Compression of raw biogas

A feasibility study

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Abstract

Noen biogassanlegg er for små til å ha eget oppgraderingsanlegg for å produsere kjøretøykvalitet biometan (>97% CH_4). Flere avløpsrenseanlegg i Østfold, Vestfold og Telemark er i denne kategorien. Problemstillingen som vurderes i denne rapporten, er om det er teknisk mulig å transportere rå biogass som ikke er oppgradert i komprimert tilstand på gassflasker. Konklusjonen er at det er mulig, under visse forutsetninger:

- Man må operere i det trykk- og temperaturområdet hvor gassene går direkte over til superkritisk væske. Gassen må inneholde så lite vanndamp at det ikke kondenseres ut vann. Mengden akseptabel vanndamp er avhengig av trykk og temperatur
- Man må benytte flasker laget av komposittmateriale fordi CO_2 er korrosivt på stålflasker. Komposittflasker er i dag i bruk for transport av oppgradert gass.

Eksempelvis kan rå biogass med mer enn 42 % metan, og dermed CO_2 er 58% eller lavere, komprimeres dersom temperaturen er over -3 ˚C.

Det anbefales at prosjektet videreføres med økonomiske estimater og en pilotinstallasjon.
Rapporten er skrevet på engelsk på grunn av samarbeid med Air Liquide.

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1 BACKGROUND

1.1 Policy

The Norwegian Ministry of Climate and Environment issued in 2014 “Nasjonal tverrsektoriell biogasstrategi [National cross sectorial biogas strategy]” to propose policy instruments to increase the production and use of biogas. In Norway, the use of upgraded biogas, biomethane, as a vehicle fuel is of special interest. Production of combined heat and power (CHP) is of less interest, as power is cheap and to less extent replaces fossil fuels as more than 98% of power produced in Norway is hydropower.

1.2 Technology, upgrading of biogas

To use biogas as a vehicle fuel it should be cleaned and upgraded. Upgraded biogas shall have at least 97% methane according to the Swedish standard applied also in Norway. For cleaning the gas water vapour, H_2S and other contaminants should be removed. For upgrading to vehicle fuel specification CO_2 must also be removed. From a technical viewpoint with regard to the functioning of engines it is not necessary to remove CO_2. Engines can run on cleaned biogas (approximately 65% CH_4 and the rest CO_2), this is well known from combined heat and power applications. However, CO_2 in vehicle fuel would take up space in the tank on the vehicle that is better used for methane.

There are several techniques for cleaning and upgrading biogas, IEA Bioenergy Task 37 reports describes the technologies [1,2]. At present upgrading is not cost-efficient for small volumes of gas. The lower volume limit for cost-efficient upgrading is in the range of 100 – 200 Nm^3/hr equivalent to 0.8 – 1.6 million Nm^3/yr. The actual limit depends on the specificities of the case considered.

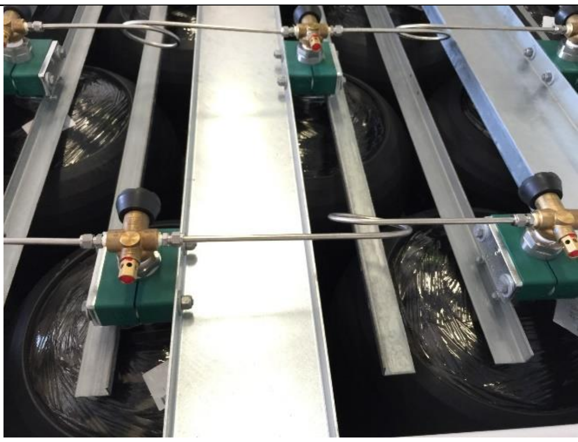
1.3 Technology, transport of compressed gas

Transport of gas is either in pipelines or as compressed gas in cylinders. In this report, we only consider compressed gas in cylinders. In Norway, the typical transport method is to have a hook skid with several gas cylinders. The cylinders are either made of steel or composite material. At least one distributor now use only composite cylinders, as it is possible get more gas on one skid. Skids with steel cylinders used in Norway typically holds 1900 Nm^3 gas, while skids with composite cylinders hold up to 5000 Nm^3. Typical pressure in these cylinders is 230 bar.

Skid with steel cylinders unloading at school to replace heating with mineral oil
Photo from presentation by AGA

Loading of skid by hook lorry
Photo Hexagon, http://www.hexagonraufoss.com/products/gas-transportation/smartstore

Skid with composite cylinders under production
Photo: Skagerak Naturgass.



Detail of pipe connection of composite cylinders
Photo: Skagerak Naturgass.

Figure 1 to 4.

2 SCOPE

In Norway and other countries there are several smaller biogas plants where the gas is not upgraded to vehicle fuel as it is not cost-efficient. Within the region covered by the Biogas Oslofjord project this is the case for several biogas plants running on sewage sludge in the towns of Porsgrunn, Larvik, Sandefjord, and Sarpsborg to name some of them. At these plants the biogas is either used for heat or CHP. Some gas is also not used but flared.

Transport of raw biogas from smaller plants to a plant with upgrading is considered in a report by Vidnes [3]. According to information received by Vidnes from company AGA it is stated that it is not possible to compress raw gas to more than 120 bar pressure, compared with vehicle fuel quality gas transported in cylinders at around 230 bar. However, a preliminary literature search in the scientific literature and discussions with professors at University College of South-east Norway working with transport of both compressed natural gas and CO_2 has lead us to test the hypothesis that it should be possible to compress raw biogas to at least 300 bar.

The scope of this study is:

1) Is it technically feasible to compress raw biogas to at least 300 bar?
2) Has the raw biogas to be cleaned of contaminants like water vapour and H_2S?

3 COMPRESSION OF GAS

3.1 Pure methane - CO_2 mixtures

Of special relevance for this report are the properties of CO_2. The critical point of CO_2 is 31.03 ˚C at a pressure of 73.8 bar (=72.8 atmosphere pressure). That means that if one compresses pure CO_2 at a temperature below 31.03 ˚C (= 304.18 Kelvin) it will turn into liquid at some pressure. This pressure will depend on the temperature, but be lower than 73.8 bar.

If the temperature is higher than 31.03 ˚C the CO_2 will not be liquefied during compression, but at higher pressures than 73.8 bar turn into a special state called supercritical fluid or dense phase.

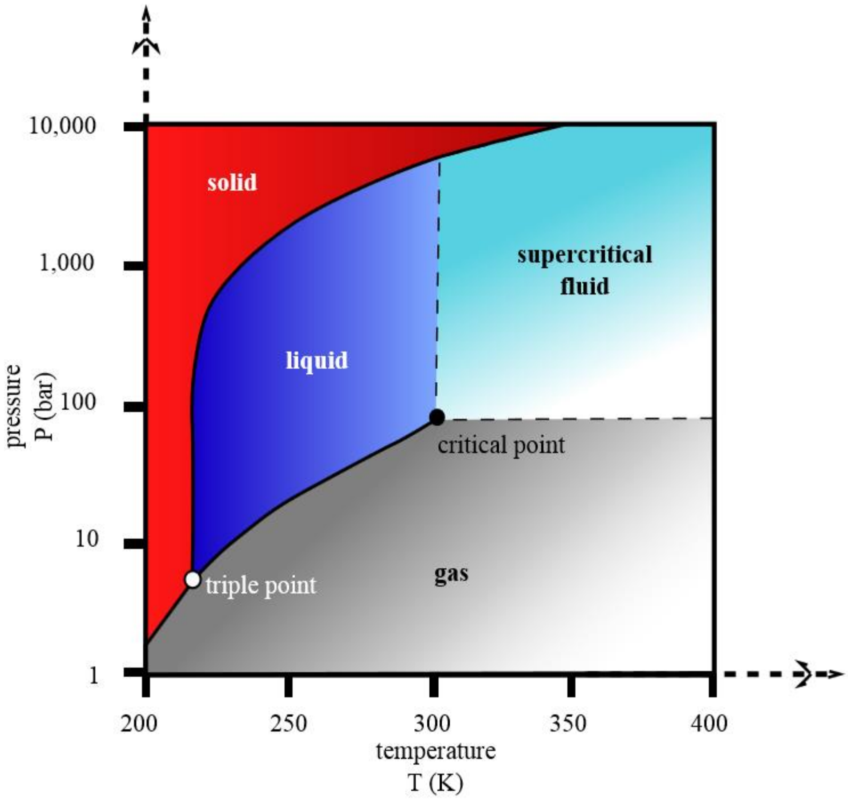


Figure 5. From Ben Finney/Mark Jacobs - Commons, Image: Carbon dioxide pressure-temperature phase diagram, https://commons.wikimedia.org/w/index.php?curid=4315735

We have been in contact with a supplier of compressors serving both the biogas, biomethane and hydrogen market, Andreas Hofer Hochdrucktechnik GmbH. According to them it is possible to compress a mixture of CO_2 and methane as long as one is operating at supercritical conditions.

The CO_2 – methane system has been studied, and there are experimental data available as well as models to explain the behaviour of the system.

The figure below from Yang et al.[4] can be a useful starting point for explaining the behaviour of the system. On the horizontal axis is given the mole fraction of methane (CH_4) present. Mole fraction (times 100) is for our purpose the same as the percentage of methane. The vertical axis gives the total pressure of the system. The unit in the original figure is MPa [MegaPascal]. 1 MPa = 10 bar, and 10 MPa = 100 bar. Let us as an example take a mixture of 45% CO_2 and 55% CH_4, then the mole fraction is 0.55, indicated by the red dashed line.

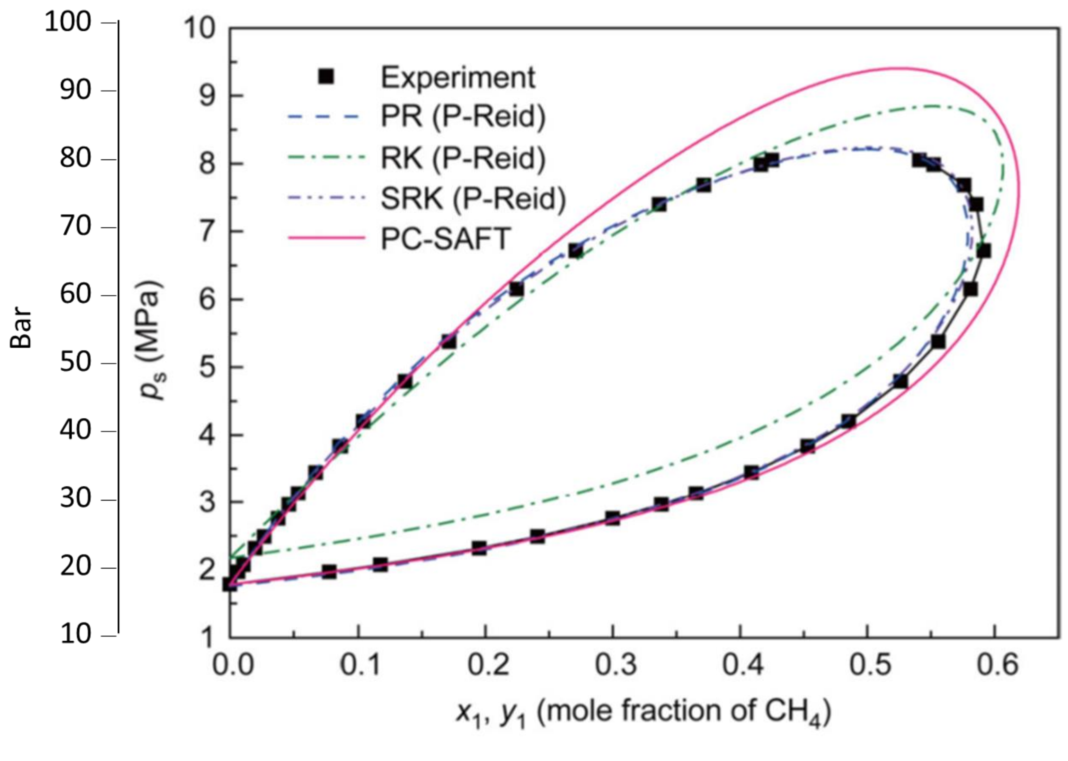


Figure 6 Mole fraction of CH_4 in both phases calculated by different Equation of States models compared with experiment (modified from Yang [4] et al.)

Let us assume that we shall compress this mixture from 10 bar to 100 bar, and at the same time keep a constant temperature of 250 K = -23 C. At the start this mixture is a gas, but when we reach approximately 52 bar, the dew point (DP) for CO_2 in the mixture is reached. Liquid CO_2 will form, with some CH_4 dissolved. We will have a two-phase system, with both a liquid and a gas phase. As we continue to increase the pressure we will reach the boiling point (BP) of the CO_2, and we will again have a system with only a gas phase. Due to the formation of a liquid phase such a system should be avoided.

If the gas mixture contained approximately 63% CH_4, and the rest CO_2, then we have a different situation. As can be seen from figure 6 we do not come into the conditions where a liquid phase is formed. Instead the gas is compressed and forms supercritical fluid (also called dense phase).

Dense phase, also called supercritical fluid, is a fourth (in addition to Solid, Liquid, Gas) phase that cannot be described by the senses. The word “fluid” refers to anything that will flow and applies equally well to gas and liquid. The dense phase has a viscosity similar to that of a gas, but a density closer to that of a liquid. There is no sharp transition from gas to dense phase.

We can then use commercial compressors available for pure gases like CO_2, CH_4 and H_2 also for this mixture of 65% CH_4 and 35% CO_2 as long as no other substances are present. The problem of moisture in the gas will be discussed below.

So far we have only discussed the system at -23 C. Privat and Jaubert [5] has made similar curves at different temperatures, Figure 7.

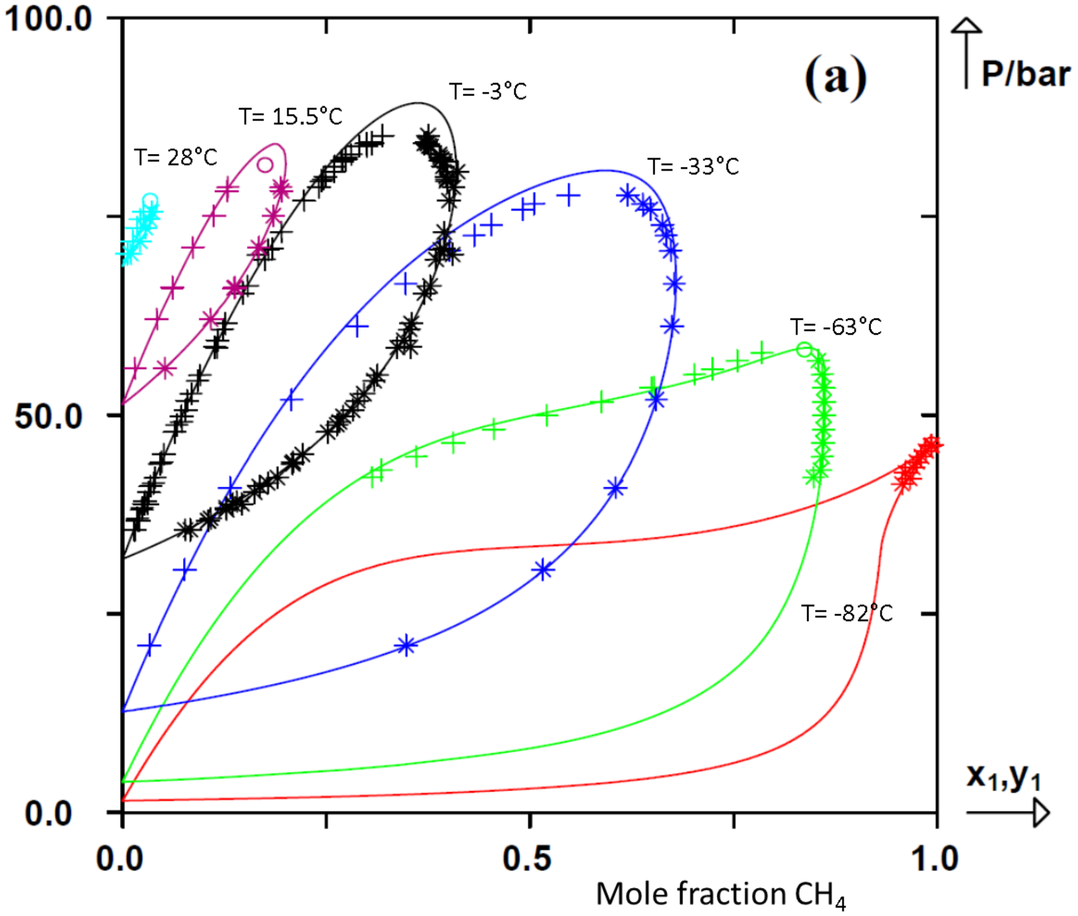


Figure 7 At temperatures above -33 C, liquid CO_2 will not form if the CO_2 concentration is below approximately 32%, and thus CH_4 higher than 68 % (from Privat and Jaubert [5]).

3.2 Water vapour

Biogas will be saturated with water vapour as it leaves the biogas reactor. Typically, the gas will be cooled before compression, and some of the water vapour will condense to form liquid water. However, the remaining water vapour will influence the properties of the raw biogas, and increase the temperature where a liquid phase will form. The model used by Privat and Jaubert[5] can also model gas mixtures with water vapour, and can be used to as basis for the selection of compressor design.

3.3 Decompression av gas

We assume that the cylinders with raw biogas are transported to an upgrading plant. The upgrading plants operate at a much lower pressure than 200 bar, and the gas decompresses when the cylinders are emptied.

As the gas expands it cools down, this is called the Joule-Thomson effect. The cooling can lead to liquid or ice formation from water vapour in the gas. The system for decompression of the gas has to be properly designed to avoid water or ice formation.

Some systems for gas upgrading operate under pressure, e.g. membranes (typically around 12 bar), "Pressure swing adsorption" and some amine systems. It is then possible to use the raw biogas directly at the required process pressure.

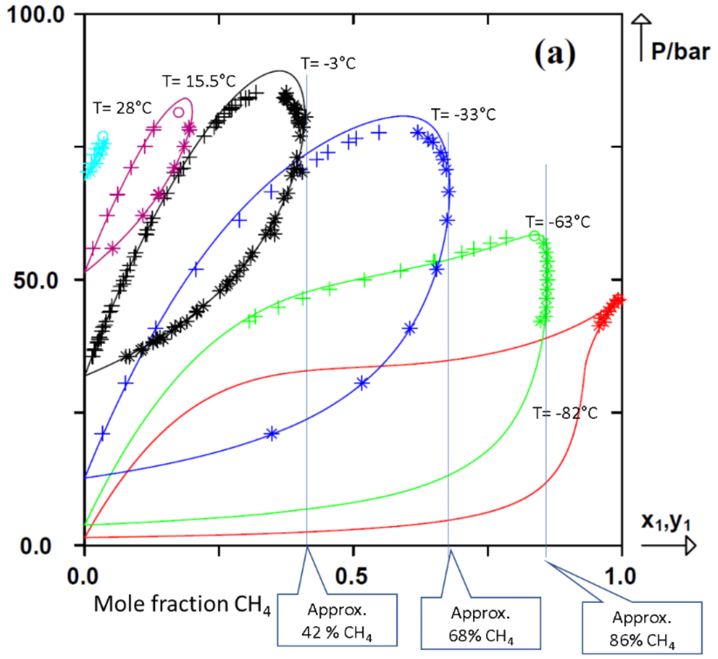
4 USE OF HIGH CO_2 BIOMETHANE

It has been suggested by Larsson[6] that in some cases partially upgraded, high CO_2 biomethane could be used as a vehicle fuel e.g. for tractors. According to Larsson the gas could contain up to 20% CO_2. It is suggested that for small scale biogas production this could be an opportunity to use low cost upgrading technology.

We can here consider a case in northern Scandinavia where temperatures in extreme situations could be 40 ˚C below zero. As the gas tank is emptied during use of the tractor the pressure will drop from the typical filling pressure of 200 bar down to 70 – 50 bar.

We have then to consider the question:

> If the partially upgraded biogas contains 20% CO_2 as suggested by Larsson, is that a problem at temperatures down to -40 ˚C?



As can be seen from figure 8:

At T = -3 °C no liquid phase is formed when CH_4 > 42 %

At T = -33 °C no liquid phase is formed when CH_4 > 68 %

At T = -63 °C no liquid phase is formed when CH_4 > 86 %

Figure 8 Phase diagram for CO_2 – CH_4 (modified from Privat and Jaubert [5]).

A crude estimate can be done by doing a linear interpolation between the two points [-33, 68] and [-63, 86]. The result for 20% CO_2 is -53 °C, indicating that partially upgraded biogas with 20% CO_2 can be used also in very cold weather.

A proper calculation should be carried out if high CO_2 biomethane is taken into use, but from the above data is seems reasonable to estimate that in Scandinavia one would be safe with regard to the formation of a liquid phase if the CH_4 concentration is at least 80%. The gas would also have to be dry to avoid formation of ice.

5 GAS CYLINDERS

Most gas cylinders are made of steel. However, due to possible corrosion by CO_2 and traces of H_2O and H_2S one should avoid steel cylinders for raw biogas.

Cylinders made of composite material is already in use for biomethane. Type 4 composite cylinders have an internal plastic liner and can be used for raw biogas according to information from Hexagon Raufoss (pers.comm.).

There are two Norwegian producers of composite cylinders:

- Hexagon Raufoss http://www.hexagonraufoss.com/about/technology/technology
- Umoe Advanced Composites http://www.uac.no/WEB/uac100.nsf/pages/home

6 CONCLUSION

It is possible to compress raw biogas, a mixture of CO_2 and methane, to at least 300 bar, and transport it in composite gas cylinders.

One should avoid operational conditions (temperature, pressure) that leads to formation of two phases (liquid and gas). Water vapour and H_2S will also influence the temperature and pressure at which two phases are formed. There exists experimental data and models that can be used to design a system to avoid two phases. These can also be used to determine an acceptable level of H_2S and water vapour given a set of conditions.

Two possible applications are considered:

1) Transport of raw biogas to an upgrading plant. In this case, some water vapour and possibly H_2S can be accepted as temperature can be controlled by proper design.

2) Use of "High CO_2 Biomethane" as suggested by Larsson for special applications depending on local small scale production of biomethane; in the case that full upgrading to standard vehicle quality is too expensive. One such application is for tractors on farms. In extreme cold operation e.g. in northern Scandinavia it may be necessary to have very dry gas to avoid ice formation, or alternatively the gas storage and fuel lines are protected against the cold.

A techno-economic analysis and/or a pilot installation is suggested as a continuation of this technical feasibility study.

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