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FiB
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Optimisation of the biogas process

Better control of the biological process will improve the economy of many biogas plants. Already today, there are various control parameters, which can improve operation, and the researchers are far advanced in the development of online systems, which will make it much easier to avoid interruptions in operation.

By Henrik Bangsø Nielsen, Kanokwan Boe and Rena Angelidaki

From time to time most biogas plants have experienced substantial declines in the gas production due to interruptions of the biological process. Often a more effective control of the process will prevent such incidents and thereby improve the economy of the plants.

Oxygen-free digestion of organic matter is a complicated process, in which the catabolic products from one micro organism serve as food for the organisms produced. The different micro organisms have different growth rates and different robustness in relation to changes in the process. As a result, uncontrolled operation of the biogas plant may result in an imbalance between the different organisms, which may lead to a process collapse.

The complex interaction between the different groups of bacteria makes it possible to take measurements of the many intermediates and end products. In this way, it is possible to gain detailed insight into the activity of the individual sub-processes and to use the different combinations as control parameters in order to obtain a better digestion process.

From the point of view of a plant manager, a control parameter must:

- give clear and early warning of a potential collapse, but on the other hand not give unnecessary warning,
- warn of an unstable process, not just a total collapse,
- reflect when the process has re-established itself after a collapse,
- be easy to measure - preferably online.

Test set-up at the Department of Environment & Resources at the Technical University of Denmark. Henrik Bangsø Nielsen to the left and Rena Angelidaki to the right.


photo: institut for miljø & ressourcer

If the above-mentioned guidelines are taken into account, four parameters are of particular interest: the methane production, the concentration of hydrogen, pH and the concentration of volatile fatty acids (VFA).

The methane production

As the end products of the digestion process mainly consist of biogas, a registration of the gas production is today the most commonly used control parameter. Usually a distinction is made between the total gas production and the relative production, which indicates the amount of methane in relation to the amount of biomass.

The total gas production may be used to gain an impression of the activity of the methane bacteria, but it does not give a precise impression of the process situation. A decline in the gas production may well be related to the methane bacteria being inhibited, but it may also be due to failure to add biomass. Overloading of the reactors will often result in increased gas production followed by a plunge and by then it may be too late to intervene. Use of the total gas production as the only control parameter is therefore not recommended.

The relative gas production reflects how effectively the added material is degraded. The obtained values can be compared with a theoretical methane yield, which can be calculated. Unfortunately, it is a rather time-consuming process, partly because the theoretical methane yield from for instance liquid manure can vary considerably. The relative gas production is therefore not practically useful for registering sudden changes in the process, although it can be quite useful for the subsequent evaluation of total collapses.

The concentration of hydrogen

Laboratory tests have determined that a low hydrogen pressure in a reactor is necessary to ensure an effective process. This is obtained when various bacteria convert hydrogen and carbon dioxide into methane and water. An increase in the hydrogen pressure may therefore be an indication of an imbalance between the different micro organisms, for instance when large amounts of easily convertible material have been added.

As hydrogen can be measured relatively easily during both the gas and the liquid stages, use of hydrogen as a control parameter has received quite a lot of attention in recent years. Unfortunately, the results have been very variable. The problem is that the concentration of hydrogen is often very sensitive to chances in the composition and amount of added biomass. Against this background, it is to be expected that the concentration of hydrogen may give rise to many false alarms. The use of hydrogen as a control parameter is therefore not realistic in Danish biogas plants and not at all as the only parameter.

Control parameter	Online	Possible applications
Total gas production	Yes	Partly applicable, but not as the only control parameter.
Relative gas production	No	Only applicable in connection with slow changes of process.
Hydrogen	Yes	Too sensitive for use in the Danish plants.
pH	Yes	Only as an indicator of the occurrence of a major imbalance.
Total VFA measurement	(Yes)	Partly applicable, but not as the only control parameter.
Individual VFA	(Yes)	Highly applicable.

Table 1. Overview of the different control parameters.

VFA and pH

Volatile fatty acids (VFA) constitute most of the intermediates in the biogas process, and among researchers there is no doubt that the VFA level is very important for the maintenance of a stable digestion process.

There has, however, been much dispute about how to use a registration of VFA. Many studies have compared the concentration of the acid level with occurring interruptions of the process. For instance, it has been mentioned that a concentration of 0.8 grams of acetate/litre biomass indicates an interruption of the process, while a pripionate/acetate ratio higher than 1.4 is a sign of imbalance.

However, it is not possible to generalise on the basis of such results, as the individual reactors each have their own acid levels dependent on the operating conditions. Instead, the VFA level of each individual reactor should be used as an indicator.

Several biogas plants measure the total acid level in the reactors from time to time. This may be done in a relatively simple way by means of titration and can give a hint of changes in the process, but it is inadvisable to use this as the only control parameter.

It is debatable whether pH can be used as a control parameter, because an increase in the concentration of acid must be expected to affect the pH. However, in Danish biogas plants most of the biomass is liquid manure, which has a high buffer capacity. An increase in the acid level will therefore not necessarily result in a substantial pH drop. Often a pH drop will not be registered until after the VFA level has increased considerably and the process has become unstable. Therefore pH is too slow to be useful as a single indicator, although it may be suitable in connection with other control parameters.

VFA online

How often is it necessary to measure the VFA concentration? During a normal stable process, where no major changes of operation are made, it will often be sufficient to measure the level approximately five times per week. However, in periods when operational changes are made, for instance by the addition of new types of waste, measurements should be made as often as possible.

Unfortunately, measuring the VFA has been regarded as complicated for many years. In practice, it has been difficult to undertake automatic sampling and the treatment of samples has itself been time-consuming.

However, in recent years, there have been developments in this area. For instance, Swedish researchers have tested the possibilities of using infra-red spectroscopy, and at the Technical University of Denmark a device for online measurement of VFA has been developed. The device has proved to be very stable on a laboratory scale and it will now be tested in a full scale plant.

Online measurement of the VFA level will make it much easier to avoid possible process interruptions, and it will be safer to add new, complex types of waste. At the same time, the use of the VFA measurements will provide various information that can be used to develop different "recipes" for regulating the operation. Greater pressure can thus be put on the reactors than today without the risk of a collapse of the process.

Unfortunately, it is likely to take some years before these systems are commonly available, reasonable priced and sufficiently reliable. Until then, much can be gained by following the below procedures:

- Generally ensure constant process temperature, agitation, load and composition of raw materials.
- Make all necessary changes on the basis of a precautionary principle and gradually, especially with regard to changes in the composition of the biomass and the load.
- Always introduce new raw materials with great care, especially if they are "potent" and contain much fat, proteins or similar s. If possible, new types of raw materials should be tested before being added by means of a simple test in a laboratory plant. Simple reasoning can be very helpful: Is this something a cow's stomach would like? Is it so "spicy" or unfamiliar that it takes some getting used to before it tastes good?

Unstable process cost DKK one million

photo: torben skøtt/biopress

In the autumn of 2004 the biogas plant in Blaabjerg experienced big problems with the biological process because of unintentional overdose of industrial waste. The accident led to reduced gas production, and periodically the gas quality was so poor that it could not be used in the engines but had to be burned in the torch, serving no useful purpose.

The process was slowly re-established, partly by diluting the biomass with water. During the entire process, the plant manager relied extensively on a so-called automatic indicator borrowed from the biogas plant in Blåhøj. This made it possible to track the concentration of VFA acids in the reactors at regular intervals.

It took approximately three months before the biological process was stable again and the gas production returned to its normal level. The total operational loss was subsequently calculated as just under DKK one million.

TS

From gas to liquid fuels

While the politicians continue to debate whether ethanol and biodiesel should be used in the transport sector, the researchers are busy developing new forms of biofuels that can be used as alternatives to diesel and petrol.

By Torben Skøtt


photo: torben skøtt/biopress

Ulrik Henriksen in front of the Viking gasifier, which produces very clean gas on the basis of forest chips. The plant, which is based on a two-stage process, has had more than 2,500 unmanned operating hours.

A couple of new names, which we might as well get used to, are methanol and dimethylether - colloquially called DME. Methanol is also known as wood spirit - an organic compound belonging to the group of alcohols, but highly toxic, unlike ethanol. Today methanol is among other things used for producing biodiesel and in California a mixture of 85 per cent methanol and 15 per cent petrol has been used in the transport sector.

Many describe DME as the engine fuel of the future and it may also with advantage act as an intermediate in a hydrogen-based energy system. It has a higher efficiency than petrol and unlike diesel produces virtually no particles during combustion.

Both methanol and DME can be made from a wide range of carbon-based substances such as biomass, coal and natural gas. The first stage of the process is the conversion of biomass into gas and the gas is then converted into liquid fuel.

In this country, the Technical University of Denmark and the company Haldor Topsøe have been particularly active in relation to the manufacture of methanol and DME. The researchers at the Institute for Mechanics, Energy and Construction at the Technical University of Denmark have considerable expertise within the first stage of the process, while Haldor Topsøe specialises in the second stage of the process.

High performance

The production of liquid fuels based on gas is not a new invention, but until now the focus has been on the use of natural gas as a raw material. No less than three per cent of the world's production of natural gas is actually burned serving no useful purpose, because it is produced in remote areas where it is too expensive to establish the necessary pipelines.

In this area, Haldor Topsøe is internationally famous for producing catalysts allowing natural gas to be converted into a mixture of DME and methanol. Most recently, the company supplied some of the technical solutions for a large plant in Qatar, which will produce liquid fuels corresponding to Denmark's total diesel consumption.

The object of the co-operation with the Technical University of Denmark is to develop a technology where the biomass firstly undergoes a thermal gasifi-

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- Continuously evaluate the gas production in relation to expectations based on the additions over the last few days, and hold back if inexplicable drops or major increases occur.
- Undertake regular VFA measurements. The VFA level should be checked on a regular basis, even if there may be long periods without "interesting" results.

VFA measurements once every week is usually sufficient to prevent acute process breakdowns. The principles of stable operation and careful addition of new types of waste are necessary to avoid sudden and unmanageable changes. One should be careful and abstain from driving in an aggressive manner when the windscreen is steamy and there is steering gear backlash. Fortunately, the brake is still working, but that is no good unless the obstacles are spotted in advance.

Rena Angelidaki, Henrik Bangsø Nielsen and Kanokwan Boe are all employed at the Department of Environment & Resources at the Technical University of Denmark, email: ria@er.dtu.dk

cation and is then converted into DME and methanol.

- Basically this involves previously known technology, but we need to examine how things can be linked in a sensible way, says senior lecturer Ulrik Henriksen from the Technical University of Denmark.

- What is exciting is that a fairly simple process allows us to convert biomass into very high performance liquid fuel. We expect as much as 80 per cent of the biomass to be convertible, which can make production very competitive in relation to other types of biofuels.

- Another possibility is to create a simpler plant, which only converts for instance 40 per cent of the gas into liquid fuels. The rest of the gas can then be utilised in a CHP plant in order to obtain overall high performance, explains Ulrik Henriksen.

There are thus many possibilities and, most importantly, it will be possible to create small, decentralised plants. In this way, methanol and DME can become important supplements to ethanol and biodiesel, not only because of the size of the plant, but also because methanol and DME are particularly suitable for wood, whereas ethanol and biodiesel are based on agricultural crops.

Gasification of biomass

Since the early 1990s, the Technical University of Denmark has played a central role in the development of gasification plants capable of converting wood, straw and other forms of biomass into gas. Among other things, it has developed the so-called Viking gasifier, producing very clean gas on the basis of forest chips. The plant, which is based on a two-stage process, has had more than 2,500 unmanned operating hours.

- The Viking gasifier produces high quality gas that will be suitable for producing methanol and DME. If the gas contains too many impurities in the form of sulphur, tar and chlorine, it will affect the working life of the catalyst and then the economic viability may be doubtful, explains Ulrik Henriksen.

One of the students at the Technical University of Denmark recently completed an exam project, which among other things included the establishment of a test plant for producing methanol and DME from gasification gas. The man behind the project is Henrik Laudal Iversen, who is today employed at the Institute for Mechanics, Energy and Construction, and who will in future undertake research into gasification and biofuels.

- If a fairly simple process produces methanol only, performance is limited to around 25 per cent, but if the production of methanol and DME is integrated in the same process the performance may increase by as much as 45 per cent. For more advanced processes, the performance levels may increase to as much as 75-80 per cent, says Henrik Laudal Iversen.

This is due to methanol being an intermediate in the production of DME. The end product therefore mainly consists of DME, while the proportion of methanol is limited.

Fuels of the future

Many regard methanol and DME as worthy substitutes for petrol and diesel. However, one problem still needs to be solved: DME has poor lubricating properties, so either the engines must be redesigned or an additive improving the lubricating properties must be found.

In the 1990s a mixture of 85 per cent methanol and 15 per cent petrol was launched in California. At the same time, cars able to run on the new fuel were introduced on the market, but it was never a big success. However, this was not due to technical problems, but the difficulty of developing the distribution network while the number of vehicles was limited. Conversely, it was difficult to persuade people to buy the new cars while the number of service stations was limited.

The well-known question of which came first, the chicken or the egg, applies to some biofuels, but not all. Most diesel cars can thus run on 100 per cent biodiesel, while petrol cars can run on different mixtures of petrol and ethanol. If most of the fuel consists of ethanol or methanol, special vehicles are required - the so-called flexi-fuel cars which can run on any mixture of methanol, ethanol and petrol.

photo: torben skøtt/biopress

Ulrik Hansen inspecting the test plant for producing methanol and DME from gasification gas.

In Sweden an act ordering the service stations to sell either ethanol or biogas as a supplement to petrol and diesel has recently been passed. Time will tell whether the driving public prefers ethanol or would rather drive on gas.

In other places, a third possibility is under consideration: The so-called Fischer-Tropsch diesel, which can be produced on the basis of gas like methanol and DME. The great advantage is that this fuel can be used in already existing diesel engines. Furthermore, it contains far fewer impurities than ordinary diesel, resulting in a significant reduction in the escape of particles.

Several oil companies are investing in the technology because of the many environmental benefits, but if the product is to compete with the other forms of biofuels, investments in very large production plants are required. ■

How to double the gas production through the addition of solid biomass

The gas production from a biogas plant can be doubled by replacing part of the manure in the plant with solid biomass from a separation plant. Tests carried out by the Danish Institute of Agricultural Sciences show that up to 60 per cent of the manure can be replaced with solid matter without causing process problems.

By Henrik B. Møller & Gitte Andersen

It is well-known that the solid part from manure separation has considerable gas potential. Laboratory tests have shown that the gas yield from plants using chemical precipitation is 5-10 times higher for the solid part than for manure with a dry matter content of 3-6 per cent.

Whether it is profitable to replace manure wholly or partly with solid biomass will depend on local conditions. Furthermore, it is important to be aware of the possible process problems that may arise as a result of a high nitrogen content in the solid biomass.

At Research Centre Bygholm, which is part of the Danish Institute of Agricultural Sciences, tests have been carried out on the replacement of pig manure in one reactor with the solid part from a separation plant, based on chemical precipitation. The dry matter content in the manure varied between 4.1 and 7.2 per cent, while the solid biomass had a dry matter content of 21-25.3 per cent. For the first 190 days 20 per cent of the manure was replaced by solid biomass. For the subsequent 90 days this was increased to 33-40 per cent, and for the last 100 days 60 per cent solid matter was added. Concurrently, another reactor was fed with pure pig manure as a reference.

Except from a few outages the temperature in the pig manure reactor was kept stable at 50°C, while the temperature in the reactor where solid biomass was added was gradually increased from 48 to 52°C. In both reactors the biomass had an average retention time of 15 days.

It was expected that the biomass would become difficult to handle when up to 40 per cent of the manure had been replaced by solid matter. However, it turned out that it could be agitated without problems, even when the total volume of biomass had a dry matter content of up to 15 per cent. The solid material resulted in a thick mash that did not separate into either sediment or supernatant, and there was no greater need for agitation than with thin pig manure.

Stable process

During the test, a number of different parameters were measured on a regular basis, including the ammonium content and the amount and composition of volatile fatty acids.

As shown in Figure 1, the ammonium content in both reactors increased during the test. This was primarily because the nitrogen content in the added pig manure was higher during the last part of the period than during the first part of the test and because an increased amount of solid matter was added to the solid matter reactor.

However, the level in the solid matter reactor is much higher than in the pig manure reactor. If less than 40 per cent solid matter is used, the level remains below 4 grams of ammonium/litre biomass, while the level stabilises around 5.4 grams at the high dose of 60 per cent solid matter.

At an ammonium content of more than 5.4 grams/litre biomass, a considerable inhibition of the biological process is to be expected at a thermophilic process. Nonetheless, it was possible to

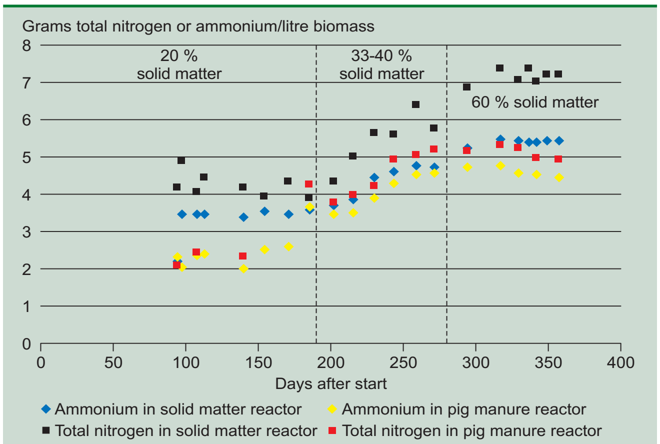

Figure 1: Ammonium and total amount of nitrogen in the two reactors with solid substance and pure pig manure respectively.

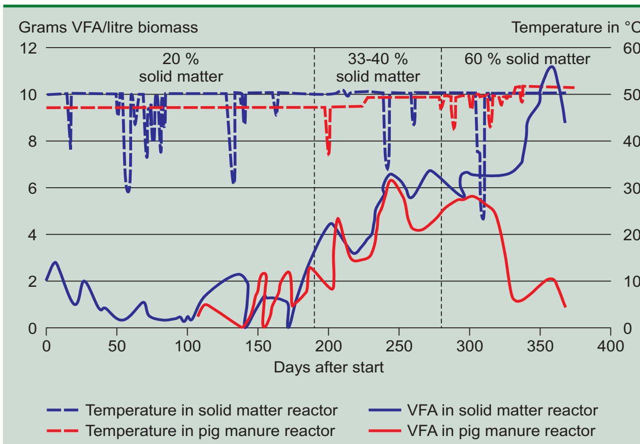

Figure 2: Reactor temperature and levels of VFA in the two reactors with solid matter and pure pig manure respectively.

maintain a stable gas production throughout the whole test period.

The level of volatile fatty acids (VFA) gradually increased in step with the amount of ammonium (Figure 2). During the period with 20 per cent solid matter, the level of VFA was low in both reactors, while it increases in the period with 30-40 per cent solid matter. However, there is little difference between the two reactors, due to the significant increase in the nitrogen level in the manure during the same period.

At the transition to 60 per cent solid matter, yet another increase in the VFA level occurs, but it remains fairly stable at 6,500 mg/litre as long as the temperature is kept at 50°C. At a temperature rise to 52°C a drastic increase in the VFA level to approximately 11,000 mg/litre occurs, but this still does not materially affect the gas production.

Gas production

The gas production per kg organic dry matter (VS) in the different periods is shown in Figure 3. Generally, the reactor with pure pig manure produced a somewhat higher gas yield than the solid matter reactor, which is to be expected, as manure has a higher content of easily convertible organic dry matter. However, both reactors show a reasonable yield throughout the whole period.

In the period with 60 per cent solid matter, 15 days of after-gasification at 30°C were included. Consequently, the overall gas yield increased to around 300 litres of methane/kg VS, which corresponds to the level from pure pig manure.

photo: kemira miljø a/s

Manure separation by means of chemical precipitation at a plant from Kemira Manure Separation.

The gas yield in relation to the reactor volume is of course much higher for the solid matter reactor than for the reactor with pure manure (Figure 4). Thus, during periods with 60 per cent solid matter, twice as much gas was produced as with pure pig manure. If the yield from 15 days of after-gasification is included, the yield is improved by up to 30 per cent, which indicates that the process at the first stage is not optimal.

Outlook

By replacing part of the manure in a biogas plant with solid biomass, the gas production of the plant can be significantly increased. By using as much as 60 per cent solid matter, a high and stable gas production can be obtained at a temperature of up to 50 °C.

Whether it will be economically advantageous to replace part of the manure with solid biomass depends on several factors, including costs for separation, distance to manure producers and opportunities for disposing of the excess phosphor.

The possibility of burning the fibre fraction after gasification will probably make it even more attractive to add solid biomass from separation plants to the biogas plants. In this way, the biogas plants will be able to involve a larger group of suppliers, as transport of solid matter is much cheaper than transport of the corresponding amount of manure, especially if the suppliers are located far from the plant.

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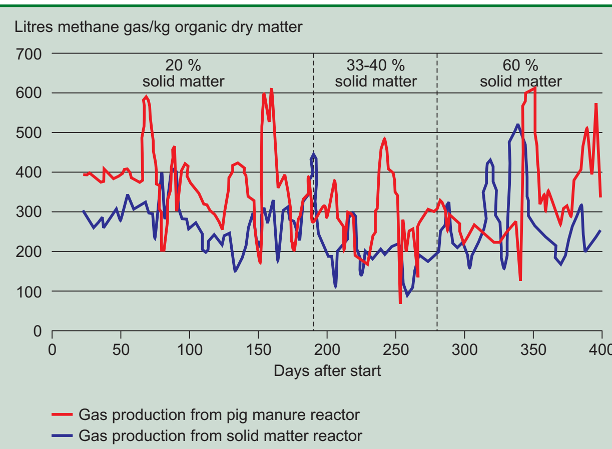

Figure 3. Gas production in relation to organic dry matter in the two reactors with solid matter and pig manure respectively.

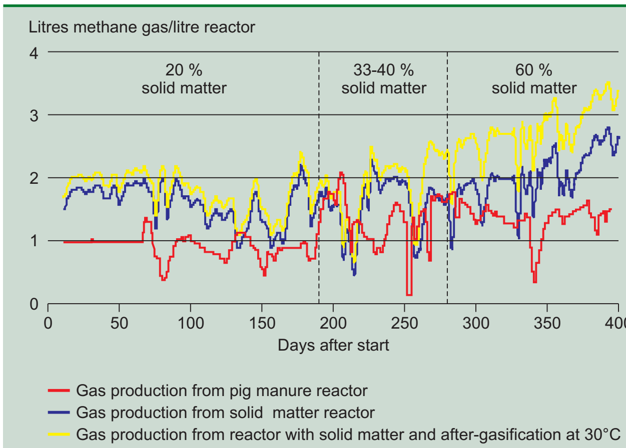

Figure 4. Gas production in relation to reactor volume in the two reactors with solid matter and pig manure respectively.

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The Stirling engine is ready for production

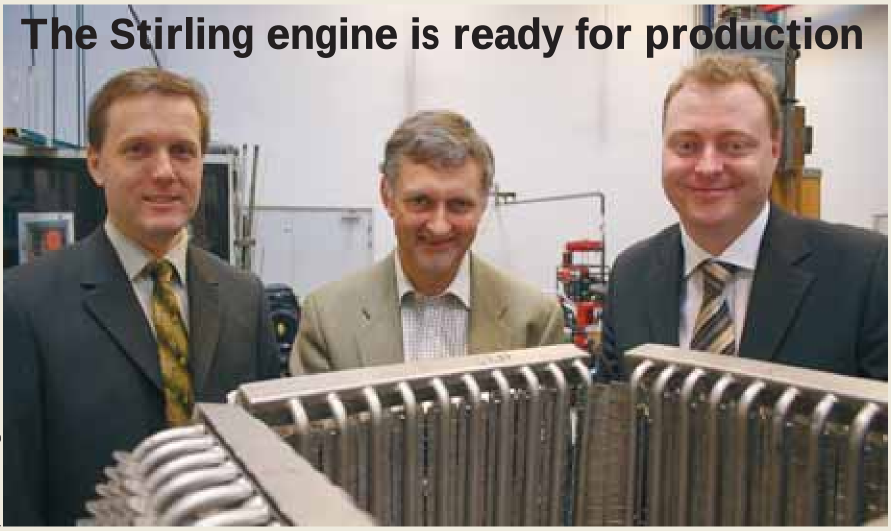

photo: stirling.dk

Three men and an engine. From the left, they are Peter Tøttrup from SEED Capital, Henrik Carlsen from Stirling Denmark and Søren Houmøller from EGJ Development.

Stirling Denmark , which develops engines for biomass, has been given a boost of DKK 12.5 million from EGJ Udvikling A/S, SEED Capital and the Danish Fund for Industrial Growth. The money is to be used on getting the technology from the test phase on to the market.

- It promises to be a breakthrough for a Danish energy technology, says Søren Houmøller, Development Manager of EGJ Udvikling A/S, who is also a member of the board of directors in Stirling Denmark.

- The technology works, the sales have started and the company has a unique position on the market, where no other technologies are capable of delivering small combined heat and power units for biofuels, he explains.

The founder of Stirling Denmark is Professor Henrik Carlsen from the Technical University of Denmark. He has led the research and development effort since the start more than 10 years ago and has received funding from the Energy Research Programme and PSO-funds from Energinet.dk.

Henrik Carlsen continues as Professor at the Technical University of Denmark and will be associated with Stirling Denmark as the person responsible for the future technological development. A chief executive officer will be appointed very soon and in addition two or three additional engineers are expected to be employed in 2006. The object is to create 40-50 new workplaces over the next 5-6 years and a similar number of workplaces with the subcontractors. The technological development will remain at the Technical University of Denmark, while production and sale will be located in the Herning area.

A Stirling engine differs from an ordinary combustion engine due to the fact that the combustion does not occur in the cylinder, but in an externally heated combustion chamber. The principle is thus closer to a steam engine than an internal combustion engine.

Stirling Denmark has chosen to integrate the engine with an electric generator and a biomass-fired boiler. In this way, a small combined heat and power unit for biofuels suitable for businesses, institutions, housing associations etc. is created.

Read more about the Stirling engine at www.stirling.dk *TS*