FINAL PUBLISHABLE REPORT

CONTRACT N° : ENK5-CT2001-30004

ACRONYM : E R O B

TITLE : Development of an Improved Energy Recovery of Biogas by Cooling and Removal of Harmful Substances

PROJECT CO-ORDINATOR : Stefan Waerdt
Pro2 Anlagentechnik GmbH
Schmelzerstraße 25
D-47877 Willich

PARTNERS :

- **SME Proposers:**
  - **Pro2 Anlagentechnik GmbH**
  - **Gascogen N.V.-S.A.**
  - **FRUEHAUF Kälte- und Klimaanlagen GmbH**
  - **Roestvaststaal Apparatenfabriek B.V.**
- **RTD Performers:**
  - **Fraunhofer-Institut UMSICHT**
  - **PHYTEC Physikalisch-Technische Anlagen GmbH**

REPORTING PERIOD : FROM 01.01.2002 TO 31.10.2003

PROJECT START DATE : 01.01.2002 DURATION : 22 months

Project funded by the European Community under the 'Energy, Environment and Sustainable Development' Programme (1998-2002)

Publishable synthesis report

Biogas as a product of the microbiological decomposition of biodegradable substances is a renewable energy source and an excellent fuel. Since the first application in the 1970s, its utilisation has grown steadily, encouraged both by environmental pressures and financial incentives. The potential resources and supplies are enormous.

Biogases consist to an essential part of methane from 40 up to 70 %. Therefore the most practical means of utilizing the energy in biogas today is to generate electricity basically in gas engines that drive generators. Unfortunately harmful substances such as organic silicon compounds prevent in many cases the utilization of the gas. Deposits of silicon dioxide cause damages in the combustion chambers of the gas engines with the result of high maintenance costs. This is often the reason why no degassing and collecting systems are installed to avoid the escape of gases from the landfills into the atmosphere. If these gases can be made available by a reliable and economical operating system, then several effects can be reached simultaneously.

The objective of the project is the development of a new economical process to minimize the problems of harmful trace components and to remove them from biogas by cooling devices before being used in gas engines. This cooling down of the biogas results in a reduction of deposits in the combustion chambers. Damages of the engines will consequently be minimized. It is intended by this new process to prolong the maintenance intervals and the lifetime of the biogas engines up to the corresponding level of natural gas engines. Today the actual lifetime of the critical motor components of the biogas engines is only about 50% compared to the corresponding lifetime of natural gas engines. The reduction of repair work in combination with the prolongation of the engine lifetime will improve the energy recovery of biogas to a very large extent.

Tests on a labscale level have proven that harmful trace components like organic silicon compounds, in particular siloxanes, can partially be condensated and removed from biogas at low temperatures. On the basis of different ways of process design the best adaptation of cooling down the gas has been determined by comparison of different refrigerating systems (compression, absorption, adsorption, etc.), kind of refrigerant, steps of cooling, direct injection of the refrigerant or use of brine coolers, measuring and control devices under consideration of frosting and defrosting of ice as well as costs involved. Different heat exchange systems (plain tubes, spiral tubes, ribs or plate-shaped surfaces) have been analysed under consideration of the required cooling temperatures, the coefficient of heat transmission, the pressure drop, the water content of the gas (ice formation), resistance against corrosion (material to be used, heat conduction), the accessibility for cleaning (draw out heat exchanger) and the costs involved.

Prototypes of model heat exchangers, using finned tubes from stainless steel grades, manufactured by a novel development of Laser-welding technique, have been connected to a laboratory refrigerating plant. On the basis of an adjustable and water saturated air flow the heat exchangers have been tested under variation of dimensions and operating parameters. Heat transfer coefficients as well as freezing and defrosting characteristics of the finned tubes have been examined and determined in a wide range of flow conditions in view of dimensioning the heat exchangers. Heat transfer coefficients up to 185 kJ/m^2hK have been achieved.

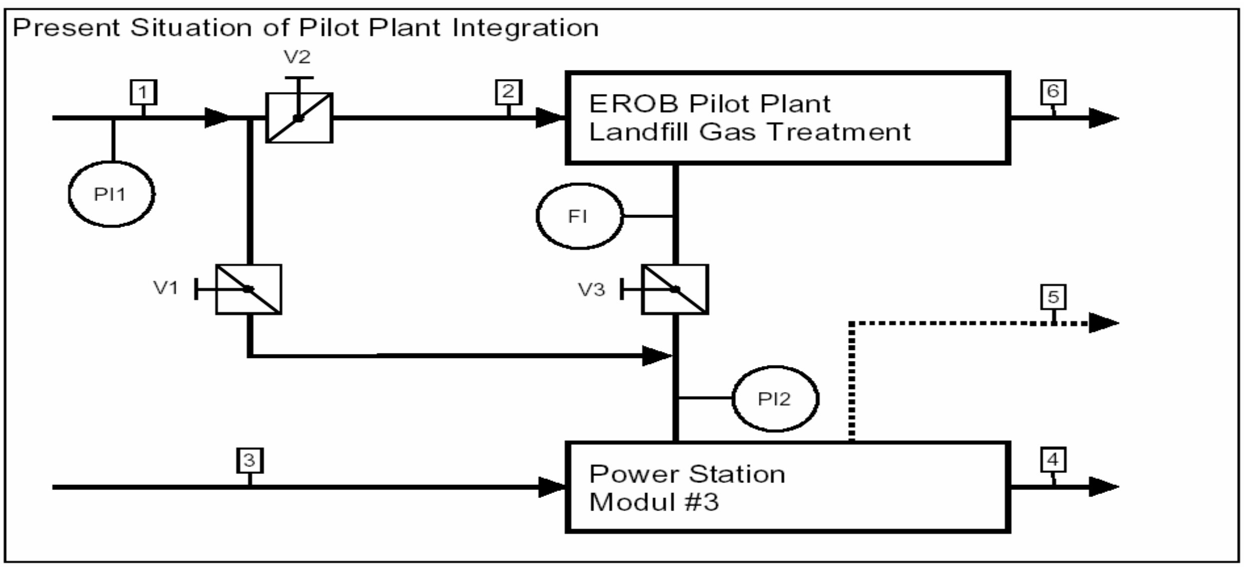
The determination of the basic technical requirements of the process has produced the following substantial results:

- Cooling down of the gas in two stages independent from each other

- Stage 1: Cooling down of the gas from about 35°C to about 5°C by a cold water scrubbing process
- Stage 2: Cooling down of the gas from about 5°C to about –10°C by alternately operated heat exchangers

In a further step an assembled laboratory setup with model plant components has been manufactured, delivered on site, connected to a landfill gas system and tested under different operating conditions. Compared to the intended production process the cooling down of the landfill gas during the test runs on site has been carried out in one stage and without the cold water washing process of stage 1. This additional washing of the landfill gas may contribute to an extra effect in the reduction of harmful substances. Promising results of the process and the tests on site have been analysed at a landfill gas temperature of –11°C. Reductions of 40 % and 80 % respectively have been achieved for the main siloxane compounds, octamethyltetracyclosiloxane (D4) and decamethylpentasiloxane (D5). No or lower reductions have been found for the less existing other volatile compounds of the siloxane family (MDM, D3, M2), trimethylsilanol as well as haloginated compounds.

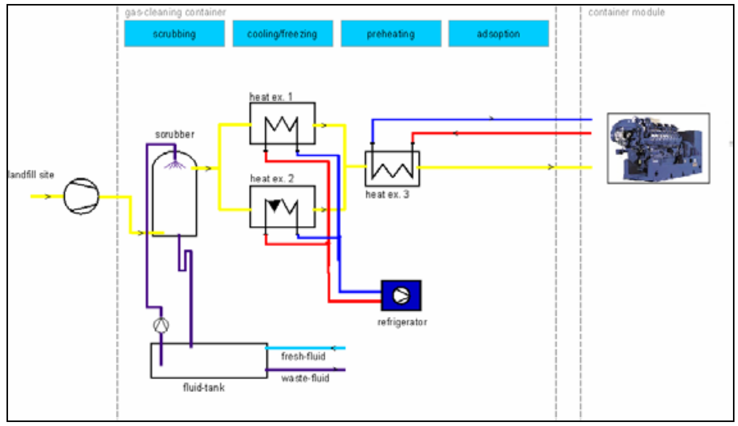
On the basis of first promising results the engineering and manufacture of a pilot plant with a throughput of 200 Nm³ biogas per hour has been realised. The pilot plant has been completely assembled and mounted in a standard 20 feet container. After extensive functional tests at the works the plant has been transported to a landfill in the vicinity of Cologne and connected to a gas engine in operation.



The Waste Disposal Centre Leppe, about 40 kms east of Cologne opened in December 1982. The terrain encloses an area of 45 hectares and has a deposit volume of 10 million cubic meters. The average gas composition of the untreated landfill gas is shown in the following:

Oxygen	**Vol. %**	**1,3**
Nitrogen	**Vol. %**	**10,6**
Methane	**Vol. %**	**49,1**
Carbon dioxide	**Vol. %**	**39,0**
Hydrogen sulphide	**mg/m³**	**3100**
Total silicon content	**mg/m³**	**28,2**

A problem of the location is the total silicon content of organic compounds that is higher than the warranty limit of the engine supplier fixed at 10 mg/m^3_{CH4}.



In stage 1 the gas is cooled down to about +5°C, in stage 2 down to about –10°C. Before entering the combustion engine in the power station the gas is warmed up again to about +5°C by a heat exchanger provided with hot water. All main functions of plant operation can be tele-serviced.

During the first test runs it became evident that this idea of gas supply to the pilot plant does not fit to the operating demands of reliability and reproduction. A smooth operation of the pilot plant necessitates a reliable control of gas flow in connection with a higher level of gas volume flow rate. An additional relatively small compressor unit will be installed in the supply pipe of the pilot plant. A flow meter will be mounted in the outlet pipe and adjusted to a desired value up to 200 m^3/h. Deviations from this desired value will be compensated by a frequency transformer resulting in the speed control of the compressor motor.

In the test run of the pilot plant, under non reproducing conditions up to now, the total silicon content of the organic compounds has been analysed and found to be reduced by about 33 percent by weight. After conversion of the pilot plant further tests will follow on the basis of a continuous operation and under optimum conditions. There is no doubt that better results will be achieved in the near future.

Samples of condensate taken at the outlet of stage 2 of the pilot plant have been analysed. Among other values a significant content of silicon of 184 and 263 mg per litre respectively has been found. As the usual content of silicon in landfill seeping water is in the order of 2 mg per litre this silicon content of the stage 2 obviously derives from condensated organic silicon compounds.

Compared to the currently applied systems the advantages of this development are the following:

- Less costs of investment and operation, higher reliability of the process by a simplified technology
- No expensive auxiliary substances like absorbents or adsorbents
- Better efficiency of the engine by water removal and cooled fuel

Furthermore the question of analysing the quantity of organic silicon compounds in the biogas has been investigated. Today there exists no standardized method. The critical topic is the way of sampling on the landfill site or the sewage plant. It has to be easy and safe in handling and should be done by the service guys on site without a special training. The following analytical methods are researched:

- Adsorption, solvent extraction:
  The sampling was done with sorbent tubes filled with Porapak Q (50/80). Using a vacuum pump 10 l of biogas were enriched of the adsorbent material, which was spiked with hexamethyldisiloxane as an internal standard. After sampling the sorbent was extracted with hexane using a ultrasonic bath. The solvent was subjected to GC/MS determination. The evaluation was done by means of the internal standard.
- Adsorption, thermodesorption:
  The silicon compounds were collected on adsorption traps as described in method 1. Afterwards the analytes were desorbed from the adsorbent agent by thermal desorption and determined by GC/MS. In detail this was done through an increase in temperature of the sorbent tubes, and then the silicon compounds were cryofocused. Subsequently through a rapid increase in temperature the vapours were carried to the analytical column under carrier gas flow.
- Gasbag sampling:
  In contrast to the methods 1 and 2 no solid adsorbent sampling was used here. The biogas was gathered in 2,5 l-gas bags. After this, the gas was directly injected in the GC/MS-system.
- Solvent absorption:
  The solvent absorption method was not used here. Brief, for accumulation the biogas is conducted through divers washing flask. Because of the impractical shipment by mail, this method was not applied.

The best method to determine organic silicon compounds in biogas has been found to be the adsorption of solid sorbents with subsequent thermodesorption or gas bag sampling combined with gas chromatography - massspectrometry.

Process calculations and simulations were carried out with Aspen Plus. Aspen Plus is a process-engineering tool for the design and steady-state simulation and optimisation of process plants. It allows prediction of the behaviour of a process using basic engineering relationships such as mass and energy balances, phase and chemical equilibrium, and reaction kinetics. Given reliable thermodynamic data, realistic operation conditions and the rigorous Aspen Plus equipment models, actual plant behaviour can be simulated. As a further result it has been found that simulation models like Aspen Plus in combination with UNIFAC are not suitable for the prediction of real removal efficiencies.