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Dry Ice and Liquefied Biomethane — Two Products from Biogas for an Energetic and Economical Upgrading of Biogas Plants

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Abstract: In the planned process biogas will be cleaned and subsequently transformed into liquid biomethane (LBM) and solid carbon dioxide (dry ice). Thus biogas is transformed in an energy rich storable and easily transportable energy carrier.

An important precondition for the process is an individually adapted gas cleaning system, which separates impurities (e.g., NH_3, H_2O, H_2S etc.) from the biogas. Subsequently the pre-cleaned biogas (now consisting mainly of CO_2 and CH_4) is fed into the liquefaction unit. Core pieces of this system are two heat exchangers connected in series with operating temperatures of about 200 and 120 Kelvin. The first heat exchanger works as a precooler and might also be used as a back-up for freezing out impurities. Triggered by the deep temperatures reached in the second heat-exchanger, the CO_2 flocculates. A purity of 99.9% CH_4 in the liquid phase could be guaranteed, as only CH_4 has its dew-point at the operating temperature of 111 Kelvin. The low pressure and the absence of toxic chemicals are further benefits of the specific process.

A high-quality cryogenic and liquid energy source arises by cutting off CO_2 and by the liquefaction of CH_4. This energy source has an upper heating value of 5.87 kWh/l at a temperature of 111 K (biogas: 0.0055 kWh/l at 300 K). By increasing the volumetric energy by the factor of 1000 (compared to biogas), transportation to highly efficient energy plants becomes reasonable.

Goals of the project are to proof the feasibility of a decentralized long-term storage of large energy amounts, to show alternative ways in using transformed biogas and an efficient usage of the energy content of the raw gas. Additional marketing possibilities of dry ice and LBM could ensure an economical operation outside the German EEG (Renewable energies act).

Key words: biogas, biomethane, liquid biomethane, carbon dioxide, dry ice, CO_2 separation, renewable energy, upgrading, cryogenics, energy storage

1. Introduction

About 25.8% of Germany's electrical power supply originates from renewable energies [1]. The major part of this energy derives from fluctuating sources like wind and solar power plants. For the future energy demand, it is desirable to store this seasonally produced energy from summer for winter. One possible solution is liquid biomethane derived from biogas plants. The liquefaction increases the energy density of biogas by the factor of 1000 (Fig. 1) and creates a fully suitable energy carrier [2].

In the planned process, biogas will be transformed into liquid biomethane (LBM) and solid carbon dioxide (dry ice). By cooling down to -162°C, it is possible to obtain one liter of LBM and about 1 kg of dry ice from

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one cubic meter of biogas (Fig. 1). Dry ice can only be obtained at low pressures up to about 0.5 MPa; however the gas conditioning works best with atmospheric pressure.

$$1\ \mathrm{m}^3_{\mathrm{biogas}} \rightarrow 550\ \mathrm{l}_{CH_4} \sim 1\ \mathrm{l}_{\mathrm{LBM}}$$

$$1\ \mathrm{m}^3_{\mathrm{biogas}} \rightarrow 450\ \mathrm{l}_{CO_2} \sim 1\ \mathrm{kg}_{CO_2\mathrm{solid}}$$

Fig. 1 Volumetric Energy Density of Biogas and Liquefied Biomethane (LBM) [2]

It is necessary to find a constant working and cost-effective process. The research focus is on the heat exchanger, especially its working parameters and conditions (i.e., surface, temperatures or pressure). Trace gases such as ammoniac (NH_3) or hydrogen sulfide (H_2S) may have negative effects on the cooling process and the energy efficiency. To avoid major efforts it is necessary to remove or reduce trace gases within the biogas in advance. Furthermore, it is of great importance to establish an adapted and reliable gas cleaning process, because high purity without undesirable trace gases is a requirement for a successful marketing of the dry ice. This must be done in accordance with the general process requirements as well as with individual parameters as the feed materials used in the biogas plant. An optimization of the operational parameters will lead to cost saving in the gas cleaning process.

1.1 Liquefied Biomethane (LBM)

LBM resembles liquefied natural gas (LNG). LBM and LNG feature a similar composition of components but reaching a higher purity of LBM (LBM: > 99% CH_4 vs. LNG: > 75% CH_4 [3]). Its high purity enables the use for industrial raw materials and for chemical processes. Due to the reduced volume, LBM is a flexible, portable, and long term storable energy carrier. The transportation of LNG and LBM is state of the art. E.g., easily transporting of about 14,000 liters of LNG and LBM over long distances by truck is possible. LNG and LBM can be stored without significant evaporation losses. For example: In the United States more than 250 LNG/LBM gas stations retain this fuel every day [4]. This common know-how can be used within this study. Due to the good transportability and storage properties, following applications are of interest:

(1) LBM can be used as a feedstock in highly efficient gas and steam power plants and as peak electricity coverage in gas power plants. Thus, biogas can contribute extensively to the demand electricity production by means of renewable energies.

(2) The upper heating value of LBM is approximately 5.8 kWh/l [5]. Therefore, LBM can be used as a substitute for fossil fuels. In the USA over 10,000 buses, vans, garbage trucks and highway tractors are running on LNG and LBM already [4]. Compared to compressed natural gas (CNG) the range can be doubled. Furthermore the emissions compared to conventional diesel engines can be significantly reduced: As a matter of fact, particulate material can be reduced by 100%. E.g., the automotive companies “Mercedes” and “Volvo” already advertised explicitly the use of LBM within their heavy traffic vehicles [6].

(3) Farmers are able to produce LBM for their own consumption.

A main aim of the study is to develop a process that is cost-efficient even for small sized biogas plants. Due to a close meshed gas grid in Central Europe, larger plants with a gas production rate of more than 250-500 m^3/h often have the possibility to feed their biogas in the natural gas grid. For small plants the established gas conditioning technologies are far too expensive. Especially for small sized plants with modular construction, LBM is suitable, which should be expandable in modular construction. A treatment plant may convert about 25 m^3 biogas per hour, which is equivalent to an electrical output of 50 kW_{el}. The limiting factor of the maximum flow rate is the performance of the cryocooler.

1.2 Solid Carbon Dioxide

Dry ice is just a byproduct of the biogas treatment. The whole process is economically dependent on the successful marketing of this product yet. Dry ice has a higher market value than liquid carbon dioxide and the main advantage of dry ice is its “residue-free evaporation”. Thanks to these properties:

(1) Dry ice can be used as a substitute for conventional ice in food storing application. Food cooled by dry ice does not take any dilution and packaging damage. Further advantages are a higher cooling efficiency (by a factor of 2.5), e.g., it is used in planes for cooling food due to its reduced weight and additional antibacterial storing characteristics.

(2) Materials such as polymers and metals can be blasted by dry ice. E.g., blasting of engine blocks without any disturbing residues.

2. Methods

Fig. 2 exhibits a flow chart planned for a large-scale industrial process. It is divided into four steps: In the **first step,** the crude biogas is converted into an almost pure mixture of methane and carbon dioxide. The gas cleaning process starts with a gross desulphurization (H_2S) by ferric chloride already within the fermenter. This is followed by ammoniac removal (gas washing bottle) and fine desulphurization (activated carbon columns). The gas is dried by a gas cooler (7°C) and additional us of a silica gel column and/or zeolites.

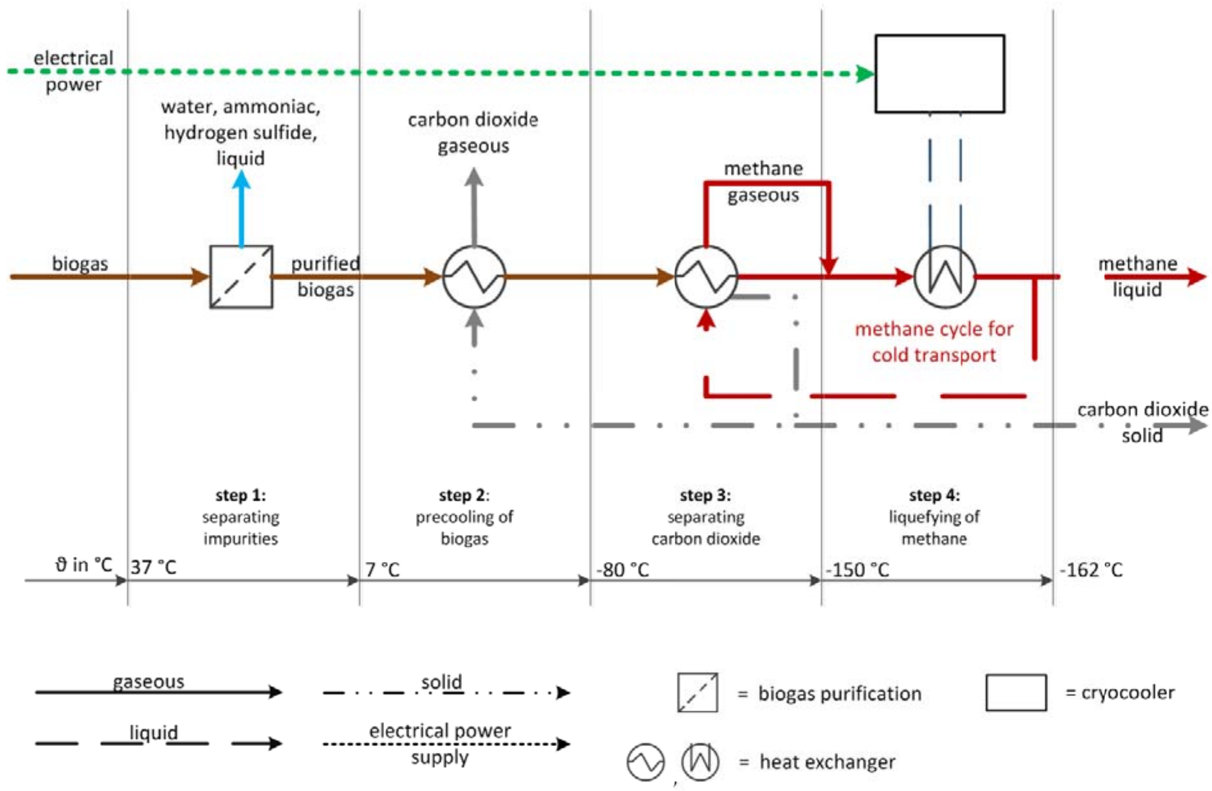

Fig. 2 Flow Chart for the Liquefaction of Biogas in Large Scale Industrial Processes

In the **second step,** the biogas is precooled by a heat exchanger. That also works as a backup unit by freezing out of possible impurities. Especially for components such as H_2O or NH_3, this process works very well. An operation of the heat exchanger with dry ice dissolved in alcohol (i.e., ethanol ore methanol) is theoretically possible. Approximately 20% of the resulting dry ice is required for pre-cooling. In this step the gas temperature reaches approximately -80°C. Methane (CH_4) and carbon dioxide (CO_2) are separated in the **third step**: CO_2 is specifically flocculated from the gas stream by a further reduction of the temperature, accomplished by another heat exchanger. This heat exchanger is the core of the purification system. Dry ice can be removed at the base of the heat exchanger setup.

The remaining pure methane has to be liquefied in **step four** at a temperature of -150°C: This liquefaction unit is a standard component. A partial flow of the liquefied CH_4 is returned to the second heat exchanger. By evaporation of the CH_4, enough energy is provided for the CO_2 to freeze out. Together with the purified CH_4, the evaporated CH_4 is liquefied again. This is also known as boil of gas, boil of chiller, or boil of cooling machine. With the liquid methane cooling a stable process with constant process conditions is guaranteed.

3. Challenges and Difficulties

3.1 Gas Cleaning

Depending on the used substrate, an individual gas cleaning process is essential for a stable process, due to different trace gas contents. On one hand, impurities can freeze on the surface of the heat exchanger. On the other hand, they can lead to a degradation of the energy balance due to longer residence times in the process.

3.2 Quality of Dry Ice

A main challenge for the gas cleaning process is the dry ice quality. Only if the requirements of the food industry [7] can be fulfilled, a successful marketing of the dry ice is possible. Due to the intersection point of the vapour pressure curves of CO_2 and H_2S, even smallest remaining amounts of H_2S in the cleaned gas will be integrated into the dry ice during the cooling process. As H_2S is highly toxic and its human odor threshold is very low [9], the gas cleaning process must lead to a nearly total separation of H_2S.

3.3 Separation of Carbon Dioxide and Methane

CO_2 resublimates by cooling down below temperatures of -78.5°C. The heat exchanger for resublimation is called two-phase heat exchanger and works from gaseous to solid state. Following scenarios can occur: The dry ice falls to the bottom and can be removed or the CO_2 freezes inside of the heat exchanger, which would lead to process termination.

3.4 Energy Balancing

In the laboratory plant, thermal losses should be as low as possible. Therefore, the system isolation could do by a high vacuum surrounding the freezing unit. High vacuum means a pressure of < 10^{-10} MPa. The vacuum must remain constant during the experimental period. Thus the energy balances reveal representative results.

3.5 Low Temperatures

Methane liquefies at a temperature of about -162°C. This temperature is not available in common system technologies of biogas plants. Therefore, special cryogenic techniques and materials are needed to enable a stable process with such low temperatures at depressurized working conditions.

4. Results and Discussion

As described above, a reliable removal and detection of H_2S and NH_3 is important. The challenge is here that the H_2S measurement methodologies for a range below one ppm are difficult to handle, especially, if online-results are required. It turned out that a combination of direct analytical methods (*Dräger* tubes and electro-chemical sensor) combined with offline-measurements (gas chromatography) allow a reliable data recording. Therefore, a mutual validation of H_2S analysis methods is possible. For gas chromatographic analysis, the dried gas samples were stored inside aluminium cans. Sampling and processing requires cautious handling and are not suitable for the daily routine on biogas plants.

For both trace gases, H_2S and NH_3, the complete removal via activated carbon is possible, but it is hard to estimate the breakthrough of the columns: An online measurement of H_2S in the required accuracy is not available and a premature replacement of the activated carbon is economically undesired. Therefore, it is of great importance to save the H_2S capacity of the activated carbon and simultaneously determine the right moment for its replacement. To lower the activated carbon consumption, rough purification steps were installed upstream. Different activated carbon types should be used to optimize the system in a physical and an economical point of view. Therefore it is also necessary to fit the operating conditions for a maximized H_2S absorption. An example for test results of an activated carbon type under different humidity conditions illustrates the dependence on physical parameters (Fig. 3). The Black columns show the cleaned gas volume (in l), white dots represent the H_2S concentration in the gas after breakthrough (in ppm). The dashed columns show the H_2S absorption (in mg) of a tested activated carbon type depending on the relative humidity (r.H.) of the biogas.

For operation a continuous process is needed. The gas-solid heat exchanger is not allowed to ice up or freeze. Therefore, it is important that the CO_2 forms snow (low density) instead of ice (high density). The density of the resulting dry ice can be influenced by various factors such as flow rate, percentage of CO_2 in the gas, test duration and temperature difference. These were also the conclusions derived in previous experiments 1997 (Cryogenics Institute in Dresden [8]).

$$\rho_{CO_2} = 1191 + 57.65w + 21.25\psi_{CO_2} + 3.40\tau - 13.67\Delta T_{GS} \quad (1)$$

As seen in Equation (1): On one hand, rising the flow rate or the content of CO_2 as well as the duration of the experiment is leading to an increased density of dry ice. On the other hand, a higher temperature difference between the in and out coming gas will reduce the dry ice density, which favours the formation of snow.

To affect the formation of snow, the surface coating of the heat exchanger is subject to experimental investigations. Coatings of the inner heat exchanger wall can be composed of various materials such as gold, silver, nano coatings of glass and plastic particles, Teflon, ceramic, or simple electro polish. Passive materials that do not allow chemisorptionas, e.g., graphite or exfoliated graphite were also under consideration. In a simple laboratory experiment, liquid N_2 is filled into a tube and gaseous CO_2 flows around the outer wall of the tube: The process of snow accumulation can be recorded visually over the duration of the experiment.

If this approach will not succeed, other tests with ultrasonic or piezo crystals will be performed. Ultrasonic technology may hinder CO_2 to get into contact with the surface of the heat exchanger. Piezo crystals are used to remove the snow on vibration at periodic intervals. Fig. 4 shows an experiment where the snow formation of CO_2 was analyzed on stainless steel by flow regulation.

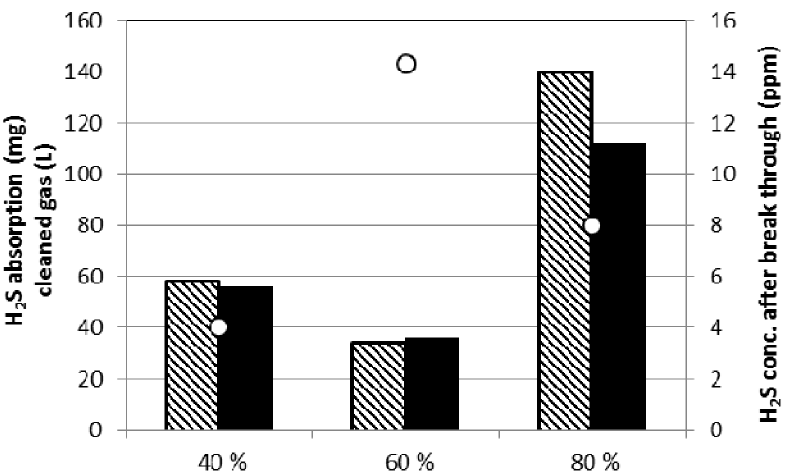

Fig. 3 H_2S Absorption (in mg) of a Tested Activated Carbon Type

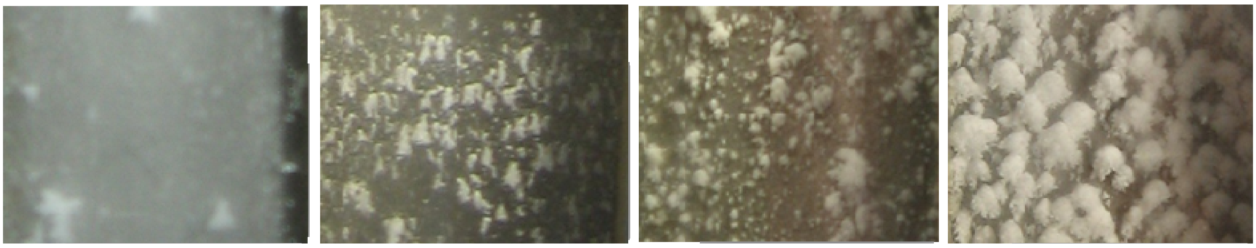

Fig. 4 CO_2 Snow Formation on Stainless Steel Monitored over the Test Period

The vapor pressure curves of the components contained in the biogas are intended to be examined more closely. In general, the interaction of the different gas components must be ensured. Further investigations are aim at the solubility and behavior of the gases during the cooling process. Predicted amounts of the required energy for the biogas conversion must be confirmed by experiments. In order to set up the energy balance, it is necessary to prove how much energy is actually required for an experimental conversion. It is expected that two cubic meters of biogas can be liquefied by converting one cubic meter of biogas into electrical power in a combined heat and power (CHP) plant. In other words: Approximately one kilowatt hour of electricity is needed to produce one liter of LBM and 1 kg dry ice.

5. Conclusion

Small biogas plants that use manure, dung and other agricultural residues are ecologically favorable. These plants would normally provide a power of about 50 kW_{el} and they perfectly fit for the designed processing modules. A case study: Analogous to a milk driver, who is passing by every day to get the milk, a truck picks up LBM (liquefied biomethane) once a week as well as for dry ice: Which can be picked up two or three times a week. The uncomplicated transport of LBM and dry ice is state of the art, even for long distances. This allows a wide range of applications (Fig. 5). High purity CO_2 can be used for cooling food or for surface treatment. LBM can be stored for several months in insulated tanks. In this way a seasonal storage from large energy amounts is possible. LBM can be used as a substitute for fossil fuels or as high-purity industrial pipe material. Furthermore, it can be used for power and heat generation with coupled refrigeration due to the storability is possible. This technique deserves to be further investigated and to be brought up to its market potential.

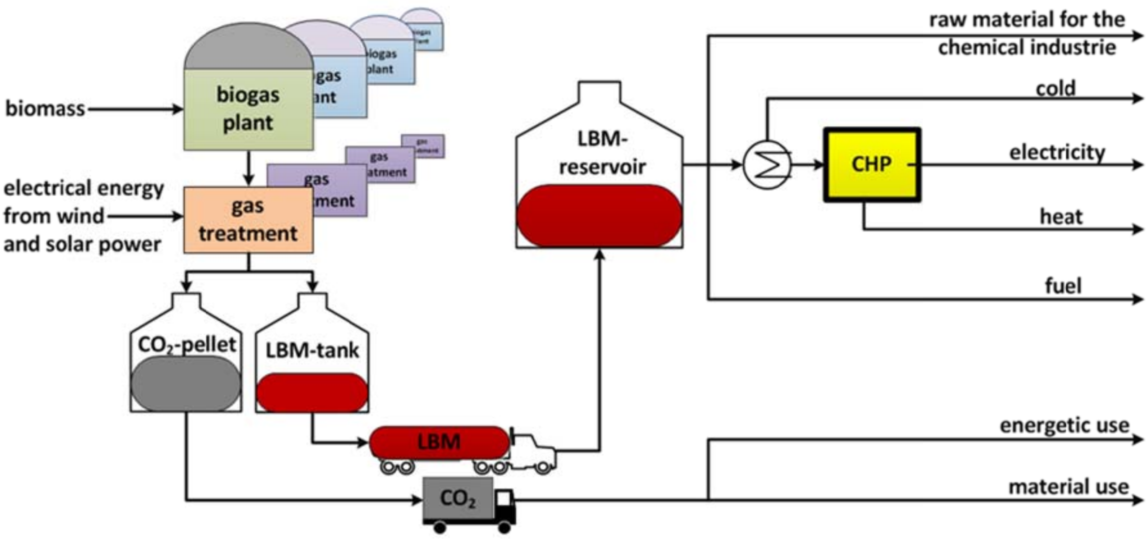

Fig. 5 Possible Scheme for the Application Range of LBM and Dry Ice [10]

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