PRESSURELESS CRYOGENIC CONVERSION OF BIOGAS INTO LIQUEFIED BIOMETHANE AND SOLID CARBON DIOXIDE

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ABSTRACT: Biogas consists of about 50 to 65 Vol.-% methane CH_4 and 50-35 Vol.-% carbon dioxide CO_2. The calorific value of biogas is therefore significantly lower than natural gas (about 36 MJ/Nm³) with 18 to 23 MJ/ Nm³. Therefore biogas for long-term storage (weeks to months) is not suitable. In the presented treatment process biogas is largely freed from water vapor and trace gases (H_2S, NH_3) and transferred by a cryogenic separation process into solid carbon dioxide (dry ice) and liquid biomethane. The cryogenic pressureless separation process based on three heat exchangers: In the first step the pre-purified biogas is cleaned at 193 K (-80 °C) of H_2S and NH_3 residues. Subsequently, the gaseous carbon dioxide is transferred by desublimation at 123 K (-150 °C) into dry ice snow. The methane contained in the residual gas is transferred at 111 K (-162 °C) into liquid biomethane. The condensation of gaseous methane to liquid methane reduces the volume to 1/600 of its original volume and creates liquid biomethane with a calorific value of 21 MJ / liter (5,9 kWh/l). Such biomethane is long-term storable and can be used as a CO_2-neutral substitute of LNG as fuel.

Key words: biogas, liquid biofuel, liquefaction

1 INTRODUCTION

The construction and operation of biogas plants in Germany is supported by a feed-in tariff for electricity of renewable sources (Renewable Energy Act) for a period of 20 years since 2000 [1]. This resulted in an installation of currently of 8928 biogas plants with a total electrical power of 4177 MW in 2015 [2].

Therefore, the biogas plants will drop out of the feed-in-tariff assured by the Renewable Energy Act from 2020 onwards and enter the “free energy market”. Thus, it is very likely that operators are confronted with the decision to shut down their plants, if they cannot find an alternative successful business model.

In addition to the electricity market, the gas market provides an alternative way for the marketing of the produced biogas. Approximately 164 biogas plants in Germany supplied biomethane into the German natural gas grid in 2014 [3]. A prerequisite is an access to the gas grid which cannot be implemented easily (or only at high expenses), especially in many smaller biogas plants in rural areas.

Up to now, there is no real alternative for smaller biogas plants (50…100 kW electrical power) apart from feeding into the national grid. Biogas could only be short term stored in the fermenter, secondary fermenter and repository (up to a few days). In addition, it has a low heating value with 5...6 kWh per standard cubic meter.

In cooperation between Finsterwalder Umwelttechnik GmbH, University of Applied Sciences Weihenstephan-Triesdorf and University of Applied Sciences Landshut a concept and laboratory installation was developed, which can separate Biogas into liquefied biomethane (LBM) and solid carbon dioxide (dry ice).

1.1 Concept

Fig. 1 displays a scheme of the developed procedure. The raw biogas from the fermenter is purified of trace gases such as ammonia (NH_3), hydrogen sulfide (H_2S) and water vapor. In the following cryogenic separation process, the purified biogas (Methane CH_4 and Carbon dioxide CO_2 gas mixture) is separated by desublimation into dry ice and condensation leads to liquefied biomethane (LBM) at different temperatures and normal pressure.

The purification of the raw biogas from trace gases and water vapor is studied at the University of Applied Sciences Weihenstephan-Triesdorf. The development of the cryogenic separation process is carried out at the University of Applied Sciences Landshut.

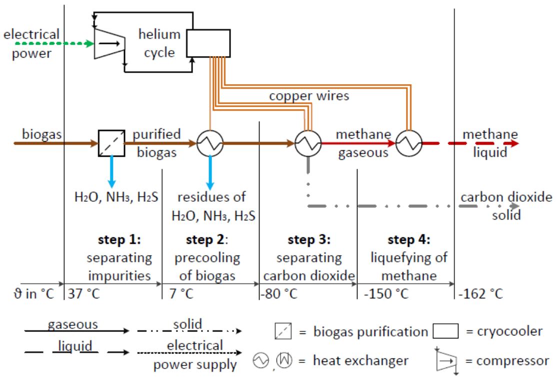

Figure 1: Flow Chart Liquefaction of Biogas

First, the raw biogas from the fermenter is purified from H_2O, H_2S and NH_3 below the limit of detection and thereby cooled down to 7 °C. In the second step, a cooling of the biogas is carried out up to -80 °C. It is possible, to reduce any residual concentrations of trace gases by condensation or freezing out. The resulting binary gas mixture of CO_2 and CH_4 is cooled down to temperatures of -150 °C. The gaseous CO_2 freezes out completely and forms dry ice. In the last step the residual gas is cooled down to temperatures below -162 °C and a condensation of gaseous methane leads to liquid biomethane [4].

1.2 LBM – Renewable alternative to LNG?

LBM (Liquefied Biomethane, often called also LBG Liquid Biogas in the literature) can be produced from biogenic gases such as biogas, sewage gas or landfill gas. The remaining residue after removal of CO_2 consists mainly of CH_4. It is converted mostly by pressure liquefaction to LBM. [5]

LNG (Liquefied natural gas) contains next to the main component CH_4, also higher homologues of alkanes (e.g. ethane, propane) and other gas components such as nitrogen. [6] LBM contains almost exclusively CH_4. By the removal of CO_2 and the liquefaction of CH_4 the volume-related calorific value can be increased by 1000 times. CH_4 has a calorific value of about 5.9 kWh/l at the boiling point (-161.5°C) and a density of 0.4226 kg/l. [7]

LNG is produced for example in Quatar and Australia in large quantities by pressure liquefaction of natural gas (241 mtpa – Million tons per year corresponds to 313 billion m³ gaseous methane). LNG is transported by tanker to Southeast Asia (China, Japan, Taiwan) or Europe. [8] Unlike LNG, which is produced from fossil natural gas, LBM comes from renewable sources and is therefore classified as a CO_2-neutral.

1.3 LBM and LNG as alternative fuels

Positive example of the reduction of carbon dioxide emissions in the transport sector is the increasing use of LNG/LBM during heavy traffic (ships, trucks) worldwide.

Compared to diesel fuels, CO_2 emissions are decreased by approximately 25%, particulate emissions by almost 100%, CO by 80% and NO_x by 90% [8]. Therefore, it can make a significant contribution to the reduction of pollutant emissions in heavy burden traffic.

1.4 Processes for preparing LBM

Neighboring European countries (Sweden, Netherlands) have already developed and operated biogas plants based on organic waste to produce LBM. For example GTS (Gastreatment Services) developed a method (GPP-system), in which pre-cleaned bio gas is produced under pressure and the proportion of CO_2 at low temperatures (-95 °C) is liquefied and deposited. The gaseous CH_4 is converted at -100 °C under pressure into LBM. The plant is in operation in Sundsvall, Sweden [9].

In Sweden Lidköping Biogas operates a biogas processing plant, in which the CO_2 is separated by water scrubbing from the prepurified biogas. The remaining CO_2 in the CH_4 stream is separated by pressure swing adsorption. Subsequently, the liquefaction of the CH_4 occurs at temperatures between -140 °C and -162 °C by use of a Brayton cycle. The energy requirement is about 1 kWh of electrical energy per Nm³ gaseous biomethane [10].

Most treatment methods for the production of LBM require enormous amounts of biogas in order to operate economically. The current lower economical limit is at a flow rate of about 200…250 Nm³ biogas per hour. This corresponds to a biogas plant size with a capacity of about 400...450 kW electrical power.

2 BIOGAS PURIFICATION

There are several possibilities to reduce the H_2S content in the raw biogas [11]. The biological desulphurization process is one of the most common method used in agricultural biogas plants [12-14], thus this is a cost effective and technically easy way to remove the H_2S from the biogas. This process has limited desulphurization effect, it is not possible to get under 10 ppm H_2S values in the raw biogas, the most common values are between 50-100 ppm H_2S [11, 15, 16]. The side effect of this process is that the not used O_2 and N_2 content of the air accumulates in the raw biogas, which can reduce the quality of the product biomethane after the biogas upgrading.

The chemical desulphurization processes have several ways to reduce the H_2S content in the raw biogas [17-20]. The two possibilities are use the chemicals directly as an additive into the biogas production and these are mixed in the digestate in the fermenter. The other way is to use the chemicals in external desulphurization units, where the produced raw biogas flows through the equipment, which is mainly a column, and the desulphurization product acts as an ad- or absorber [20]. Chemical additives used in the fermenter directly are usually Fe^{3+} or Fe^{2+} based, where the Fe^{2+} reacts with the Sulphur content of the produced biogas directly in the digestate [11]. The end product is FeS. Agricultural biogas plants use normally a by-product of the drinking water pretreatment $Fe(OH)_3$, which is pulverized and can be used without serious safety precautions [17]. Another widely used chemical desulphurization product is $FeCl_3$ or $FeCl_2$, which is an acid [16], so the usage occurs higher health risk. Both of the chemical additives can reduce the H_2S content of the raw biogas up to 100 ppm.

The most common fine chemical desulphurization method is the use of activated carbons directly before the biogas utilization [11, 13, 17, 21, 22]. Several cogeneration units to reach the strict exhaust gas directives regarding the formaldehyde values use activated carbons. It is possible to reach lower than 10 ppm H_2S in the product biogas to extend the lifetime of the CHP´s catalyzer [17]. The activated carbons are used in columns as a filling material and act as an absorber. The H_2S content of the raw biogas is bound in the extended surface of the AC [11]. The target H_2S content in the product biogas is under 10 ppm.

The cryogen biogas upgrading process can work with higher H_2S content (even more than 100 ppm) in the raw biogas, but we considered the use of the produced ice as a cooling material in the food industry. To avoid bad smell of the dried ice caused by the H_2S content of the raw biogas, the product biogas must be completely H_2S free. This can be only reached by the use of AC. The product biomethane must reach the minimum quality requirements of the natural gas [14], such impurities as O_2 or N_2 content should be avoided if possible. The biological desulphurization is not recommended because of the air used in the process. Chemical desulphurization was used in the biogas production process as pre-treatment.

Laboratory scale raw biogas purification system

The laboratory raw biogas purification system had three main components: quality and quantity measurement, biogas cooling and the desulphurization units. These parts all had subsystems to ensure an accurate measurement of the biogas purification system to choose a cost effective way of the raw biogas pretreatment to remove the H_2S and other unnecessary components in the biogas which can effect the dried ice quality.

The raw biogas from the continuously stirred 200 liter net volume fermenter was led directly in a gas washing bottle, where the biogas was cooled down from the fermentation temperature to the ambient temperature. The biogas was still saturated with water vapour. The condensate water was removed from the bottle on a regular basis. In the next cooling stage the raw biogas was diverted into a double walled gas washing bottle. The biogas was cooled down to a constant temperature of 288 K with cooling water, which was provided by a Julabo FL300 external cooler. As a next step the biogas was diverted into the desulphurization system. The column filled with the different activated carbons was placed in a water bath with a constant temperature of 290 K, provided by a Julabo EH tempering unit. With this double cooling and heating up method it was possible to ensure constant raw biogas temperature and humidity content of 75% during the trial phase. The amount of the produced and the desulphurized raw biogas was separately measured with two Ritter TG1/5 gas counter. The quality of the raw biogas directly from the fermenter, the cleaned biogas after the desulphurization unit was measured with an Awite AwiFlex series 7gas analyzer. Following biogas components were measured: CH_4, CO_2, O_2, H_2, H_2S. An Ahlborn almemo 2890-9 data logger was used to save the ambient temperature and the biogas humidity content, measured by 2 Ahlborn FHAD 46-7 sensors.

13 different activated carbons were tested in two separate desulphurization test series with two different column volume, with an AC filling weight of 5 and 55 g. In the first stage in a smaller column the ACs were tested for its desulphurization capability without any O_2 content in the raw biogas. In the next phase the ACs were tested in a column size as it is described in the ASTM D6646 - 03(2014) standard [13].

Results

After the first AC testing round only 6 from 13 AC was capable to remove the H_2S completely from the raw biogas. 7 of the ACs were not able to reduce the raw biogas H_2S content under 100 ppm. The other ACs bound capacity had a wide range from 0,003 to 0,066 g H_2S/1 g of AC. Producers of the ACs estimate an average of 20% H_2S bound rate regarding the net weight of the AC [7, 10, 14]. This result shows, that the strict condition of O_2 free raw biogas has a downgrade effect on the desulphurization capacity of the ACs.

Discussion

The desulphurization of the raw biogas under the strict condition without O_2 is possible with several commercial ACs. The results show, that the H_2S bound capacity of the investigated ACs are clearly lower as the producers estimate it. Even if the ASTM D6646 - 03(2014) standard is used for testing the ACs, it is inaccurate, because a mixture of gas contains O_2 is used. The relatively high O_2 content in the test gas is not similar to standard biogas composition and can result better H_2S removal grades. We recommend to develop a standard method to test the ACs for use with biogas, to ensure a better comparison possibility.

3 CRYOGENIC TREATMENT OF PURIFIED BIOGAS

3.1 Design of the laboratory installation

Prior to the implementation of the explained concept (1.1) for the cryogenic gas separation installation following points have to be clarified:

Operation of the system with synthetic biogas (CH_4 / CO_2 mixture) and with pre-purified biogas

As maximum gas flow rate up to 60 standard liters of biogas per hour have been set for the laboratory installation for the cryogenic gas separation. The biogas can be mixed synthetically by mass flow valves of pure CH_4 and CO_2 in any concentration ratio. A 250 liter laboratory biogas fermenter with subsequent fine purification of the gas ensures the supply of purified biogas. The installed gas management system allows the detection of gas quantities and as the measurement of gas pressure and temperature (fig 2).

Figure 2 Gas management system

The control of the gas quantity ratio CH4 / CO2 is carried out by two mass flow valves. For the management of the entire laboratory installation the program LabVIEW® is used with corresponding National Instruments hardware (Compact Rio). Three gas expansion tanks (1 liter, 0.5 liter and 0.25 liter) provide a gas buffer in order to avoid pressure fluctuations and to determine the volumes of the individual components exactly. Prepurified biogas from the digester is transmitted to the valve terminal.

In addition, a supply is realized with nitrogen gas to allow the purging of the laboratory plant with nitrogen and discharge any residual gas amounts of CH_4 from the installation. This avoids explosive gas mixtures of oxygen and CH_4 in the case of opening the laboratory test rig. An installed burst pressure protection allows the discharge of gases pressure surges into the open.

Cold supply and insulation of the heat exchangers

For the liquefaction of methane, a temperature level of -162 °C must be achieved in the third heat exchanger at ambient pressure. Cooling is realized with a Gifford-McMahon cryocooler. A compressor supplies compressed helium gas at 2.500 kPa which relaxes in the cooler to 100 kPa. Here the radiator heat is extracted and it can be temperatures down to -240 °C achieved. The compressor is connected to an 8 kW-water-air cooling unit. A continuous operation of the heat exchangers is only possible if convective heat transfer from the surrounding can be avoid Therefore, a vacuum bell is used for isolation of the three heat exchangers (fig. 3).

Figure 3 Heat exchangers in the opened vacuum bell

Radiative losses can be substantially avoided by use of a radiation shield (fig. 4)

Figure 4 Vacuum bell with radiation shield

The radiation shield is made of a copper-clad iron grid wire, which is wound with a capacitor film (coated with aluminum plastic film). The plastic layer ensures the prevention of conductive heat transfer to the inside of the shield.

Cold supply of the heat exchangers

The Gifford - McMahon cryocooler can only be operated at a constant temperature level (approximately -240 °C). However, all three heat exchangers require different temperature levels (-80 °C, -150 °C, -162 °C). Therefore, copper wires (fig. 3) are used to realize the heat transfer from the three heat exchangers to the cryocooler. Depending on the number of connected strands different temperature levels can be achieved. All heat exchangers are equipped with heating cartridges and temperature sensors (Pt 100). This allows a temperature constancy of +/- 0.1 K.

Heat exchanger for desublimation of carbon dioxide

The tube heat exchanger made of stainless steel is operated in such a way that temperature levels of approximately -150 °C are kept constantly. At this temperature, carbon dioxide can be almost completely frozen out as dry ice. The cooled gas mixture of CH_4 and CO_2 (-80 °C) is injected from the top into the tube. Then CO_2 crystallizes as a solid dry ice on the coated surface (Teflon) of the inner tube. The residual gas, which consists mainly of CH_4, is drained on the rear side of the tube heat exchanger and enters the he subsequent heat exchanger for liquefying the CH_4.

The lower end of the heat exchanger is closed by a vessel for collection the falling dry ice. For removal the vessel can be separated. The collecting vessel is made of copper. A container manufactured from PTFE is used for its thermal isolation.

Furthermore, a vacuum-tight optical access port (glass window) has been fitted in the middle of the heat exchanger. It is used for the visual detection and documentation of the formation of CO_2-cristals. Fig. 5 shows a cross section through the vacuum bell with the heat exchanger used.

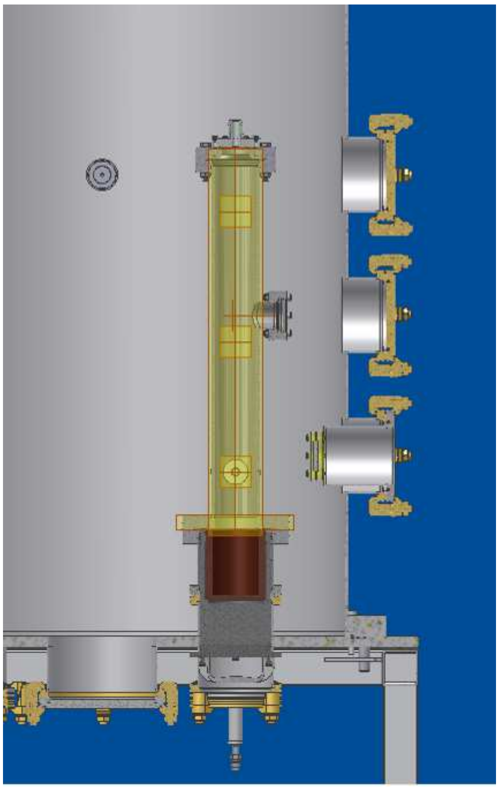

Figure 5 Tube heat exchanger in the vacuum bell

Heat exchanger for liquefying of methane

The methane-containing gas resigning from the tube heat exchanger is condensed in the following liquefaction unit at -162 °C to liquid biomethane. Fig. 6 shows the design of the liquefying heat exchanger.

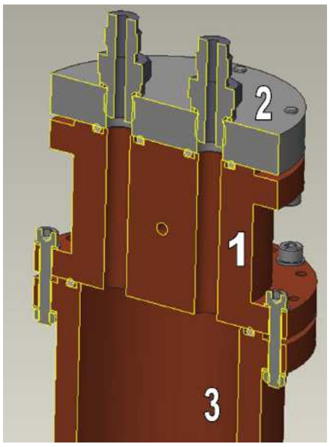

Figure 6 Heat exchanger for liquefying of methane

The heat exchanger exists of three components:
condenser (1), mounting plate (2) and container for the collection of liquid CH_4 (3) with the possibility for the withdrawal of LBM. The heat exchanger has a connection for the methane-containing gas and as a connection for gaseous nitrogen. In the event of critical pressure rise or decay originating from condensation of CH_4, nitrogen gas can be supplied or removed by this connections to guarantee a pressure balance on surroundings pressure. This method avoids regasification of CH_4 at subpressure. In the lower part of the collective container there is a decision system of the LBM, which allows its transfer in a transport vessel cooled with liquid nitrogen for analysis purposes.

Fig. 7 shows the transport vessel for the LBM, which is connected with the valve of the collecting vessel temporarily. It is cooled in a Dewar vessel with liquid nitrogen. The pressure relief valve is visible at the left edge of fig. 7, which in case of pressure rise with warming boil-off gas can escape and thus prevented a rupture of the transport vessel.

Figure 7 Transport container for LBM with overpressure protection

Gas detection system

Two mass flow control valves are used for the quantitative determination of the quantities of gas for experiments with synthetic biogas (binary gas mixture with variable concentrations of CH_4 and CO_2) in the area of gas supply to the gas management system. This system allows an exact adjustment of the composition of the gas volumes of CO_2 and CH_4.

A mass flow meter for determining gas quantities is installed to measure residual gas of the pipe from the laboratory system to the vacuum bell, so that the amount of residual gas according to the cryogenic gas separation can be determined. For the determination of the gas composition after the cryogenic gas separation are two IR gas sensors for CO_2 and CH_4 (measuring ranges: 0..5 and 0..100 Vol %) used by Dynament Ltd. [25]. The tolerance specified by the manufacturer is in the range of 0..5 Vol.-% approx. +/-50 ppm and in the measuring range from 0..100 Vol.-% approx. +/-1000 ppm. To ensure the validity of the results, the biogas analyser SWG100 MRU is used for measuring (Company MRU Messgeräte für Rauchgase und Umweltschutz GmbH) [26]. In addition to CH_4 and CO_2 (IR sensors) oxygen (0…25 Vol.-%) and hydrogen concentrations (0...1000 ppm) are measured in the residual gas (electrochemical sensors).

Both measurement systems are designed for continuous operation and can be calibrated periodically to reduce the uncertainty to a minimum.

3.2 Determination of suitable surface materials for the separation of CO_2

For a later implementation of the results of this project in a demonstration plant, it is important to clarify whether or not a continuous separation of solid CO_2 is possible. A stubborn layer of dry ice at the heat transfer surface should be avoided, as it would lead to blockage by freezing of the heat exchanger. Ideally, microcrystalline dry ice which is liable not to the surface and is continuously removed from the surface is created. Following questions were to be clarified:

- Is it suitable for metallic surfaces?
- What are the effects show coatings for deposition of gaseous CO_2?

Twentyfour cylindrical objects are made of different metals without or with different coatings (E.g. graphite, PTFE, Nano finish) as tube heat exchangers, which are sealed on the underside. These were attached to the metal lid of a glass vessel (Aquarium) without contact with the ground.

The jar was filled completely with gaseous CO_2 at the beginning of the tests. During the tests streamed gaseous CO_2 with different volume flows in the glass jar. The tube heat exchangers are in the mounted condition during the experiments with liquid nitrogen (-196 °C) be filled. With increasing length of time it came depending on the coating either for the forming of a firmly adhering layer of dry ice or falling microcrystalline dry ice, which is collected at the bottom of the glass container (fig. 8).

Figure 8.. Test of different surface coatings to the CO_2 capture

Following results could be observed in these experiments:

- A stubborn ice layer of dry ice on the tube heat exchangers is formed on metal surfaces (stainless steel, copper, gold or silver coatings).
- High CO_2 flow rates and high concentrations of CO_2 also lead to the formation of firmly adhering layers of ice on all tested 23 tube heat exchangers.
- Low flow rates and low CO_2-concentrations enable the formation of dry ice snow on coated tube heat exchangers (E.g. PTFE).

3.3 First results of gas separation experiments

The results listed here relate to experiments to a synthetic gas mixture of 55 Vol.-% CH4 and 45 Vol.-% CO2. A total flow rate of exactly 60 l/min gas mixture is basis of separation attempts.

In Fig. 9, the purity of CH_4 is displayed according to the cryogenic treatment. In the pictured test duration the residual concentration of CO_2 is on average less than 2000 ppm or 0,2 Vol.-%. The purity of CH_4 is consistently 99.8% and more. The deviations in the CH_4 concentration can be explained only as a measurement error. An even higher purity is expected at lower flow rates. A faster flowing through the reactor, however, leads to higher concentrations of CO_2 in the purified product gas.

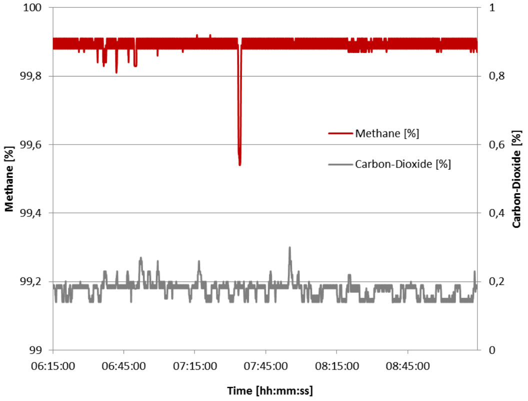

Figure 9 Concentrations of CH_4 and CO_2 in a gas separation experiment

The crystal formation of CO_2 remaining in the reactor can be evaluated visually with the help of the sight glass unit. Thus, the design theory [27, 28] can be confirmed that local excesses can occur with laminar flow. The snow formation in the gas stream or loosely adhering CO_2 snow on the heat transfer tubing are the consequences. In Fig. 10 is this phenomenon figurative over the course of time.

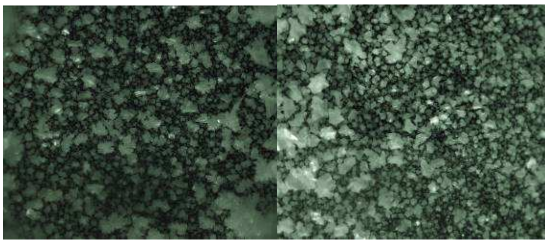

Figure 10 Formation of solid CO_2 crystals at the surface of the heat exchanger tube

The icing-up of the heat exchanger can be temporarily avoided by operating in the laminar flow range with high probability. A long-term operation of the cryogenic heat exchanger unit (over 10 hours) seems to be possible. The disadvantage of the low flow rate compensates for almost with the advantage of very high purity. The dry ice is available at regular intervals at the bottom of the heat carrier.

4 OUTLOOK

A combined biogas cleaning (cooling, charcoal silica gel) enables an efficient preparation of the raw biogas even without the use of oxygen to below the limits of detection of trace gases such as NH_3 and H_2S. This is a prerequisite for a subsequent successful cryogenic gas separation of CO_2 and CH_4. Marketable products (dry ice and liquid bio-methane LBM) can be produced only with a binary gas mixture almost completely cleaned of trace gases such as H_2S and NH_3.

To avoid a freezing of the heat exchanger for the deposition of dry ice, various coatings of the heat exchanger were examined. With a surface coating of the heat exchanger with PTFE turned out to be suitable. A freezing up of the heat exchanger for the deposition of CO_2 can be avoided with synthetic biogas in the laminar flow area. Also a residual gas can be thus produced, which has a purity of almost 99.9 Vol.-% CH_4.

In the next step, purified biogas from the digester should be used in further experiments to the cryogenic separation and should be compared with the presented findings. Similar results are expected, which can provide important information for the construction of a demonstration plant.

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