within the space of the two central photo-interrupters. When the pressure of the biodigester returns to exceed the ambient pressure, the drop exceeds again the central photo-interrupter, which would have to reverse its motion, and interrupts the beam of an external photo-interrupter. In this way, the solenoid control logic returns to its basic form.

The evolved version of the drop gas meter is shown in the next figure (fig. 2.13).

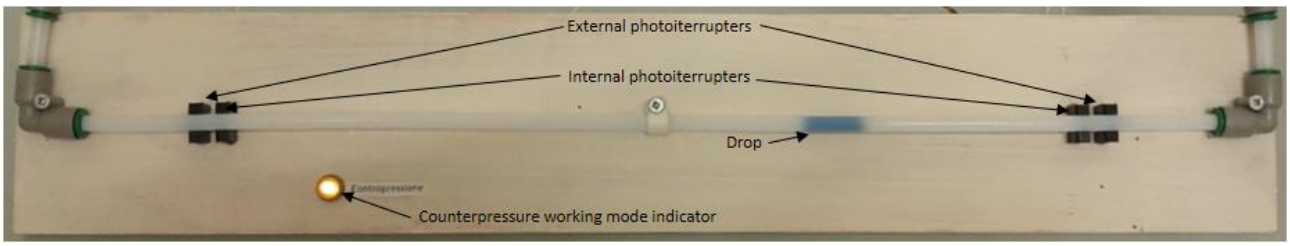

Figure 2.13: Evolved version of the drop gas meter

In detail, during the basic functioning of the system, when the drop interrupts the light beam of the interior left photointerrupter, the left side of the PTFE tube is connected with the biogas source while the right side of the tube is connected with the external environment. In this way, the drop is pushed by the pressure of the biogas source and moves to the right. When the drop interrupts the light beam of the interior right photointerrupter, the right side of the PTFE tube is connected with the biogas source while the left side of the tube is connected with the external environment. In this way, the drop is always pushed by the pressure of the biogas source and moves to the left. So, there is an external overpressure and the drop reverses its motion and moves back toward the biogas source. In this manner, it ends with stopping the light beam of one of the external photointerrupters, which in turn inverts the logic previously described. When the drop interrupts the light beam of the interior left photointerrupter, the left side of the PTFE tube is connected with the external environment while the right side of the tube is connected with the biogas source. In this way, the drop, pushed by the pressure coming from the external environment, moves to the right. When the drop interrupts the light beam of the interior right photointerrupter, the right side of the PTFE tube is connected with the external environment while the left side of the tube is connected with the biogas source. In this way, the drop is still pushed by the pressure coming from the external environment and moves to the left. Then the pressure of the biogas source exceeds again that one of the external environment, the drop reverses its motion and interrupts the light beam of one of the external photointerrupters, which reverses again the logic and brings it back to the basic version.

2.2.3 - The spoon gas meter

2.2.3.1 - Concept and evolution of the spoon gas meter

The spoon gas meter is the last meter to be developed. In particular, some laboratory measurement systems of methanogenic power are of this type, although it was not possible to examine in detail any of these.
Conceptually, the meter is constituted by a container, filled with liquid, in which a mobile object, shaped as an overturned spoon, is immersed. The concavity of the spoon is facing downwards and it is positioned to cover the inlet port, that is connected to the gas source. When the gas enters, it fills the cavity of the spoon which starts to rise upwards allowing the exit of accumulated gas. When this has happened, the spoon falls down and it is ready for a new cycle. It's important to notice that the gas meter must be equipped with a system capable of blocking the flow of gas when the spoon is in motion in order to avoid not counted gas pass through the system.
Given these premises, the construction of such a device seemed immediately quite complicated for the available technology, especially in view of the fact that it was necessary to realize a perfectly reproducible system. Particularly problematic was the choice of the gas interrupting device, which could be mechanical (i.e. driven by the motion of the spoon) or take place through a solenoid valve (which had to be able to be activated as soon as the spoon was beginning to rise). In addition, it was necessary a system to count the rises of the spoon.
As regards the gas interrupt system, the choice made was to prevent its use through the implementation of a symmetrical system constituted by a double spoon. This device was designed to ensure that, when the first spoon starts to get up, the gas flow is immediately picked up by the second spoon; in this way an explicit interruption of the gas is no longer necessary.
Unfortunately, the first attempts to build such a device, carried out initially with the classics teaspoons for food and then moved on to the plasticine, have produced quite disappointing results.
With the progress of the tests it was finally possible to obtain, by gluing pieces of hard plastic, a device that was at least mechanically functioning, even if still not equipped with a symmetric behavior. The first version of this spoon gas meter is shown in the next figure (fig. 2.14).

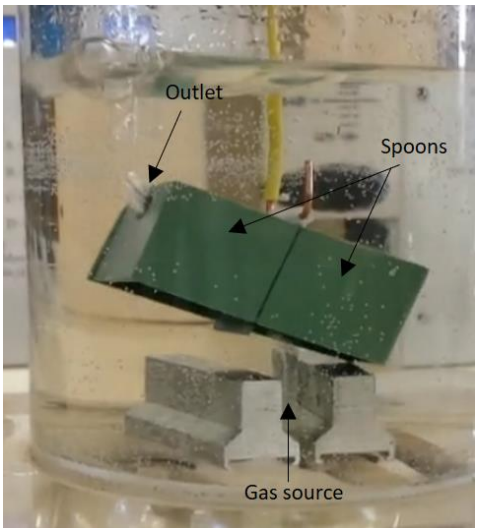

Figure 2.14: first version of a mechanically functioning spoon gas meter

In general, however, the reproducibility, for a craft system was a great problem. After several attempts and research, we realized that the only way to build a system with the desired characteristics was to use a 3D printer. After choosing the 3D printer type on which to focus (the cheapest), I was addressed to an architectural firm whose kind owner, after listening the requests (in particular, the fact that it would be take several prints before getting a gas meter with the desired characteristics) proposed to cure the assembly of a 3D printer and the possibility of a temporary use of it. Unfortunately, a longer time than expected was spent before being able to get a printer that worked satisfactorily. Moreover, once completed the selected printer, it was necessary also to restore a second printer. Some of the pieces of this second printer were used to understand and solve problems showed by the corresponding elements belonging to the first printer. A figure either of the created or of the printer restored is shown below (fig. 2.15).

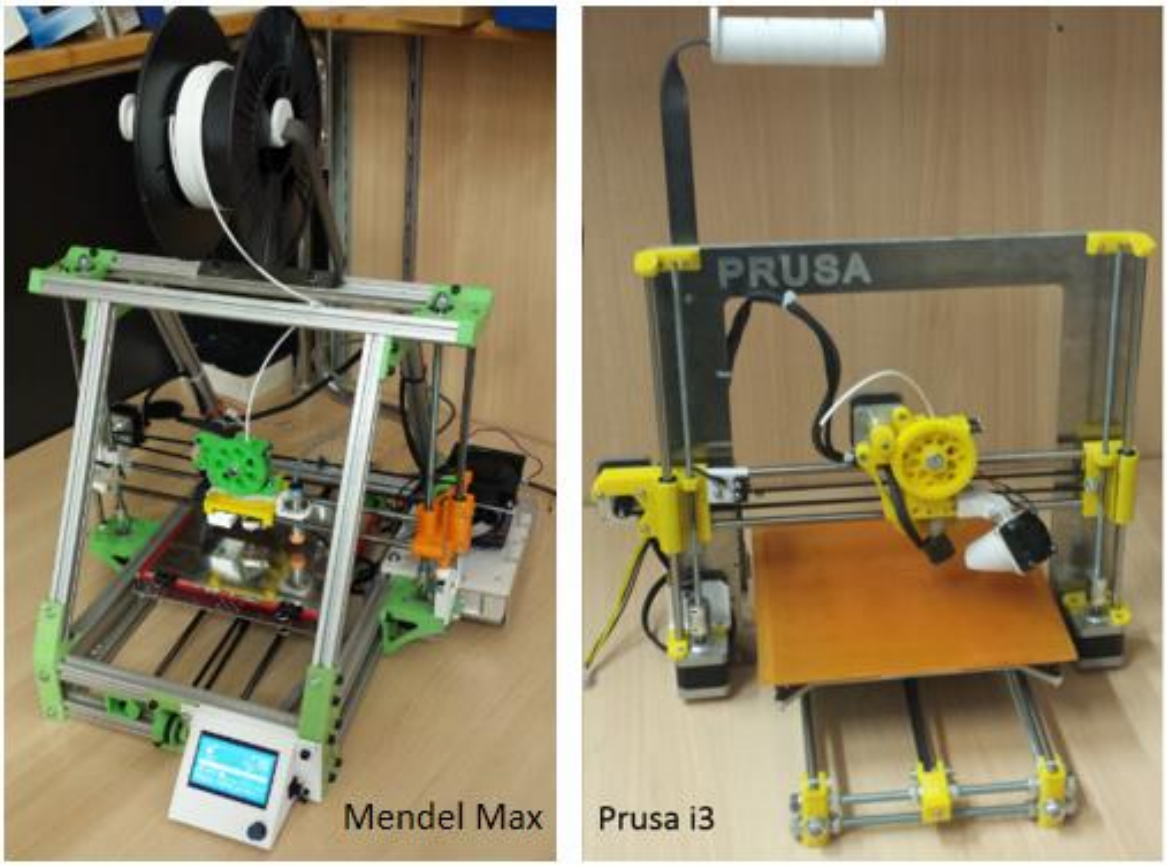

Figure 2.15: 3D printer made (Mendel Max) and restored (Prusa i3)

It was possible to print with the 3D printer the first version of the spoon gas meter, in particular, for the counting of the cycles, the established technology of the photo-interrupter was used and for this reason the spoon has been equipped with a vertical bar line which, serves also to reduce the transition time of the mobile element, a concept that will be well described in the next paragraph. A figure of the first spoon gas meter, made with the 3D printer, is shown below (fig. 2.16)

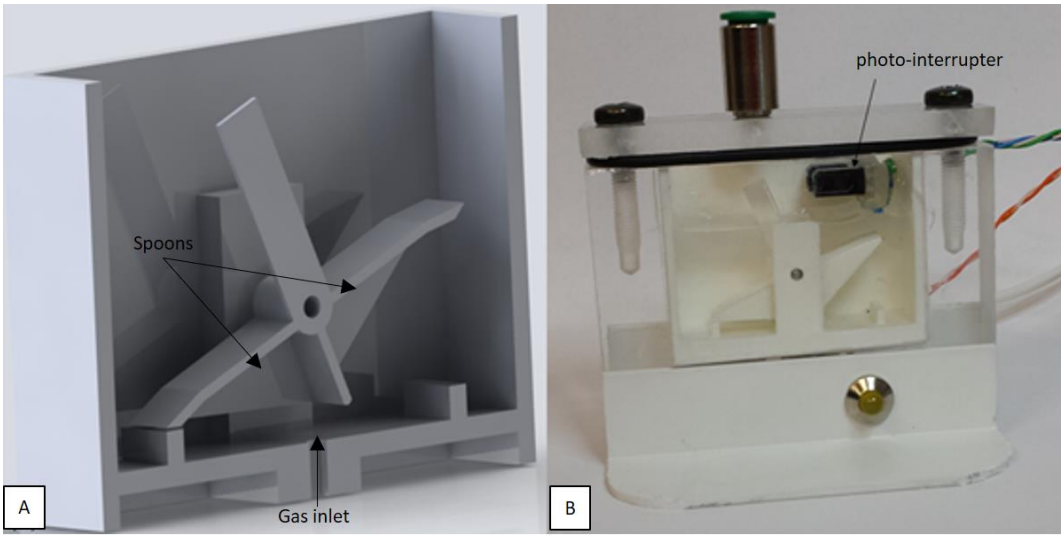

Figure 2.16: First 3D printed version of the spoon gas meter. A: the project design. B: the real device

Unfortunately, despite the excellent mechanical operation, the system showed some sealing problems. Moreover, after few hours of operation, it is formed a slight condensation on the optical switch that altered its operation. To solve this leakage problems, it was decided to design a removable container (that maintains the possibility to inspect the movable spoon) capable to capture the gas leaving the spoon and immersed in the liquid almost to the base of the spoon. As regards the problems related to the malfunctioning of the photo-interrupter, the first choice was to replace it with a simple contact switch. To perform this, two different potential copper rigid bars were inserted within the container and two conductors able to short-circuit them have been inserted at the ends of spoons, with the purpose of having a signal for each position change of the mobile element. A figure of the spoon gas meter with the described modifications is shown below (fig. 2.17).

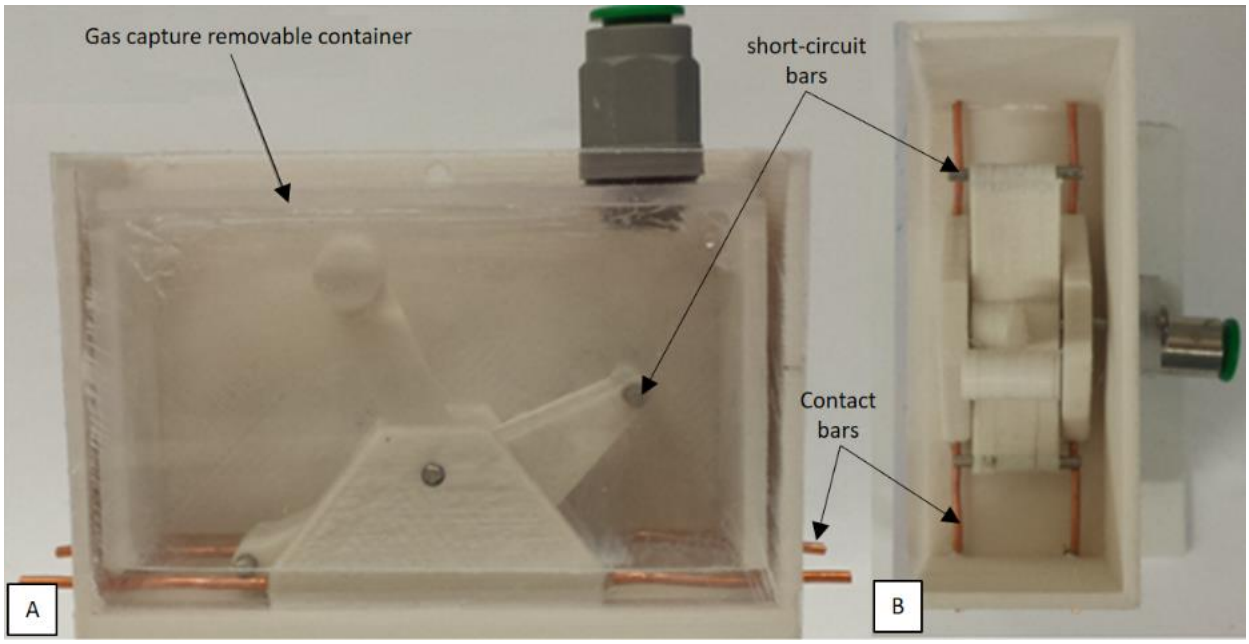

Figure 2.17: First evolution of the spoon gas meter. A: front view; B: top view

With this new approach, the leakage problem could be considered solved while this is not true for a part of the signal. In fact, the electrical contacts produced only a slight impulse, also quite dirty, so it needed a new idea to solve this second issue.

The solution adopted has been to design a new device equipped with two rods hinged to the base that, according to the position, can interrupt the light beams of two photo-interrupters placed outside of the

container that are not in contact with the liquid. A figure of the double spoon gas meter project with the external photo-interrupters is shown below (fig. 2.18).

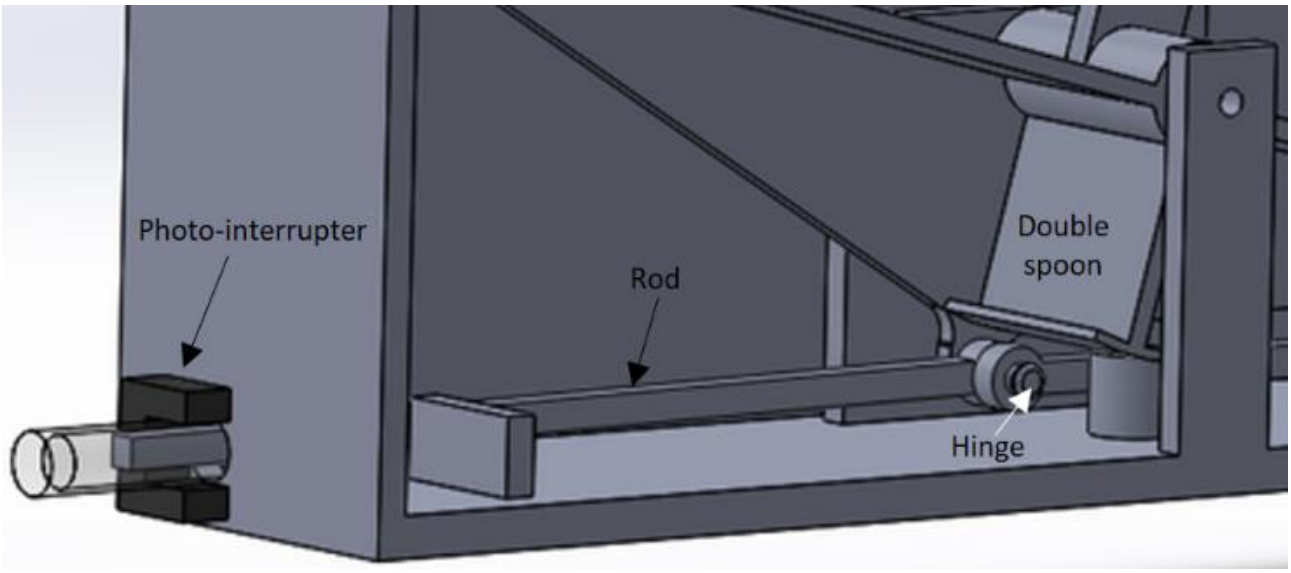

Figure 2.18: Particular of the hinged rod and the external photo-interrupter applied to the spoon gas meter

With this solution, the problem of a simple and robust method for determining the gas meter's cycles could be considered solved.

At this point, it was possible to concentrate on the careful improvement of the mechanical operation of the device. In particular, it was tried to evaluate some possible solutions to reduce the transition period of the mobile element.

The first solution was to equip the double spoon with a weight (ballast) placed at a certain distance above the center of rotation of the mobile element. In this way, in stable state the application point of weight force is at maximum distance from the center of rotation, which means a maximum holding torque exerted by the weight. Instead, when the spoon starts to move upwards, the application point of weight force moves closer to the center of rotation so the holding torque decreases more and more and the transition period can be very rapid (a detailed description of this mechanism will be given in the next paragraph). The second solution was to add a sort of further external spoon to the mobile device that serves to collect the air harvest in the main spoon as soon as the double spoon starts to move.

In this way, it was thought that the application point of gas buoyancy force moves in a short time further away from the center of rotation with a consequent increase of the ascent torque. A figures that illustrates these two types of modifications is shown below (fig. 2.19).

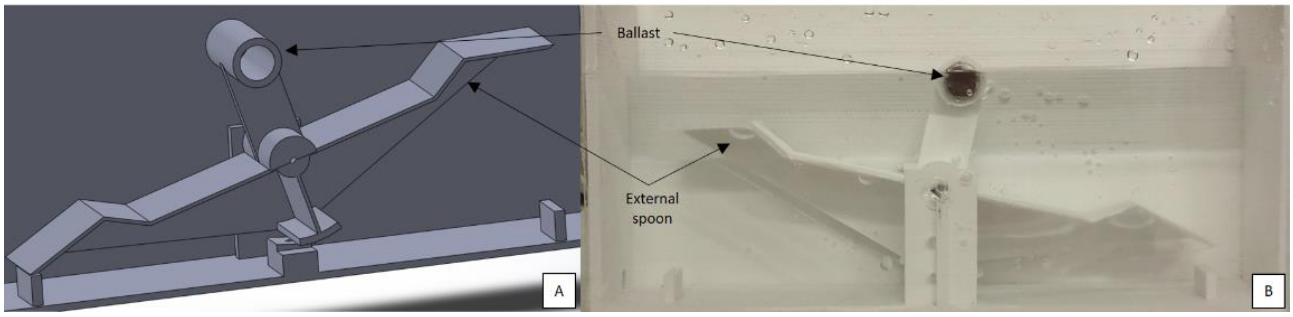

Figure 2.19: Additions of the ballast and the external spoon to the double spoon gas meter. A: the project design, B: the real device

The various tests carried out with and without ballast by using different models of double spoon with and without the external spoon showed that the ballast improves the transition speed, while the external spoon does not appear to have a similar positive effect. The transient in this second case was in fact substantially equal to the basic double spoon model. Moreover, not all the gas collected from the external spoon was then released during the ascent phase, in fact some bubbles remained trapped in the external element; an evolution of the project would have been necessary, but given the lack of interesting results, this direction of study was not undertaken. In conclusion, for the final version of the gas-meter the external spoon was not used, instead the ballast was maintained.

The last type of spoon made and studied was the single spoon mobile element. At the beginning of the work, the use of a single spoon had been discarded because , an easy and convincing way to stop the gas flow was not found with this design when the mobile element is in motion. Clearly, this condition does not constitute a problem at low flow rates, because the transient time is very fast compared to gas influx. However at high flow rates, the transient time becomes comparable to the gas influx and part of the gas may pass through the gas meter without being counted. Since the main advantage of the spoon gas meter is the constructional simplicity due, in particular, by the absence of solenoid valves. Even in the single spoon version, this philosophy of simplicity must be maintained for which the use of solenoid valves has been immediately excluded. Moreover, the 3D printer offered the possibility to realize even components with very complex shape. For this reason, it was thought that by increasing the geometric complexity of the movable element, only this could block the passage of gas when the spoon is rising without the use of solenoid valves. The basic idea was to equip the single spoon of a sort of trap, that would capture the gas that might escape when the spoon is in the ascend phase and then release it when the spoon is in descent phase. A figures that illustrates the first design of the single spoon gas meter is shown below (fig. 2.20).

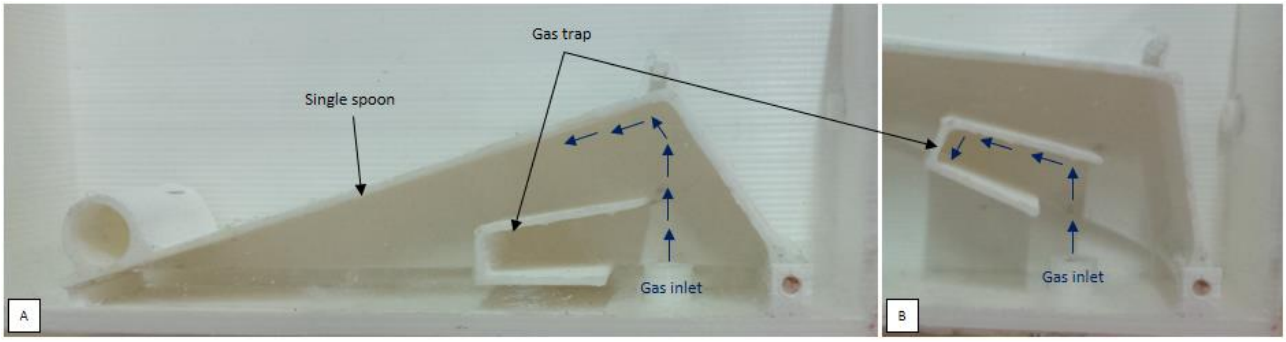

Figure 2.20: First version of the single spoon gas meter. A: Spoon normal position. B: Gas entrapment

Practically, when the spoon is in its normal position, the gas fills the main space of the mobile element. Instead, when the spoon is in the ascent phase, the main space of the movable element is obscured by the trap that provides to capture the gas that otherwise would pass through the meter without being counted. After that, when the spoon is in the descend phase, the trap releases the captured gases which provides to fill the main space of the mobile element. Unfortunately, the realization of a fully functioning device based on a single spoon was much more difficult than expected. In fact, various projects and prints are needed to achieve a mechanically acceptable behavior. In the first models often the air don't leave completely the trap or the spoon and moreover the trap was unable to capture all the gas.
The evolution of single spoon models until to obtain an acceptable mechanically operating device is shown in the next figure (fig. 2.21).

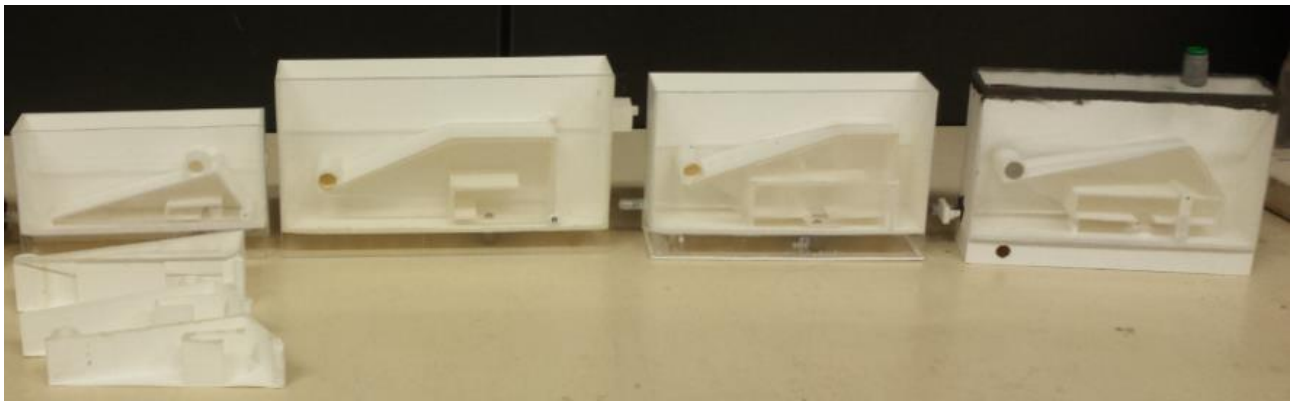

Figure 2.21: Evolution of the single spoon gas meter

In the final version of the system, the gas is always forced to cross the trap and to enter in the main spoon, even when the mobile element is in its stable position. After several attempts, this approach is the only way to ensure that the trap functions properly by capturing all of the gas that enters in the spoon during its ascent phase. For the correct operation of the system, another important aspect is the position where to place the openings that allows gas to pass from the trap into the main spoon. Initially, it was simply placed at the end

of the trap, in a position which remains lower down when the spoon is in its unstable position. However, with this configuration, even when the trap entered in action some gas bubbles could still pass through it. To solve the problem, it was thought to move forward the spoon's center of rotation and place the opening of the trap immediately after it. The observation is that while in the previous case, with the opening placed before the hinge, the center of the opening moves upward when the spoon is raised, now with the opening placed after the hinge, the center of the opening moves downward when the spoon is raised. Whereas the gas, or rather the liquid which surrounds it, is moving with a certain inertia, the fact that the opening moves downward limits the undesired leakage of the gas from the trap more than when the opening moves upwards. Experimental tests have confirmed the better behavior of the system with this change than the previous one. Relatively to the spoon design, the spoon's main area has the shape of a triangle with the top vertex aligned with the center of rotation. This has the aim to favor the escape of gas towards the outside. Finally, in order that the device can operate correctly, it was necessary to dimension properly the trap in such a way that it is able to contain all the gas at the maximum flow rate expected that can enter during the transitory of the movable element.

The area of the main spoon must be sized to contain all the gas contained in the trap and in addition the gas that can enter, always at the maximum flow rate expected, before the spoon begin to rise. The size of these areas must take account of the presence of a ballast which serves to promote the rapid descent of the spoon, that would otherwise be too slow, the spoon must be filled with a greater amount of gas to overcome the weight force of the ballast. The operating phases of the last version of the single spoon are shown in the following figure (fig. 2.22)

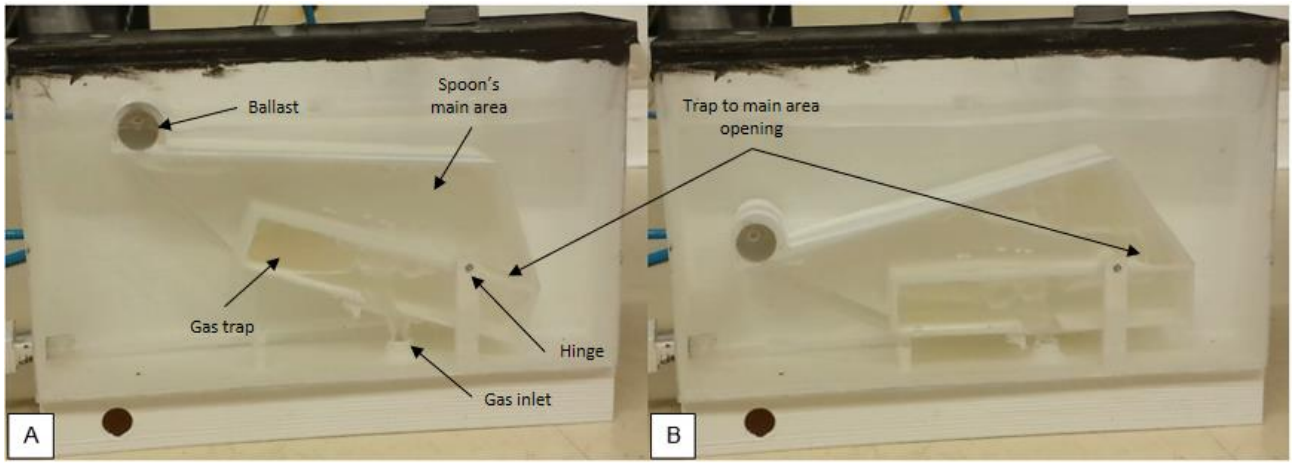

Figure 2.22: Single spoon with bubbles trap. A: the capture phase. B: the release phase

To achieved a good mechanical operation of the gas meter based on the single spoon, the device has been subjected to a comparison of performance test with the double spoon gas meter. Unfortunately, the results showed the presence of strong fluctuations of the new system versus the flow despite a constant input flow

rate. Not knowing where to take action in order to solve this problem despite the hard work done so far, the evolution of the project was stopped. The results of these tests are shown below (fig. 2.23 – 2.24)

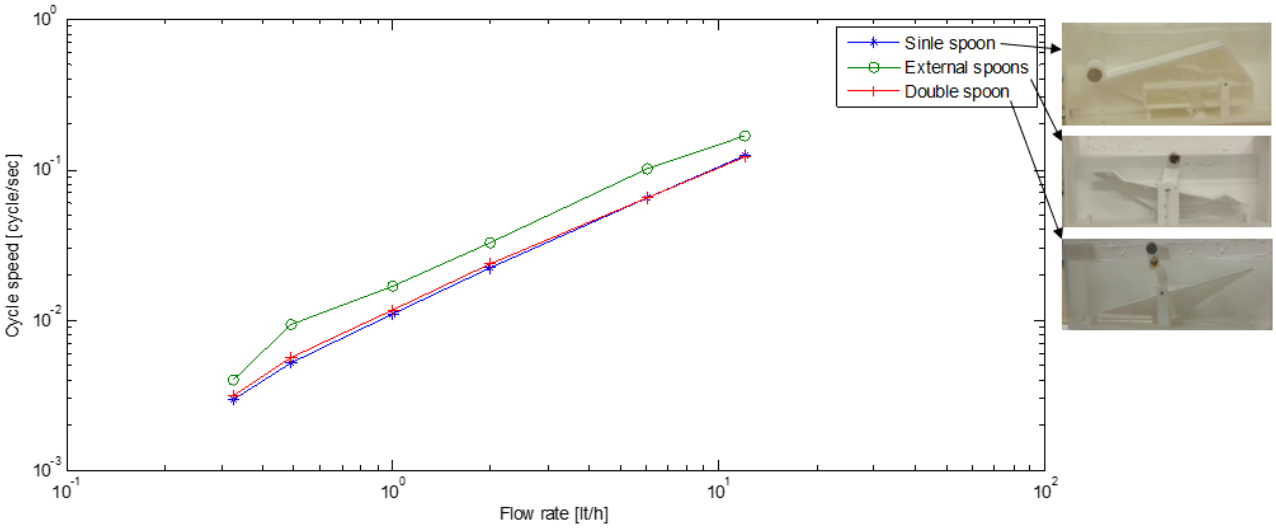

Figure 2.23: Behavior of the single spoon, double spoon with external spoons and basic double spoon gas meters, in terms of number of cycles per second at various flow rate

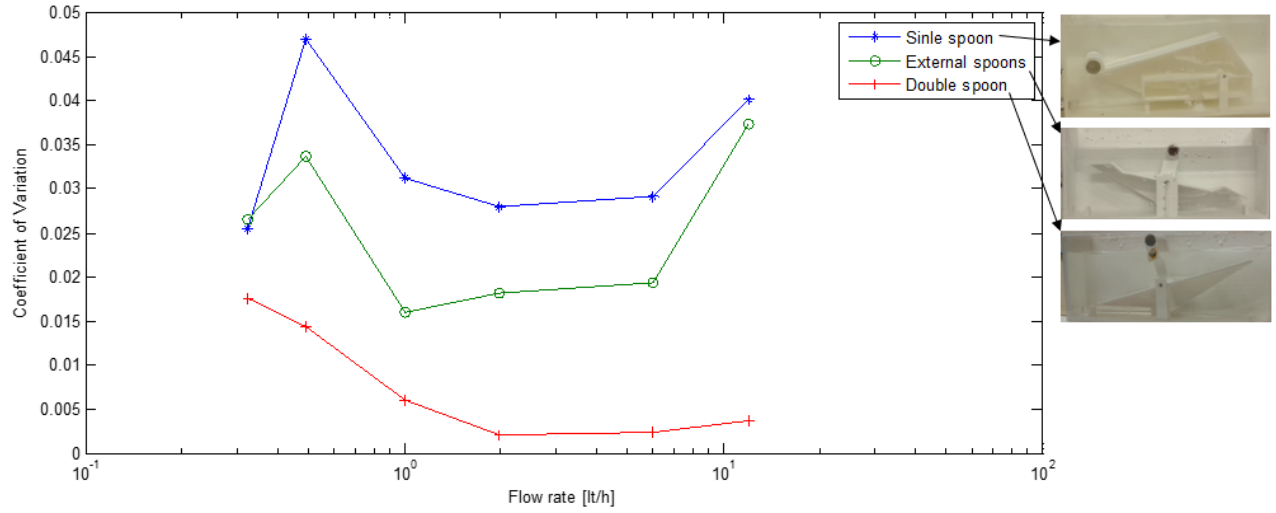

Figure 2.24: Coefficient of variation, at various flow rates, of the single spoon, double spoon with external spoons and basic double spoon gas-meters

The first graph shows the trend of the cycle speed of the gas meters with the increase of the flow rate. In particular, all the three systems showed a quite linear behavior with a slight exception for the double spoon with external spoons gas meter. The second graph shows instead the trend of the coefficients of variation with the flow rate. In this case, it is interesting to note that the highest values are achieved by the single spoon gas meter, while the lowest value is shown by the basic version of the double spoon gas meter. This

model is then the version with the best performance, so its construction and operation will be described in detail in the following paragraph.

2.2.3.2 – Detailed description of the final version of the spoon gas meter

The spoon gas meter is the simplest of the meters described here and it has been adopted by the most commercial systems used in laboratories to study biogas production. Since our aim is not to emulate/duplicate commercial products, but rather to understand limits, criticalities and benefits of different techniques, we produced few "spoon setups" with a home-made 3D printer after a rough analysis of the physical quantities involved.

Our setup consists of a container, a liquid with appropriate characteristics, a volumetric cell shaped as a symmetrical double spoon, two photo-interrupters and a microcontroller for data acquisition. The container is filled almost completely with a displaceable liquid, an oscillating double symmetrical spoon is placed in its interior, totally submerged in the liquid. The double spoon has two rods hinged to the base that, according to the position, can interrupt the lights beams of two optical switches. The container has two ports, the inlet port is connected at the bottom to the gas source and outlet port is located at its top and releases the gas outside the meter. The inlet port is aligned with the rotational center of the double spoon. The double spoon has two stable states and in each state only one of the two spoons can be filled by the gas coming from the inlet port. When a spoon is full of gas, it moves upwards losing the exposure to the inlet port, which is acquired by the second spoon in a very short time. In this way, the gas contained in the first spoon is released while the gas coming from the inlet port starts to fill the second spoon and the system is ready for a new cycle. To make the system work properly, it is essential that the transition from one state to another one is performed as fast as possible, so the double spoon is equipped with a weight placed in a central position (ballast) to obtain this effect. In the stable position, the ballast is located on the same side of the spoon which is filled with gas and thus exerts a torque (holding torque) which keeps the spoon in place. Moreover, in stable state the application point of weight force is at the maximum distance from the center of rotation, for which the holding torque exerted by the weight is maximum.

When the spoon starts to move upwards, the holding torque decreases more and more because the application point of weight force moves closer and closer to the center of rotation. In addition, the spoon is designed in such a way that, when it moves up, the application point of gas buoyancy force moves further and further away from the center of rotation, so that the ascent torque increases. In other words, when the spoon starts moving, the holding torque is in constant decline while the ascent torque is in constant increase, so that the transition period can be very rapid. In particular, when the half rotation point is passed, the holding torque become negative, that is, the weight force drag the other spoon in position.

The hearth of the spoon gas-measuring system is shown in the next figure (fig. 2.25).

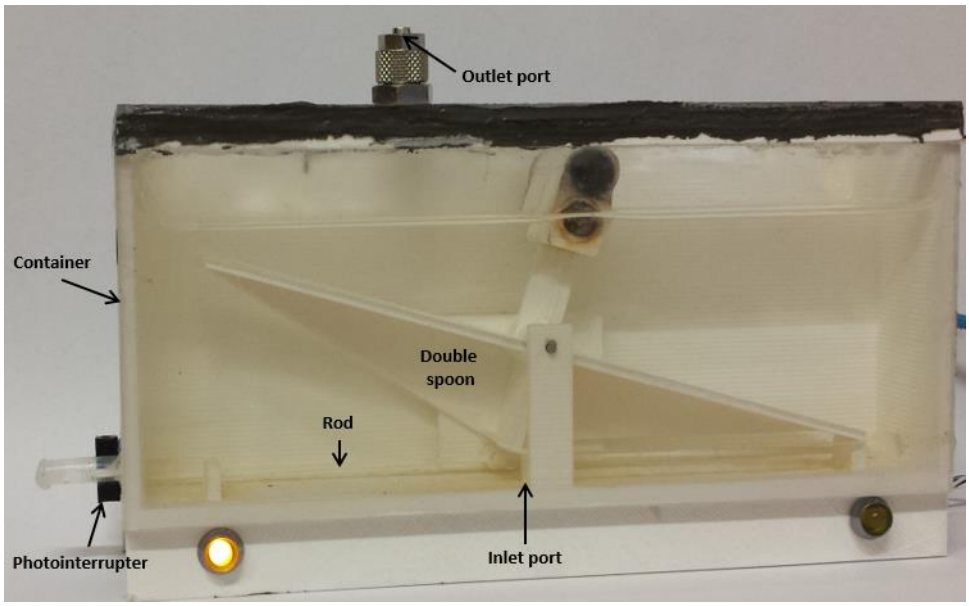

Figure 2.25: Spoon gas meter: components display

In our implementation, the gas meter is able to measure flows up to 12 l/h, its measuring resolution is about 30 ml and the backpressure imposed by the gas-meter is approximately 80 mm of water (785 Pa).
Constructively, the container is a polylactic acid (PLA) prism 3 mm tick, with 190 x 45 mm base side lengths, and 90 mm high made with an Open Source fused deposition modeling (FDM) 3D printer, specifically the Mendel-Max model. In the middle of the vertical planes, at a height of 32 mm, two 2 mm hole represents the center of rotation of the double spoon and the rear one is externally closed by a cap to allow the insertion of the fulcrum rod with no leakage. The base presents a hole 4 mm in diameter, which represents the inlet port. To allow the gas source connection a gas-tight joint (Pneumax T1504M5) is glued into the hole. Also the upper plate present a 8.5 mm hole which represent the outlet port, with another gas-tight joint (Pneumax TC0618) screwed into the hole. The symmetrical double spoon is the movable element of the system, it performs a rotary motion of about $\pm 15°$. The two spoons are shaped as right triangles with sides of 80 mm and 25 mm, when the water depth is 23 mm. The ballast consists of two steel cylinders, with diameter of 10 mm and 8 mm and vertical hooks at 25 mm and 35 mm respectively, above the rotation center. The gas-barrier liquid is the same used in the bell gas meter. The system does not need a dedicated control electronic since registration of the “pulses”, released by the optical switches, can be performed directly by the Arduino hardware.

2.2.4 – Practical considerations on counterpressure

Regarding the considerations on the practical operation of the gas-meters, it should be noted that they may be subject to malfunctions in case of external counterpressure, due to the atmospheric pressure increases. That may occur, for example, at night or during a thunderstorm due to a lowering of the ambient temperature that causes an increase in air density and consequently of its weight. The result is an increase of the atmospheric pressure. In this case the liquid contained, in different quantities, in all meters presented might pour into the biodigestion cells causing the arrest of the measuring system, which should then be manually reset by re-inserting a new liquid. To solve the problem, the use of a common non-return valve may not be as effective. These valves in fact contain a spring, which presses a ball against a seal, whose strength can only be won if the digester reaches a certain pressure. This situation is to avoid especially in laboratory experiments, it is a good idea to remove that spring or alternatively use non-return valves which are devoid of it. Unfortunately this type of non-return valves have some disadvantages, they can be used only in a certain position and, in any case, following the tests carried out it has seen they are not always capable to stop completely a gas at low pressures and flow rates.

A possible solution could be to immerse the non-return valve in a liquid container. In normal conditions, the gas product by the cells bubbles in the liquid while, in the case of counterpressure, the liquid will try to pass through the valve without success, because of its higher density and surface tension. A similar effect can be obtained by placing the liquid container downstream of the valve. Also in this alternative version, in the case of backpressure, the liquid pushed towards the valve would improve its sealing behavior. A scheme of the solutions descried are shown in the next figure (fig. 2.26)

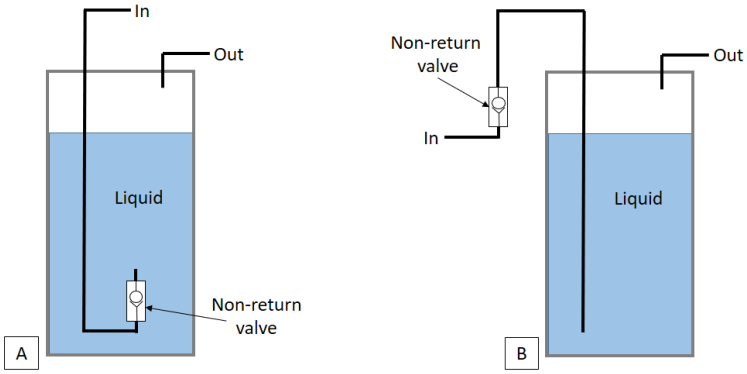

Figure 2.26: Non return valve immersed in a liquid (A), or with the liquid container downstream (B), to counteract the gas reflux

In the case of the bell and spoon gas-meters, it is sufficient to solve this problem by placing them at least one meter below the biodigestors, so that, in the event of counterpressure, the weight of the liquid that goes back from the meters to the cells is sufficient to balance the back pressure.

2.3 - DESCRIPTION OF THE GAS FLOW CALIBRATORS

In order to test the performance of the gas-meters at various flow rates, it is needed a test system that would guarantee a constancy of the input stream towards the various devices within few hours.
Several calibration systems with different degrees of complexity have been reported [B24-B27].
In this work, three types of gas flow calibrator were used. The first is a differential pressure flow generator, the second is a commercial Bronkhorst mass flow controller and the third is a piston flow generator.

2.3.1 - Description of the differential pressure flow generator

In this first gas flow calibrator, the flow rate is obtained by controlling the pressure difference.

2.3.1.1 - The initial failed project of the pressure flow generator

The first ever solution adopted in the absolute was to connect the gas-meter under test to a simple mechanical pressure regulator, connected in turn to the compressed air line present in the laboratory.
Analyzing the results of this first set of tests, we noticed, however that they showed some important oscillations that were initially attributed to pressure fluctuation of the air line.
To solve the problem, it was decided to build a pressure regulator with a feedback system.
This regulator was constituted by a microcontroller that, on the basis of information supplied by an absolute pressure sensor (specifically a BMP180 [B31]) placed inside a tank, provide to control to a solenoid valve, connected in turn to the compressed air network.
Such solenoid valve operated at the input of compressed air in the tank in order to reach the desired pressure value; the gas-meter under test was always connected to the tank.
The tests on the new pressure regulator, although showed some improvements in the behavior of the gas-meters, proved also the persistence of some abnormal oscillations.
The problem consists in the fact that the pressure sensor performed only a measurement of the absolute pressure of the tank, while the operation of the gas-meter depends on the pressure difference between its input and output.
In conclusion, in order to make the correct calibration tests it was necessary to control also the ambient pressure.
To do this, it was decided to replace the initial absolute pressure sensor with another one that measures relative pressure (specifically a PR-Keller 41X [B32]).

The use of this sensor, equipped with a more sophisticated language based on the RS485 protocol, required the construction of a dedicated electronic circuitry equipped with a suitable voltage regulators, in particular a RS485-TTL converter was used for the communication between the sensor and the microcontroller. At this purpose, the previous sensor connection was much easier because it was directly connected to the microcontroller.

To solve further anomalies shown in the preliminary tests, it was also decided to add a flow regulator to obtain a better flow adjustment.

The final version of the calibration system is shown, together with the block diagram, in the following figure (fig. 2.27)

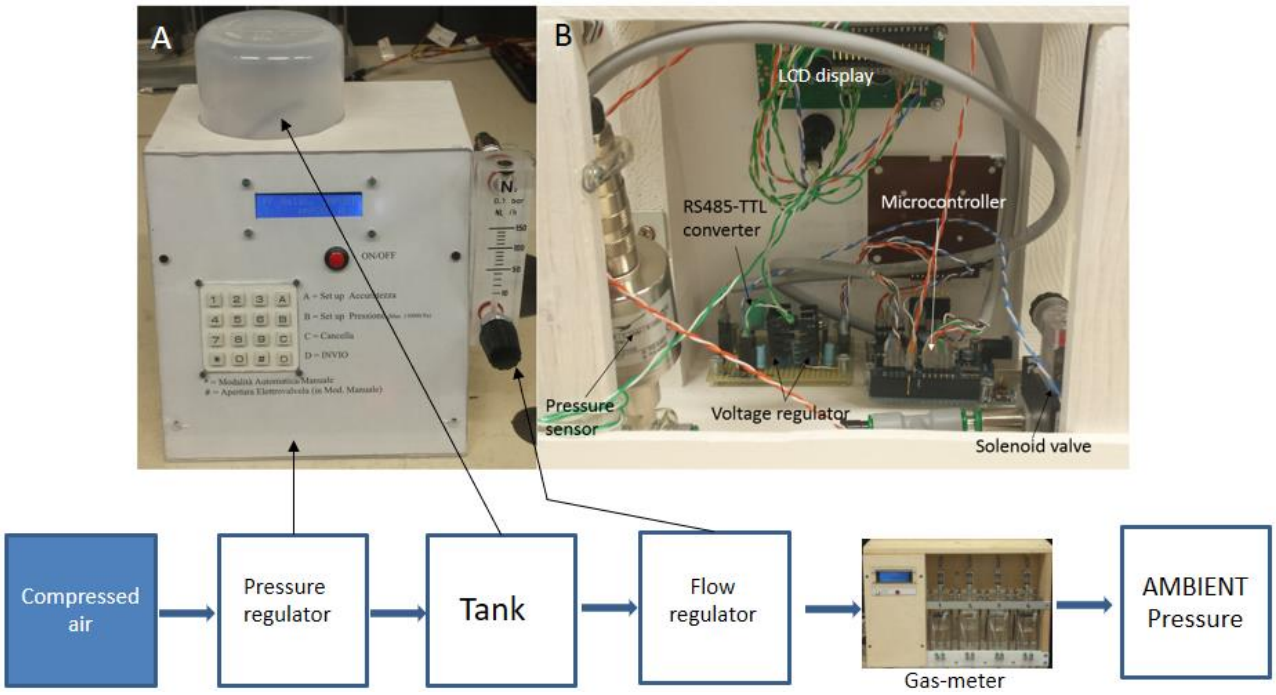

Figure 2.27: Pressure regulator with feedback control and its and block diagram; A: front view. B: rear view

Subsequent tests performed subsequently showed that this system was able to produce a constant flow at high flow rates, but nevertheless fluctuations remained at low flow rates.

In fact, this system shows an underlying problem due to the fact that the tank could be automatically pressurized (by the solenoid valve connected to the compressed air), but not automatically depressurized, because this operation exploits the gas escaping from the tank into the gas-meter under test.

At high flow rates, this technique allowed to maintain constant the tank overpressure with respect to the environment.

In fact, if the ambient pressure increase, the solenoid valve increases its pressurization cycles, while if the ambient pressure decrease, the solenoid valve simply decreases its cycles.

But at low flow rates it is not capable to operate properly because, if the ambient pressure increase, the solenoid valve increases its cycles and if the ambient pressure decrease, the solenoid valve decreases its cycles until to stop, but this may not be enough to depressurize the reservoir to the desired level.
In this case, it is necessary to wait the depressurization actuated by the output flow from the tank, but this process occurs at low rates and it can take a long time to complete, so the constancy of the overpressure within the environment is lost.
In conclusion, two solutions were possible, the first consisted to add a depressurization solenoid valve, while the second one was to place the gas meter under test between two tanks held at different and known pressure values.
In particular, the second technique seemed able to guarantee the best result so it was decided to choose this approach and to abandon the system built.

2.3.1.2 - Concept of the new pressure flow generator

The basic idea for testing the gas-meter is to connect it to two tanks, each tank is set with a pressure value selected by the user.
In order to operate the gas meter, both tanks must be set at a higher pressure compared to the ambient.
This approach allows to protect the components of gas meter, specially the solenoid valves.
Each tank is equipped with a solenoid valve, in the high pressure reservoir the solenoid valve serves to pressurize it, while in the low pressure reservoir the valve depressurizes it.
It will be advisable to perform some vacuum cycles before starting to collect data on the gas meter; this step is necessary to allow that the low pressure tank reach the set value, because its pressurization takes place only due to the flow passing through the gas meter.
Each tank is connected to a relative pressure meter (Keller PR-33X) through which a computer controls the solenoid valves.
The main difficulty of this project was the realization of a program that controlled the various systems at the same time. For this purpose, it was decided to use the graphic language LabView because the manufacturer of the these systems already supplies some subroutines ready to be integrated into the main program.
In the case of the pressure sensors subroutine, however, this subprogram allowed to acquire only data from a single sensor at time, so it was necessary to modify the subroutine to make it capable data from more sensors.
With respect to the flow generator, all the components (except for the computer) are enclosed within a controlled thermal environment and furthermore the flow adjustment are performed by a mechanical

flowmeter. This component is necessary to reduce the fluctuations, but it constitutes the main limit of the system since limits the user-settable flow rate at the minimum value of 0.6 ln/h.
For these reasons, it is necessary the construction of alternative gas flow calibrators, capable operate at lower flow rates.
A detailed description of these gas flow calibrators, will be provided in the following section.

2.3.1.3 – Detailed description of the final version of the pressure flow generator

As aforementioned, the first gas flow calibrator is a laboratory-made flow generator operating at a constant differential pressure. It is composed of two pressurized tanks, a mechanical flowmeter, two pressure transmitters, two solenoid valves, an heater capable to maintain the surrounding environment at constant temperature and the electronics for the instrument control and data acquisition.
The gas-meter under test is placed between the two tanks, so the inlet and outlet pressure of the meter are determined by the pressure values set in the tanks. A mechanical flowmeter is placed between the high pressure tank and the inlet of the gas-meter, it allows a precise flow regulation. The pressure in the high pressure tank is driven by a solenoid valve which is in turn controlled by a computer. A pressure transmitter is connected to the tank and sends pressure data to the computer allowing a feedback control.
The solenoid valve is connected to the compressed air by means of a mechanical pressure regulator that lowers the pressure value by one order of magnitude to avoid excessive fluctuations in the tank. On the other side, the pressure in the low pressure tank is controlled by a second solenoid valve, also controlled by the computer, that releases gas when a pressure overshot occurs. Also the low pressure tank is connected to a pressure transmitter which sends data to the computer allowing the feedback control. The whole system is covered by a plastic casing which minimizes the heat losses and maintains constant the environment temperature.
A block diagram of this differential pressure flow generator is illustrated in the next figure (fig. 2.28)

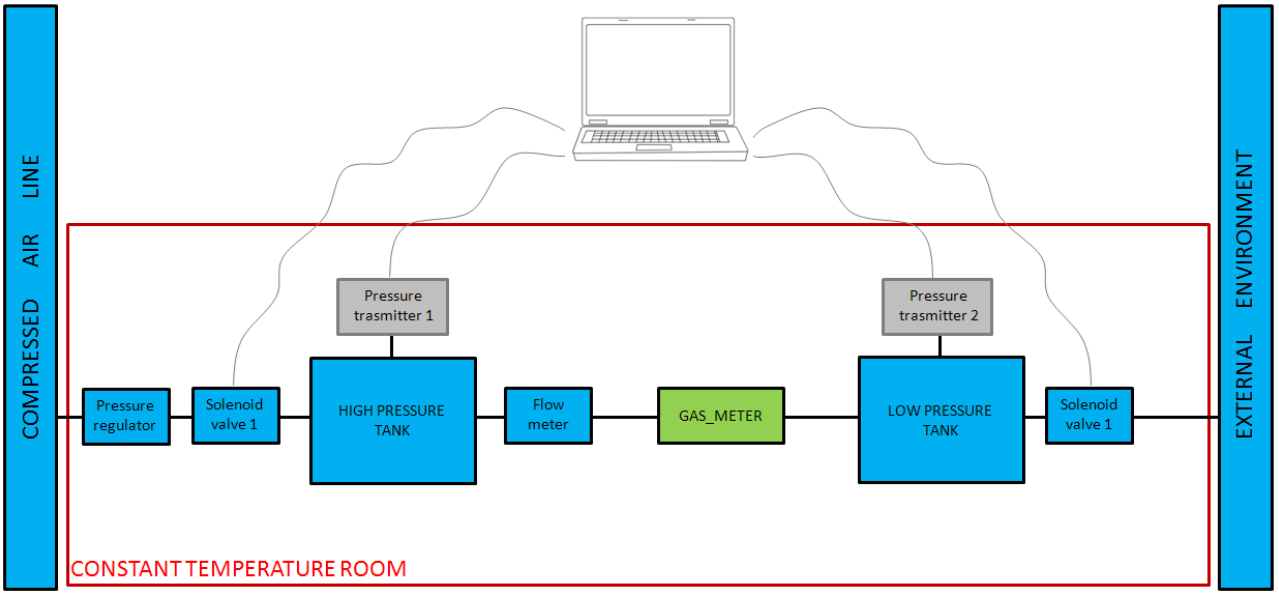

Figure 2.28: Block diagram of the differential pressure flow generator

In detail, the pressure regulator is a Pneumax regulator model 17109A that lowers the compressed air pressure from 6 to about 0.5 bar. The high-pressure tank is a steel tank with 11 It capacity, pressurized to a value of 1000 mm of water (i.e. 9806.38 Pa); the low-pressure tank is also a steel tank with a capacity of 4.8 lt that it is pressurized to a value of 100 mm of water (i.e. 980.638 Pa). The two pressure transmitters are Keller model PR-33X, which measure the atmospheric pressure with an accuracy of 0,05 %FS; the device consists of a floating piezo-resisitive transducer with an integrated microprocessor that compensates the temperature dependency and the non-linearity of the sensor [B30]. The pressure transmitters are directly connected to the computer where a in LabVIEW program read the pressure values and use them to drive the solenoid valves.

The principle of the flow meter is the opposition between the downward force of gravity and the upward force of the flowing fluid. When the flow is constant, the float stays in a position that can be related to the volumetric flow rate; this position is indicated on a graduated scale. This dynamical balancing requires a vertical measuring tube to keep the gravity force fully in effect. Two flowmeters were used to cover all the range of desired flow rates, the first has a work range from 0.6 to 4 l_n/h and the second a work range from 6 to more than 12 l_n/h, which is the maximum flow measured by the gas-meters.

The solenoid valves are two Pneumax electrically driven valves model N331.0B. These valves work with a 24 V power supply and cannot be controlled directly from the computer, so to drive these valves we used two solid-state relay (Opto22 DC60MP) with the control pin connected to two digital I/O pins of an Arduino Mega 2560 board, connected in turn to the computer. The program loaded on the Arduino board is directly controlled by LabVIEW software so that the solenoid valves can be actuated when the pressures of the two tanks came out from the respective set point value; the differential pressure between the two tanks is always kept below 20 mm of water (196 Pa).

All the components (except for the computer) are enclosed within a pliable transparent plastic Bubblewrap, used in general to pack fragile items, which provides the thermal insulation. Inside this plastic case we placed a heater consisting of two 240 V, 200 W Heater Mats (RS 245-641). These elements are attached on the bottom of a stainless steel plate on which are also placed two fans with related heat sinks.

The temperature Controller Eurotherm 3216 is connected to a thermocouple, positioned at the center of the test chamber, it drives the heater by means of a high power solid-state relay Crydom D2425PG holding the internal temperature near 25 °C and suppressing the variations driven by room temperature (typically by less than 0.5 °C).

The system made can generate flow rates from 0.6 to 12 l_n/h, the three gas-meter types have been tested with the following flow rates: 12, 4, 2.5, 1 and 0.6 l_n/h.

The actual components of the pressure flow generator are illustrated in the next figure (fig. 2.29).

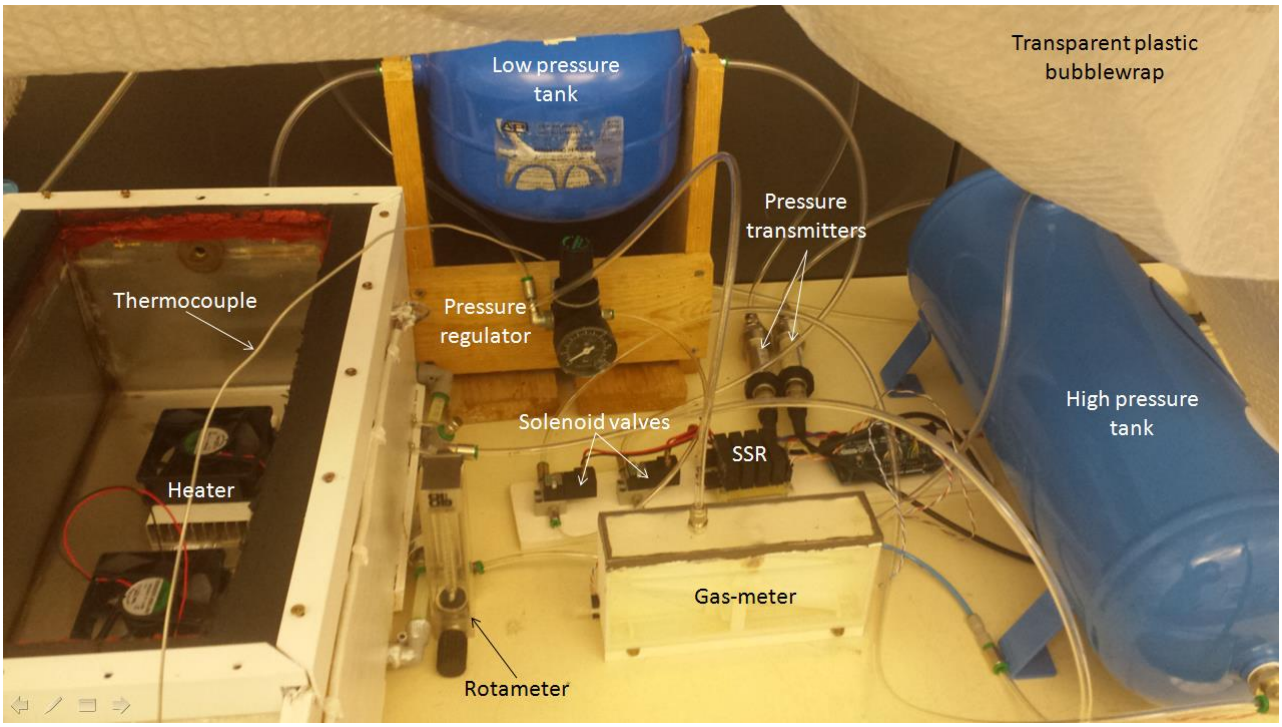

Figure 2.29: Actual components of the pressure flow generator

A picture of the system's coverage followed by an images of the LabView control panel program are shown below (fig. 2.30-2.31)

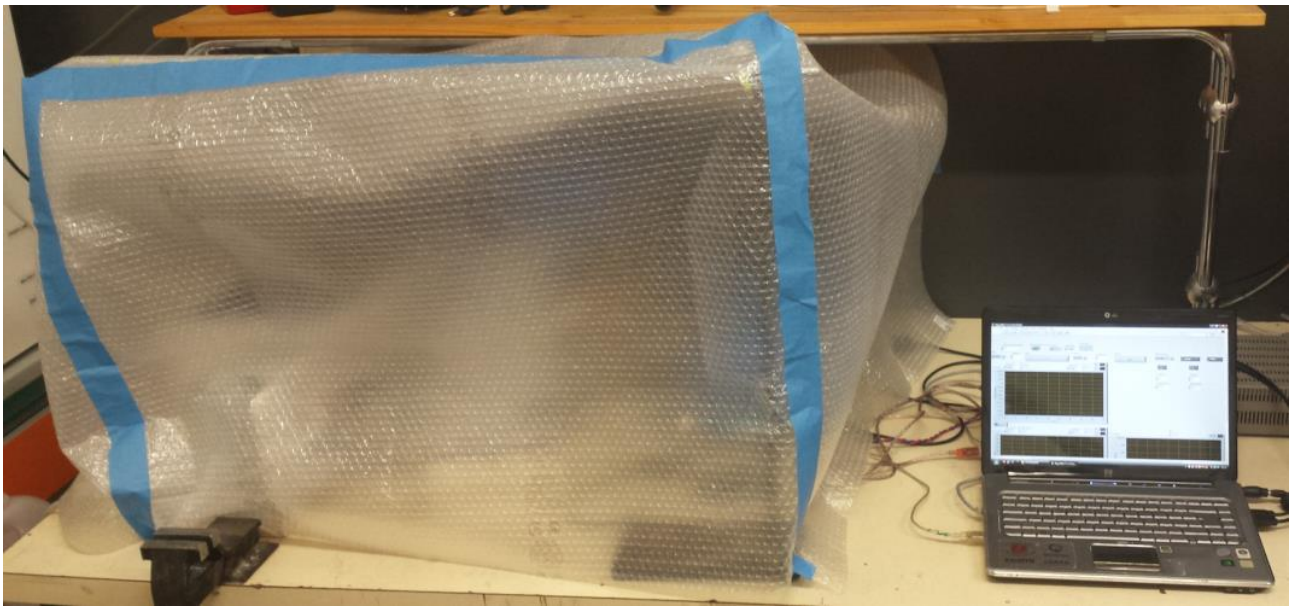

Figure 2.30: Thermostatic chamber of the pressure flow generator

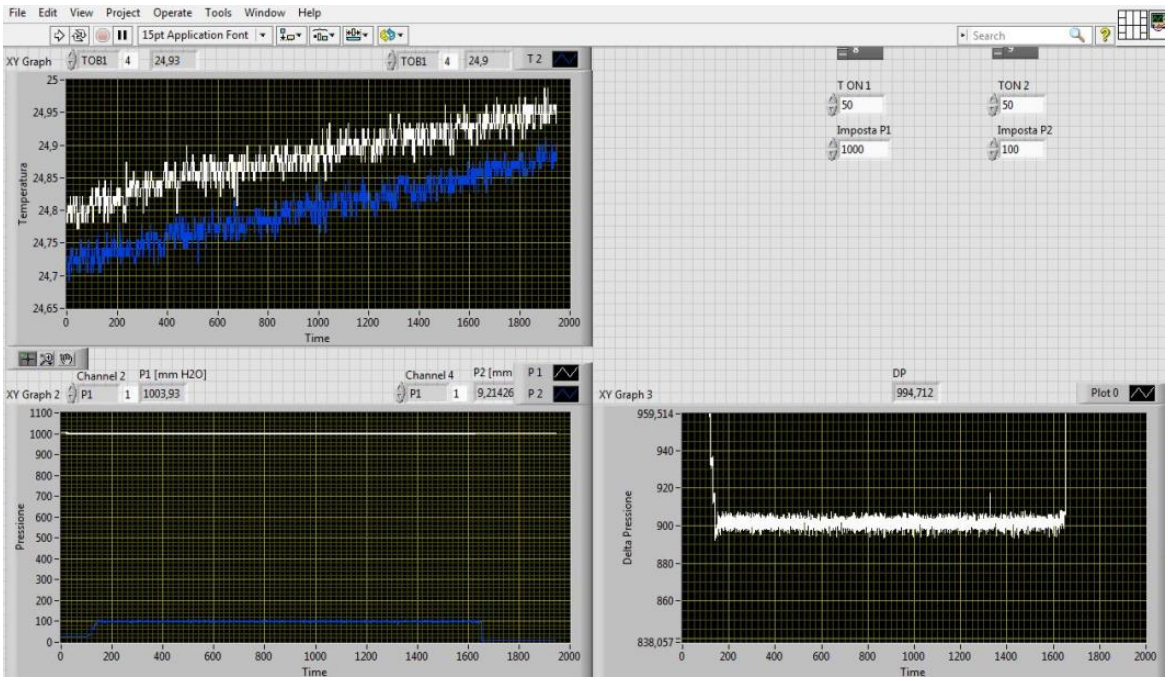

Figure 2.31: LabView program screen of the pressure flow generator

2.3.2 - Description of the mass flow controller

In this second commercial gas flow calibrator, the heat conductivity of gas is used to determine the mass flow and the solenoid valve is driven on the basis of this parameter.

2.3.2.1 - Detailed description of the mass flow controller

This second gas flow calibrator is a commercial Bronkhorst mass flow controller (MFC) model F-201C-FGB-22-V, capable of generating a gas flow rate up to 300 ml_n/min (i.e. 18 l_n/h). The flow controller is a Thermal Mass Flow Controller, it uses the heat conductivity of the gas fluid to determine the mass flow [B28, B29]. It consists of a mass flow sensor, a precise control valve and a microprocessor based PID controller. The thermal mass flow sensor consists of a stainless steel capillary tube with two resistance and two thermometer elements. From the main channel, a part of the gas flows through this sensor and is warmed up by the heating elements; consequently, the measured temperatures that depend on resistors drift apart. The temperature difference is so directly proportional to mass flow through the sensor. In the main channel is present a laminar flow element consisting of a stack of stainless steel discs with precision-etched flow channels. Thanks to the perfect flow-split, the sensor output is proportional to the flow rate of the total gas mass.

Each of these flow controllers has been calibrated with a specific gas. If we use another gas, it's necessary to modify the conversion table of the controller to obtain the proper flow value. In the present work, we use pure nitrogen supplied in the range of 1-5 bar, since compressed air is typically added with trace of lubricant oil that can damage the mass flow controller.

All three gas-meter types have been tested with the following normal flow rates: 12, 6, 2, 1, 0.5, and 0.25 lt/h. The maximum flow rate is determined on the basis of the maximum flow processable by the gas-meters, which is approximately 12 lt/h; while the minimum flow rate is determined on the basis of the minimum current supplied by the current signal generator (which does not allow to obtain flow rates lower than 0.25 lt/h).

The mass flow controller test case and the details of MFC used are showed in the next figure (fig. 2.32)

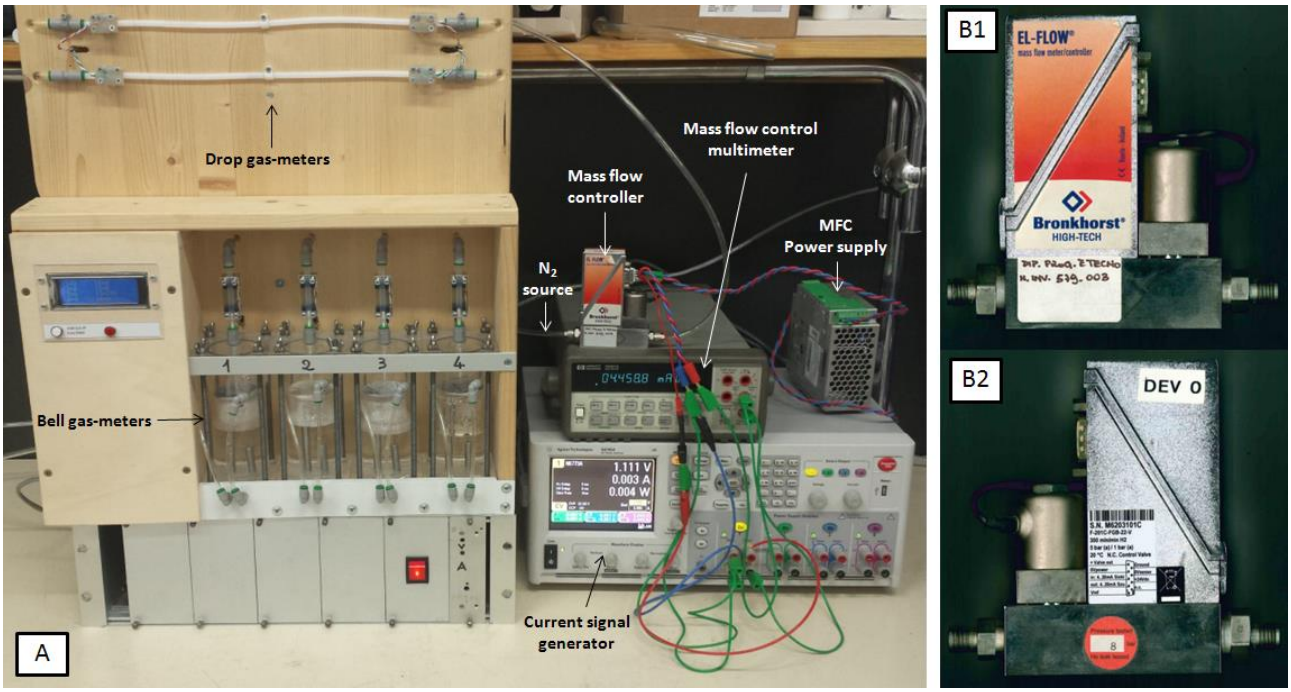

Figure 2.32: Mass flow controller. A: Test case. B1 and B2: Bronkhorst mass flow controller front and rear

Although this system has the advantage of a high accuracy, the minimum flow rate that can be generated is slightly lower than that one achievable with the previous system, so a further flow calibrator, is necessary to addresses this problem.

2.3.3 - Description of the piston flow generator

In this third gas flow calibrator, the flow rates is obtained by controlling the feed rate of a piston stem.

2.3.3.1 - The initial failed project of the piston flow generator

The last type of flow calibrator investigated is a piston flow generator.

The first approach selected was to reactivate an old system, made about 8 years before, with the aim to investigate the ability of some metal matrix to absorb hydrogen.

This system consists of a cylinder with two chambers, separated by a sliding piston, and various pneumatic valves that manage the gas flow. The piston had the aim to pressurize the hydrogen gas that must be absorbed by the metal matrix and the pneumatic valves drive the gas-flow, through some measuring systems, towards the external test chamber where is located the metal matrix under test. All the elements above

described are then enclosed in a thermostatic environment. The components of the system described are showed in the next figure (fig. 2.33)

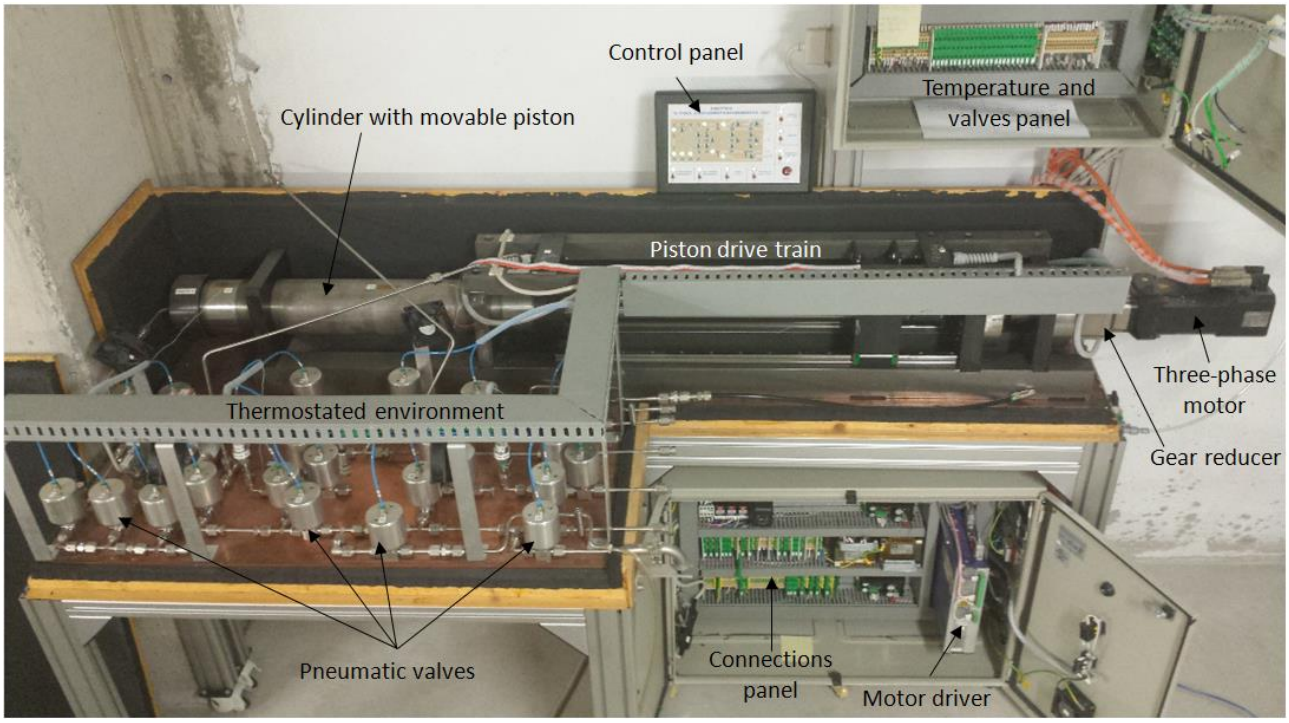

Figure 2.33: Components of the system reactivate

In particular, the cylinder had been specifically realized, it is constituted by a 800 mm long and 120mm external diameter steel tube. The movable piston is placed at the interior of this cylinder and is externally connected in turn to the drive train, that begins with a three phase Danaher motor, model DBL4, whose speed is decreased by a 100:1 gear reducer connected to a sophisticated recirculating ball screw which ends with the piston. The engine is equipped with position sensors and is driven by a suitable electronic controller. All systems are fixed onto a copper plate under which some heaters are glued which serve to keep the whole device at the desired temperature.

The piston obviously was the component of main interest.

The idea was to connect one of the two chambers of the cylinder at the inlet of the gas-meter and the other chamber to the outlet of the gas-meter so that they will be able to generate a flow of gas that circulates within a closed circuit and it is independent of ambient pressure. An intuitive scheme of the connections is shown in the next figure (fig. 2.34)

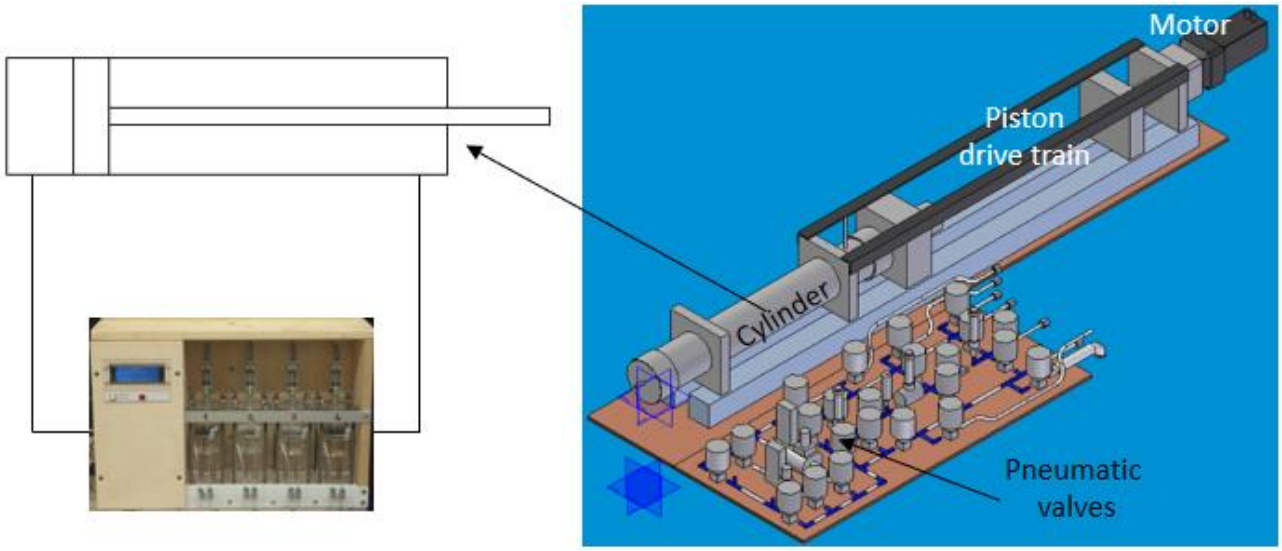

Figure 2.34: Connections concept between the test system and the meter

The pneumatic valve circuit could be used to maintain a constant gas flow direction and independent of the advancement direction of the piston. Finally the thermostatic environment, after being expanded to incorporate the gas-meter, it would be capable to reduce gas-flow fluctuations due to temperature oscillations.

Unfortunately, the system described had both hardware and software problems. In fact, the pneumatic valves showed anomalous behavior due the long period of inactivity, in particular imperfect or absent opening/closing; while part of the electronic control of the device was not supported by the latest versions of the software responsible for its management.

In addition the project, had been closed before the actual activation of the machine and unfortunately the software for the comprehensive management of the instrument was never completed. For the sake of completeness, some subroutines screens are shown in the next figure (fig. 2.35)

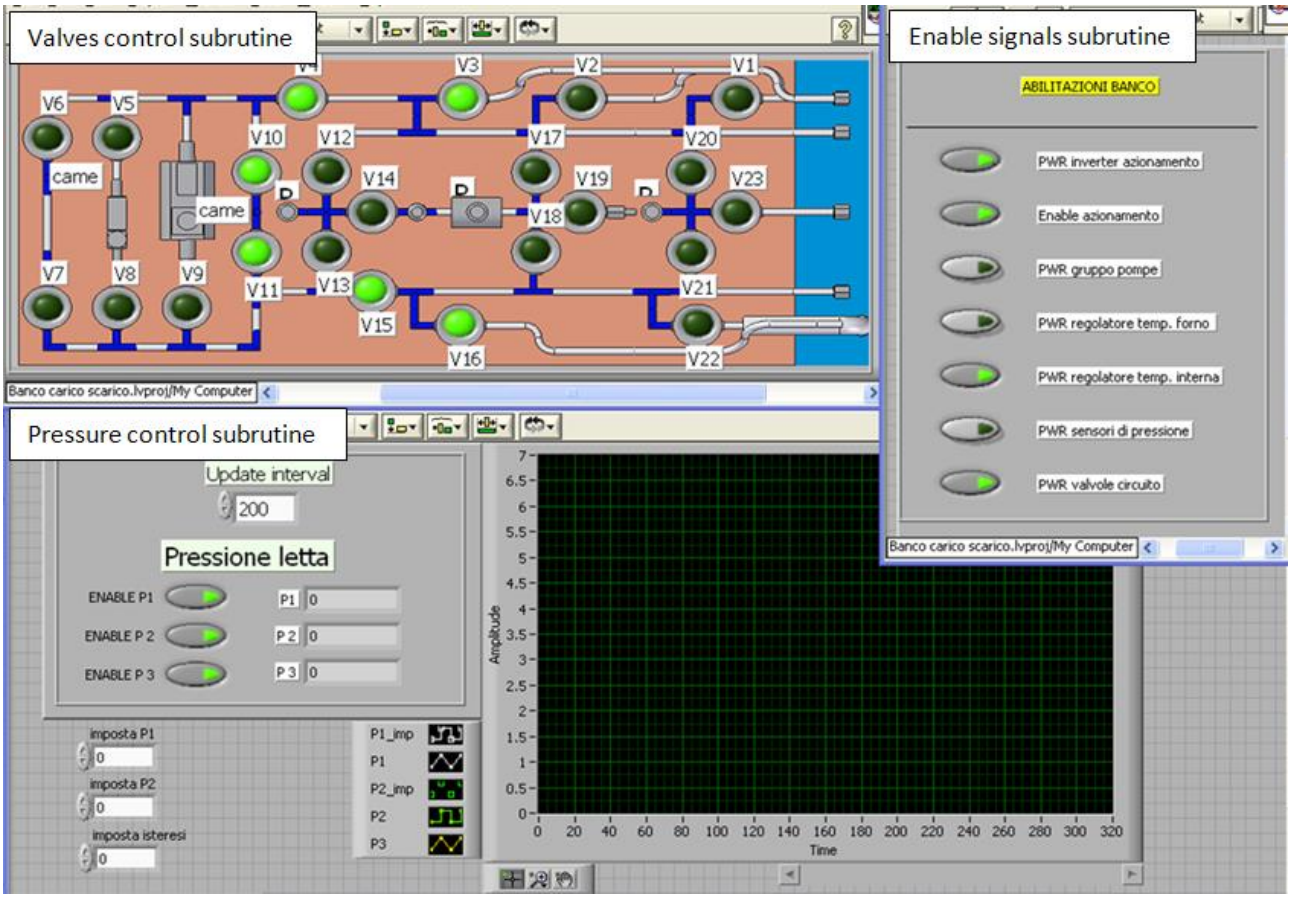

Figure 2.35: Subroutines screens of the system

The main effort was therefore the study of the LabView language, in order to complete the final program of the instrument; but the reactivation was already taking much longer time than expected.

Moreover, while the system begins slowly to operate, the electronic controller of the engine which, by the drive train, actuates the advancement of the piston rod, has stopped working during a test run and it was not able to start it again.

In the long period devoted to the reactivation of the device, it was clear that it would be hard to resolve a electronic failure. In fact some components were old and also enough complex, so their repair would not be compatible with the available budget; also the electric circuit diagram of the device was lost so it was difficult to identify the connections to be checked and to understand the cause of the failure. As a result of these considerations, it was decided that the best solution was to build up a new system with a complete and safe control of hardware and software.

2.3.3.2 - The concept and evolution of the new piston flow generator project

Certainly the hardware and software complexity of the previous project had been one of the main causes of its failure. To solve the problem, it was decided that the new project should be as simple and inexpensive as possible.

So, syringes equipped with large capacity have been chosen in replacement of the steel cylinder with two chambers. Although the market offers syringes where the air tightness is guaranteed, for budget reasons the choice fell on the syringes of the type used to harvest oil from car engines, where the air tightness is not guaranteed. These syringes were positioned in opposition, i.e. with the stems connected one to another; those stems are then connected to a threaded carriage. The threaded carriage begins with two stepper motors housed, together with the rest of the electronics, in a well ventilated area separate from the syringes. This choice was based on the fact that in a situation of continuous operation, the stepper motors get quite overheated and it this set-up could affect their operation. The two engines are keyed to two threaded screws (supported by appropriate elements), that are fitted into the threaded carriage that moves the stems. This mechanism allows to convert the rotation of the step motor in a linear translation of the carriage and consequently of the stems. Following is an image of the first version of the piston flow generator (fig. 2.36)

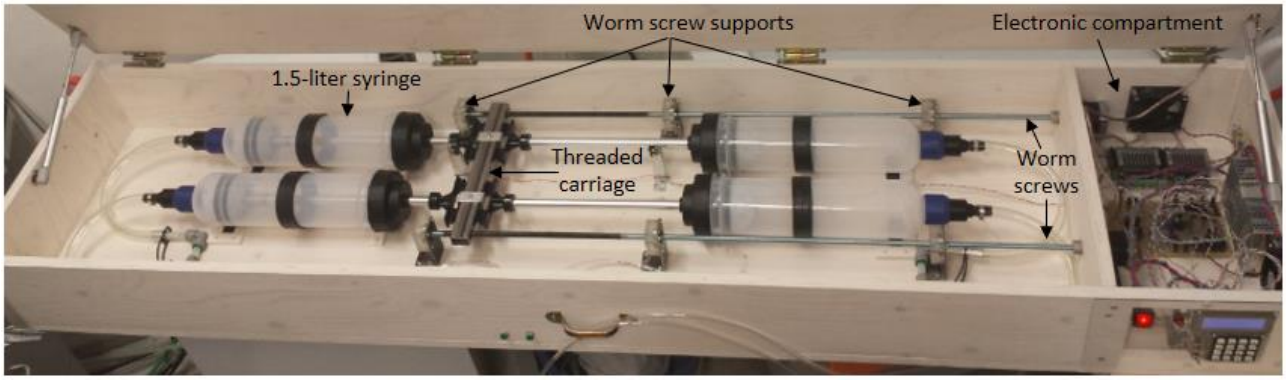

Figure 2.36: First version of the piston flow generator

As regards the electronic circuit, the heart of the system is a microcontroller capable of emitting a pulse train that determine the direction and the rotation speed of the step motors. These impulses are received by the engine driver that directly control the motors. The system is designed to operate without the use of a computer, in fact the microcontroller parameters can be set via a keypad and an LCD display can shows the main device information. Inside the electronic compartment, a 24 V power supply provides the voltage necessary for the operation of the motors and, via a voltage reduction circuit, also the voltage required by the microcontroller. Finally, two fans create a constant air flow that cools the various components described. An image of the electronic circuit is shown below (fig. 2.37)

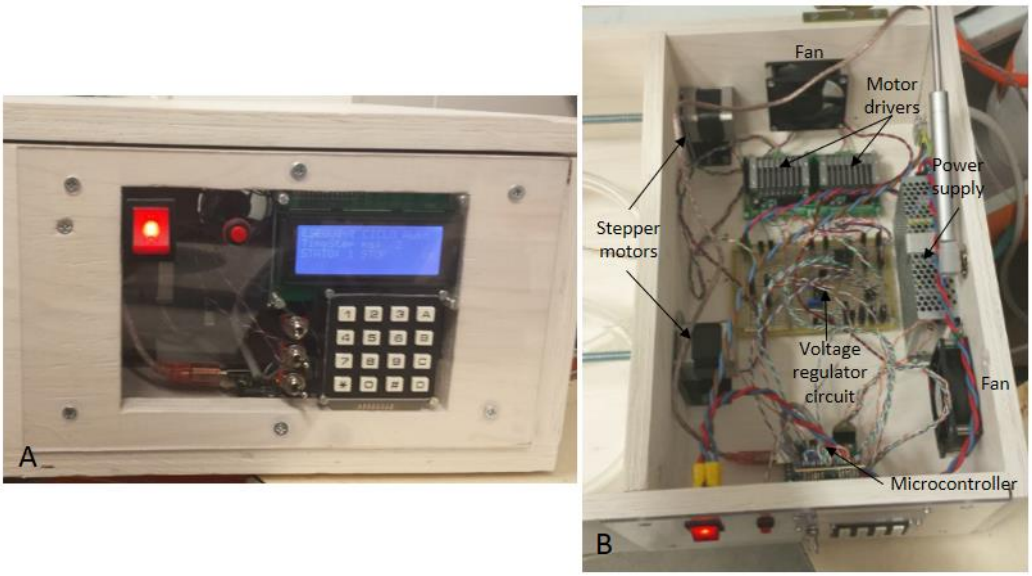

Figure 2.37: Electronic system: A: Front panel; B: Circuit Components

Preliminary tests of the system have shown its correct mechanical operation, however, it has unfortunately occurred a problem in the air-tightness of the plunger. To solve the sealing drawback, two gaskets on the plunger head were replaced with new larger models, without obtaining the expected results. By filling the entire syringe of water, it was found that the losses originated not from the contact area between the gasket and the cylinder, but from the contact area between the piston and seals. Because in that area there were smudges, i.e. vestiges of the plastic printing step, the areas were thrown by the University Mechanical workshop; however this operation, greatly worsened the system losses. To solve this problem, it was decided to insert a little amount of mastic into the spoiled gasket housing. At the beginning the solution seemed to work, in fact the tests carried out by filling the syringe with water showed no loss, but it was not a lasting solution. In fact few hours were sufficient because the mastic, compressed by the seals, began to rise from the excavation reaching the cylinder. This was a critical condition because the presence of adhesive between the gasket and cylinder entailed, when reached by the piston, its immediate arrest of it, so a considerable force is needed to unlock the system and resume its operation. The following image shows the mastic during ascent (fig. 2.38)

Figure 2.38: Detail of the mastic ascent

The solution of this second problem started by trying to remove all the mastic, especially the part placed on the cylinders that continually blocked the plunger. Unfortunately, no solvent present in the laboratory (even acetone) was able to eliminate such material, at the end of a long research it was discovered that the best approach is to rub oil with a cloth. In fact the oil surrounds the mastic particles preventing its sticking onto the surface and allowing its removal.

So, we abandoned the use of the mastic and passed to the utilization of the silicone; also in this case, the application an uniform layer of this material constitutes a particularly difficult operation, which was done through a suitably shaped tool, as shown in the following image (fig. 2.39).

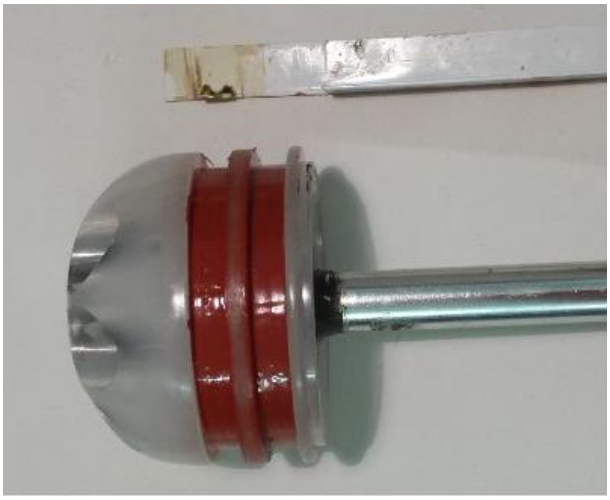

Figure 2.39: Detail of silicon deposition within the housing seals

After several attempts devoted to find the right thickness, (if the layer too thick, the plunger does not move, if it was too thin, there were still losses) this approach allowed to solve permanently the problem of air leaks as shown in the following figure (fig. 2.40). This image shows the trend, after an initial pressurization, of the syringe internal pressure and temperature, detected by a suitable sensor (Keller PR-33X), versus time. It is possible to note that the pressure follows the temperature but it does not drop even after nearly a day of test period.

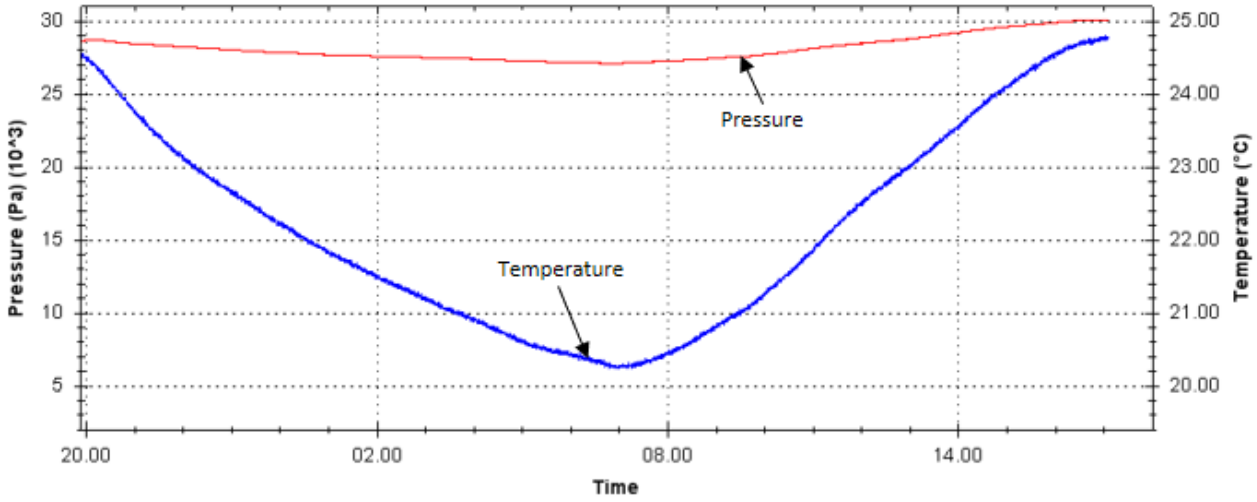

Figure 2.40: Trend of the sealed syringe pressure and temperature after a little initial pressurization

If on one hand this solution has allowed to solve definitively the losses, on the other hand another set of problem, however, was just arosen. In fact the increased size of the gaskets, coupled with the increased thickness of their housing, due to silicone, led to enhance the strength needed to move the plunger, so the stepper motors were no longer able to support it.

Anyway, our tests showed that the extra effort required to the motors was not so high; in fact, the system was able to operate for a few minutes by lubricating appropriately these syringes.

Then, the first choice has been to change the motors with more powerful models; this operation required the construction of a new specific control board that is shown in the next picture (fig. 2.41).

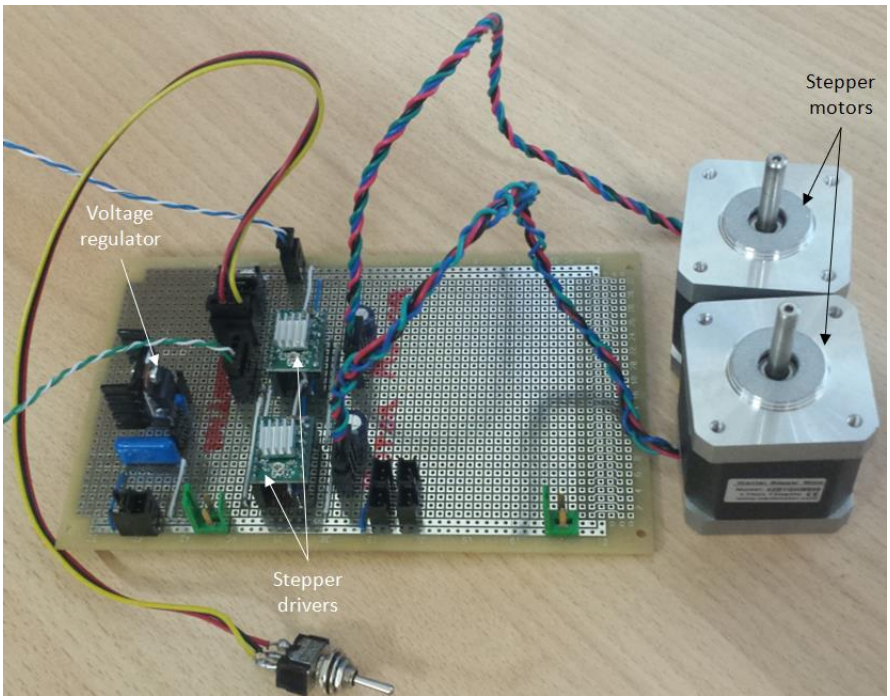

Figure 2.41: New control board for the new motors

Unfortunately, these new stepper motors were not yet able to move the stems and the switching to even powerful models was not possible because this would mean to rebuild the entire system since, with the current distribution of the components, larger engines would not enter in it.

After several attempts, in which we tried to reduce the thickness of the silicon under the gaskets, without going below certain levels in order to avoid the problem of air-losses and after trying different types of oils and greases to promote the sliding of the plunger (the best effect was obtained with the silicone grease) it was decided, to change the typology of syringes.

In particular, it was decided to focus on medical syringes, where the air-tightness is guaranteed and among them the 100 ml models (the greater capacity available in pharmacies) are chosen. Then to increase the overall volume of the system, it was decided to couple three pairs of syringes mounted on a specific support. It is necessary to note, however, that even with three syringes for side, the total volume required is one order of magnitude lower than that of previous syringe model. This involved the fact that the duration of the test was too little, i.e. the number of cycles of the meters was too limited (an order of magnitude less than in the previous case) to obtain a statistical significance. To solve this problem, it was thought to provide the system with a series of pneumatic valves that take steps to reverse the gas circuit in order to obtain a stream to be sent to the gas-meters, that was always in the same direction, regardless of the direction of advancement of the plungers. The following image shows the construction details that was discussed until now (Fig. 2.42).

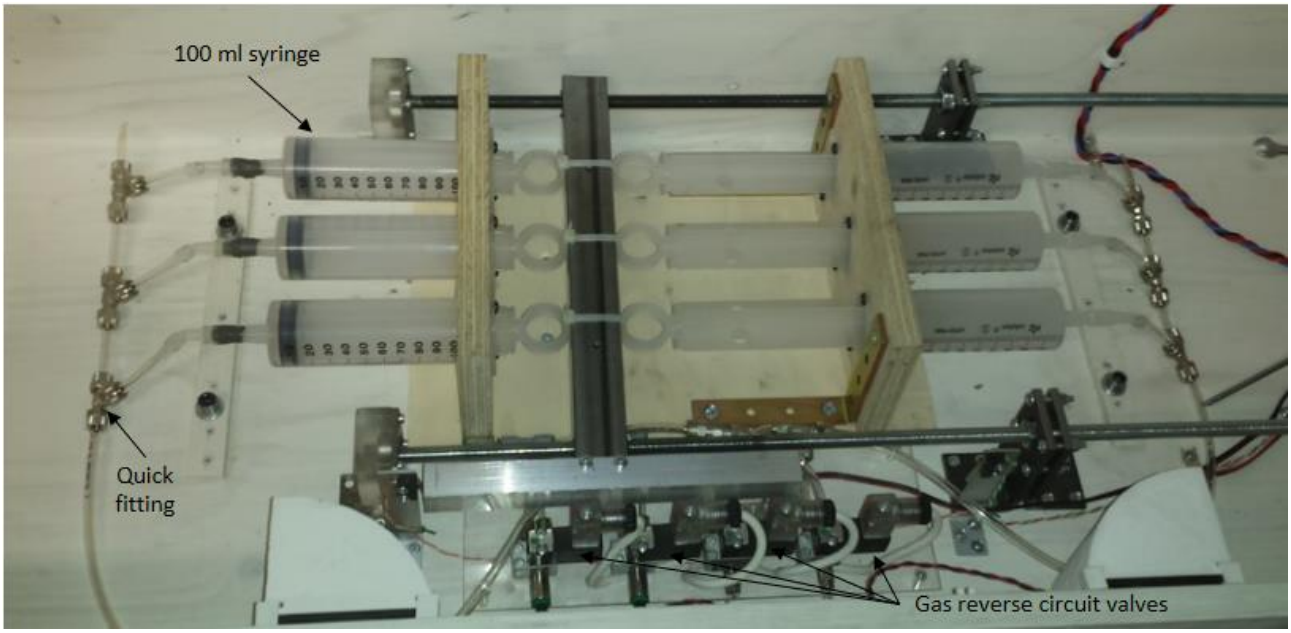

Figure 2.42: System with six 100 ml syringes and a gas reverse circuit valves

Where possible, only quick fittings are used and all components were then immersed in water to test the air-tightness.

As expected, the practical tests have shown that this system would not be able to produce a uniform flow and the cause was the presence of the circuit inversion system. In fact, this system produces fluctuations that alters the behavior of the flow-meter bringing it to produce an unacceptable result.

The following figure (fig. 2.43) shows the cycle speed trend of the bell gas-meter at the flow rate of 1 lt/h. The most evident particular is the presence of three falls, each corresponds to a gas circuit inversion occurred during the test.

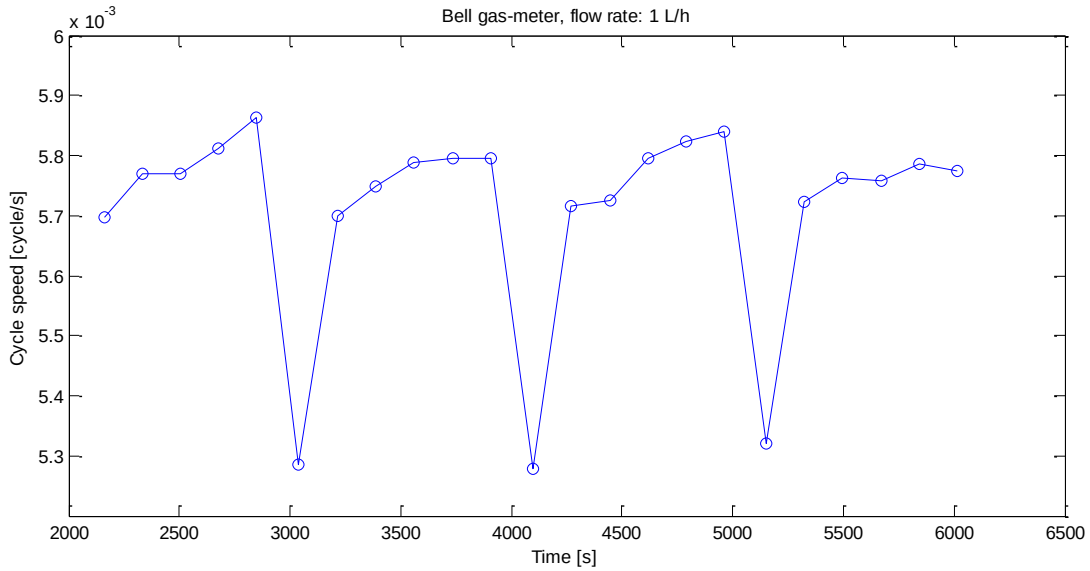

Figure 2.43: Cycle speed trend of the bell gas-meter

Although the presence of the gas reversing circuit allows to increase the number of cycles performed by the gas-meter during the test, which would otherwise have been only 5 or 6, the results show a non-uniform flow that is not suitable to test the performance of the various gas-meters, at least without the use of an important data postprocessing method. For this reason it was decided to remove the 100 ml syringes and return to the previous ones.

With this choice, however, the problem of the motors not able to operate the device has come back. To solve the problem without changing the engines (there was not enough space), it was decided to add a reduction gearbox. In particular it was chosen a 25:1 planetary gear, where the ratio was calculated as the greatest reduction that still allows to have double the maximum flow rate required for testing. Specifically two elements were purchased, each one applied to the engine head, as shown in the following figure (fig. 2.44)

Figure 2.44: Planetary gearbox applied to the stepper motor

Previously, all the axial load of the threaded carriage was discharged on the motors bearings, however, since the increase of the forces in play, it was decided to discharge all of these forces onto a suitable support. To achieve this effect, one of the bearings that hold in position the worm screw has been trapped between two L-shaped brackets and the threaded bar was then secured to the bearing by means of two counter-tight bolts. The mentioned supports are shown in the following figure (fig. 2.45).

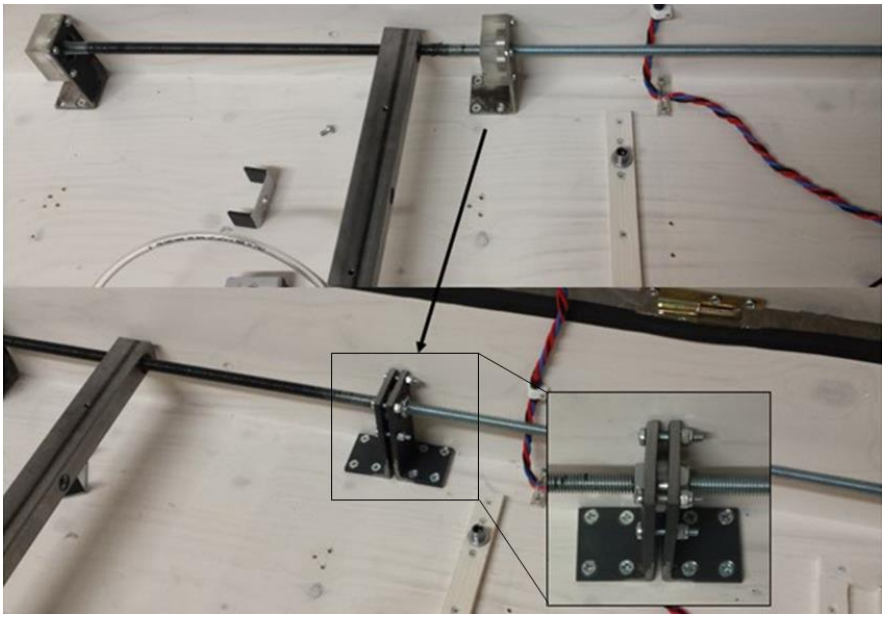

Figure 2.45: Axial load discharge support

At this point, we believed that the system was ready for operation, but we were still troubled by the fact that a big problem might have been overlooked, but due the long delay that had built up, we nonetheless decided to start with the test campaign. For the first few days the system has behaved properly, but in the end, after the umpteenth test, all the uncertainties came to fruition as it is clearly shown in the following image (fig. 2.46)

Fig. 2.46: System damage following the arrest of one of the stepper motors

The fundamental mistake was that there was not a system which binds the two engines to run at the same speed. Certainly the two motors were receiving the same train pulse but if, for any reason, one should ever block, nothing could prevent to the forces in play to destroy everything and this was just what happened. In fact, for reasons of cost, the two gear units purchased were already used, and also while tested them, we noticed that one of them showed a slight resistance in a certain point of rotation and for this reason it was completely disassembled, cleaned, checked and relubricated (fig. 2.47), but clearly it was not enough to make it work properly.

Figure 2.47: Planetary gear disassembled and cleaned

To permanently resolve the problem, it was decided to delete one of the motors and the relative faulty gearbox unit and to transmit the rotary motion from a worm screw to the other by means of a high loads toothed belt. The detail of the modified system is shown in the following image (fig. 2.48).

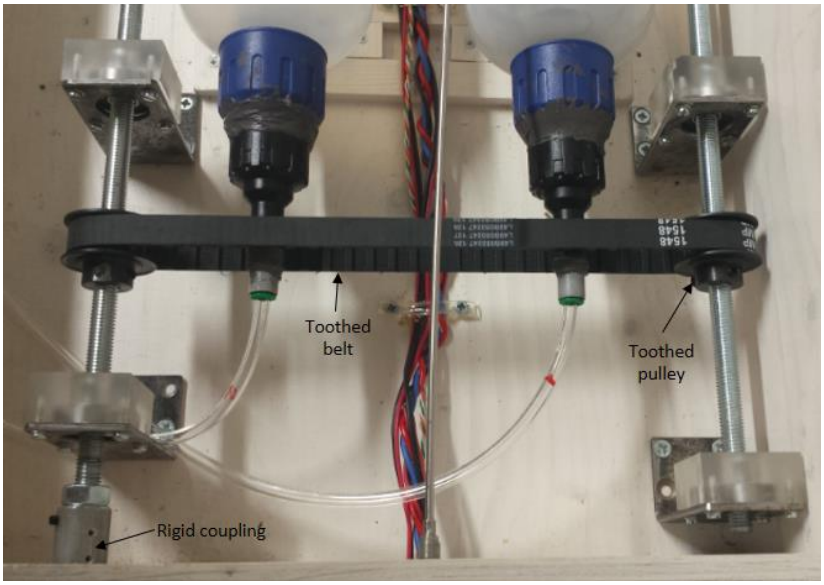

Figure 2.48: Detail of the belt drive system

In this case the remaining engine and gearbox had to carry twice the load, and this was noticed immediately since the spring coupler, that joined the reducer to the worm screw, and served to compensate any misalignment between these two elements, was no longer able to handle the load and is continually broken after each replacement. To solve the problem, it was decided to replace the coupler with a more rigid element, as it is shown in the following image (fig. 2.49).

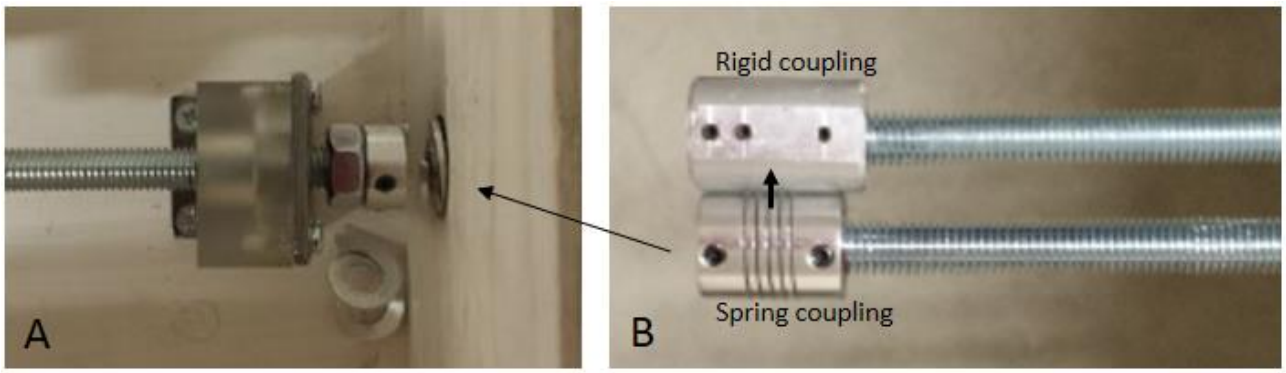

Figure 2.49: A: Result of the spring coupling overloading. B: Replacing the spring coupling with a rigid coupling

This operation has allowed to get finally a fully working system and practically unstoppable, except perhaps for a slight clicking sound due to some misalignment problem, but which has never given problems. The

system was also then completed with a heater operated by a temperature controller to limit the thermal oscillations. For a viewing of the final system, see the next section.

2.3.3.3 - Detailed description of the final version of the piston flow generator

As aforementioned, the third gas flow calibrator is a laboratory-made piston flow generator.
It is composed of four syringes, two worm screw, a threaded carriage, a stepper motor with gear reducer and motor controller, a timing belt with two pulley, four solenoid valves, a system for temperature control, and the electronic circuitry.
In this flow generator, two pairs of syringes with the stems connected in antiparallel way are fixed in a container. The stems are tied to a threaded carriage, driven by two threaded screws and moved by a step motor. This mechanism allows to convert the rotation of the step motor in a linear translation of the carriage and consequently of the stems. Inside the syringe, the head of each stem ends with a gas-tight sliding piston that can generate a gas flow rate when it is in motion. The antiparallel arrangement of the syringes entails that, when the pistons move, a pair of syringes behaves like a flow source while the other pair behaves like a flow sink. It is possible to test gas-meters with a constant flow, not affected by changes in ambient pressure, by connecting the inlet of the gas-meter under test with the source of syringe flow and the outlet of the gas-meter with the syringe flow sink and by keeping constant the speed of the stems.
Moreover, the whole system is enclosed in a thermally controlled environment so the obtained results are not influenced by fluctuations in ambient temperature. The main components of the piston flow generator and the overall external view of the system are illustrated in the next figures (fig. 2.50-2.51)

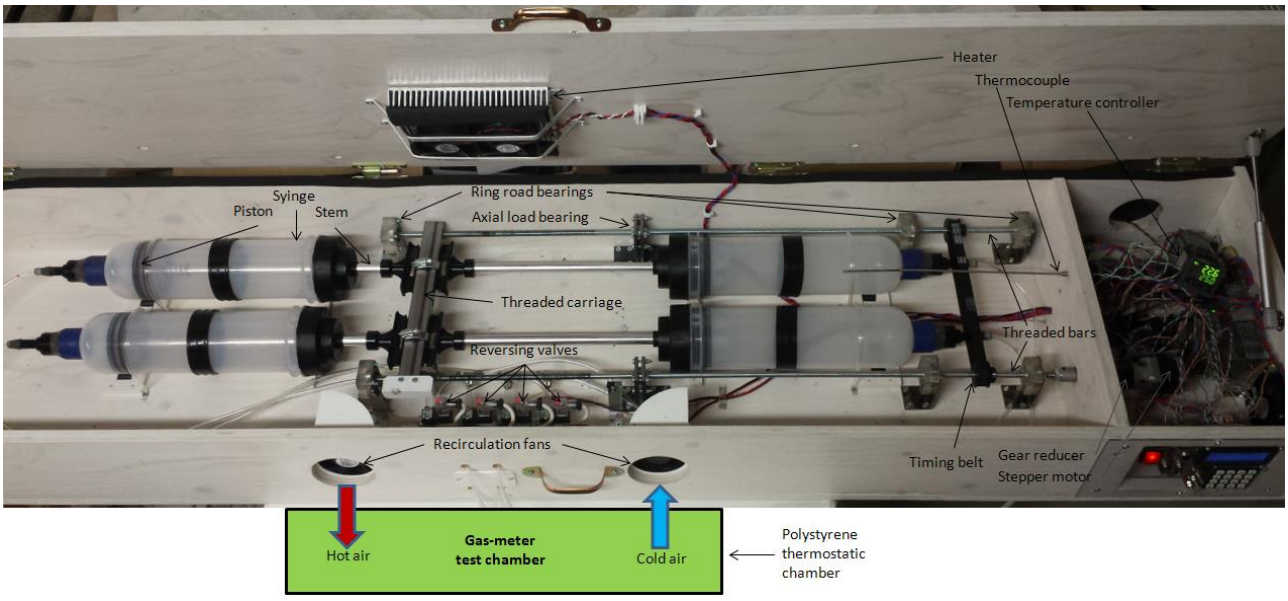

Figure 2.50: Components of the piston flow generator

Figure 2.51: overall external view of the piston flow generator

We used four 1.5 lt volume Pastorino E200231 syringes that were chosen for the low cost; unfortunately they did not ensure a good gas seal since they are designed mainly for liquids transfer applications.
Consequently, we have to replace the original sliding seal of the pistons with new u-type gas-tight piston seal in order to obtain an adequate gas tightness; a gas-tight joint Pneumax T081006 was also glued at the end of each syringe. The stems of the syringes are connected to the threaded carriage by means of hose clamps.
The stem drive train begins with a 1.24 w Vexta stepper motor (model PK545NAW) whose speed is decreased by a 25:1 gear reducer connected by means of a torque coupling to a worm screw, which is constituted by a 1 meter long threaded bar with M10 diameter. A second identical worm screw is rotationally connected to the previous one by means of a timing belt model L with 64 teeth, 9.525 mm pitch and 12.07 mm development. A pulley L050 with 10 teeth diameter of 29 mm is mounted on each worm screw where the belt is assembled. Each worm screw is held in place by 4 identical bearings (model 6000-2RSH SKF); three of these (in particular the two closest to the belt) must withstand only a tangential load while the one closer to the center of the system must absorb all the axial load. The worm screw is fixed to this last bearing by means of two nuts that are tightened counterclockwise; the bearing is in turn clamped between two 6 mm tight

teams which prevent the axial displacement. The carriage is a rectangular steel profile, 2 mm thick 30 x 20 mm side length, inside which are positioned two non-rotating threaded bushings; the worm screws are placed within them. When the worm screws are set in rotation, they are screwed into the bushing causing the carriage to move.

Two electro-mechanical end-stop switch are placed at the two ends of the translational space; each of these, when activated, block the stepper motor and prevent the further advancement of the carriage.

The four syringes are connected to four solenoid valves, suitably connected to each other, so they can reverse the gas flow circuit when they are activated. In this way, the inlet and the outlet of the system are always located on the same ports, regardless of the advancement direction of the carriage.

Custom electronic circuitry, whose main component is a microcontroller Arduino UNO board, controls the activation of the solenoid valves by means of a solid-state relay Opto22 DC60MP and the carriage speed by sending appropriate signals to the motor controller.

The device is equipped with a heater consisting of a 240 V, 200 W Heater Mats RS 245-641 attached on the bottom of a finned aluminum plate on which two fan are placed. The temperature controller Eurotherm 2416 is connected to a thermocouple placed in the center of the two right syringes and drives the heater by means of a solid-state relay Opto22 MP240D4 holding the internal temperature at 25 °C.

On the long side of the syringes container, two recirculation fans are placed to maintain uniform the temperature of the test chamber. The test chamber is a parallelepiped of 750 x 580 mm base length and 1 meter high, it is obtained made by joining together 40 mm thick polystyrene panels.

This system can generate flow rates up to a maximum of 48 l_n/h by connecting together two syringes of each side; it is also possible to keep separate two pairs of syringes, so the maximum flow rate is reduced to 24 l_n/h but it is possible to test simultaneously two meters. All three gas-meter types have been tested with the following flow rates: 12, 6, 2, 1, 0.5, 0.17, 0.08, and 0.04 l_n/h.

2.4 - TEST RESULTS AND EVALUATION

The performance of three gas meters have been tested using three flow calibrators described above.

The results show that all three gas-meters have a quite linear behavior with the flow rate and such behavior is evident within all three the calibration systems utilized. Figures 2.52, 2.53 and 2.54 show these results in terms of number of cycles per second, they are obtained varying the flow rate in the each gas-meters through its calibration system.

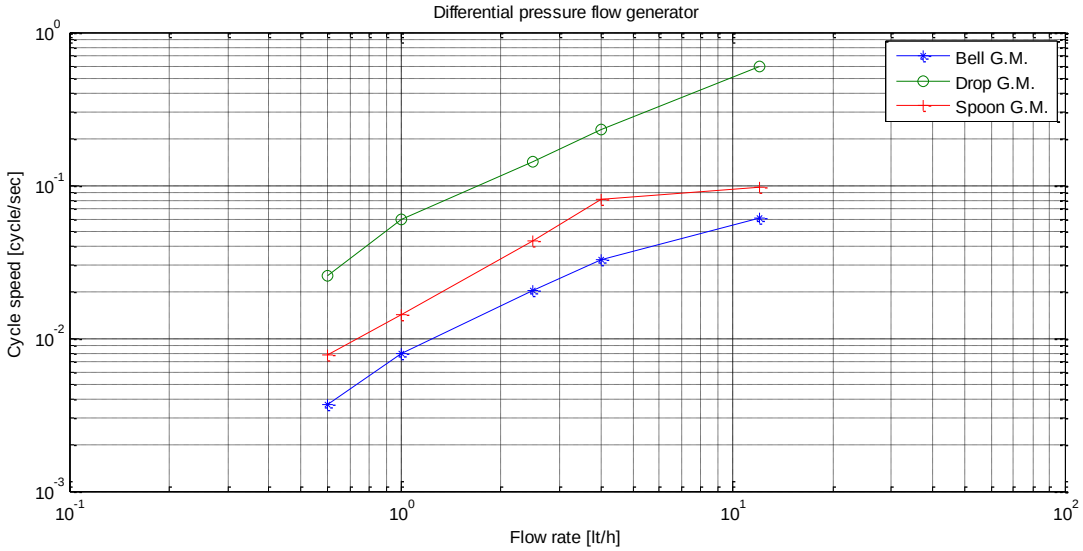

Figure 2.53: Behavior of the bell, drop and spoon gas-meter in terms of number of cycles per second at various flow rates, obtained utilizing the differential pressure flow generator as calibration system

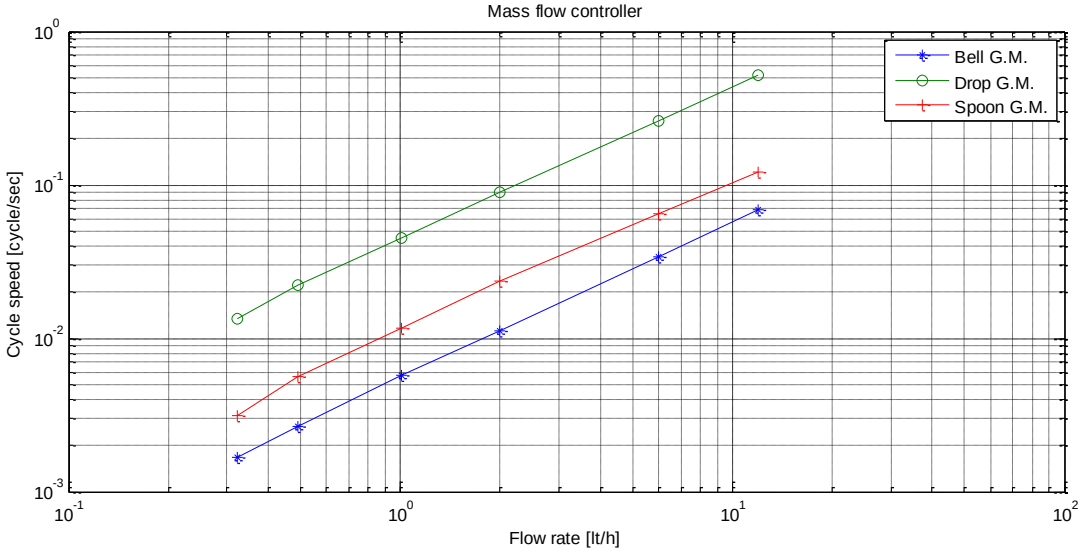

Figure 2.52: Behavior of bell, drop and spoon gas-meter in terms of number of cycles per second at various flow rates, obtained utilizing the mass flow controller as calibration system

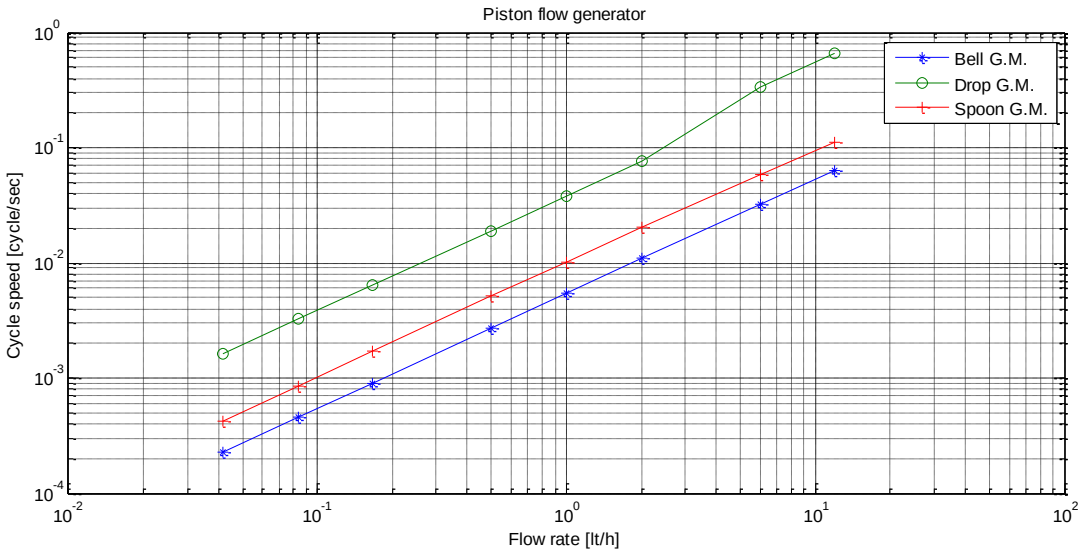

Figure 2.54: Behavior of the bell, drop and spoon gas-meter, in terms of number of cycles per second at various flow rates, obtained utilizing the piston flow generator as calibration system

In addition to these tests. It was also investigated whether the gas volume processed by the single gas-meter at each cycle is maintained constant or less with the various flow rates. To do this, two flasks connected at the bottom, one of which is filled with water, were placed at the exit of the gas-meter under test. The gas flow coming out from the gas-meter enters into the first container and pushes part of the water present in it into the second one. By weighing the second flasks, we can estimate the total gas volume passed through the gas-meter, and dividing it by the total number of cycles performed we obtain the volume of gas processed at each cycle.

Figure 2.55 shows the scheme of the system just described.

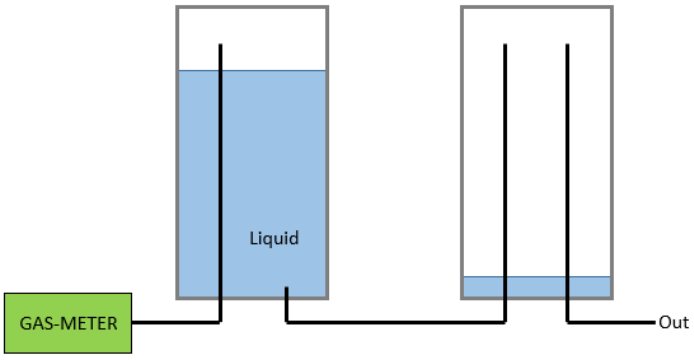

Figure 2.55: Scheme of the two flasks utilized to study the steadiness of the volume of gas processed at each cycle by the gas-meter

Comparing the values obtained at various flow rates, it can be seen that the bell gas-meter always shows an error less than +/- 1.5%, which rises to a +/- 2% in the case of the spoon gas-meter. In both cases, the error is quite comparable to the repeatability error obtained by re-running the same test for several times.
The situation is slightly different for the drop gas-meter. In this case, tests have shown a linear increase of the volume of the gas processed at each cycle with the flow rate. This effect begins to emerge with flow rate above 1 lt/h to reach values close to 7.5% for flow rates of 12 lt/h. With flows below 1 lt/h, the error, as in the case of the other meters, is comparable with the repeatability error (i.e. around a +/- 2%).
Figure 2.56 shows the volume increase of gas processed at each cycle by the drop gas-meter versus the flow rate increase.

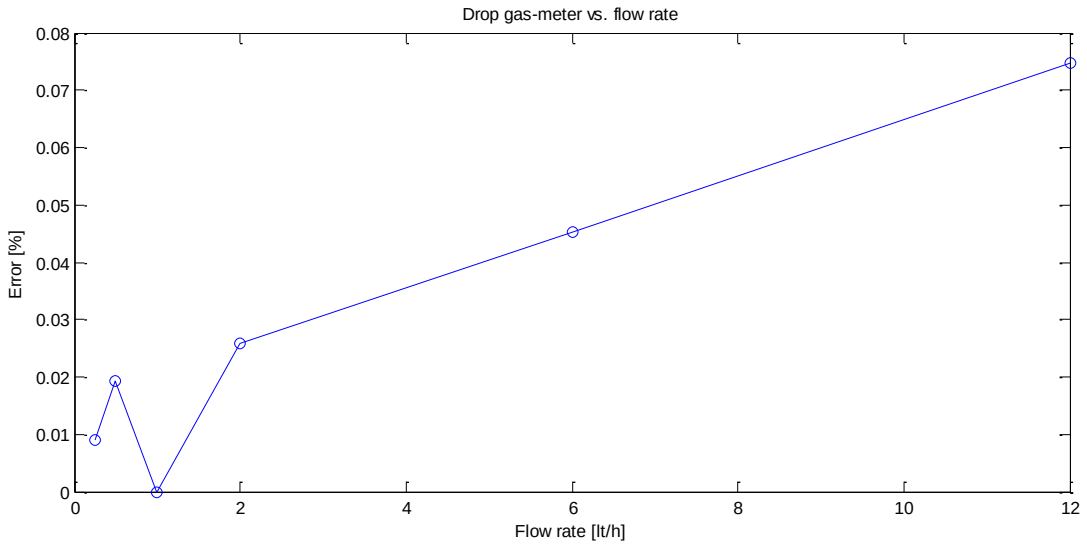

Figure 2.56: Error reported at the flow rate of 1 lt/h of the volume processed at each cycle by the drop gas-meter at various flow rates

This situation is probably due to the fact that, with the increase of the drop speed, the friction force also increases requiring a larger pressure differential, and a gas volume larger than the nominal one that passes in standard conditions through the meter.
In conclusion, while for the bell and the spoon gas-meter the calibration can be performed by referring to a single value of the flow rate, in the case of the drop gas-meter we need a calibration curve of the unit volume vs the flow rate.

Regarding the comparison between the different calibration systems, the main aspect to consider is whether they are able to produce a constant flow gas, i.e. without oscillations induced by the environment due to changes in temperature or pressure, or to the gas-meter itself because of its operating characteristics. The results show that in all the gas-meters the variation coefficients reach their maximum value when we used the piston flow generator as a calibration system. This is probably due to the high void volume contained in

the syringes, which acts as a reservoir and favors the alternate operation of these meters. In fact, in all the gas-meters, with the exception of the drop gas-meter where the curve trend is the same for all calibration systems used; the gas must win a certain pressure given by the liquid contained in it to actuate the gas-meter, and this can give rise to the noted oscillatory behavior. Oscillations increase when tanks are inserted in the measuring circuit.

Figures 2.57, 2.58 and 2.59 show the coefficients of variation (calculated as the ratio between the standard deviation σ and the absolute value of the mean |μ|) at various flow rates of the three calibration systems, applied to each of three gas-measurers

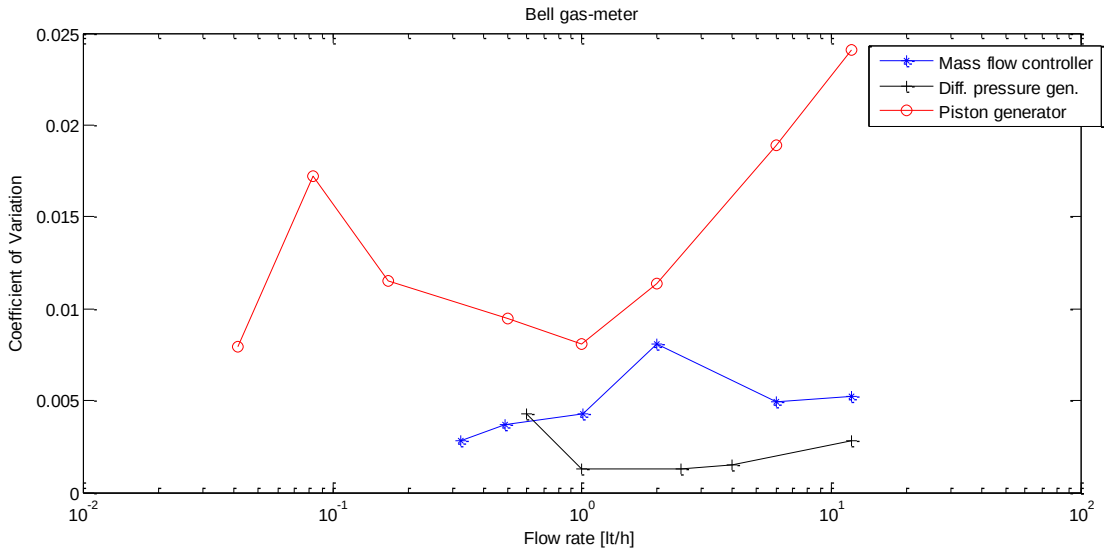

Figure 2.57: Coefficient of variation, at various flow rates, of the three calibration systems applied to the bell gas-meter

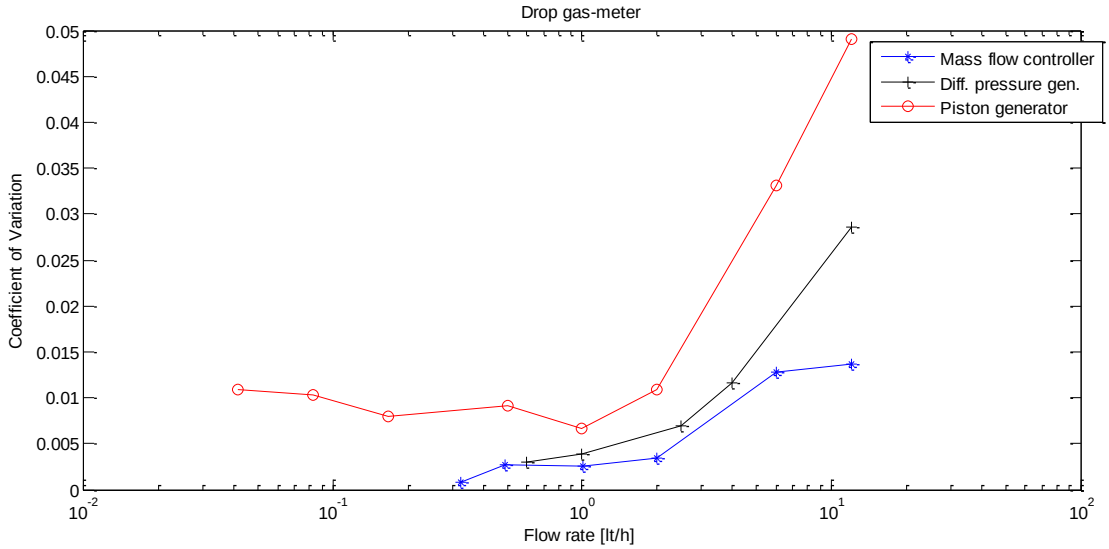

Figure 2.58: Coefficient of variation, at various flow rates, of the three calibration systems applied to the drop gas-meter

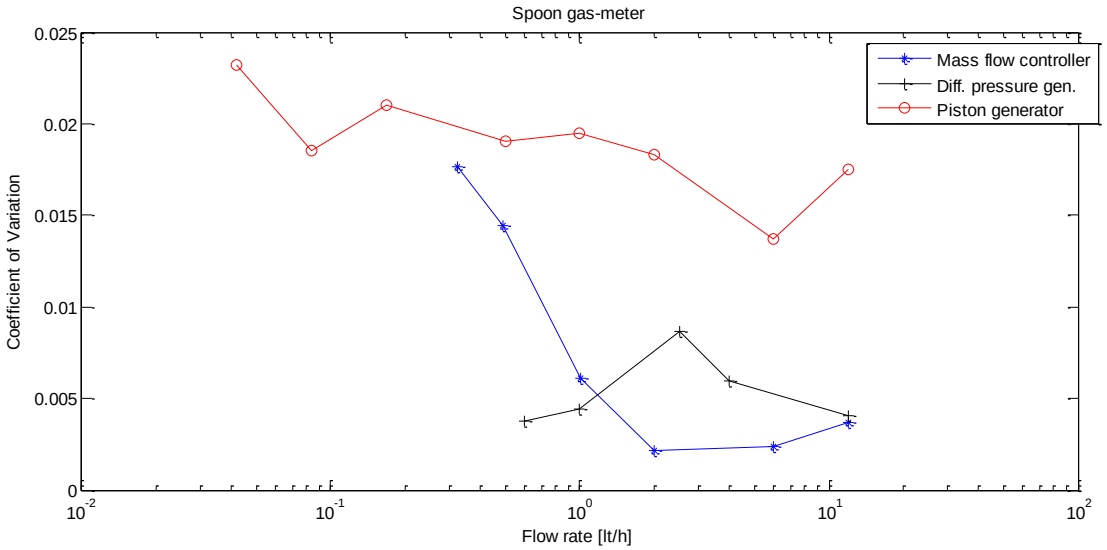

Figure 2.59: Coefficient of variation, at various flow rates, of the three calibration systems applied to the spoon gas-meter

Another particular observation concerns the operating pressure of the gas-meters. In this regard, the drop gas-meter has a very low operating pressure, which correspond to few millimeters of water, while it amounts to a few centimeters in the other meters. This minimizes the overpressure induced in the biodigestion cells and this peculiarity enables to use this gas-meter to study in detail the evolution of the biogas/biomethane production even in small size biodigestion cells.

2.5 - CONCLUSIONS

The three gas-meters described are all able to monitor precisely the gas production from anaerobic digestors at a laboratory scale. All meters have a quite linear behavior with the flow rate, with the exception of the drop gas-meter where a calibration curve of normal volume vs flow-rate is needed. However, the great advantage of this gas-meter is the low operating pressure, (equal to few millimeters of water), while it amounts to a few centimeters in the other cases. The bell gas-meter presents instead a greater linearity while the spoon gas-meter is characterized by a greater simplicity of construction. As regards the calibration systems, all these systems have been able to evaluate the performances of our meters. The differential pressure flow has the advantage of simple construction, but it can generate only a limited range of flow rates, the mass flow controller has greater accuracy, but it is made with expensive commercial modules; the piston flow generator has the greatest measurement range among all but it is somehow less accurate.

Chapter 3

STUDY OF SUBSTRATES METHANOGENIC POWER

3.1 – INTRODUCTION

Biomethane, namely methane obtained through the upgrading of biogas, is gaining more and more interest as an alternative and renewable source to the natural gas. Carbon dioxide is the most present pollutant, that must be removed for obtaining the biomethane, may be present in concentrations up to 50%. The elimination of this molecule from the gas stream is therefore a fundamental step in the purification process. The extraction problem of carbon dioxide from biogas is certainly much less complex than the extraction of CO_2 from a gas stream coming, for example, from a combustion process.

In this case, the high temperature of the gaseous flow and the presence of various dangerous or corrosive substances increase greatly the difficulties that must be faced and technologies necessary for this purpose.

The biogas produced during the anaerobic digestion is at room temperatures and ambient pressure; moreover it fairly easy to produce and manage inside a laboratory. Typically what is done in a laboratory is to study in small scale digesters with dimensions of a few liters, while commercial digesters have the size of hundreds of cubic meters. Biogas is almost exclusively produced in large plants that collect the organic matter from various companies and municipalities. There are also plants of smaller size that can be used by an individual farm, but hardly digesters have low dimensional levels, since the production of biogas could have excessive fluctuations. In this paper, we focus on the research and the study of very simple and effective carbon capture technologies that could be applied to small plants suitable, to be used in condominiums, plants that today are not commercially available. The first problem to be faced was the study of anaerobic digestion in laboratory systems intended as biogas source together with the purification devices. In particular, we focused on chemical carbon capture systems for their constructive simplicity and the high degree of CO_2 purification trying to find a partial solution to their high cost which constitutes at the moment the main limit to their application.

3.2 - PRELIMINARY TESTS

Since our purpose was to apply the CO2 capture technology on biogas, a study of methanogenic power of the substrates was necessary with a focus on the precautions to be taken to maximize their production. Below we will list the instrumental and the equipment used for the preliminary tests and the more advanced experiments.

3.2.1 - Description of the first experimental set up

The first set of preliminary tests for studying the biogas production process was carried out in a previous work, but the description of the experimental setup and the results obtained are useful for understanding many of the choices made later. In this experimental setup we used, as biodigestion cells, some plastic containers of 500 ml volume on top of which a gas-tight opening had been created to allow the biogas escaping. The containers (with a maximum number of eight elements) were immersed inside a thermostated bath of handicraft construction. The bath was made of a stainless steel tub with dimensions of 200 x 400 mm base square and a 150 mm height, it was assembled by the Faculty workshop. Under the tub were glued two resistors 240 V, 200 W (RS 245-641) driven by a solid state relay (Crydom D2425) controlled by a thermostat (Euroterm 2216) with a thermocouple inserted in the bath. The gas generated in the small biodigestion cells was sent directly to the flow measuring system to control the biogas production. In order to measure the biomethane production, a bubbling cell of 500 ml filled with 300 ml of KOH 28% w/w was interposed between biodigesters and the gas meters. The gas measuring system was simply based on the principle of liquid displacement. The main component consists of a pressure cooker full of water. The gas entering the cooker pushes the liquid, through the suction pipe, outside it and then inside in a bottle that was weighed 1 or 2 times per day.

Since the bottle was placed under the cooker to prevent that the liquid gets sucked down, we placed a vent connected to the atmosphere in a raised position along the liquid path. The relative pressure between the inside and the outside of the pot was measured by means of a "U" shape water gauge pressure.

Before weighing the bottles, the pressure inside the pot was balanced with the external ambient pressure. This was achieved by plugging and lowering the vent to the atmosphere of the conduit that leads the liquid under the bottle, so that the water was sucked. Unfortunately, as the vent element was bound to the same support of the "U" shape gauge, it was necessary to unscrew the entire device and then reassemble it when the measure is completed. Unfortunately, this system was very onerous and inaccurate and this explains the great amount of work, described in the previous chapter, for the development of an automatic measurement systems for the

biogas/biomethane flow rate. A figure with the detail of the components is shown below (fig. 3.1) together with a figure of the overall system (fig. 3.2).

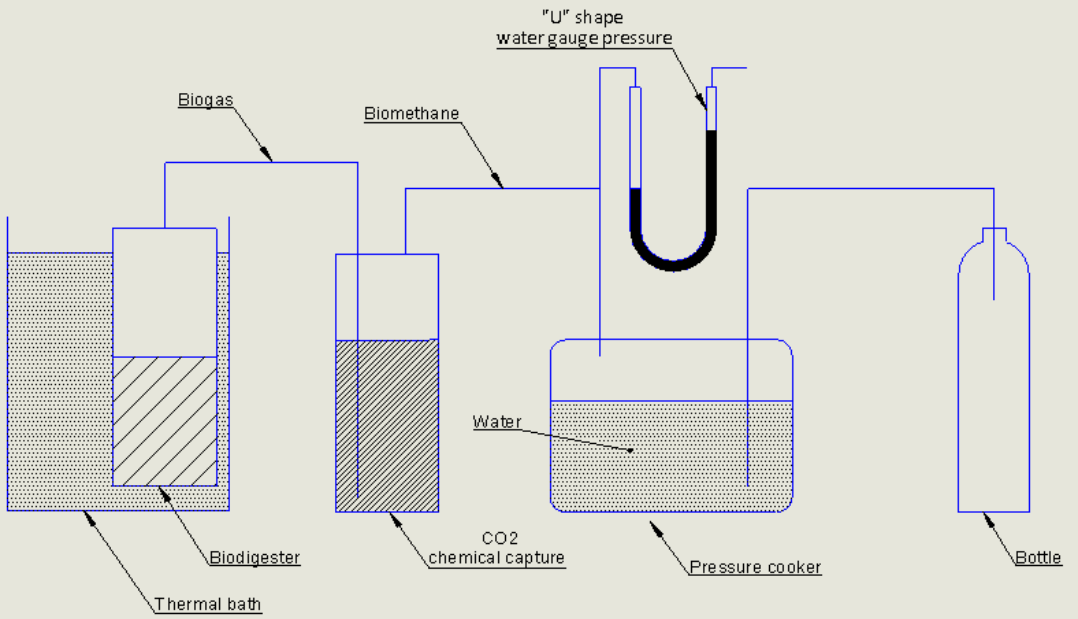

Figure 3.1: Scheme of the preliminary test setup

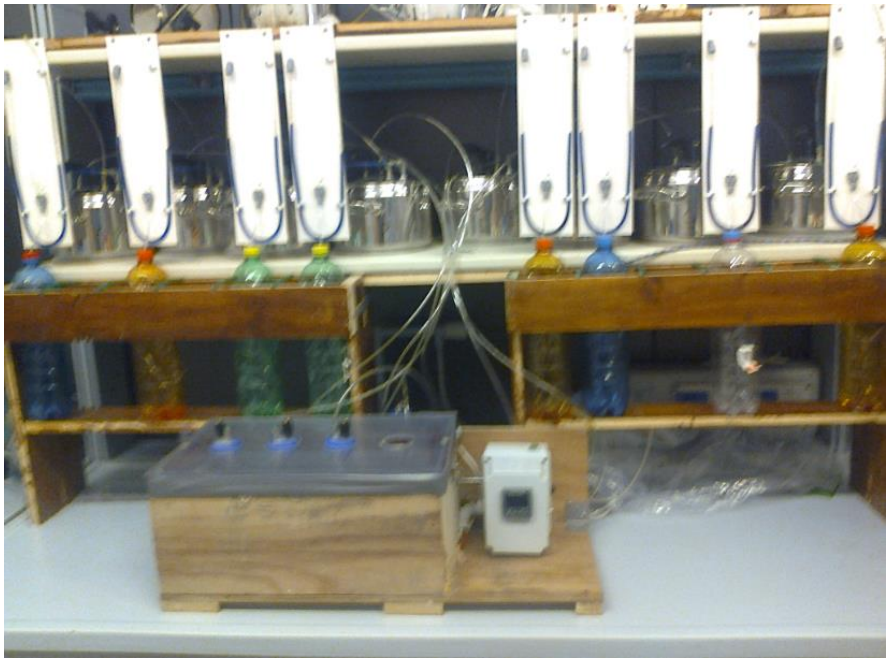

Figure 3.2: Real system

3.2.2 - Preliminary test results

The purpose of the preliminary tests was to verify the correct implementation of techniques suitable to create an environment capable of maximizing the methanogenic production. With this purpose, a study of the cumulative biogas and biomethane production of the available substrates, compared with the typical values of the literature, ranging from 200 and 1000 cc/g of SV, was done.

Four types of substrates were used for the tests that, renewed (regenerated) from time to time, will be maintained for all the other experiments. Such substrates are manure, mud, sewage and OFMSW (Organic Fraction of Municipal Solid Wastes), that have been used individually or mixed together in varying quantities to find out their peculiar effects in the biogas production.

For the first test, the following mixtures of substrates were used: manure-OFMSW-mud, manure-mud, mud, mud-sewage, mud-OFMSW, manure-sewage (3:1), manure-sewage (2:1), manure-old sewage (2:1).

The tests had been carried out in thermophilic environment (55 °C) with CO_2 capture performed by bubbling KOH and it lasted for more than a month.

The graph (fig. 3.3) of the cumulative production of biomethane, expressed in cubic centimeters per gram of initial volatile substance, is listed below.

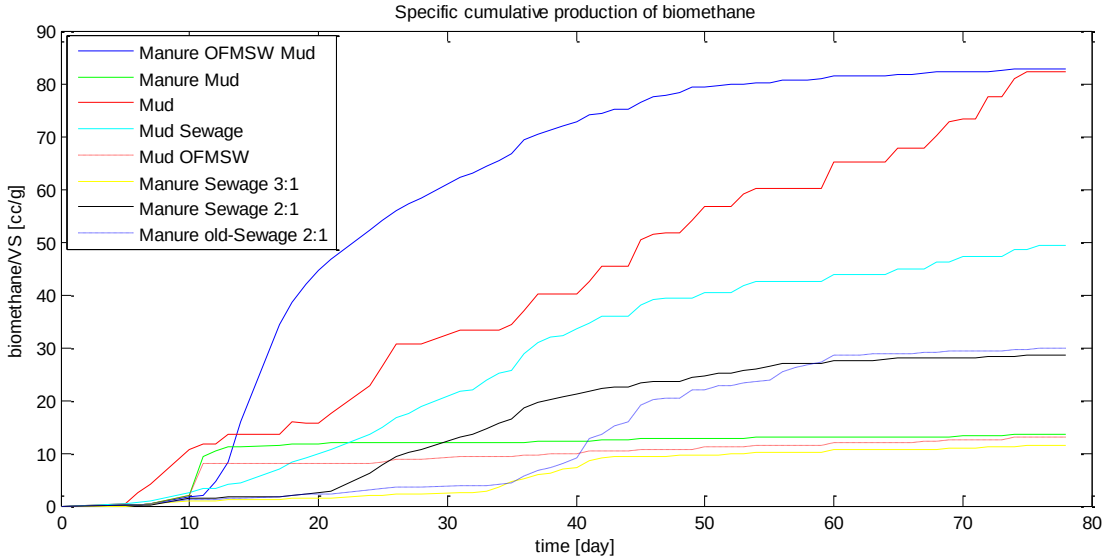

Figure 3.3: Specific cumulative production of biomethane obtained from the first preliminary test

The results showed rather limited yields, except for the samples containing the sludge; in particular, the best result was obtained for the mixture manure-OFMSW-mud. The reason for the poor production of the vast

majority of the cells was probably due to the not optimal pH of the substrate. This aspect had been overlooked, but its importance would become clear in the next test.

The conditions in which the second test was carried out were similar to the previous one. The substrate mixtures, however, were changed; in particular the mixtures of substrates used were: manure, manure-OFMSW, manure-mud, manure-sewage, mud-OFMSW, manure-OFMSW-mud, mud-sewage, OFMSW-mud-sewage.

Below is the graph (fig. 3.4) with the results always expressed in cubic centimeters per gram of initial volatile substance.

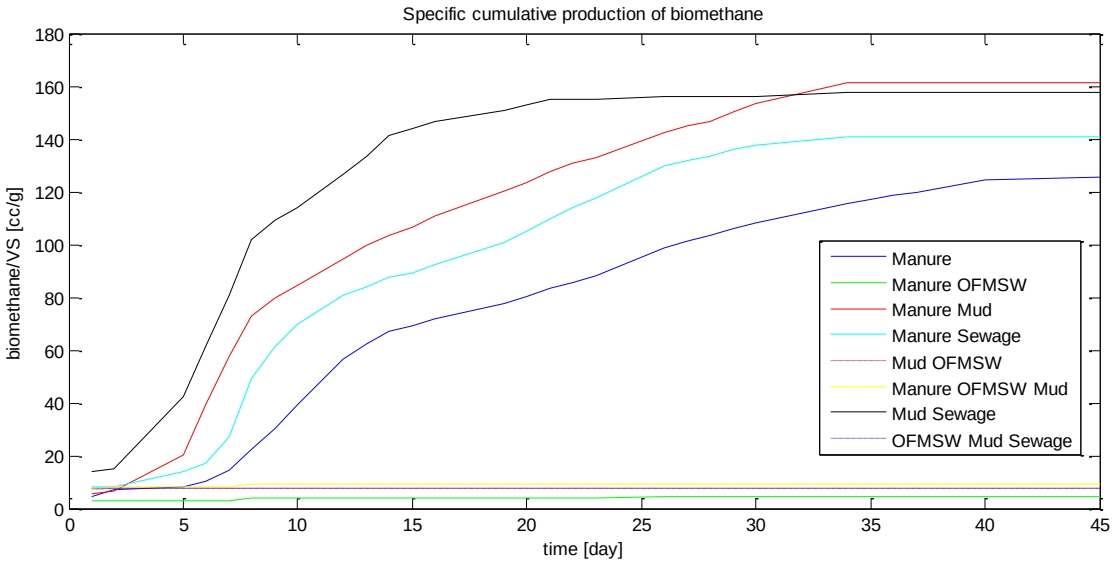

Figure 3.4: Specific cumulative production of biomethane obtained from the second preliminary test

Analyzing the results, it seemed more evident than in the previous case, that in the samples containing OFMSW the activity stopped in a few days. This apparent coincidence prompted to investigate the inhibitory characteristics of the OFMSW that include a pH measure, that resulted very low (around 4).

Unfortunately, the increase of neutrality by addition of KOH during the test run did not led to a recovery of the digesters activity.

In conclusion, the preliminary tests allowed to understand the importance of mud as an element capable of providing adequate bacterial flora necessary to get the best biogas production. The other observation was the need to correct the pH of the substrates, especially in the case of OFMSW. While the third and last observation was, as already introduced, the need to have an automatic measuring system of gas flow.

3.3 – TEST WITH AUTOMATIC READING OF GAS PRODUCTION

3.3.1 - Description of the new apparatus

The new measuring apparatus was a system with greater dimensions than the previous one. It was always made up of 8 biodigestion cells but the capacity was 2 liters. These cells are obtained by assembling three main elements: an acrylic tube, 10 mm thick and 135 mm long with outside diameter of 120 mm and two acrylic square plate, with 40 mm thickness and 160 x 160 mm side length, attached at the ends of the tube. The lower plate is permanently glued while the upper plate connects to the top of the tube trough a rubber gasket and four tensions screws to allow the gas access.

The holes for the biogas escape are present on the upper plate. The high thickness of the acrylic components is sized to ensure the sinking of the cells in the liquid bath more than on the resistance of the internal pressure. The innovative feature that distinguishes these cells is the fact that are equipped with a device for mixing the organic substance. In fact, in the first chapter we had discussed how in the process of biodigestion the longest and most onerous phase was represented by hydrolysis; this is a surface phenomenon that can be encouraged by the mixing the substrate. Typically, the classical approach is the use of an electric motor whose shaft is connected to a kind of whisk, immersed in the biodigestion cell. However, this system may present gas sealing problems in the area where the shaft of the motor passes through the cover of the digester. To solve this problem, we decided to use the same biogas produced in the cell as a means of substrate mixing. The heart of the device utilized is represented by a membrane micropump that aspires the biogas from the reactor head, compresses it, and places it on the bottom through the channels formed in the base. Dispersers are screwed at the end of the channels, they serve to allow the escape of gases to and prevent the entry of solid particles that may clog the channels. The effective operation of the device is shown in the next figure (fig. 3.5).

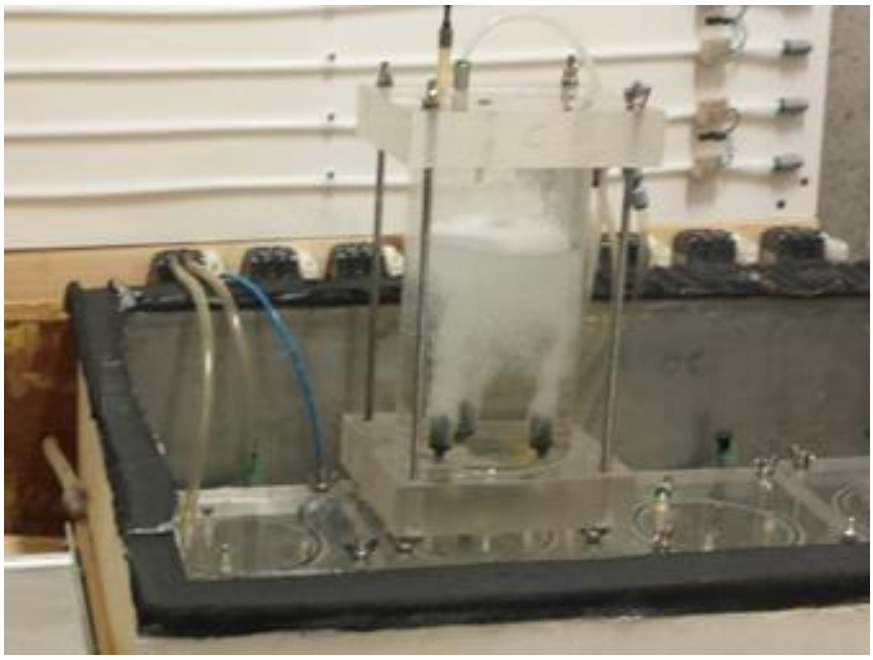

Figure 3.5: Biodigesters mixing system

As regards the activation of the pumps, a variable voltage supply, necessary to adjust the gas flow and the magnitude of the mixing, was not initially available, so the pumps could not be fed simultaneously. To solve the problem the pumps was subdivided in four groups of two elements, that were cyclically fed. In particular, each group was provided with its own solid-state relay (OPTO22 DC60MP), controlled by a microcontroller (Arduino UNO), which was used to actuate a pair of agitators for two minutes, while in the following six minutes the other pumps were gradually activated.

Returning to the general system, the thermostated bath consists of a large stainless steel tub with 800 x 500 mm side length, 400 mm high heated by four resistors 400 W 240 V (RS 245-663) glued at the bottom. These resistors were driven by a solid state relay (Crydom D2425) always controlled by a thermostat (Euroterm 2216e) equipped with a thermocouple placed inside the liquid bath.

The innovative aspect of this system is represented by its automatic measurement of the gas flow. These systems were made up by the basic versions of the bell and drop gas meters reproduced in series. The need of their respective evolutions had not yet emerged at this time. In particular, the measurement system is formed by eight drop gas meters, which operation and components are described in the related paragraph. The bell gas meter had been reproduced as a series of 16 elements, each one is equipped with a simplified components. In fact, the version described in the previous paragraph, consisted of a special electronic system capable to control the solenoid valve that guide the gas flow to the bell, a microcontroller was entrusted with the simple task of data recording. For practical reasons, it was decided to delete the electronic system and to manage the control of the

solenoid valves with a microcontroller, that was connected to 16 solid state relay (OPTO 22 DC60MP). The intention was to use the bell gas meter to measure the biogas and to perform the measurement of the biomethane with the drop gas meter. As in the previous case, the capture of carbon dioxide was performed by bubbling it in 300 ml of potassium hydroxide. In particular we realized an array of 16 bell gas meters to increase the number of tests, so we added to the eight acrylic cells other eight cells realized starting from simple bottles of plastic. The diagram of the path followed by the gas and the real final system are shown in the following figures (fig. 3.6 – 3.7).

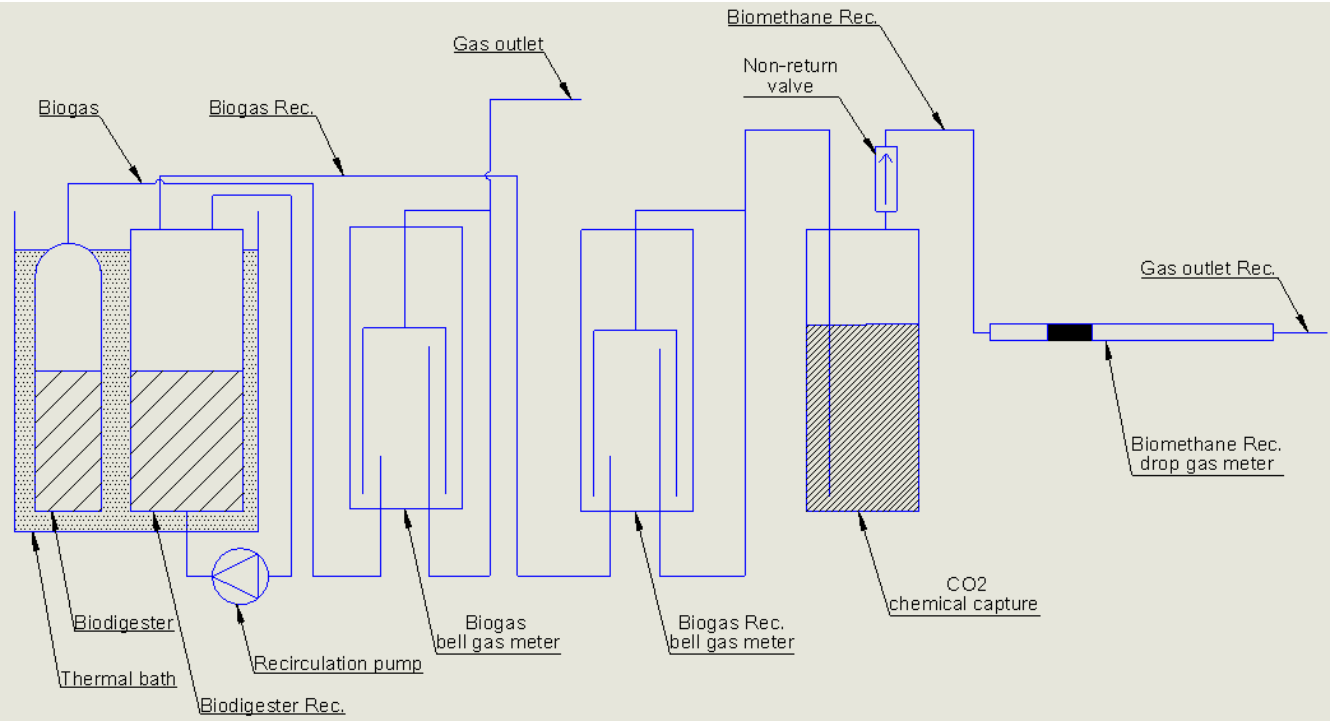

Figure 3.6: Scheme of the path followed by the gas in the new apparatus for the measurement of the methanogenic power; the gas and the devices related to the cell with the recerculating system are described with the term "Rec."

Figure 3.7: Real system for the measurement of the methanogenic power

As shown by the previous figure (fig. 3.7), the bell gas meters were placed under the thermostatic tube to avoid malfunctions related to counterpressure phenomena while, in the case of the drop gas meter, this problem has been solved with the addition of springless non-return valves without any other expedient.

3.3.2 – Test results

The first results that we discuss in this paragraph are related to non-shuffled cells, they consist of simple bottles filled with about 1.5 kg of material placed in thermophilic environment (55°C). The substrates used and their combinations are shown in the following table (tab. 3.1), together with the calculated values of TS % and VS%.

Cell	Substrate	TS%	VS%	VS/TS%
A	Manure	13.66	11.37	83.24
B	Manure-OFMSW (1:1)	16.4	13.06	79.63
C	Manure-Mud (1:1)	9.75	8.1	83.08
D	Manure-Sewage (2:1)	10.41	8.14	78.19
E	Mud-OFMSW (1:1)	11.03	8.26	74.89
F	Manure-OFMSW-Mud (1:1:1)	11.75	9.1	77.45
G	Mud-Sewage (1:1)	4.37	3.01	68.88
H	OFMSW-Mud-Sewage (1:1:1)	9.56	6.94	72.59

Table 3.1: Substrated used with TS% and VS%

Unlike what happened in the preliminary test, the pH of each substrates was corrected and brought to neutrality before the start of the test. As expected, the substrates containing OFMSW are those that required more intervention. The millimoles of NaOH used for each matrix are shown in the following figure (fig. 3.8).

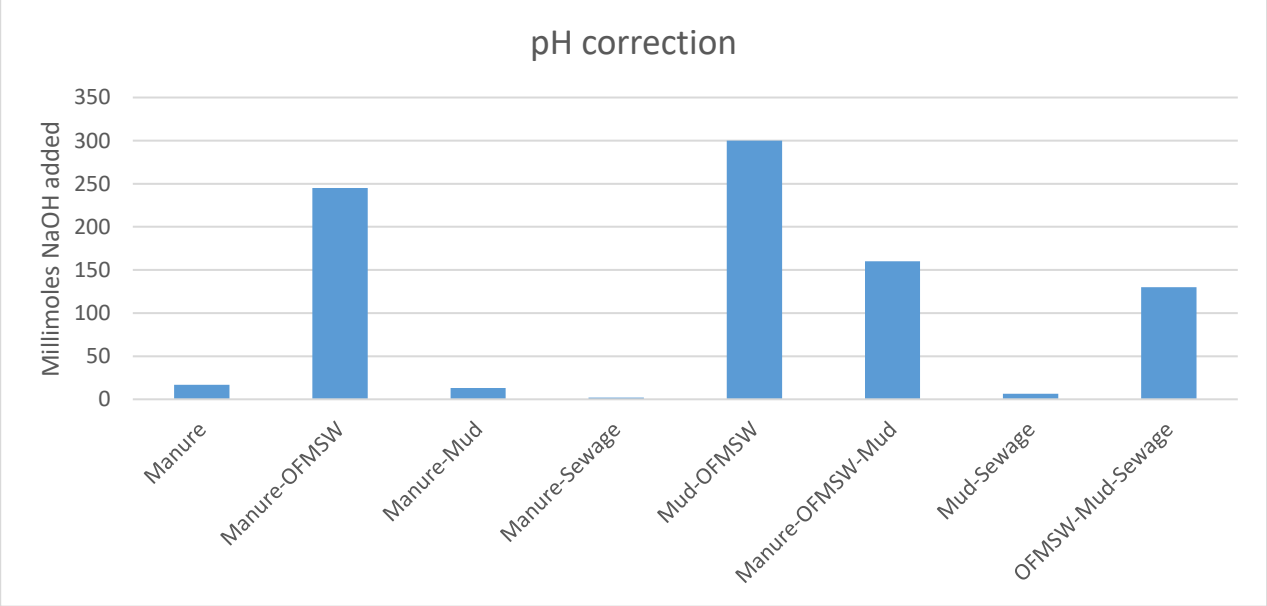

Figure 3.8: Millimoles of NaOH added for pH correction

The results obtained in terms of biogas cubic centimeters per gram of initial volatile substance are shown in the following figure (fig. 3.9).

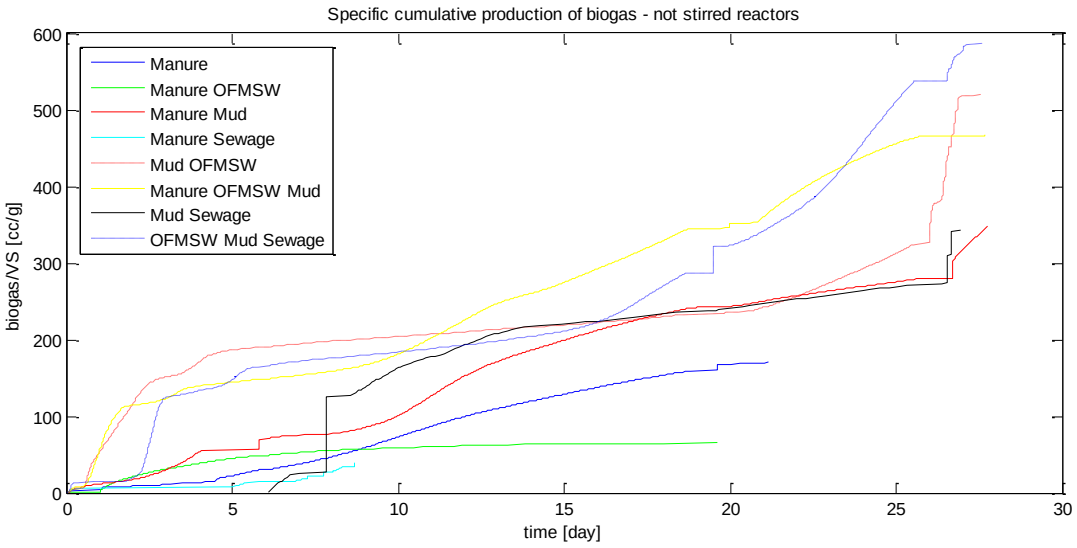

Figure 3.9: Specific cumulative production of biogas with non-shuffled cells

The “leaps behavior” is due to system bottlenecks that, in some cases, have even caused the explosion of some bottles. In particular, the sample A exploded, due to a shutter problem, in the first days and immediately replaced. The sample C exploded after about 4 days when it produced approximately 7000 cc of biogas. The bottle was replaced, part of the matrix was recovered and put it in a new bottle with addition of the lost material. The recording system was not interrupted in both cases. The sample D exploded during the fifteenth day after a period of apparent inactivity. The best performance was shown by the wet process loaded with OFMSW-Mud-Sewage in equal parts (sample H). Even the semi-dry processes with Mud and OFMSW (Samples E, F) have shown excellent performance at around 500 biogas cc / g (VS).

The dry process with manure and OFMSW (sample B) instead produces about 1/6 compared to the best samples. A similar behavior is shown by the Manure-Sewage matrix (sample D): in this case the graph is stopped on the eighth day since the gasometer had any shot until the bottle explosion on the fifteenth day.

It seems that the combination more favorable to the process is the one that matches OFMSW and Mud: the samples E, F, H as a matter of fact, show a very high initial production of biogas - up to about 100 cc / day biogas / g (SV) - that brings in about 5 days to complete almost 50% of the process. It seems that the only manure is not capable to trigger effectively the methanogenesis (see samples A, B, D), but this may be due to the fact that it was a material with few weeks of ageing.

As regards the shuffled cells, they have been initiated after a few weeks. They were filled with about 600 g of material, starting by the same previous substrates and with the same combinations. In fact, the TS% and VS% content and also the millimoles of NaOH were completely analogous to the previous cases.

The initial goal was to measure of both biogas / biomethane production, however the second measure was not carried out because the drop gas meters stopped working within a few days because of the presence of external

pressure phenomena that resulted in the release of the drop. The results obtained, in terms of cubic centimeters of biogas per gram of initial volatile solids, are shown in the following figure (fig. 3.10).

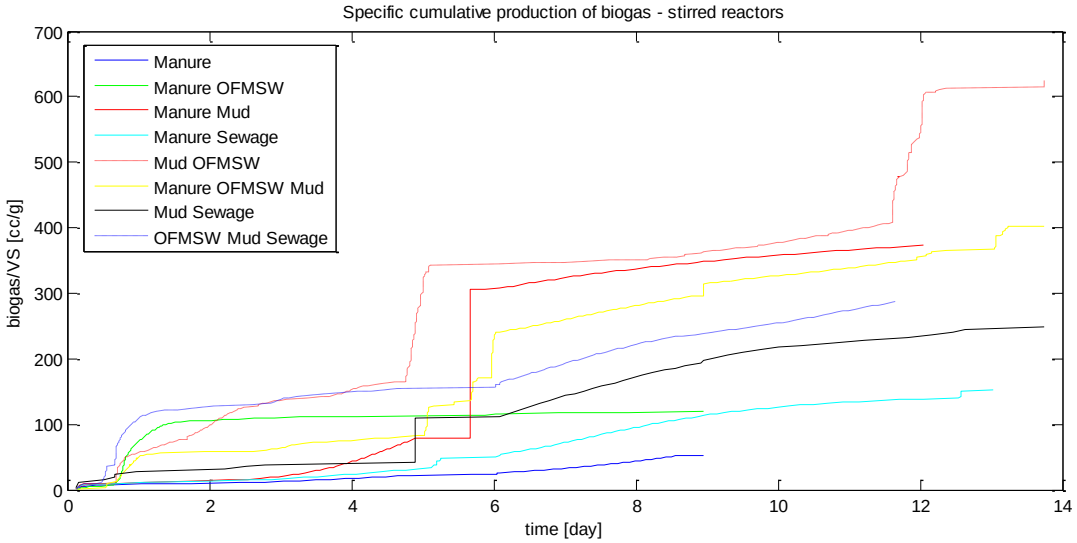

Figure 3.10: Specific cumulative production of biogas with shuffled cells

Also in this case, there is a leaps behavior due to system bottlenecks which, however, thanks to the increased robustness of the cells never caused explosions. The best performance was obtained from the semi-dry process, it consists of Mud-OFMSW (sample E) which produced nearly 1/3 of biogas more than other, the total was about 600 cc / g (VS). It is interesting to note then that, thanks to the reshuffling, this biogas occurred in times almost halved compared to the previous case. The productions of semi-dry processes of samples C, F and H were also good, all these samples contained Mud, which produced biogas from 250 to 350 cc / g (VS). However, the performance of the wet process were slightly lower, they were formed by combining Mud-Sewage (G sample) that produced about 200 cc biogas / g (VS). However, we observed a very low production of the samples A and B due to the inability of the aged manure to effectively trigger the methanogenesis.

3.4 - FINAL EXPERIMENTAL SETUP

3.4.1 - Description of the evolved apparatus

The previous experimental setup manifested several problems, in particular often the outflow biogas pipe had engorged and also in the case in which a real obstruction had not occurred, the ducts and also the gas meters

(especially their pneumatic valves) were very dirty at the end of the test. The bell gas meter worked rather enough well, even if few unexpected failures occurred, but they were probably due to management of the entire system performed by the microcontroller. To solve these problems, further changes to the experimental setup had been decided. In particular, to limit the obstructions in the gas outflow pipe, the diameter of the tubes was increased from 3 to 6 mm, and a trap for non-gaseous substances was installed at the exit of the biodigestion cells. This trap was constituted by a gas-tight glass bottle, placed outside of the thermal bath, within which the gas was flowed from the bottom to the top so any solid or liquid particles remain trapped inside it. With regard to its use, the trap was used at first to remove non-gaseous substances from the gas flow that passes through the mixing pumps, to decrease the likelihood of its damage. In particular, during the first experiment with this new device the output of the biodigestion cells was directly connected to the traps, then, from each of them came out two tubes, one went to the mixing pump and the other to the measuring system. The gas path diagram is shown in the next figure (fig. 3.11).

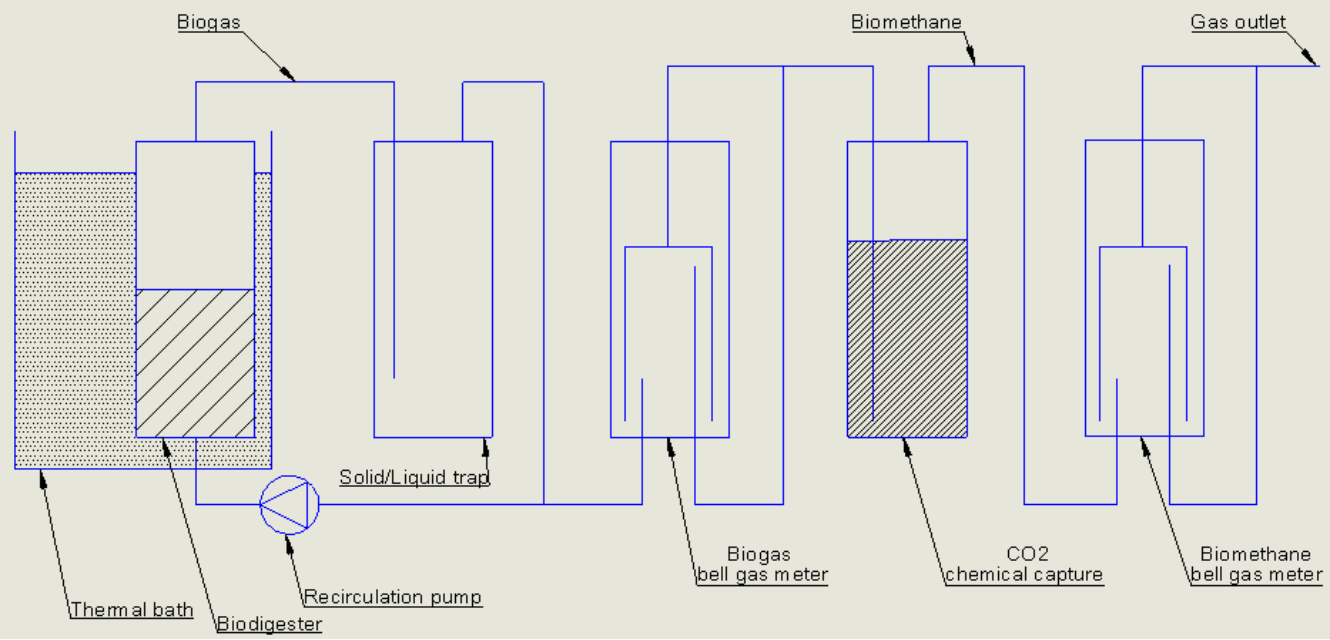

Figure 3.11: Gas patch in the system with the trap connected also to the pump

Unfortunately, the fact that the water-saturated biogas came out at a temperature of about 55 °C to an environment at 15 °C had been underestimated. The result was that the high gas flow rate circulated by pumps, coupled to the temperature difference of about 40 ° C between the inside and the outside of the cell, made sure that in less than a week the liquid contained in the cells were all accumulated in the traps, stopping the production of biogas during the test.

By opening the digesters, the various substrates are presented fairly dry. The traps filled with liquid and an example of dehydrated substrate are visible in the next figure (fig. 3.12).

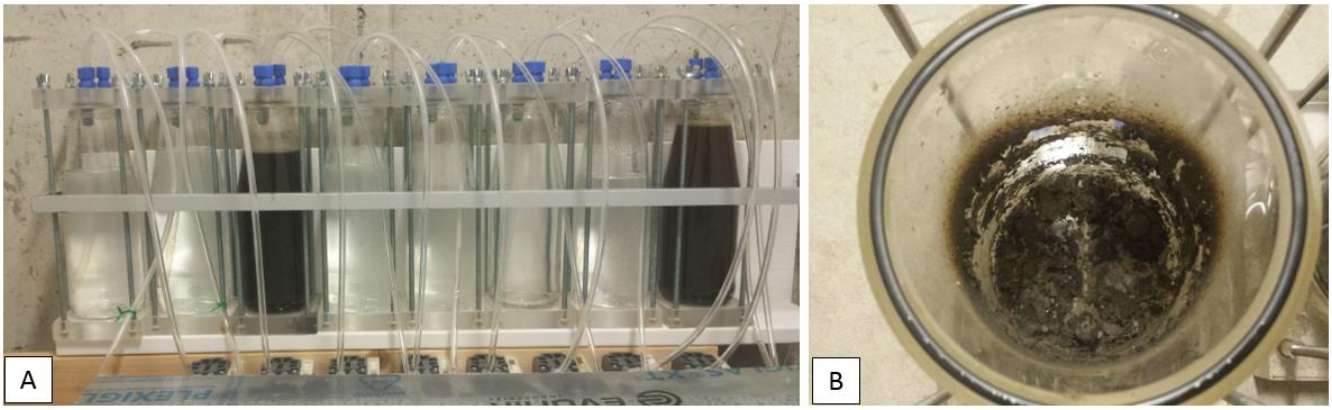

Figure 3.12: A: traps filled with liquid. B: dehydrated substrate

After this experience, the trap was used only to clean the biogas directed towards the gas meters, while the pumps were connected directly to the biodigestion cells, as in the first version of the system, when their use was introduced. The final pattern of the gas path is shown in the following figure (fig. 3.13).

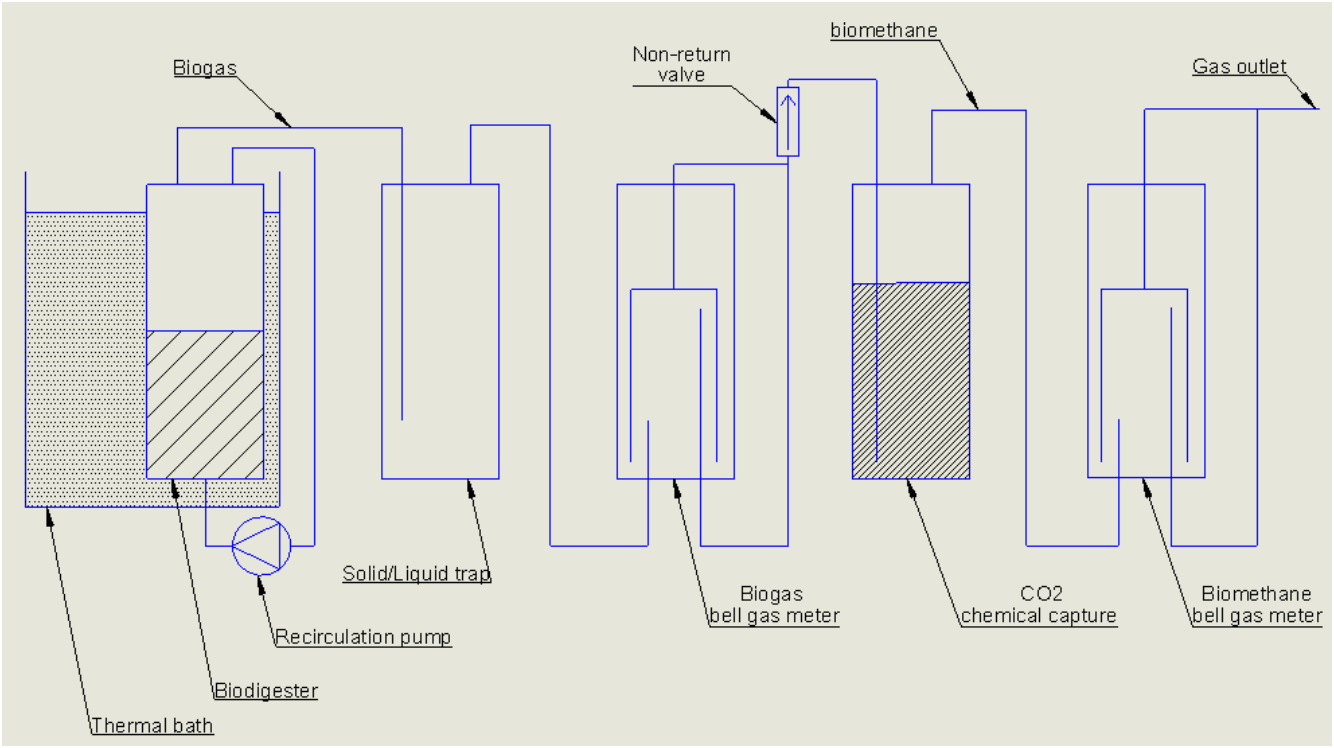

Figure 3.13: Gas patch of the final system

With regard to the recirculation pumps, previously an adjustable voltage supply was used to power them. However, it was not able to provide enough current to guarantee the simultaneous operation of all pumps. A new power circuit was then specially built. After various researches, it was decided to base this circuit on switch voltage regulators (series LM2576-XX) that, unlike the classic voltage regulators (series LM78XX), allow, in front of a more complex circuit, to have much higher power.

Such controllers were located downstream of a 24 V power supply. In particular a single switch adjustable regulator (LM2576-ADJ) was entrusted with the task of providing a variable voltage 3-20 V to all pumps. For the correct operation of the regulator, it's necessary to dimension capacitors and inductances, but the datasheet of the component provides all the information necessary for this purpose. In the practice, the voltage can be adjusted by acting on a potentiometer and, it can be displayed by a voltmeter on the front panel of the thermal bath. There is also a curiosity about this circuit. In the previous version, it was used a solid state relay to command the seats resistors under the tub, which required a control signal in continuous low voltage. This signal was provided by a very cumbersome rectifier inserted in the same control panel. To gain space for the new circuit, it was decided to remove the solid state relay, and also the cumbersome rectifier, and replace it with a mechanical relay that could be controlled in AC current by the thermostat. With this solution the thermal bath worked well anyway, but when we added the new version of the 16 bells measuring system, this system (that in the preliminary tests seemed to work well) began to show an unjustified arrest phenomena. At first we thought that the problem was within the measuring system, and the focus was also on the microcontroller of which the system was provided. Unfortunately, even after rescheduling several times and even replacing it twice, the problem persisted, it is evident that the cause of this malfunction should be seeked elsewhere. This problem was due to the mechanical relays that produced an electromagnetic pulse which evidently disturbed the operation of the microcontroller. To solve the problem the mechanical relay was then replaced again with a solid state relay. Then it was provided, always by means of the switch voltage regulator (in particular the LM2576-05 model) with a compact 5 V power supply in substitution of the cumbersome rectifier, and the problem was no longer presented. The evolution of the circuit and the front panel is visible in the following figure (fig. 3.14).

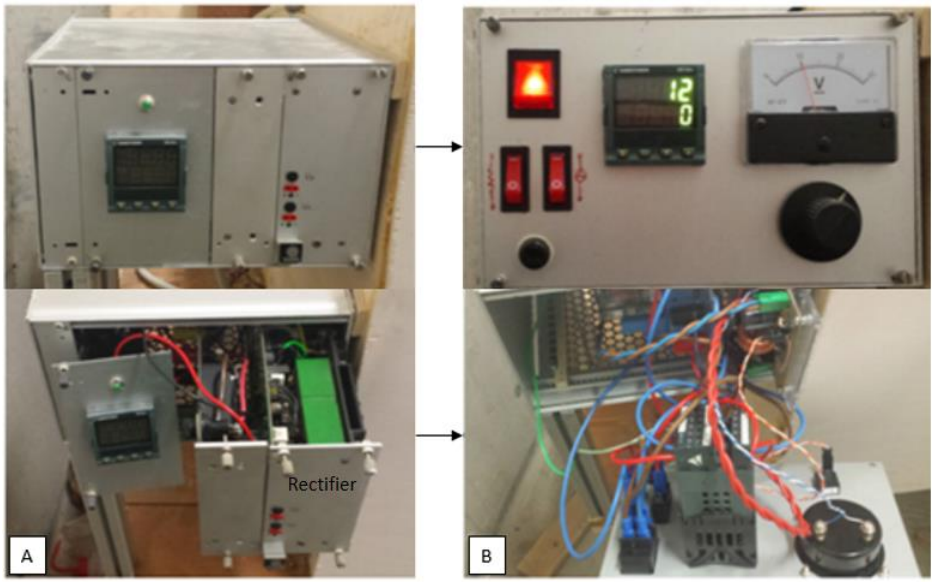

Figure 3.14: Thermostatic bath panel evolution. A: previous version. B: new version

As mentioned above, in addition to the thermal bath circuit, it was decided to also reconstruct the entire 16 bells measurement system. In fact, the earlier version had given some problem and almost all the valves, as well the body of the same gauges, appeared soiled by organic material, for which it was still necessary to disassemble the whole apparatus. For the new version, it was decided to use the microcontroller only for the acquisition and storage of values and not also for managing the solenoid valves of the. For this reason a new electronic circuit, was constructed, which is able to operate autonomously the solenoid valves. To simplify the system, the 16 bells were divided into four groups of four elements and a special electronic form was created for each one of those. Each form requires a 5V power supply, which serves for the electronics to operate, and a 24 V power supply, which serves for the solenoid valves. The voltage at 24 V was provided from a power supply connected to the network, while the 5 V was obtained by means of a voltage regulator (LM2576 series) placed downstream to the 24 V power supply. Inside the microcontroller there was a website that allowed to download the saved data. In addition, it was also provided a control display, located in front of the system, which show of the total cycles made by the measuring instruments. The 12 V required by the microcontroller was initially provided by a classical voltage regulator, however, there were continual arrests because of the overheating of this component. For this reason it was decided to replace all the controllers of the series LM78XX with the series LM2576-XX. The evolution of the power supply circuit is visible in the next figure (fig. 3.15).

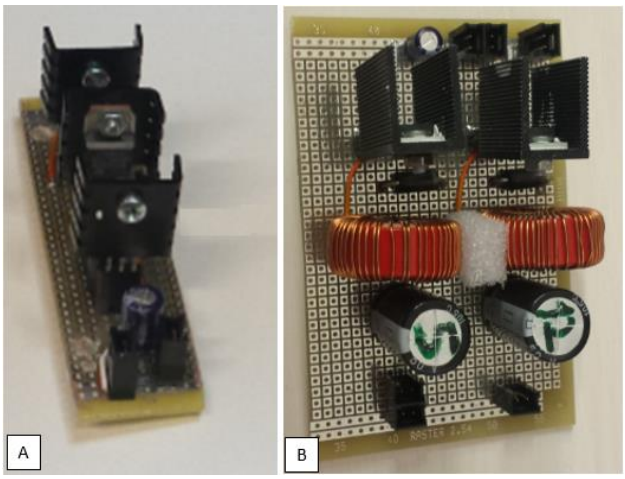

Figure 3.15: evolution of the supply device for the system with 16 bell gas meters. A: previous version. B. new version.

The carbon dioxide capture cells were then positioned in front of the thermal bath in order to facilitate the identification of any problems occurred during the operation. In this new version it was decided to insert non-return valves before capture cells so that, in case of backpressure, the liquid contained in the cells will be forced to cross the valves that have, in this way, a better seal. It is well known that the liquids have a higher density and a higher surface tension compared to the air. The final system for the measurement of the biogas and biomethane is shown in the next figures (fig. 3.16 – 3.17).

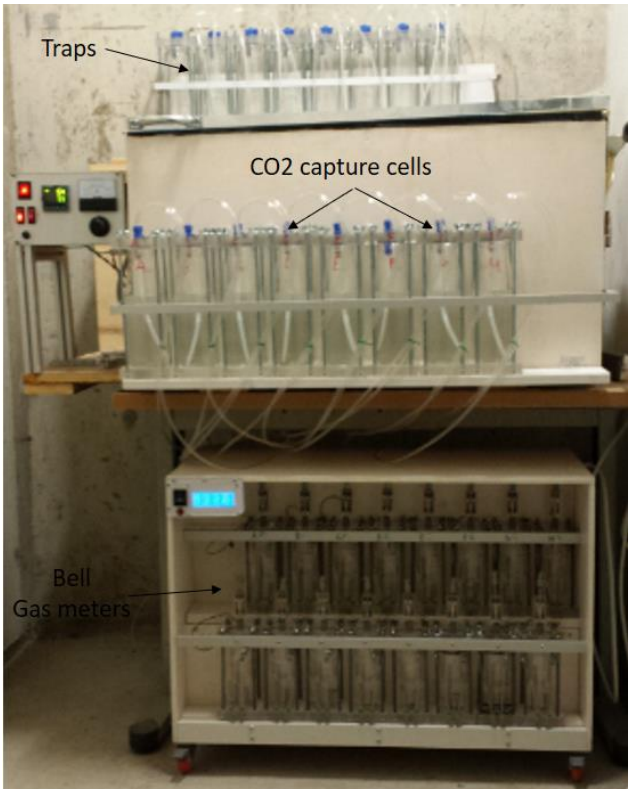

Figure 3.16: Real system

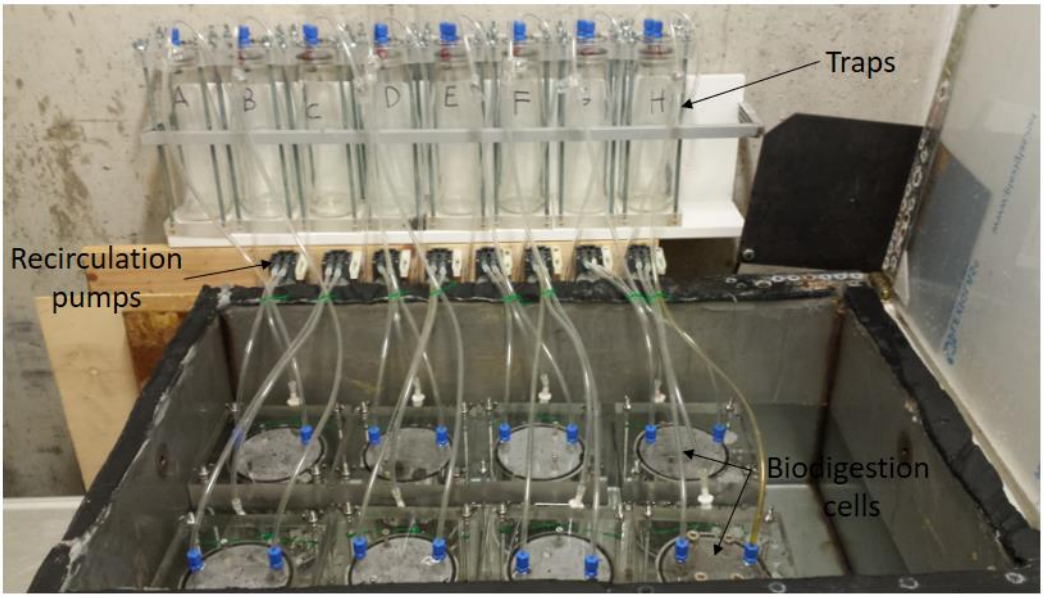

Figure 3.17: Internal view of the thermostatic bath

3.4.2 – Test results

The experiment with the improved version of the measuring system was conducted several months after the previous test. All substrates have been renewed, but the combinations were the same of the previous cases. In this test we have been used only 8 cells with shuffled system, which were filled with about 600 g of substrate maintained in a thermophilic environment (55°C). Among all the results presented, this was the only one where was possible to perform simultaneously a measurement of biogas and biomethane products. In particular, for the measurement of biomethane, the biogas was bubbled inside some capture cells containing 500 ml of NaOH 25% w/w. The combinations and the value of TS% and VS% are reported in the following table (tab. 3.2).

Cell	Substrate	TS%	VS%	VS/TS%
A	Manure	26.35	20.43	77.53
B	Manure-OFMSW (1:1)	15.95	12.28	76.97
C	Manure-Mud (1:1)	16.68	12.12	72.67
D	Manure-Sewage (2:1)	18.51	14.89	80.42
E	Mud-OFMSW (1:1)	6.30	3.82	60.66
F	Manure-OFMSW-Mud (1:1:1)	11.31	8.17	72.25
G	Mud-Sewage (1:1)	8.48	6.42	75.63
H	OFMSW-Mud-Sewage (1:1:1)	8.72	6.21	71.23

Table 3.2: Substrated used with TS% and VS%

Also in this case that the pH adjustment took place before starting the test and, as in the previous case, the biggest change has been observed in matrices containing OFMSW even if the proportions with the other substrates were lower than in the previous case, probably due to the different collection period of the material. The millimoles of KOH used for each matrix are shown in the following figure (fig. 3.18).

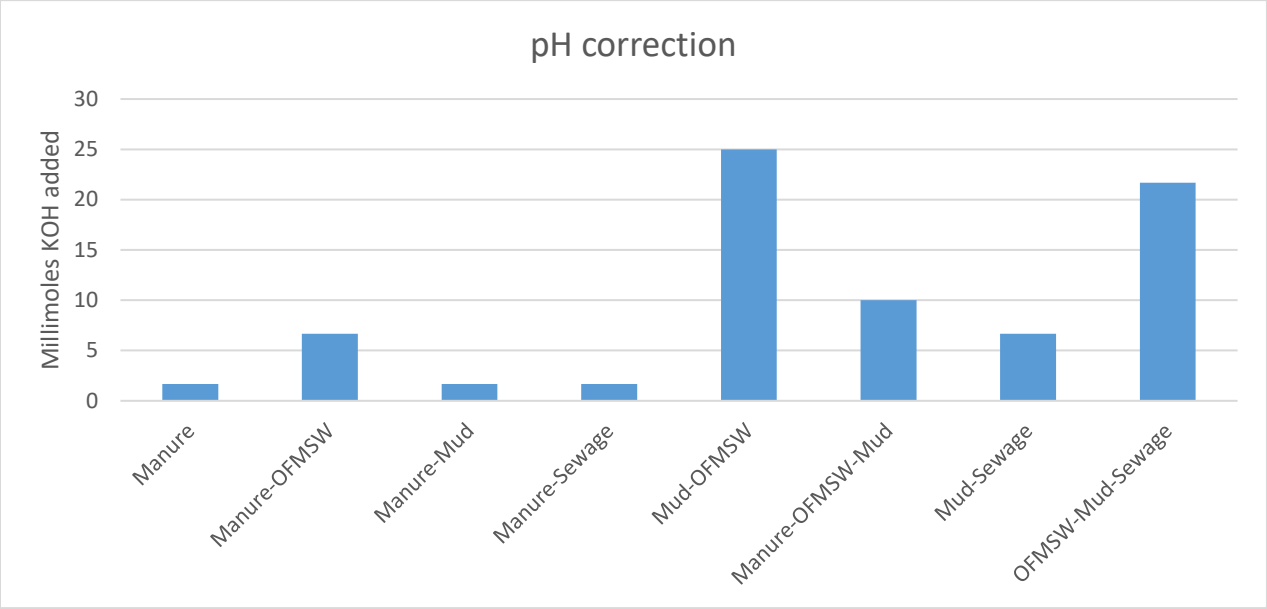

Figure 3.18: Millimoles of KOH added for pH correction

The results obtained, in terms of cubic centimeters of biogas per gram of initial volatile substance, are shown in the following figure (3.19).

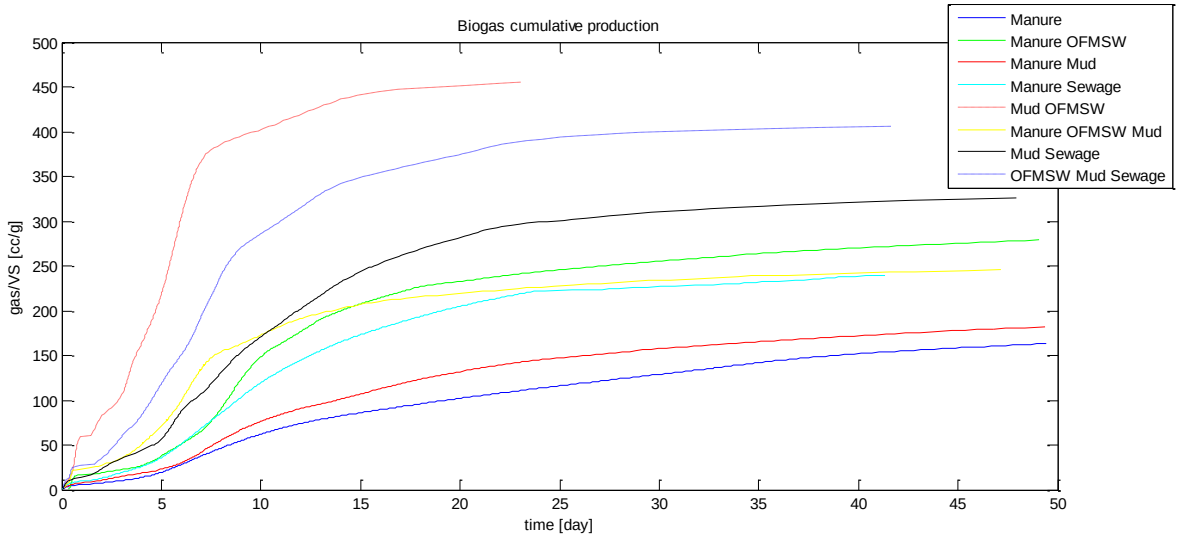

Figure 3.19: Cumulative production of biogas with shuffled cells

The first observation is the absence of the leaps behavior typical of the previous test. This is due to the larger air conduit and the presence of a trap for non-gaseous substances. Also in this case the highest production was obtained from the wet process with a Mud-OFMSW mixture (Sample E) that produced about 450 cc biogas / g (VS), 80% of which in the first six days of activity. Very good results have also been obtained from wet processes H and G, with productions respectively of about 400 and 300 cc biogas / g (VS). Quite similar were the production of the semi-dry B and F samples and dry sample D, which amounted to values around 250 biogas cc / g (VS). Very less have been instead the production of dry and semi-dry sample A and C, which have been of the order of 150 cc biogas / g (VS). Unlike all the tests carried out up to now, it was also possible to learn about the production of biomethane. This quantity, along with the production of biogas, is reported, for each substrate, in the following graphic matrix (fig. 3.20).

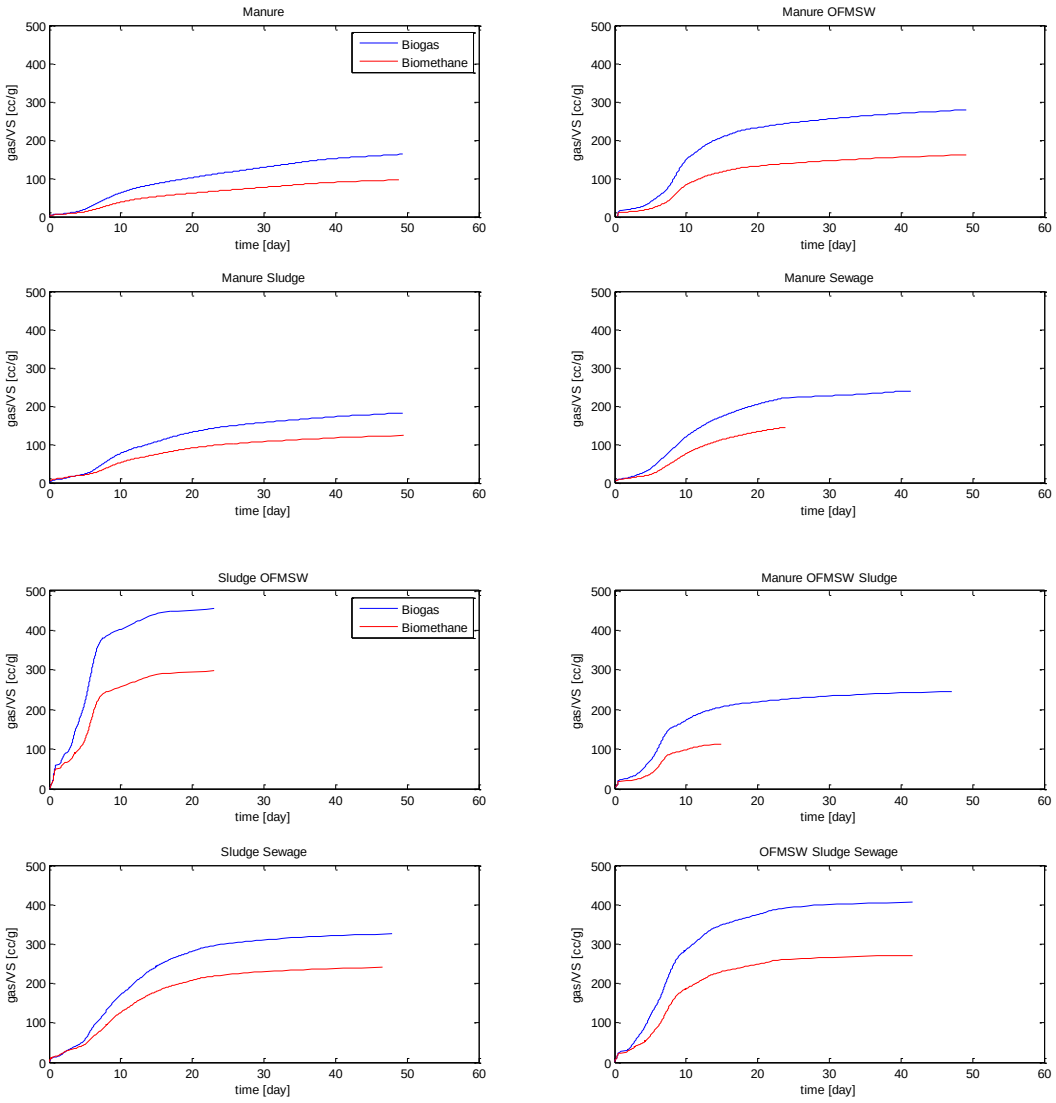

Figure 3.20: Cumulative production of biogas and biomethane with shuffled cells

The cumulative production of biomethane is summarized in the chart below (fig. 3.21).

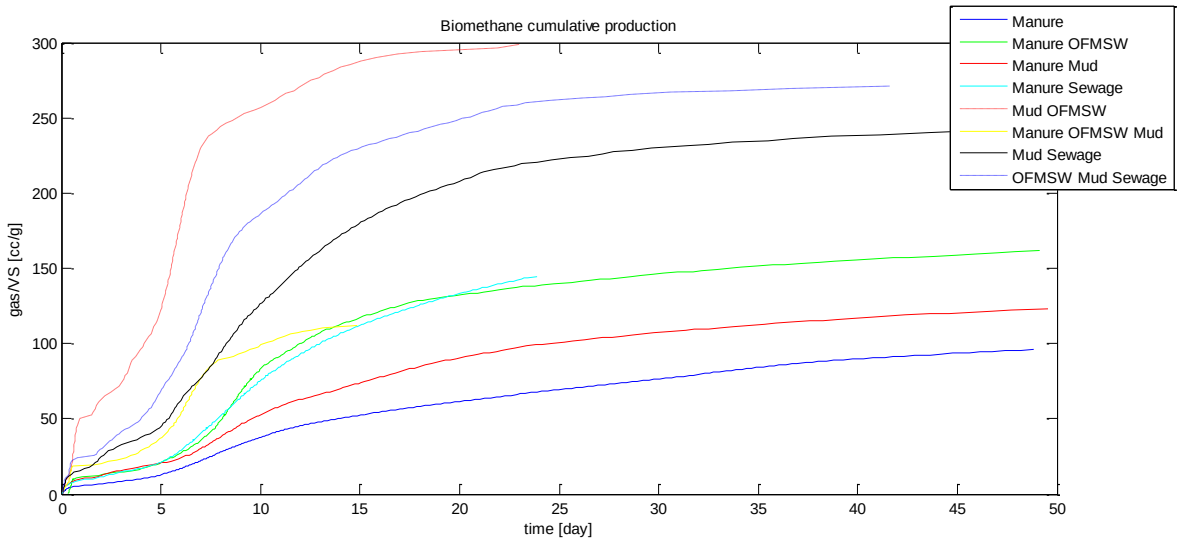

Figure 3.21: Cumulative production of biomethane with shuffled cells

Trends are substantially the same as described for the production of biogas. In particular, the percentage of carbon dioxide captured in the case of each substrate is visible in the figure below (fig. 3.22).

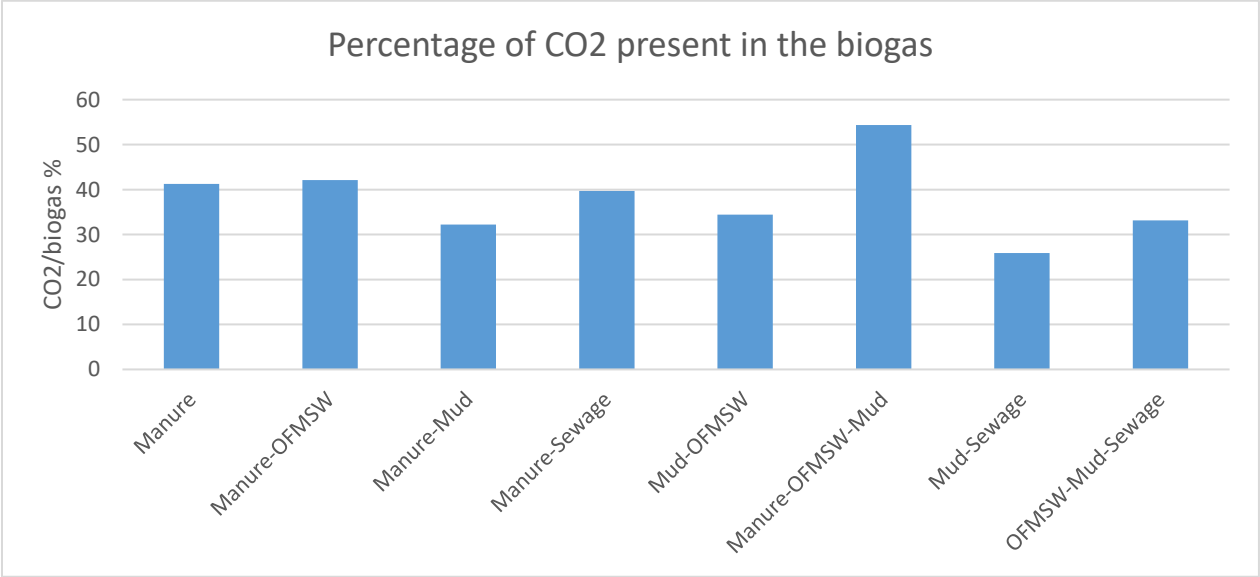

Figure 3.22: Percentage of CO2 present in the biogas

In all cases, with the exception of the wet process containing Mud-Sewage (sample G), the carbon dioxide percentage is above 30%. In particular, the percentage of carbon dioxide is 40% in the dry process containing Manure (sample A) and semi-dry processes Manure-OFMSW and Manure-Sewage (samples B and D). This

composition, richer in carbon dioxide is , however obtained from the semi-dry process containing Manure-OFMSW-Mud (sample F) which is extent of almost 55%.

Finally, as regards the flow rate of biogas and biomethane, the following matrix graphs (fig. 23) shows these data for each substrate.

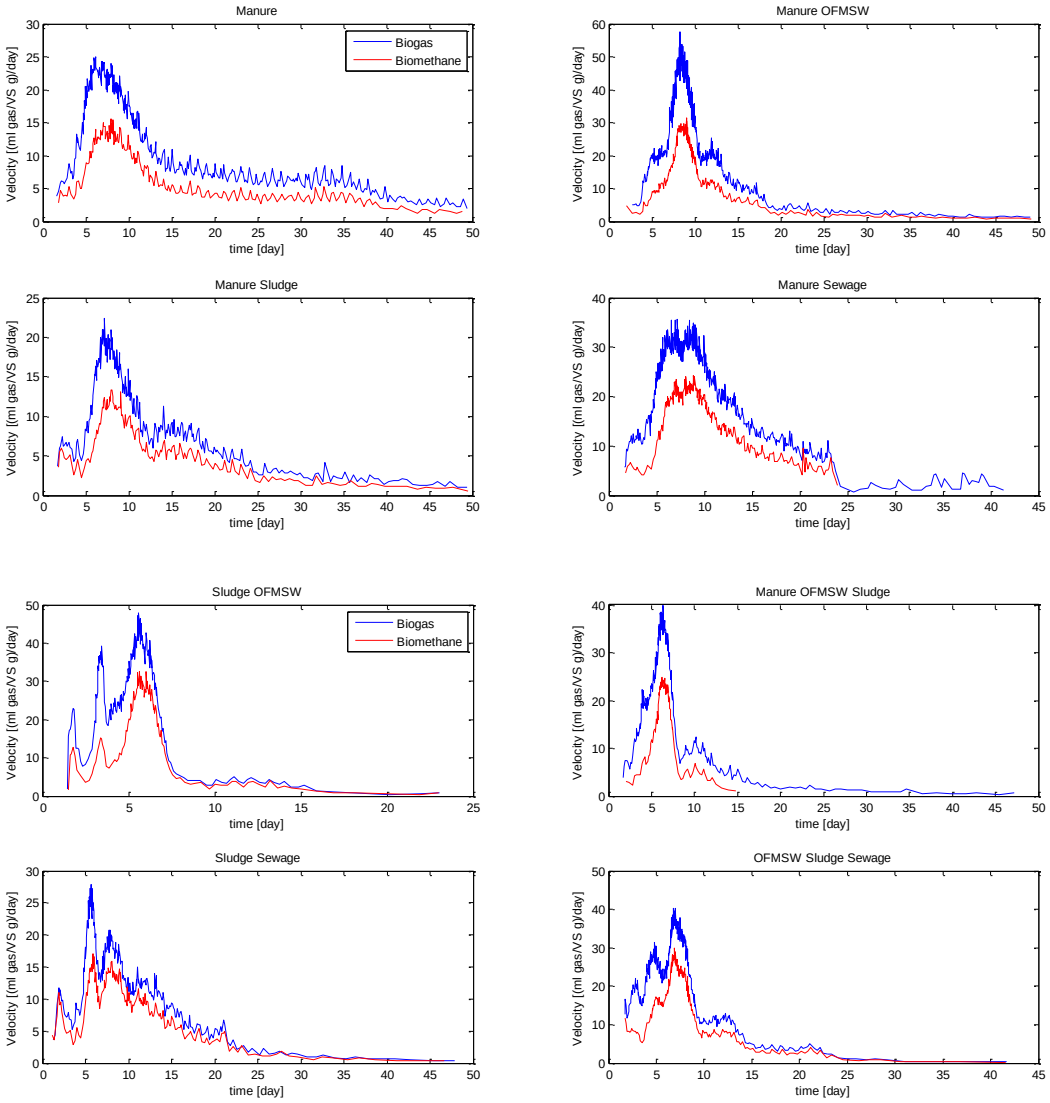

Figure 3.23: Biogas and biomethane production rate with shuffled cells

This trend can better highlighted from the following graph (fig. 24), relative to production of the sole biogas

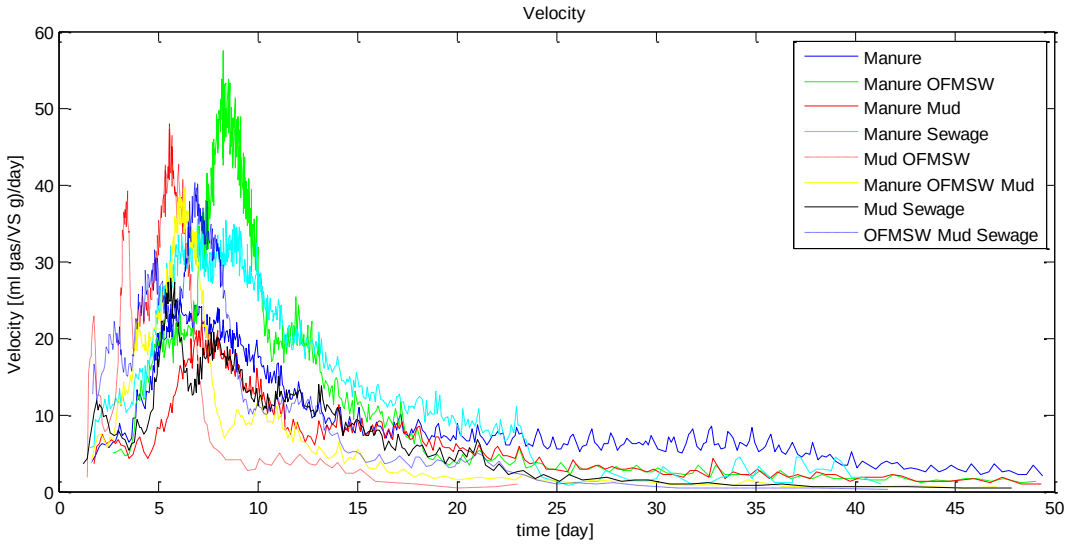

Figure 3.24: Biogas production rate with shuffled cells

The substrate which reaches the greater speed of production is the Manure-OFMSW mixture (sample B), that reaches the peak at about 9 days since the departure. Immediately after the Manure-Mud substrate (sample C) is characterized by the highest cumulative production, it reached the peak velocity around the sixth day. The interesting observation, however, is that after the 10th day, all the samples show a clear decrease in the production speed that remain substantially constant after the 20th day.

3.5 - TEST WITH A LARGE CAPACITY LABORATORY DIGESTER

3.5.1 – Description of the 30 lt digester

For a system closer to the real case of a small digester, a new biodigestion system with 30 lt capacity was realized. This digester is obtained starting from a stainless bin for volatile liquids, which constitutes the biodigestion cell, to which was taken off the bottom. Around this component, six resistors have been arranged.

These resistors were initially actuated by a mechanical relay but, regarding the problems generated in the previous case, it was replaced with a solid-state relay. This relay is controlled by a thermostat, equipped with ~~a~~ thermocouple inserted inside the digester. In this system the thermal bath is not present since the resistors heat the directly digester.

Even this system is equipped with a mixing device that uses, as in the previous case, a pump that picks up the biogas from the upper part of the cell and reinsert it through the bottom by two ducts that begin directly from the lid to limit the holes at the base of the container. The lid consists of a plexiglass plate in which are formed

the holes for the outflow of the biogas and those for the suction and the emission of the recirculation pump. Also this system is fitted with a trap for non-gaseous substances that escapes together with the biogas. The flow measuring device is integrated in the system and consists of two bell gas meters that are used for the measurement of the biogas and, after the capture of carbon dioxide, of biomethane respectively. With regard to the capture system, it is always a bubbling type, consisting of a glass cell, identical to those described previously and placed in the same compartment where the meters are housed. The electronic system, using of switch voltage regulators supplies both a variable voltage 3-20V to power the recirculation pump, a 5 V and 24 V for the bell as meters and a 12 V for the microcontroller .

Also in this case the microcontroller has only the task of saving the data and downloading them to an appropriate Internet site located inside it. There is also a display that shows in real time the number of cycles completed by the meters and the voltage supply of the pump. The actual 30 lt digestion system is shown in the following figure (fig. 25).

Figure 3.25: Real 30 liters digester

3.5.2 – Test results

The test with the 30 lt digester was launched simultaneously with the previous test. In particular, the system was filled with about 20 kg of Manure-Mud mixture, mainly to avoid the complex operation of pH correction it could be difficult to fulfill on such large volumes. The table with the values of TS% and VS% is showed below (tab. 3.3)

Substrate	TS%	VS%	VS/TS%
Manure-Mud (1:1)	16.80	12.20	72.62

Table 3.3: Substrated used with TS% and VS%

The results obtained, in terms of cubic centimeters of gas per gram of initial volatile substance, are reported in the following chart (fig. 26).

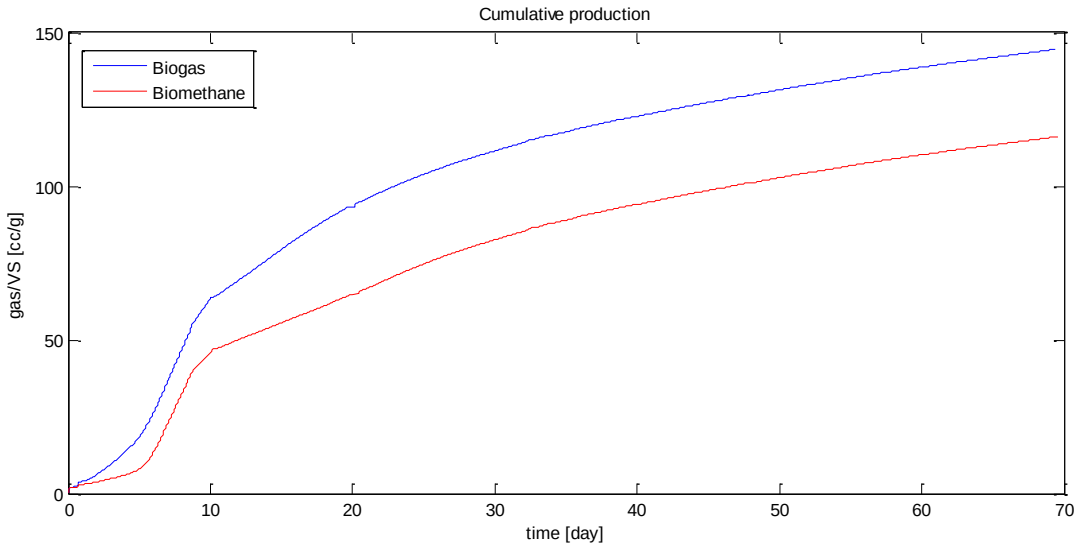

Figure 3.26: Cumulative production of biogas and biomethane

As seen in the cases with small cells, the production of biogas is divided into two phases, the first lasts until about the tenth day and is characterized by rapid growth of the biogas produced, The second starts from the tenth day to the end and it is characterized by a progressive slowing down of the production. The performances are quite scarce, around 150 cc biogas / g (VS), and 100 cc biomethane / g (VS), similar to those that occurred in the 2 lt cell containing the same mixture. The percentage of carbon dioxide contained in the biogas is instead slightly lower, at around 20%;

3.6 – CONCLUSIONS

As regards to the biodigestion systems, tests have shown the capacity of our Laboratory made systems to produce and measure without particular problems, after various improvements, biogas and biomethane generated from various substrates. About the substrates, the tests showed that it is possible to obtain yields of biogas as those expected in times of the order of ten days with thermophilic processes and agitation of the organic matter. From these tests it is also found that Mud represent the best substrate for triggering the methanogenesis process, while Manure and Sewage gave lower results. The OFMSW substrate seems to be capable of providing the increased amount of organic matter which consequently ensures an increased biogas production. Unfortunately, the insertion of such substrate may result in lowering of pH to a level that stops the biodigestion process. For this reason, it is necessary to neutralize the pH of the mixture containing OFMSW. The tests have also shown that seemingly identical samples or similar, can have very different behaviors. Finally, it is useful to point up that the shuffling allows almost to halve the time of the biogas production.

Chapter 4

AMMONIA CAPTURE

4.1 – INTRODUCTION

Among the available technologies for CO_2 capture and sequestration, the ammonia scrubbing process provides the advantage of a high CO_2 loading capacity and absorption efficiency with no absorbent degradation [D2-D12]. However, this process still suffers from an unfavorable energy balance due to NH_3 loss and regeneration and for the cost related to its separation from concentrated CO_2 that must be compressed and sequestered [D1]. One of the current objectives is to lower the process costs based on this capture method. About this, some laboratories are developing a new technology of CO_2 capture which combines the necessary CO_2 abatement with the production of commercially valuable products [D13-D15].

Indeed turning carbon dioxide into a feedstock for producing useful commodity chemicals in mild conditions would circumvent most of drawbacks for energy consuming steps of CO_2 desorption, absorbent regeneration and CO_2 transportation and disposal in geological cavities, oceans or elsewhere [D1].

At this regard, it is necessary to observe that the ammonia at room temperature and pressure is in gaseous form, however, a process involving the use of ammonia directly in this state is scarcely suited for practical carbon capture applications because the low reaction rate of CO_2 and gaseous NH_3 causes a severe loss of NH_3 and consequently a scarce CO_2 removal efficiency, accompanied by the difficult removal of solid ammonium carbamate from the absorbent reactor [D16]. Instead the situation improves greatly when using the ammonia dissolved in a liquid. In fact some studies [D17] reported that the absorption of CO_2 by NH_3 aqueous solutions, in a wide range of concentrations (from 0.85 to 10.0 M) occurs with high efficiency and load capacity producing solutions of bicarbonate, carbonate and carbamate ammonium salts. The ratio of produced salts depends on the amount of absorbed CO_2 with respect to the concentration of the free NH_3 in solution, but the important observation is that all these salts have some industrial applications. Indeed ammonium bicarbonate is a marketable product with a variety of uses (it has been used as a nitrogen fertilizer in China for over 30 years [D18]. Recently, the use of both ammonium bicarbonate and carbamate has been patented for the recovery of freshwater from seawater by forward osmosis [D19]. Ammonium carbamate has been also tested as a NH_3

generator for NOx abatement in diesel exhaust gases, to recover manganese from steel-making plant slag and for soil remediation [D20]. Moreover, ammonium carbamate is the intermediate for the production of urea, the most used nitrogen fertilizer worldwide (more than 108 metric tons per year) [D21]. In fact, the commercial production of urea is based on similar patented processes where carbon dioxide is reacted with excess of ammonia (NH_3 /CO_2 molar ratio up to 4) at high temperature (450–500 K) and pressure (150–250 bar) to produce ammonium carbamate, which is then dehydrated to urea.

The production of urea could be then already an application to which allocate the salts of ammonium carbamate that are produced by the capture of carbon dioxide into ammonia. It is useful to observe that the ammonium salts have a high solubility in water, however, by using liquid solutions in which ammonia is dissolved such as (i.e. ethanol–water, anhydrous ethanol, 1-propanol and N,N'-dimethylformamide (DMF) [D1] etc.) it is possible to obtain the crystallization of salts which can be easily separated from the solution. This would allow an efficient recycle of the unreacted scrubbing solution, providing the basis for the realization of a continuous process.

4.2 - REDUCING AMMONIA VOLATILIZATION

Among the most interesting processes, the carbon dioxide capture into ammonia is the only one to be really taken into consideration due to the easy retrieval of raw material and its simplicity of application to the biodigestion systems present in our laboratory. Like all chemical capture systems, also ammonia capture provides high load capacity and efficiencies in the capture of carbon dioxide, but in also involves high management costs. This process is very energy consuming mainly for the cost of cooling equipment, required to limit the loss of ammonia through volatilization, but also for the costs related to the regeneration of the substance. Regarding the latter aspect, the capability to produce, in the form of precipitated, molecules with a certain commercial interest, constitutes an excellent prospect as it allow the complete elimination of the regeneration costs, since this operation is no longer necessary. The other issue to be addressed, remains the expense containment due to ammonia refrigeration. In the course of this work this aspect is faced through the assessment of alternatives and economic solutions. To reduce the volatilization of a gas dissolved in a liquid the classical approach, alternative to refrigeration, is to create a certain overpressure on this liquid. However, even this choice is difficult to apply, especially in the specific case of biogas, since it means to establish an internal overpressure into the biodigester and also require the use of valves and pressure control systems which would complicate the system, a negative condition especially in small plants. A very simple solution, potentially able to limit volatilization of ammonia by means of a slight overpressure, and without any increase in the system complexity, is to cover the liquid with a less dense and immiscible substance, so that it can float above. Classic cooking oil was chosen as a liquid

substance to validate this hypothesis because it's readily available, biodegradable and equipped with almost all the features necessary for this purpose. In particular, after having completed the preliminary tests to get familiar with the oil covered ammonia capture, we can conclude that this technique will be applied to the biodigestion cells available in the laboratory in order to obtain a test very close to real case of use.

4.3 - PRELIMINARY TESTS

To verify and quantify the ability of a layer of oil to limit the volatilization of the ammonia dissolved in the underlying liquid, it's was performed a comparison test between a cell with the presence of oil and one without it. For this purpose two 750 ml cells were prepared. Both were filled with 500 ml of concentrated ammonia 30% and only at one were added 200 ml of cooking oil. After taking note of the liquid level and the weight of the cells, they were allowed to stand under a fume hood for 10 days. The situation at the beginning and end of the 10 days is shown in the next figure (fig 4.1).

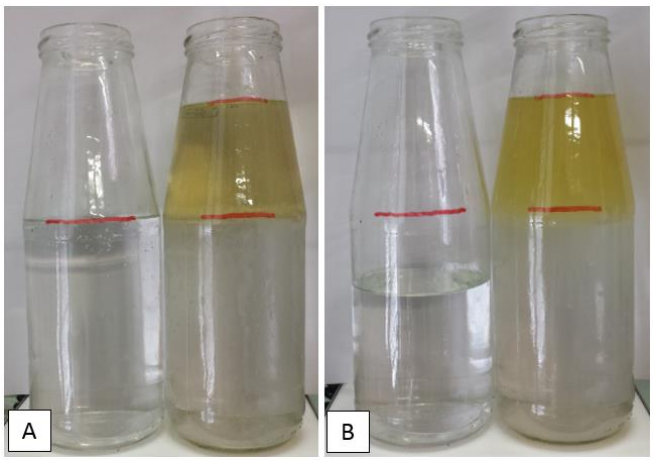

Figure 4.1: Effect of oil coverage in reducing ammonia volatilization. A: initial situation. B: situation after 10 days

It is possible to notice, after a period of 10 days, the evaporation of part of the liquid is evident in the cell without the oil coverage, while this phenomenon seems not to be present in the cell with oil coverage. Such visual evidence was also confirmed by the analysis of the cell weight. In particular, the oil-free cell showed a weight reduction of 30%, while the other one only of 0.2%.

Since the results on the ability of the coverage oil to limit evaporation of the ammonia have been successful, further tests closest to the real situation were conducted. As previously mentioned, the carbonates formed

following the carbon capture into ammonia are very soluble in water. To promote their precipitation (a fundamental operation to allow their easy removal), the literature allows to choose between various solvents [D1]. Among these, ethanol was chosen for its easy availability. This solvent, according to the literature [D1] should be present in a concentration of around 80% to ensure a complete precipitation of the carbonates. Unfortunately, the ethanol is lighter than oil, so this implies limit in its use.

Fortunately, the ethanol is fully miscible in water and, immiscible in oil so a compromise solution can be found. This solution consists in mixing water, in which the ammonia is dissolved, and ethanol so that the overall density of this mixture is still higher than that of the oil. After that various tests were carried out. it was seen that the mixing value can reach more than 60%, (however, is a advisable not to exceed 50%). This is because although at 60% the separation between the oil and the mixture is evident, this optical distinction among fluids with different density takes a long time to be recover, when disturbances occur, like passage of the gas bubbles, This happens in a much less evident way if the ethanol do not exceed the 50% of in the mixture. A new test was carried out to verify if even with a relatively low concentration of ethanol a good formation of precipitate is maintained and also to test the ammonia capture performance. Typically, the synthetic biogas is used in the laboratory for these tests is obtained by mixing 50% carbon dioxide and 50% methane. In the case under discussion, simple compressed air was used in place of methane, because it was not available. The gas flow was composed of a mixture of 50% carbon dioxide (purity 99.5) and 50% of compressed air; the pressure of these gases has been set to 2 bar. The gases passed through two independent mechanical flowmeters to adjust the flow rate and then mixed and sent to the test system. This test system used two capture cells, one of ammonia and one of sodium hydroxide and three bell gas meters. In particular the first bell gas meter measured the incoming gas flow to the ammonia capture cell, the second gas meter the outgoing gas flow from the previous cell and also the input gas to the sodium hydroxide capture cell and the last gas meter the outlet gas from the system. In particular the sodium hydroxide capture cell contained 500 ml of NaOH 25% w/w. Due to the high concentration of the reagent, the reaction with carbon dioxide is favored so all the CO_2 that passing in this cell is captured.

Regarding the ammonia capture cell, it was filled with 500 ml of 2 M solution of ammonia formed from a 50% by volume of water where the ammonia gas and a 50% ethanol were dissolved. The 500 ml of ammonia solution were then covered with 200 ml of cooking oil. The test was conducted for a period of about 5 hours using two flow rates; the initial rate was about 1 lt/h which at half of the test, was increased by acting in equal measure on the flow meters, up to a flow rate of 4 lt/h. The outline of this second preliminary test and an image of the real system are shown in the following figures (fig. 4.2 – 4.3).

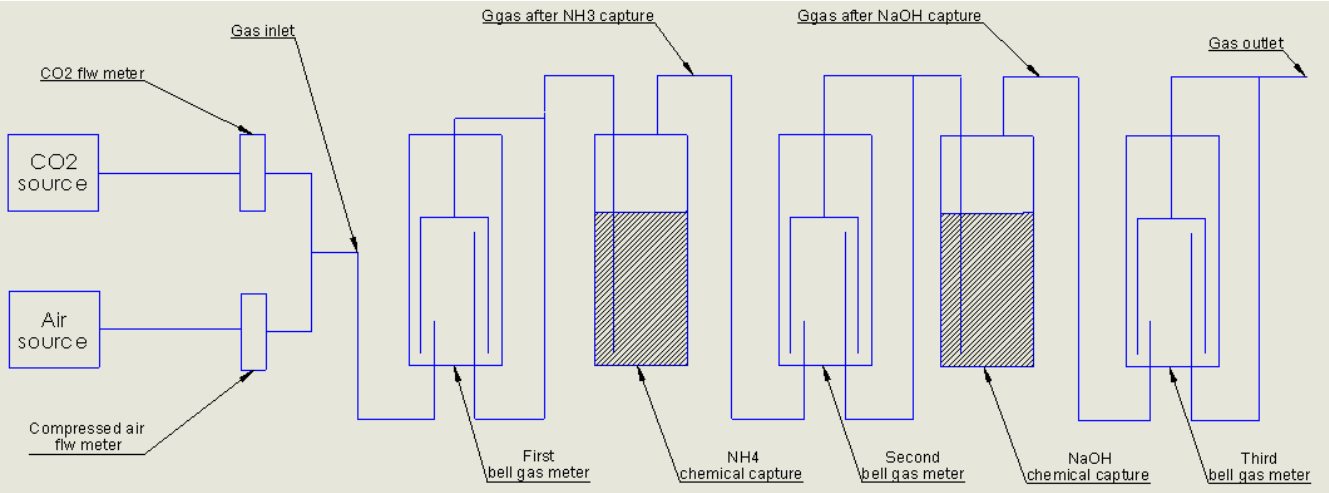

Figure 4.2: Apparatus scheme for the preliminary tests

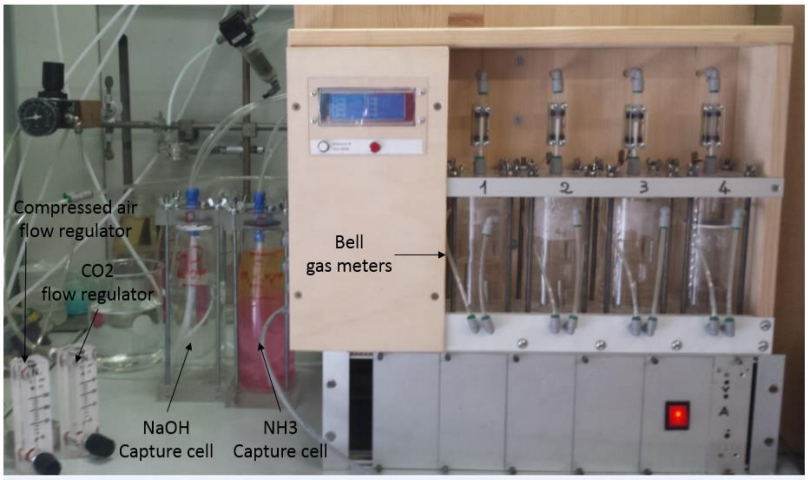

Figure 4.3: Real system

The results have shown that the volume of output gas from the system was exactly half the volume of the input gas. For this reason we can conclude that all the carbon dioxide inserted has been captured by the two cells. With reference to the performance of the ammonia capture cell, as long as the flow rates is kept low, the ammonia was able to capture almost all of the carbon dioxide that crossed it. In fact, the gas flow coming out from this cell was the same that flowed out of the sodium hydroxide capture cell. When the gas flow rate was increased, the ammonia capture cell was no longer able to capture all the carbon dioxide that crossed it and the flow coming out from this cell was greater than that came out of the sodium hydroxide capture cell. In particular, calculations showed that, with the system described, the ammonia capture cell was able to capture the 98.5% of carbon dioxide until the flow rate was maintained at 1 lt/h, but then declined to 70% when the flow rate went up to 4 lt/h. The results discussed are shown in the next figure (fig. 4.4)

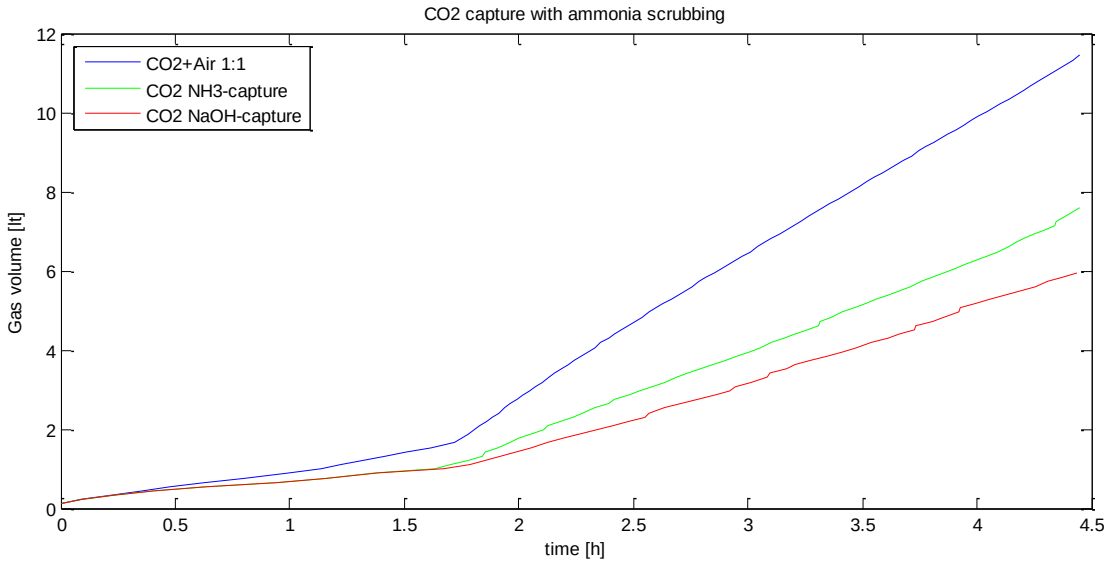

Figure 4.4: Gas volume trend through the different meters

The last consideration concerns the presence of precipitates. In fact, by observing the bottom of the ammonia capture cell, it was evident the presence of a solid precipitate. To check if the result would have been better with a concentration of ethanol of 80%, it was decided to withdraw part of the mixture, constituted for 50% of ethanol and to add an additional solvent to bring the concentration to 80%. After leaving to stand for a few hours, it was observed that the bottom of the container showed no presence of a solid precipitate.

The presence and absence of precipitate on the bottom of the containers can be seen in the following figure (fig. 4.5)

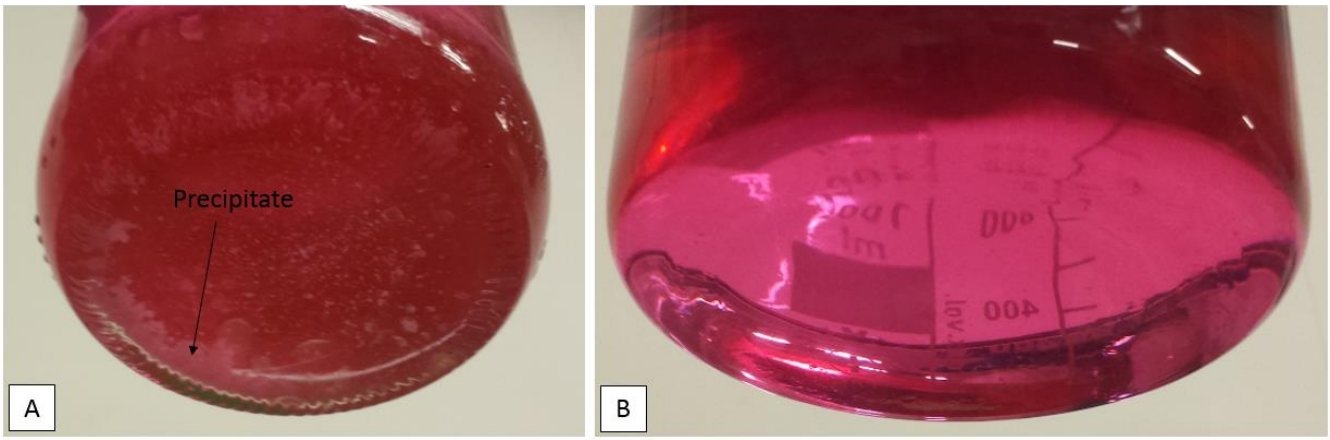

Figure 4.5: A: evidence of precipitate in the ammonia cell with 50% ethanol; B: absence of precipitate in ammonia cell with 80% ethanol

4.4 - TESTS WITH REAL BIOGAS

After the positive results of the preliminary tests, a new experiment including ammonia capture cells applied to the real biogas has been prepared. The objectives of this experiment were basically two. The first was to verify the capacity of the oil substrate to limit the ammonia volatilization for a long period of time (from two weeks to two months) as is the case of refrigeration. The second was to verify if actually an ethanol concentration of 50% was sufficient to ensure the complete formation of the solid precipitate. For the first goal, the reduction in weights between a cell with oil and a cell, with the same concentration of ammonia of the previous one but empty of oil and cooled to about 0 °C, would have been compared. For the second goal, the weight of the precipitate, recovered from an oil covered cell with 50% ethanol would been compared with that of a cell, in identical concentration of ammonia, but with 80% ethanol without oil coverage and cooled to about 0 °C.
Practically as biogas source was used 5 cells from 2 liter, all filled with 600 g of Mud-OFMSW 1:1 mixture which, in general, has always given the greater productions in the shortest time. As in the preliminary test, this system involved the use of two capture cells for line, one of ammonia with various other substances and one of sodium hydroxide, which ensures the complete capture of the carbon dioxide. Three bell gas meter with the task of measuring respectively the incoming gas flow, the gas flow after the first capture cell and gas flow after the second capture cell, are present for each line. The following table (tab. 4.1) shows the concentrations and the substances present in the ammonia cells and if they are chilled or not.

Concentration of ammonia [M]	Concentration of ethanol [% v/v]	Oil coverage	Cooling to 0 ° C
15 M	0%	present	absent
2 M	50%	present	absent
15 M	0%	absent	present
2 M	50%	absent	present
2 M	80%	absent	present

Table 4.1: Substances present in the ammonia cells and their operating conditions

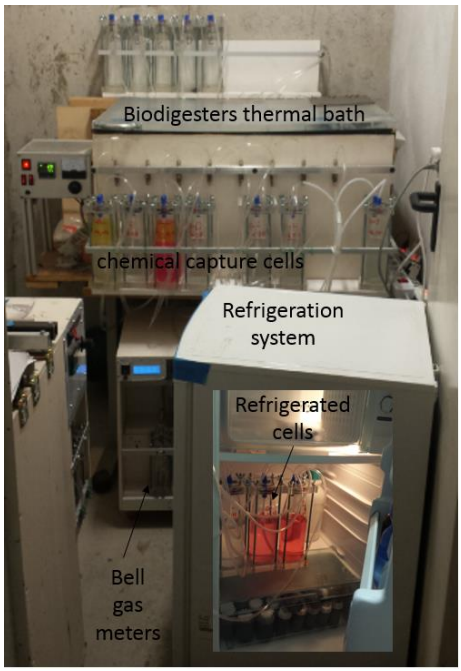

Figure 4.6: Real system

Unfortunately, in preparing the first charge, an error was occurred in the pH adjustment (this is a critical step for substrates rich in OFMSW) in fact after five days, still no cell started to produce biogas and the measure of the substrate pH showed a very low value (about 4.5). We were then obliged to empty the cells and make a new charge of digesters, being very careful to pH adjustment, so this time it seemed to go better. Unfortunately, because of the bad odors caused by the two phases of the digester loading, occurred within a few days, so the entire system has been turned off before having sufficient data to make any considerations. Unfortunately we were not able to find a suitable environment to avoid the presence of bad odors, so this was the last experiment with real cells of biodigestion.

4.5 - CONCLUSIONS

Among the systems of carbon dioxide capture, the chemical capture devices offer the best performance in terms of easiness of application and load capacity. Unfortunately, these techniques suffer from large costs caused mainly by expensive processes required by the material regeneration. For this reason, the current research on chemical capture systems is addressed to ensure that the carbon dioxide capture takes place through the formation of compounds characterized by a commercial value. Among the various chemical capture systems, ammonia capture has been investigated mainly for the ease of chemical component retrieving and for its

implementation simplicity . Additionally, this system seems very interesting since the capture of carbon dioxide takes place through the formation of precipitates of a certain industrial interest, for example the production of urea, which might allow the closure of the carbon dioxide cycle without complex systems for the permanent gas storage; (very compelling problem that is not solved in other techniques). The need to refrigerate the ammonia capture system for limiting the gas volatilization has been overcome by using an oil substrate that, due to its lower density and immiscibility with other liquids present in the capture cell, allows us to form a simple and economic barrier to the gas volatilization, as confirmed by preliminary tests. The experimental tests show also that, the presence of ethanol, useful to favor the precipitation of solid carbonates, can not exceed 50% v/v, since otherwise the mixture with ammonia would become lighter than the oil and should be to overcome it, forming an important amount of precipitate that does not increase in an evident way bringing the ethanol concentration to 80% v/v.

These preliminary tests are not exhaustive and would require tests with real biogas for several weeks in order to have a more complete view of the applicability of the proposed system.

GENERAL CONCLUSIONS

The purpose of this work was to study some simple chemical capture systems used for the sequestration of carbon dioxide present in biogas. We started with building biodigestion systems to be used as a source of biogas. At this early stage the dynamics of biodigestion process were also examined. The preliminary tests with the first small biodigestion system equipped with a manual measurement of the biogas flow rate, through liquid displacement devices, had shown the importance of carrying out either the check or the correction of the substrate pH, which must be brought to neutrality before starting the process.

Late corrections are irrelevant and do not lead to any result in terms of production. In particular, we have seen how the more problematic substrate is OFMSW that at the beginning has a very low pH (around 4). Then the mixtures that contain it must be subjected to a heavy pH correction. Despite these problems, however, OFMSW is the substrate which provides an increased amount of organic substance and the best productions in terms of cubic centimeters per gram of initial volatile substance. From the tests, we then observed that, among the various substrates, Mud provides the best bacterial population.

Where Mud is present, the production process triggers more quickly, while manure and slurry show lower performance. The mixture that gives the most increased production is a combination OFMSW-Mud, where OFMSW provides organic matter and Mud provides the bacterial population. Preliminary tests showed also the need to dispose of an automatic measuring system of the biogas flow rate. As commercial solutions could not be applied because they are too expensive or have too limited flow range, we have developed our gas meters. These meters are all based on the principle of liquid displacement, which works as a gas barrier and were called bell, drop and spoon gas meter, on the basis of the different type of mobile element used. These meters were tested with three different calibration systems, some built specifically and based respectively on the principle of thermal mass flow sensing, constant differential pressure and mechanical displacement. The results showed that all three gas meters are able to monitor precisely the production from anaerobic digestors at a laboratory scale. In fact, they have all an error that does not exceed +/-2%, and a quite linear behavior versus the flow rate, with the exception of the drop gas-meter for which a normal calibration curve of volume vs flow-rate is needed. However this gas-meter shows a very low operating pressure, which is a few millimeters of water, while in other instruments it amounts to few centimeters. Instead, the bell gas-meter presents a greater linearity while the spoon gas-meter presents a greater simplicity of construction. As regards the calibration systems, all systems have been able to evaluate the performances of the meters. The differential pressure flow has the advantage of the simple construction, but it can generate only a limited range of flow rates; the mass flow controller has

greater accuracy, but it is made with expensive commercial modules; the piston flow generator has the greatest range of measurement among all but it is somehow less accurate, compared with the other two. The bell and drop gas meters, being the most innovative, have been applied to the biodigestion systems. This situation made possible to identify the main problems caused by the external overpressure which still influenced the behavior of the meters and to solve them definitively. The final choice was the application of the bell gas meters to the biodigestion system, it allowed the completion of studies on variables that influence the biogas production.

In particular, we confirmed that the presence of a thermophilic environment and a mixing system allow to reduce drastically the production times. After building a reliable system that can be used as a biogas source and acquiring the knowledge to manage it, we switched to study chemical capture methods. Among these, the method of capture in the ammonia has been selected for its interesting potential, ease of procurement and implementation. The main problem which prevent the application of this technology the cost of ammonia regeneration. However several researchers argue that this problem can be addressed with the production of substances with commercial interest (such as urea), where regeneration is no longer necessary. The tests with ammonia takes place in a refrigerated environment its great volatility. As an alternative to chilling, we have proposed the use of a thick layer of oil which acts as a barrier to ammonia volatilization, but still allows the passage of gas bubbles in a capture whirl system. Despite preliminary tests has been encouraging, the tests with biogas were not carried out for force major reasons (bad smell issued in the environment) that forced the permanent arrest of all digesters in operation.

Acknowledgements

I would like to thank Professor Marco Savini and Professor Marco Villa for allowing me to experimentally study all the phenomena to which I was interested, and for the great support and availability always widely and promptly provided to me during the various activities. I sincerely thank Professor Paolo Nelli for great encouragement, the kind availability and indispensable help always spontaneously and courteously offered during my activities. I would like to thank Prof. Remo Garattini for the great assistance and for the economic support. I wish to thank Architect Fabio Corna for lending of the 3D printer, training and for the kind assistance given in the resolution of various problems. An important thanks goes also to the Engineer Massimo Lorenzi for his great help to solve software errors and inaccuracies in the writing of the various programming codes used in this work. Moreover I thanks Engineer Alessandro Pasta for the contribution to find innovative solutions, Mr. Enzo Biondi, Engineer Daniele Di Marco and Engineer Luca Gritti, for the support to the realization of mechanical components. Generally I like to make my thanks to all the teachers, the technicians, students colleagues and the people who, over the years, I have had the pleasure to know and admire. Finally, I would like to thank the reader for having devoted to me a good part of his time, offering me the privilege of its availability and curiosity.

Bibliography

[I1] KS Lackner. Carbonate chemistry for sequestering carbon fossil. Ann Rev Energy Environ 2002; 27: 193-232

[I2] House KZ, House CH, Shrag DP, Aziz MJ. Electrochemical acceleration of chemical weathering as an energetically feasible approach to mitigating anthropogenic climate change. Environ Sci Technol 2007; 41: 8464-70

[I3] S. Marini, C. Strada, M. Villa, M. Berrettoni, T. Zerlia. How solar energy and electrochemical technologies may help developing countries and the environment. Energy Conversion and Management 87 (2014) 1134-1140

[I4] Yohannes Kiros, Massoud Pirjamali, Martin Bursell. Oxygen reduction electrodes for electrolysis in chlor-alkali cells. Electrochimica Acta 51 (2006) 3346–3350

[A1] Henze, D.K., J.H. Seinfeld, N.L. Ng, J.H. Kroll, T.-M. Fu, D.J. Jacob, and C.L. Heald, 2008: Global modeling of secondary organic aerosol formation from aromatic hydrocarbons: High- vs. low-yield pathways. *Atmos. Chem. Phys.*, **8**, 2405-2420

[A2] Ostrem, K. & Themelis, Nickolas J., 2004. " GREENING WASTE : ANAEROBIC DIGESTION FOR TREATING THE ORGANIC FRACTION OF MUNICIPAL SOLID WA STES" . Available at: http://www.seas.columbia.edu/earth/wtert/sofos/Ostr em_Thesis_final.pdf

[A3] D.J. Batstone, J. Keller, I. Angelidaki, S.V. Kalyuzhnyi, S.G. Pavlostathis, A. Rozzi, W.T.M. Sanders, H. Siegrist and V.A. Vavilin. The IWA Anaerobic Digestion Model No 1 (ADM1). Water Science and Technology Vol 45 No 10 pp 65–73

[A4] Bilitewski**,** Bernd**,** Härdtle**,** Georg**,** Marek**,** Klaus. Waste management. 1997

[A5] Mata-Alvarez. Biomethanization of the organic fraction of municipal solid wastes. 2003 IWA Publishing. Printed by TJ International (Ltd), Padstow, Cornwall, UK

[A6] Verma, S. 2002. Anaerobic digestion of biodegradable organics in municipal solid wastes. M.S. Thesis, Columbia University, New York, NY

[A7] Lettinga G, Rebac S, Zeeman G (2001) Challenge of psychrophilic anaerobic wastewater treatment. Trends Biotechnol 19, 363–70

[A8] Wellinger A, Kaufmann R (1982) Psychrophilic methane generating from pig manure. Process Biochem 17, 26–30

[A9] Salsali, Hamid; Parker, Wayne. Proceedings of the Water Environment Federation, Residuals and Biosolids Management 2004, pp. 106-121(16) (WEF, 2004)

[A10] Persson, Johnsson, Wellinger: IEA Bioenergy Report-Task 37, December 2006.

[A11] Schweigkofler, Niessner: Removal of siloxanes in biogases. J Hazard Mater 2001;83:183–96.

[A12] Deublein, Steinhauser: Biogas from wastes and renewable resources – Wiley-VCH, 2008

[A13] Malpei, Vismara: Biogas da frazioni organiche di rifiuti solidi urbani in miscela con altri substrati – DIIAR, CIC, 2007

[A14] Deublein, Steinhauser: Biogas from wastes and renewable resources – Wiley-VCH, 2008

[A15] Miltner, Makaruk et al: Biogas upgrading for transportation purposes - Vienna University of technology, 2009

[A16] Harasimowicz, Orluk et al: Application of polyimide membranes for biogas purification and enrichement – Warsaw University of Technology, 2007

[A17] Bounaceur, Favre, Roizard: Biogas, membrane and carbon dioxide capture – Nancy Université, 2008

[A18] Deng, Hagg: Techno-economic evaluation of biogas upgrading process using CO2 facilitated transport membrane - Norwegian University of Science and Technology, 2009

[A19] Stern, Charati et al: Performance of a bench-scale membrane pilot plant for the upgrading of biogas in a wastewater treatment plant - Syracuse University USA, 1998

[A20] http://www.chemicalogic.com/Documents/co2_phase_diagram.pdf

[A21] Wellinger, Lindberg: Biogas upgrading and utilization - IEA Bioenergy Report-Task 24

[A22] Appels, Baeyens, Dewil: Siloxane removal from biosolids by peroxidation - Energy Convers Manage 2008;

[A23] Niall MacDowell, Nick Florin, Antoine Buchard, Jason Hallett, Amparo Galindo, George Jackson, Claire S. Adjiman, Charlotte K. Williams, Nilay Shah and Paul Fennell. An overview of CO 2 capture technologies. Published on 01 September 2010 on http://pubs.rsc.org | doi:10.1039/C004106H

[A24] Accettola, Guebitz, Schoeftner: Siloxane removal from biogas by biofiltration: biodegradation studies - Springer-Verlag 2008

[A25] Feasibility study – Biogas upgrading and grid injection in the Fraser Valley, British Columbia – Electrigaz, 2008

[A26] http://www.wtert.eu/default.asp?Menue=13&ShowDok=12

[A27] Marco Frigerio. 2009. Biometano per autotrazione: tecnologie, analisi energetica, analisi economica e calcolo degli incentivi. Available at: https://www.politesi.polimi.it/bitstream/10589/253/1/2010_05_Frigerio.pdf

[A28] J. de Hullu, J.I.W. Maassen, P.A. van Meel, S. Shazad, J.M.P. Vaessen. Comparing different biogasupgrading techniques. Eindhoven University of Technology, July 3, 2008

[A29] Dr. Alfons Schulte-Schulze Berndt, Intelligent Utilization of Biogas -Upgrading and Adding to the Grid, Jonköping, May 2006

[A30] Deanna M. D'Alessandro, Berend Smit, and Jeffrey R. Long. Carbon Dioxide Capture: Prospects for New Materials. Angew. Chem. Int. Ed. 2010, 49, 6058 – 6082

[A31] BC Innovation Council (2008). Feasibility Study – Biogas upgrading and grid injection in the Fraser Valley, British Columbia

[A32] Benjaminsson, J. and Anders D. (2008). "Upggradering av biogas. Kusrsuskompendium"

[B1] W.L. Hochfeld, Growth & Synthesis: Fermenters, Bioreactors & Biomolecular Synthesizers, 1st ed., Interpharm Press, Buffalo Grove, 1994, p. 79.

[B2] J. Liu, G. Olsson, B. Mattiasson, A volumetric meter for monitoring of low gas flow rate from laboratory-scale biogas reactors, Sensors and Actuators B: Chemical 97 (2004) 369–372.

[B3] http://www.smcusa.com.

[B4] http://www.abb.us/instrumentation.

[B5] http://www.aerzenusa.com.

[B6] http://www.clarksol.com.

[B7] http://www.dwyer-inst.com.

[B8] http://www.koboldusa.com.

[B9] L. Van den Berg, C.P. Lentz, R.J. Athey, E.A. Rooke, Assessment of methanogenic activity in anaerobic digestion. Apparatus and method, Biotechnol. Bioeng. 16 (1974) 1459–1469.

[B10] R. Moletta, G. Albagnac, A gas meter for low rates of gas flow: application to methane fermentation, Biotechnol. Lett. 4 (1982) 319–322.

[B11] U. Dissing, T.G.I. Ling, B. Mattiasson, Monitoring of methanogenic processes with an immobilized mixed culture in combination with a gas-flow meter, Anal. Chim. Acta 163 (1984) 127–133.

[B12] M.D. Erdman, S.R. Delwiche, Low-cost digital counting interface for fermentation gas measurement, Biotechnol. Bioeng. 27 (1985) 569–571.

[B13] M. Glauser, B. Jenni, M. Aragno, An inexpensive, automatic gas meter for laboratory-scale methane digesters and other gas-evolving systems, J. Microbiol. Meth. 2 (1984) 159–164.

[B14] A. Beaubien, C. Jolicoeur, J.F. Alary, Automated high sensitivity gas metering system for biological processes, Biotechnol. Bioeng. 32 (1988) 105–109.

[B15] B.K. Nilsson, I. Bjerle, H.T. Karlsson, A simple meter with zero pressure drop for gas flows, Ind. Eng. Chem. Res. 27 (1988) 1553–1555.

[B16] I. Angelidaki, L. Ellegaard, B.K. Ahring, Compact automated displacement gas metering system for measurement of low gas rates from laboratory fermentors, Biotechnol. Bioeng. 39 (1992) 351–353.

[B17] Jing Liu, Gustaf Olsson, Bo Mattiasson, A volumetric meter for monitoring of low gas flow rate from laboratory-scale biogas reactors. Elsevier Sensors and Actuators B 97 (2004) 369–372

[B18] R.O. Cadena Pereda, E.M. Rivera Munoz, G. Herrera Ruiz, Automatic volumetric gas flow meter for monitoring biogas production from laboratory-scale anaerobic digester. Elsevier Sensors and Actuators B 147 (2010) 10–14

[B19] Noel Bignell, Yong Moon Choi, Volumetric positive-displacement gas flow standard. Elsevier Flow Measurement and Instrumentation 12 (2001) 245–251

[B20] A. Martínez-Sibaja, A. Alvarado-Lassman, C.M. Astorga-Zaragoza, M. Adam-Medina, R. Posada-Gómez, J.P. Rodríguez-Jarquin, Volumetric gas meter for laboratory-scale anaerobic bioreactors. Elsevier Measurement 44 (2011) 1801–1805

[B21] Tamás Tauber, Brigitta Berta, Zsolt Szabó, József Kovács, Károly Márialigeti, Erika M. Tóth, A simple and novel volumetric method to metre low gas flows from laboratory-scale bioreactors and its application on laboratory sludge digesters. Appl Microbiol Biotechnol (2011) 90:1453 – 1461

[B22] BS ISO 1598 5:2004 Plastics - Determination of the ultimate anaerobic

biodegradation and disintegration under high-solids anaerobic-digestion conditions - Method by analysis of released biogas.

[B23] Guidance on monitoring MBT and other pre-treatment processes for the landfill allowances schemes (England and Wales), The Environment Agency, UK.

[B24] M. Glauser, B. Jenni, M. Aragno, An inexpensive, automatic gas meter for laboratory-scale methane digesters and other gas-evolving systems, Journal of Microbiological Methods 2 (1984) 159–164.

[B25] CHEN Pan-pan, CHENG Jia, WANG Wen-lin, SHEN Wen-xin, XIE Dai-liang, Design and Uncertainty Evaluation of the Tiny Gas Flow Calibrator. International Conference on Information Sciences, Machinery, Materials and Energy (ICISMME 2015)

[B26] Robert F. Berg, Stuart A. Tison, Two Primary Standards for Low Flows of Gases. J. Res. Natl. Inst. Stand. Technol. 109, 435-450 (2004)

[B27] Paul D. Levine, A new approach to gas flow calibration. Elsevier, Measurement 43 (2010) 1644–1648

[B28] http://www.bronkhorst.com/en/products/theory/thermal_mass_flow_measurement/

[B29] Datasheet F-201CV Mass Flow Controller for Gases

[B30] http://www.keller-druck.com/picts/pdf/engl/33xe.pdf

[B31] https://www.bosch-sensortec.com/bst/products/all_products/bmp180

[B32] http://www.keller-druck.com/home_e/paprod_e/41x_e.asp

[D1] Francesco Barzagli, Fabrizio Maniand Maurizio Peruzzini, From greenhouse gas to feedstock: formation of ammonium carbamate from CO2 and $_{NH3}$ in organic solvents and its catalytic conversion into urea under mild conditions, Green Chem, 2011, 13, 1267

[D2] J. E. Pelke, P. J. Concannon, D. B. Manley and B. E. Poling, Ind. Eng. Chem. Res., 1992, 31, 2209–2215;

[D3] A.-C. Yeh and H. Bai, Sci. Total Environ., 1999, 228, 121–133;

[D4] K. Thomsen and P. Rasmussen, Chem. Eng. Sci., 1999, 54, 1787–1802;

[D5] A. Perez-Salado Kamps, R. Sing, B. Rumpf and G. Maurer, J. Chem. Eng. Data, 2000, 45, 796–809;

[D6] H. P. Huang, Y. Shi, W. Li and S. G. Chang, Energy Fuels, 2001, 15, 263– 268;

[D7] H. Huang, S.-G. Chang and T. Dorchak, Energy Fuels, 2002, 16, 904–910; J.-W. Lee and R.-F. Li, Energy Convers. Manage., 2003, 44, 1535–1546;

[D8] A. Corti and L. Lombardi, Int. J. Thermodynam., 2004, 7, 173–181;

[D9] Y.-F. Diao, X.-Y. Zheng, B.-S. He, C.-H. Chen and X.-C. Xu, Energy Convers. Manage., 2004, 45, 2283–2296;

[D10] K. P. Resnik, J. T. Yeh and H. W. Pennline, Int. J. Environ. Techol. Manage., 2004, 4, 89–104;

[D11] L. Meng, S. Burris, H. Bui and W.-P. Pan, Anal. Chem., 2005, 77, 5947–5952; J. T. Yeh, K. P. Resnik, K. Rygle and H. W. Pennline, Fuel Process. Technol., 2005, 86, 1533–1546;

[D12] V. Darde, K. Thomsen, W. J. M. van Well and E. H. Stenby, Int. J. Greenhouse Gas Control, 2010, 4, 131–136.

[D13] F. Mani, M. Peruzzini and P. Stoppioni, IT FI2007A000199, 2007;

[D14] F. Mani, M. Peruzzini and P. Stoppioni, Energy Fuels, 2008, 22, 1714–1719;

[D15] F. Mani, M. Peruzzini and F. Barzagli, ChemSusChem, 2008, 1, 228–235.

[D16] X. Li, E. Hagaman, C. Tsouris and J. W. Lee, Energy Fuels, 2003, 17, 69–74.

[D17] F. Mani, M. Peruzzini and P. Stoppioni, Green Chem., 2006, 8, 995–1000.

[D18] C.-K. Li and R.-Y. Chen, Fert. Res., 1980, 1, 125–136.

[D19] R. L. McGinnis, US 2001-265745 20010201; J. R. McCutcheon, R. L. McGinnis and M. Elimelech, Desalination, 2005, 174, 1–11.

[D20] I. H. Warren and E. A. Devuyst, Trans. Soc. Mining Eng., 1972, 252, 388–391; N. Breuer, C. Schiller and C. Oediger, FR 2003-5411 20030502.

[D21] Urea: 2010 World Market Outlook and Forecast (http://www.mcgroup.co.uk/).