Baltic Biorefinery Symposium

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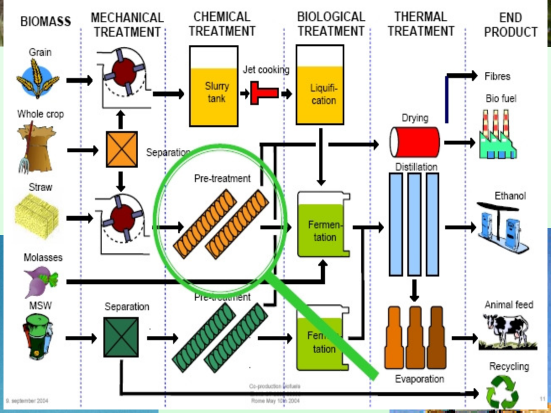
Symposium – Workshop – Study Tour

Baltic Biorefinery Symposium

Harvest of energy maize

Ribe Biogas Plant



IBUS concept

AgroFerm A/S, Esbjerg

Studstrup Power Plant

Aalborg University Esbjerg
Denmark

26th - 28th of May
2005

Baltic Biorefinery Symposium
26–28 May, 2005
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Proceedings

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Opening of the Baltic Biorefinery Symposium

By
Peter Gæmelke
President of Danish Agricultural Council

It is a great pleasure for me to be invited to welcome you all to the Baltic Biorefinery Symposium. I hope you will have some good days here in Denmark and that you will have good discussions and find prosperous solutions for the future.

The European nations, the member states of the European Union and countries all over the world are these years facing tremendous challenges regarding the creation of a sustainable society.

All over the world it is realised that we have to face the problems of the past and current use of fossil resources. We have to change our societies, the industry and way of living in a more sustainable direction.

It is obvious that the reliance of fossil resources for industrial products and energy, which was the basis for the industrial society in the last century must be relived of a sustainable society based on renewable resources in the coming century.

In this respect there is no doubt that biomass from agriculture and forestry will play a key role and lay down the basis for development.

The role of agriculture is changing in these years. Farmland can no longer be seen as the growth medium for crops for food and feed. Farmland now has a much broader and multifunctional role as the key element in the landscape and as a steward or manager of the natural resources and habitats. A further important role of future agriculture is as a supplier of biomass from energy crops, industrial crops and by-products from food and feed production.

The multifunctionality is therefore not only in regard to the use of the land. It is indeed also the case in relation to the utilisation of the harvested biomass. It is important to make the best of it – in order to optimise the value of the crop and the income for farmers and the employment in the rural areas.

This change of agriculture to a multifunctional supplier of biomass for food and feed, industry and energy is depending on a number of items.

First and foremost the development needs a scientific effort. A targeted effort from dedicated researchers on universities and in industry is necessary to overcome the technical barriers and make the bio-economy competitive with the oil economy.

Secondly industry and consumers must be willing to pay a premium price for the sustainable products. There must be a market for the products and this must be promoted by the third level: The governments or intergovernmental bodies such as the European Union must set up the necessary framework conditions that will make the bioenergy economically feasible.

A coherent policy is needed. I believe we are now at a point where moderns societies are prepared for the necessary reorientation from a fossil based society – oil economy – to a sustainable bio-economy based on use of renewable resources.

The EU framework programmes for research and development has for many years had the objective to promote the idea of biorefineries and other uses of renewable resources. This will also be the case in the seventh framework programme where bio-economy will be an important issue.

The EU has adopted ambitious targets regarding renewable energy. This is the case with an overall objective of 22 per cent of the energy supply and 12 per cent of the electricity consumption. Furthermore there is an indicative target of biofuels for transportation increasing from 2 per cent in 2005 to 5,75 per cent in 2010.

This directive on promotion of liquid biofuels will call for a substantial increase in production of energy from agriculture – probably requiring an acreage increasing from 4 mill. hectares in 2005 to 9,5 million hectares in 2009.

This is a substantial increase and it will require large investments in production facilities, new infrastructures and decisions among us farmers to grow other crops – or to focus on new outlets of our current crops.

There is, however, enormous potential in European agriculture. In EU-15 there was in total 130 mill. hectares of farmland. This was increased to 188 mill. hectares after the enlargement.

It will also stimulate research and industrial development by creating a market for new outlets. And it will call for the development where the most competible and sophisticated integrated solutions will win.

In addition to the decided targets for renewable energy the Midterm Review of the Comman Agricultural Policy has historically important developments.

The de-coupling of the payment scheme means that the EU does not interfere in the farmer's decisions regarding what to grow. This means that in addition to growing nonfood crops on set aside land, it will promote the possibilities for producing nonfood products and food on the whole agricultural area. In addition there is a further premium of 45 Euro per hectare for energy crops grown on not set aside land.

This co-ordinated stimulation of the research, the market and the agriculture is the key to obtain the development. What is crucial is, however, to maintain the target.

Many countries have decided to promote renewables. This is also the case in Denmark. We have been pioneers in using straw and wood for heat and electricity and manure and organic waste for biogas. We have also had targeted nonfood research programmes which have been important in building up capacity and intellectual platforms.

The basis for industrialisation and development of new industries and hence employment and export of equipment and knowledge has, however, been spoiled as the policy for promotion has shifted to a policy that stops the development.

Therefore in addition to the importance of a coherent policy between agricultural policy, energy policy, taxation, research etcetera it is essential to have a constant policy of promotion. This policy must include targeted policies on four levels the local or regional level with focus on rural development national level with focus on framework conditions EU with focus on coherent policies regarding agriculture, environment, energy and research, and finally globally with emphasis on fair trade conditions within WTO.

But as I stated earlier: I believe time is maturing the concept of integrated biomass utilisation as a key technology in a sustainable society.

We still need development of the possibilities. Therefore research and demonstration of new technology is essential.

I believe this seminar will bring us forward. I'll therefore leave the floor to presentation of new research results and fruitful discussions that will bring us all forward.

Biomass in the Context of Biorefineries. Optimal Biomass production for Energy Utilisation and New Products

J.B. Holm-Nielsen

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Introduction

In the conditions of global warming and increasing release of CO_2, CH_4, N_2O and other greenhouse gasses there is a tremendous need for actions to be taken. Newly tendencies of such actions have started in countries like Germany and Austria, where farmers are making paradigm shifts from food and feeding producers towards biomass producers, at higher levels of land productivity, for the energy demands and needs, and for new biorefinery products.

In Europe renewable energy production will constantly increase due to restricted use of fossil carbon resources world-wide and a prosperous future for various renewable energy technologies among others solar power, wind power and biomass based energy systems. At the same time we don't have to forget creation of new employment, as contrast to stagnation, and that EU needs developments towards advanced technology societies, in the context of decentralisation of energy recovery resources, which have to be sustainable, in contrast to the fossil fuel century we have just passed.

How to produce biomass for biorefineries and examples of resource potentials?

In all countries, in temperate, sub tropic and tropic climate zones, there are various medium to high potentials of producing biomass for a broad variety of demands, except in arid and semi arid climates, where the deserts and steps are widespread.

If good growing conditions such as sunlight, temperature above 5 ºC and sufficient water in the root zone, in the top soils, are available, besides recycling of nutrients from the societies and in some cases addition of chemical fertilisers, we have the basic conditions in place for biomass production from efficient photosynthesis.

In table 1 and 2 a case example from Denmark is given. This is a picture of potentials and possibilities for the future European paradigm shift towards biomass production for energy and new biomass based products.

In earlier decades all efforts were concentrated on production of food, and for feeding an increasing population and an increasing animal production. At the same time all energy demands and supplies were fulfilled by fossil carbon sources.

Table 1. Example of how the entire area of Denmark is utilized, including future possible changes. The survey balances as well interests of agricultural and forestry production and nature conservation and environmental interests.

Area usage; units in 1.000 ha	**1995**	**2005**	**2025**
Arable land	2.290	2.035	1.770
Fallow / brackish	220	150	0
Non-food, single/mutiannual	30	150	300
Permanent grassland	200	325	450
Agriculture total	**2.740**	**2.660**	**2.520**
Forestry / woods	500	550	650
Fences, ditches, field roads	113	123	133
Heath, dune, bog	200	205	210
Lakes, streams	65	75	95
Buildings in rural areas	230	230	230
Cities, roads, holiday cottages	460	465	470
Total area	**4.308**	**4.308**	**4.308**

Source: The Danish Board of Technology, “Biomasse til energiformål – et strategisk oplæg”

From 2005 to 2025 the tendency will be that there will be no more fallow land. Part of the arable land resources, in the range of 10-20-30 percent of the categories of arable land, fallow and non-food areas will in the next two decades be utilized for energy farming, cultivation systems aiming at maximum energy storage in organic biomass with acceptable quantities of medium to high net yielding crops per hectare. These kinds of crops will be grown and handled much more rational than traditional food crops and as cheap as possible at the input side, to gain as favorable energy output and balance as possible.

Table 2. Danish gross energy consumption of present years compared with a survey of future scenarios of either light green or dark green scenarios. One scenario features how to run the society without any kind of fossil fuels. In these scenarios is included highly efficient utilisation of energy sources by all means as well as energy savings at all levels.

Unit: PJ per year	**1992 *)**	**2003 *)**	**2030 Light green scenario**	**2030 Dark green Scenario**
Oil	348	342	246	0
Coal	324	176	22	0
Natural gas	95	191	146	0
Biomass	54	88	119	6-7 (137)
Biogas	<1	4	-	45 (90)
Liquid biofuels	-	2	-	22 (47)
Solar heating	<1	<1	4	40
PV (Solar cells)	-	-	4	25
Windpower	3	20	32	90
Net power import	13	- 31	0	0
Total	**776**	**793**	**573**	**229 (429)**

*) Figures from the Danish Energy Authority

Source: The Danish Board of Technology, “Fremtidens vedvarende energisystem”

In table 2 can be found the energy net consumption derived from biomass in the span of 119 – 137 PJ of biomass year 2030. In combination with 300.000 – 500.000 ha arable land dedicated for energy and biorefinery farming, in the long term it will be more than realistic to reach between 120 – 140 PJ biomass energy production, or even higher, under Danish conditions. This means that such a society can be organized and managed on conditions of between 50 – 100 pct. renewable energy sources. At the same time the dependencies of fossil carbon sources will be minimized throughout the years, as can be seen in the statistical data from year 1992 and year 2003, where the coal dependencies have been decreased nearly to the half of the consumption in 1992.

The future will be much more diversified, where regenerative carbon sources will be based on biomass sources of various kind, naturally adapted to the different growing conditions in the changing climate conditions and with a broader utilisation of biomasses for food, feed, fibres, fuels, fertilisers etc, after passing different, more or les advanced steps of biorefining

Table 3: The table contents 19 European Countries out of EU-25, registrated data of total area of land use. Areas of specific interests for biomass production conditions are the columns of arable land, and partly forest areas and permanent grassland areas. The fallow areas will quite soon be integrated in arable land or non-food areas.

Unit: 1.000 ha	**Total area**	**Agriculture area**	**Arable land (% of total area)**		**Forest (% of total area)**		**Permanent grass (% of total area)**		**Fallow**
Country									
Austria	8.386	3.375	1.380	16,5 %	3.260	38,9 %	1.917	22,9 %	108
Belgium	3.053	1.390	846	27,7 %	607	19,9 %	521	17,1 %	26
Cyprus	925	144	88	9,5 %	-	-	1	0,1 %	8
Denmark	4.310	2.689	2.494	57,9 %	473	11,0 %	184	4,3 %	202
Estonia	4.523	890	676	15,0 %	2.251	49,8 %	194	4,3 %	33
Finland	33.815	2.222	2.122	6,3 %	22.487	66,5 %	25	< 0,1 %	202
France	54.909	29.632	18.271	33,3 %	15.375	28,0 %	10.046	18,3 %	1.348
Germany	35.703	17.042	11.813	33,1 %	10.531	29,5 %	5.013	14,0 %	850
Hungary	9.303	5.865	4.516	48,5 %	1.772	19,0 %	1.061	11,4 %	183
Ireland	7.027	4.410	799	11,4 %	-	-	3.220	45,8 %	0
Italy	30.133	15.620	8.450	28,0 %	6.855	22,7 %	4.365	14,5 %	681
Malta	32	10	9	27,5 %	-	-	-	-	<1
Netherlands	4.153	1.932	1.005	24,2 %	352	85,2 %	881	21,2 %	30
Poland	31.269	18.392	14.046	44,9 %	9.028	28,9 %	4.078	13,0 %	1.676
Portugal	9.191	3.795	1.578	17,2 %	3.465	37,7 %	1.429	15,5 %	551
Slovenia	2 027	510	173	8,5 %	1.283	63,3 %	307	15,1 %	1
Spain	50.502	25.353	13.245	26,2 %	16.460	32,6 %	7.030	13,9 %	3.510
Sweden	44.996	3.054	2.694	6,0 %	22.323	49,6 %	372	0,8 %	266
United Kingdom	24.291	16.522	6.452	1,9 %	-	-	10.019	41,2 %	43
Summary	**358.548**	**152.847**	**90.657**	**-**	**116.522**	**-**	**50.663**	**-**	**9.719**

J.B. Holm-Nielsen and Michael Madsen, Bioenergy Department, SDU, Denmark
Source: Basic data from Eurostat, data from 2001.

From table 3 can be surveyed the biomass potentials for biorefinery purposes. E.g. Germany, a large central European country has 11.8 mil. ha of arable land. Future biomass potentials in Germany for energy crops is stipulated to be up to 2.0 mil. ha or 17 pct. of the arable land in the medium long time span. From this area can be derived and produced a corresponding energy production of 40 pct. transportation fuel or 20 pct. of primary energy consumption.

Table 3a and 3b: Scenarios of area utilisation of arable land from 19 EU countries for energy crop production, and the potentials of energy recovery form these areas expressed as mil. tons of oil equivalents at 3 different crop yielding levels.

Area used for energy prod.	10 % of arable land in EU-19	20 % of arable land in EU-19	30 % of arable land in EU-19
Yield pr. ha			
10 t TS pr. ha	1.632 PJ	3.263 PJ	4.895 PJ
20 t TS pr. ha	3.264 PJ	6.527 PJ	9.791 PJ
30 t TS pr. ha	4.895 PJ	9.791 PJ	14.686 PJ

Note: The energy potential is based on straw; 18 MJ pr. kg TS. The total arable area of EU-19 is according to table 3 estimated to 90.657.000 ha.
J.B. Holm-Nielsen and Michael Madsen, Bioenergy Department, SDU, Denmark

Area used for energy production	10 % of arable land in EU-19	20 % of arable land in EU-19	30 % of arable land in EU-19
Yield pr. ha			
10 t TS pr. ha	36 mil. TOE	73 mil. TOE	109 mil. TOE
20 t TS pr. ha	73 mil. TOE	146 mil. TOE	219 mil. TOE
30 t TS pr. ha	109 mil. TOE	219 mil. TOE	328 mil. TOE

TOE: Ton oil equivalent ~ $4{,}48 \cdot 10^{10}$ J
J.B. Holm-Nielsen and Michael Madsen, Bioenergy Department, SDU, Denmark

In the coming 10 -20 years it will not be unrealistic to see an increasing utilisation of crops for energy and industrial purposes. Scenarios of 10 -20 -30 pct. of arable land shifting from food and feed towards energy farming will gradually occur. Another large European country, Ukraine is rapidly developing in the same direction like the EU countries. In such a large, fertile agricultural country it is stipulated that introduction of renewable energy sources will grow as fast as in many EU countries, and in the table below biomass will cover nearly 50 pct. of the renewable energy resources. Energy cropping will even increase this potential when energy crops are integrated in large scale biorefinery systems in Ukraine.

Table 4: Renewable energy sources (RES) in Ukraine. Calculations and predictions until 2030

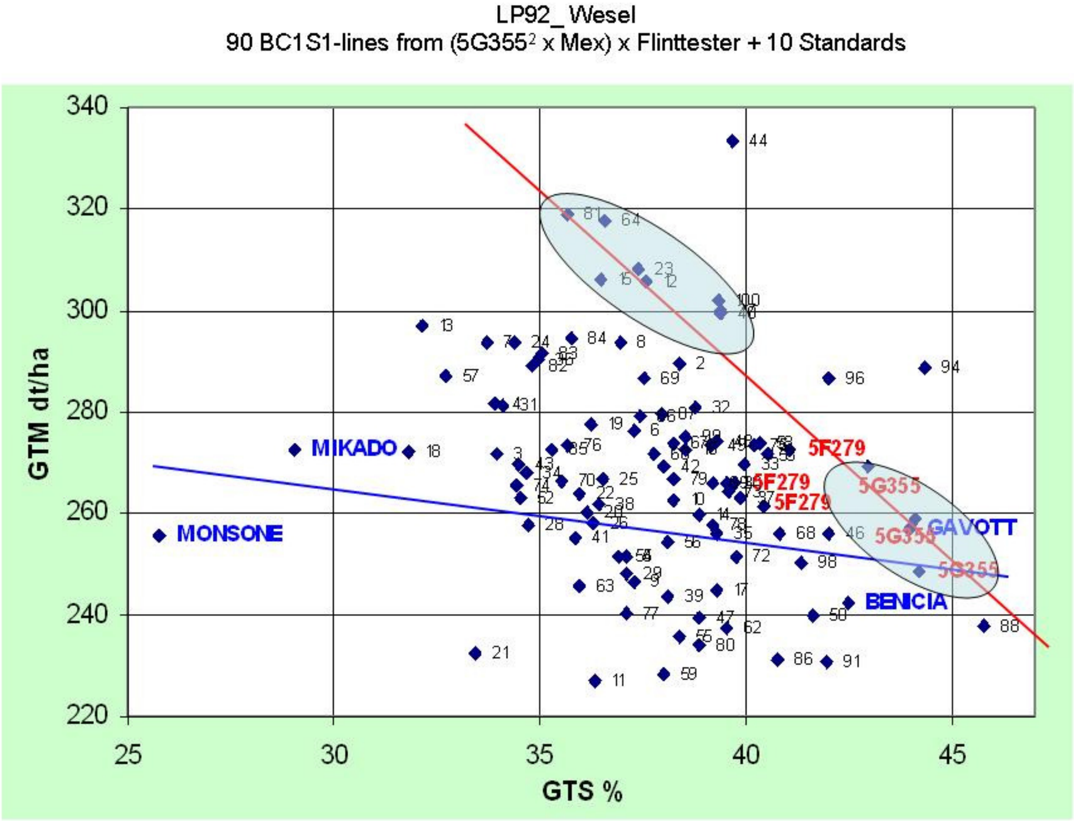
Type	Technical potential		Heat and electricity production from RES							
			2001		2010		2020		2030	
	Mln t coal eqv	%	Mln t coal eqv	%	Mln t coal eqv	%	Mln t coal eqv	%	Mln t coal eqv	%
Wind energy	15.0	23.8	0.012	0.2	0.22	3.2	1.00	7.0	2.15	10.0
Photovoltaic	2.0	3.2	-	-	0.001	0.02	0.01	0.1	0.03	0.1
Small hydro	3.0	4.8	0.17	3.1	0.15	2.2	0.48	3.4	0.65	3.0
Big hydro	7.0	11.1	4.36	78.7	4.8	68.6	5.6	39	6.53	30.2
Solar heating	4.0	6.4	0.002	0.04	0.12	1.7	0.7	4.9	1.28	5.9
Biomass	**20.0**	**31.7**	**0.99**	**17.9**	**1.66**	**23.8**	**6.3**	**43.9**	**10.13**	**46.9**
Geothermal	12.0	19.0	0.004	0.1	0.034	0.5	0.247	1.7	0.83	3.8
Total	63.0	100	5.54	100	6.99	100	14.34	100	21.6	100

Note: 1 toe = 1,43 t coal eqv.
Source: Geletukha et.al. The Institute of Engineering and Thermophysics of National Academy of Science of Ukraine, Scientific Engineering Center “Biomass”.

Case example of plant breeding gene pool potentials exemplified by maize/corn crop varieties.

The gen-pools are not yet developed for dedicated biomass production. For decades crop breeding was dedicated for specific tasks of optimal production yields for starch, vegetable oil, sugar, proteins and not for the total crop yield, including the interesting lignocelluloses complexes in steams and leaves and the entire crop biomass. A future perspective for biomass utilisation includes the whole crop, with as effective and/or robust conversion into photosynthesis products, at as good rates as will be possible, due to various growing conditions. Potentials are not yet very well developed in the plant breeding and cropping sectors of agriculture.

Below is a plant breeding company example of new maize varieties. The breeding incentives for energy maize varieties include **a.** short-day genes, **b**. tolerance towards cold growing conditions in late varieties, **c.** nutrient/water efficiency. Commercial energy maize varieties, as an example, will be on the market in 2007. The figure below shows how to grow not 15-20 t of TS/ha, but an increasing trend towards 30 t of TS/ha in the future.



LP92_ Wesel
90 BC1S1-lines from (5G355² x Mex) x Flinttester + 10 Standards

Source: Dr. Ernst Kesten, KWS Saatgut AG, Einbeck, (D)

Harvest of energy maize

Source: Dr. Ernst Kesten, KWS Saatgut AG, Einbeck (D)

Future perspectives for biomass utilisation in the energy and industrial sectors.

The potential to upgrade biomass for biofuels is evident, and can be converted in conventional used technologies, as example fermentation processes for fuels to the transportation sector. At the same time the developments are well on the track for new harvest and conversion technologies. Biofuels and fuel cells can reduce CO_2 emissions significantly from the transportation sector, as we have seen in stationary systems such as biomass for heat and electricity production systems. (Larsen et al., 2003)

Developments and implementation of improved growing systems for the purpose of biomass production for biorefinery utilisation will get more and more into focus due to increasing demands for biofuels and a variety of biorefinery products. The commitments for making this kind of shift in the way of widespread using sustainable resources in much larger scales have grown and will grow in this and the coming decade, mainly due to increasing needs of growth in living conditions in big countries like China and India, and all over the unindustrialized world and because fossil fuels will be completely inadequate in the medium to long term.

What is a Biorefinery?

The basic conceptual idea of biorefinery is illustrated by the flow sheet below, from the survey conducted by the research group – The Biomass Institute, SUC, (DK) back in the early 90'ties and after that realized in the full scale: The green juice – amino acid , Lysin plant, Agroferm Ltd. Other ideas are realized as joint biogas plants in Denmark like Ribe, Linko, Lemvig, Blaaberg and Thorsoe biogas plants, to mention only some examples.

In this decade, interesting ideas are under development in new concepts like energy crop biorefineries for gaseous and/or liquid biofuels. A new integration is under R D & D realisation, for conversion of lignocelluloses products like straw, wood chips and whole crop silage for conversion into biofuels and biogas. All initial products will be used for either bioethanol for the transportation sector and biogas for combined heat and electricity production or the natural gas grid and biofertilizers for recycling to the arable land.

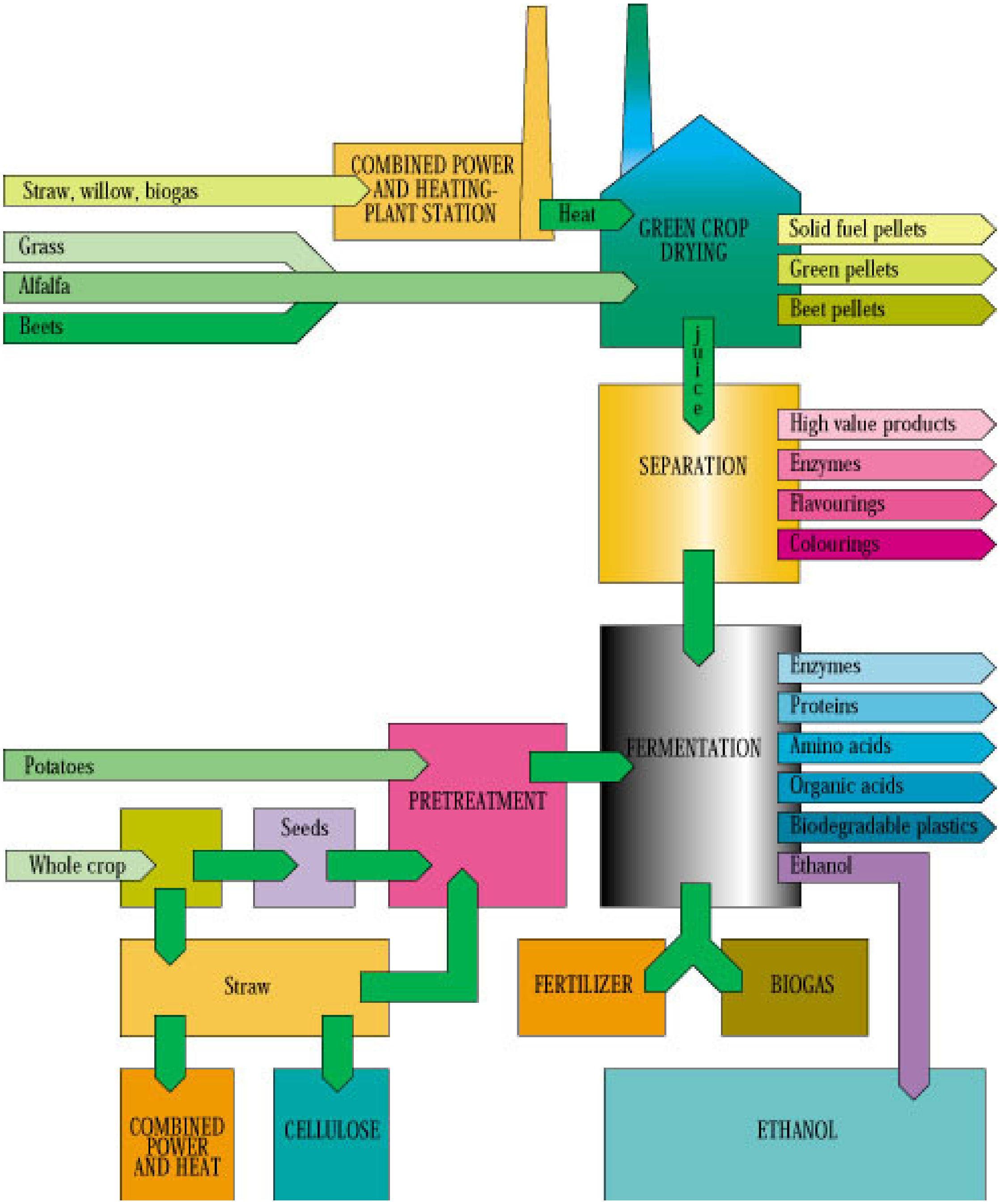


Figure: Ethanol in the Green Biorefinery
Source: Pauli Kiel et. al. Biomass Institute, SUC, 1994

Summary

Biorefineries are thoroughly integrated thinking and utilization of biomasses of any kind for new products, for industrial and energy use. A terminology as biomass for food, feed, fibers, fuels, and future industrial applications is going to be realized and implemented at increasing speed in this and the coming decade. A full paradigm shift is well underway from fossil fuel dependencies towards biomass and accompanying renewable energy recourse based economies.

Optimal utilization of biomass converted to valuable industrial and energy products, as high valuable replacements for fossil fuel products – the world is getting greener and more sustainable if we are doing a more progressive and faster effort, bearing a more balanced future in mind, environmentally as well as economically speaking internationally.

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From Sugar Factories to Biorefineries

How to bring about a change in paradigms step by step and how to involve farmers in the process.

Jens Born

CATS at FH Flensburg University of Applied Sciences

We observe a lot of constraints concerning the future of our industrial world:

1. The foreseeable finiteness of fossil organic resources as our most import organic raw material source.
2. The greenhouse effect, which changes our climate
3. Increasing economic restrictions for farmers (decreaing share of value addition, arable land which will be idled, decreasing subsidies)

The more or less common alternatives are

1. sustainable[1] resource management which will be based more and more on renewable resources
2. Reduction of greenhouse gas production
3. New sources of income for farmers and other people living in rural areas

The increasing use of biomass, products from arable lands and forests, biological residues, like straw, and biological wastes, as renewable resource for technical purposes, as fuels, chemicals, and materials is possibly the most basic contribution to realise the mentioned alternatives in the near and mid range. So as before the industrial age until 150 years ago farmers and forest owners will be important suppliers of basic raw materials in the future. Based on the demand of sustainability the future use of organic raw materials can be integrated in naturals cycles, and source and sinks of greenhouse gas emissions will be balanced. But until recently, the conversion of biomass into fuels, chemicals, and materials is, particularly for mass production, not competitive. Biorefineries may be a competitive alternative.

The industrial way of production and application of fossil resources was superior, because of the conformity between the technological demand of centralisation (from steam engines to gigawatt power plants) and raw materials coming from point sources (especially crude oil and gas, which can be pumped even over long distances). The techno-economic development results most efficiently in the economy of scale or – more simple – big is beautiful. On the other hand organic fossil resources had been pretreated by nature millions of years ago, i.e. their application was superior to the use of untreated biomass (fluid, high heating values, less diversified mixtures) in principles as long as it is easily available.

To overcome the disadvantages of the industrial way of production: missing sustainability and finiteness of the resources it is based on, one has to develop a new way of production, which contents not only the basic advantages of both, a highly efficient technology based on renewable resources, but also will overcome the disadvantages of both and the missing links between them, i.e. economy of scale versus wide areas as raw material sources. The best example to illustrate this dilemma is the experience mankind has made with the integration of flexible wind energy systems into electric grids based on static centralised GW-power plants.

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[1] Which will be used always following the definition of the Brundtland commission [1]

Learning from history – how to make the application of biomass superior

Raw materials usually are mixtures of more or less diversified components. The oldest technical way to get the component(s) of interest is to extract them mechanically, thermally, or chemically. Even in the first time of the industrial age, one extracted the interesting components, like benzene or aniline, from coal, one distilled wood to get methanol, and even today one extracts wood to get celluloses, or sugar cane and sugar beets to get sugar [2]. Beside the main product process is focussed normally more than 50% of by products results additionally, which may be valorised or are wastes in the worse case.

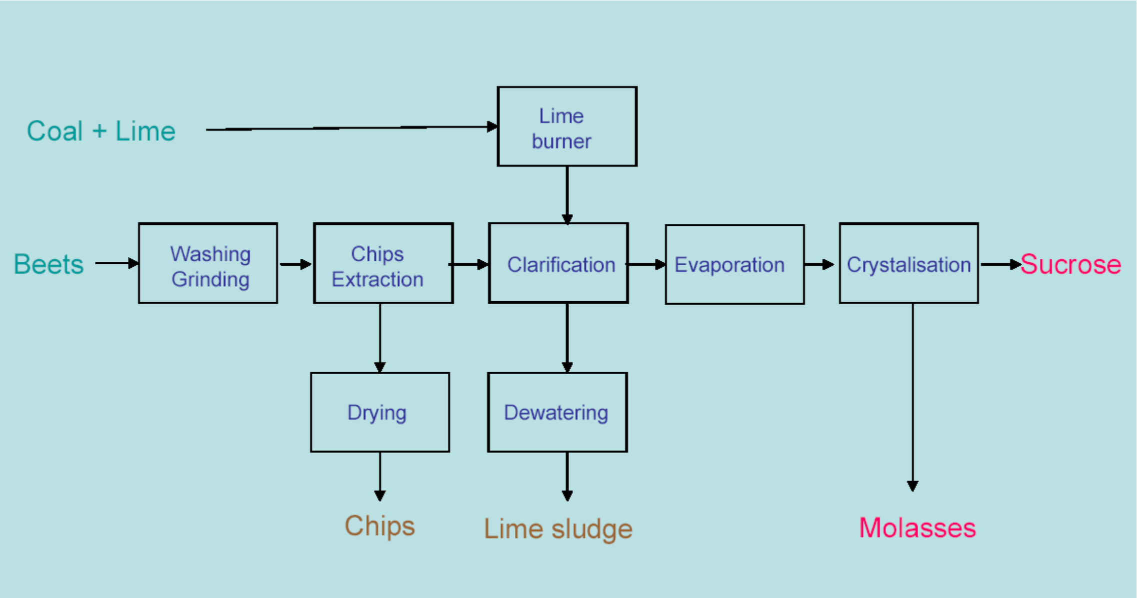
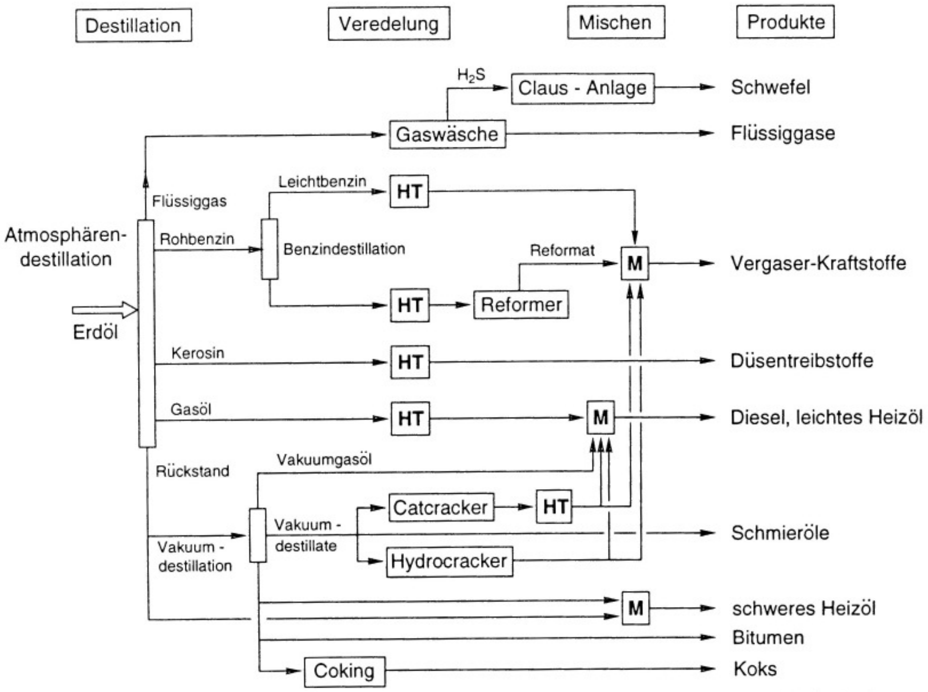


Figure 1: Sugar Factory

With the rise of chemical industries in the second half of the nineteenth century a competitive alternative to extraction was origined: based on (around 15) molecular small components which might be extracted very easily from coal and especially from crude oil one began to synthesize the components of interest. This alternative way was often much cheaper, i.e. withless expenditure, the quality of the products usually was higher, and it was especially possible to get new components with really new or better properties, like polymers, dyestuffs and so on. Based on the knowledge of chemical synthesis, catalysts were invented, which made it possible not only to convert reactants into products with less energetic effort, but also to crack the residual components of the crude oil into additional yields of the small molecules already mentioned as well as into tailor made mixtures like gasoline and gasoil of high quality. So fuel refineries as well as petrochemical refineries totally convert the crude oil into an economically most profitable and well balanced portfolio of products, nearly free of wastes [2].



Vereinfachtes Blockschema einer Kraftstoff-Raffinerie (**HT** Hydrotreater, **M** Mischer)

Figure 2: Fuel Refinery [3]

The conclusion is, that the concentration of the technical effort onto the most profitable and well balanced portfolio is superior to the concentration of the technical effort onto one product. However, until recently this statement will only be true under the restriction onto mass production, caused by the economy of scale. Sugar factories as well as refineries are in principle finalised technologies, i.e. the chance to realise significant innovations is low.

Biomass conversion processes and their integration into biorefineries

As mentioned earlier processes as well as processes to convert biomass are designed under the prerequisite to get a maximum yield and quality of only one lead product, like saccharose, Cellulose, biogas, biodiesel and so on. This strategy of production has some important drawback:

1. A huge output stream (up to 85% of feed stream) of different kinds of wastes, which may be valorised more or less (high quality glycerol, C-source for all kinds of fermentation processes, but also and most common as feed and fertilisers)
2. Production time tables are highly dependent on harvesting times and storage properties of feedstock
3. Profitability depends changing prices for the lead production because of low flexibility

Those kinds of processes are only competitive, if there exist no alternative products, like in Cellulose industries, or if they are subsidized by the legislation, like sugar industries, and biofuels.

Biomass has to become an all around competitive alternative to crude oil as feedstock for organic fuels, chemicals, and materials in order to change the game to a long-term sustainable and secure base of feedstock for the future. I.e. it is quite sure, that biomass conversion and utilisation of the future will be really different compared to the time before the industrial revolution and even compared with its processing nowadays, and it is quite sure that centralised product strategies has to be moved to more or less decentralised ways of production. Some important ideas and developments can be recognised, which will have strong influence on future conversion of biomasses:

1. It is possible to realise products in two ways: extraktion or synthesis, which additionally opens the way to new, unknown molecules as well as to use the feedstock completely within integrated production networks.
2. Chemical industries as well as living systems synthesis strategies are founded onto a small number of small key molecules, which are starting points for the synthesis of all products within the portfolio of the particular system
3. The utilisation of biomass is of greater variety than the utilisation of fossil organic feedstock. One recognises utilisation cascades, which are founded onto the deepness of change of the biomass. (For example wood can be used as timber, as sources of wood fibers, as source of Cellulose, as C-source for fermentations and basic chemicals, as source of syngas, or as direct source for energy production [4].)

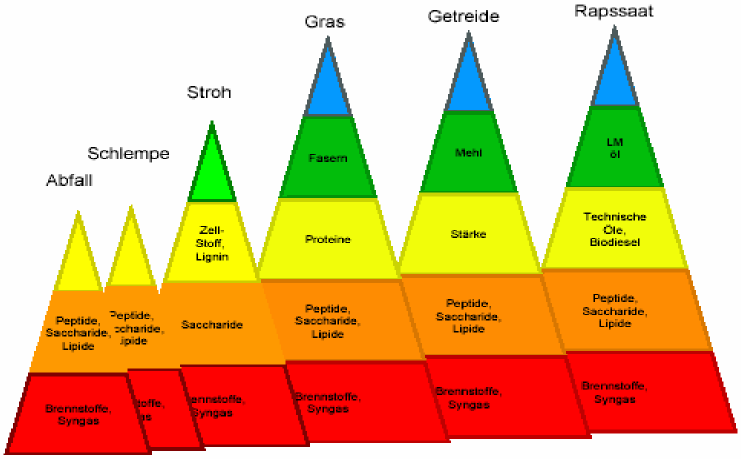


Figure 3: Utilisation cascade of differnt kinds of biomass [5]

4. The renaissance of industrial biotechnology, which at its best is nanotechnology, will offer the possibility of more environmentally friendly processes and products, higher production yields, more flexibility within similar equipment environment, less energy use
5. Process intensification will combine several consecutive unit operations within one procedure, particularly the combination of membrane technology with fermentations and chemical reactions
6. The design of processes and process equipment, which in particular will be as simple and robust in utilisation as refrigirators or washing machines, the economy will be replaced by the economy of number in some instances

Biorefineries, which can be defined as the integration of different, more or less flexible processes of biomass conversion based on mass and heat exchange networks with the aim to apply and convert feedstock completely and sustainably into a portfolio of most profitable products, seem to be a proper solution considering the mentioned ideas and developments.

The definition combines the future needs to use biomass as basic organic feedstock with the success factors of petrochemical and fuel refineries. There a lots of definitions published in literature, and there are even more processes which can be classified as biorefineries but which are not named biorefineries. A lot of companies from food and feed industry, especially, tried to apply or comercialise their byproducts as feedstock for new processes.

- Grappa is a spiritual product from waste in (italian) wine production
- Almost all rural biogas plants use their liquid/solid effluent as fertiliser
- Press cake of biodiesel plants is sold almost always as cattle feed
- The German Nordzucker found Amino, a company producing amino acids from molasses
- Lactose from whey was used since decades as fillers in pharmaceutical industries
- Vanillin is produced from the black liquor of Cellulose industry

Most of these initiatives are more or less singular, inherent, i.e. directed by the core conpetencies of the companies, and often they are driven by costs for wastewater and solid wastes. But there seemed be at least one example concerning a biorefinery directly competing to petrochemical industry:

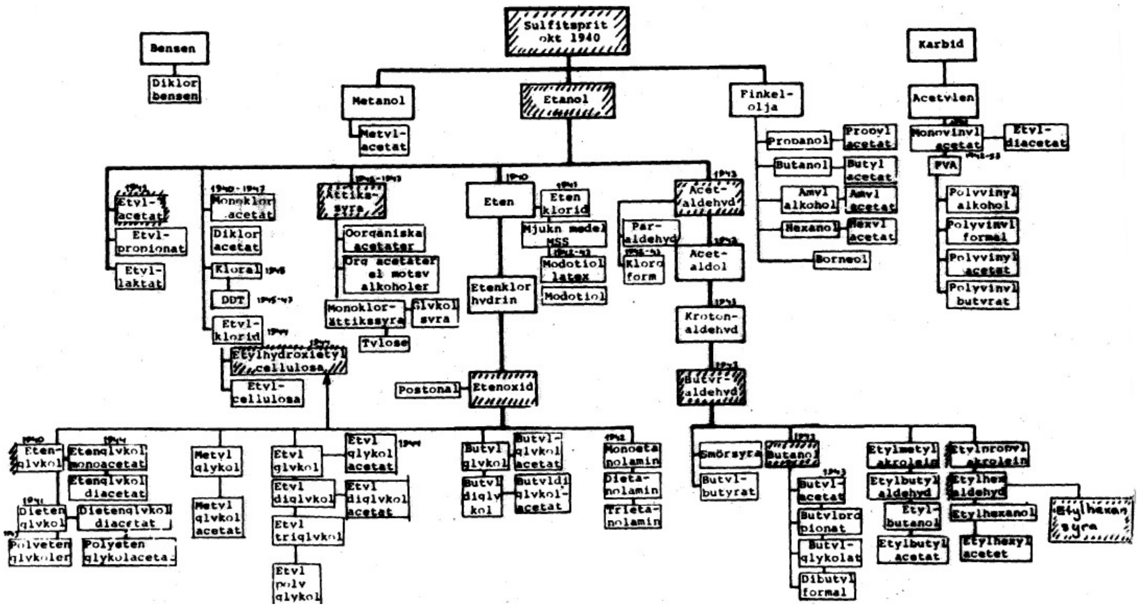


Figure 4: MoDo refinery [6]

An astonishing great diversified portfolio of products was realised in the middle of the last century. Until today there are still three products synthesized.

Biorefinery as a concept

Thinking about biorefineries there are three basic concepts under discussion:

1. Based on the kind of feedstock:
    - Lignocellulose feedstock biorefinery
    - Green biorefinery
2. Based on traditional industries
    - Conversion of waste streams and different kinds of feedstock for value-added chemicals by food industry
    - Application of new chemical core components and monomers from biomass by chemical industry

3. Based on strengthening the economy of rural regions
   - More or less small and decentralised units
   - Involving the farmers as owners, actors, and suppliers
   - Recognising the fact that the price of feedstock increases with the amount converted within the factory

The first concept is a more or less academic model (no business man will think first at feedstock, but on profitabel products. One biorefinery constructed in this kind of thinking the 2B biorefinery in Schaffhausen (Switzerland) filed for bankruptcy last year, because of the far too low product prices which can be realised for its cash cow.) Most effort will be done following the second concept [7]. We should concentrate on the third concept (which sometimes will be discussed in the constraint of the first, academic concept).

In Germany, but also in Switzerland (as mentioned), in Austria, in Italy, in the US and in some developing countries, those concepts to strengthen rural economy are under discussion, under construction or even realised. My main interest is to simulate different kinds of biorefineries

Some experiences from Schleswig-Holstein

In 2004 the regional government published the results of a feasibility studies: "Feasibility of Biorefineries in Schleswig-Holstein" [5]. It is not only a collection of examples of biorefineries in order to identify success and risk factors but also to develop scenarios to introduce biorefineries in the state based on the estimation of the state of the art of different kinsds of technologies.

Particularly the farmers and their commercial organisations ar interested in finding new fields of application of their products, beginning with wastes, like manure, ongoing with cereals and silage, which will be gasified partly in biogas plants. They found a Biodiesel producer called Marina Biodiesel, which will be one of the biggest in Germany in the near future, and they are thinking about Bioethanol. All these products are applied as fuels driven by national and european regulations to reduce CO_2 emissions. This process will develop new business structures, new kinds of production networks, and knowledge in a different section of economy, which is really strange for them. But all of them know, that this subsidized fuel production will not be profitable in a long term. So concepts of realising rural biorefineries which should be first based on energy production and in the long run onto value-added chemicals and materials, are of strong interest for them. Some months we invited an Italian company IBETECH to present its business concept of a biorefinery which processes cattle feed, Proteins, and Bioethanol (which may be substituted by ABE fermentation for example). The concept seems rather interesting, but it has the drawback, that energy consumption is based on fossil resources.

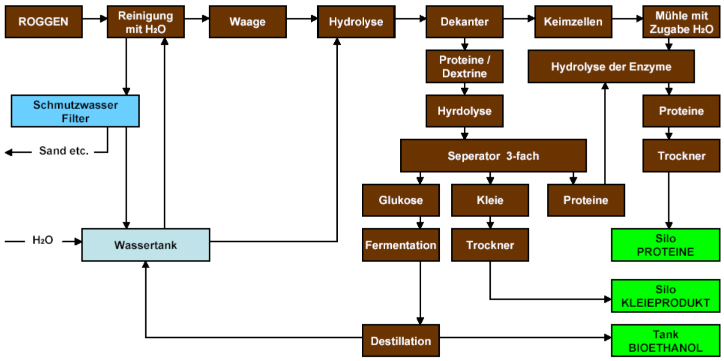


Figure 5: IBETECH biorefinery [8]

A different, but until now most optimistic realisation of a rural buiorefinery was installed in an old ethanol distillary, after the liberalisation of the alcohol market in Germany in 1999. They decided to diversifiy their business not only to more than potatoes as feedstock of alcohol production, so they are able to produce al over the year, but also to start the production of biodiesel. The residues from the alcohol plant and the reestrification of plant oil are fed into a Biogasplant together with manure.

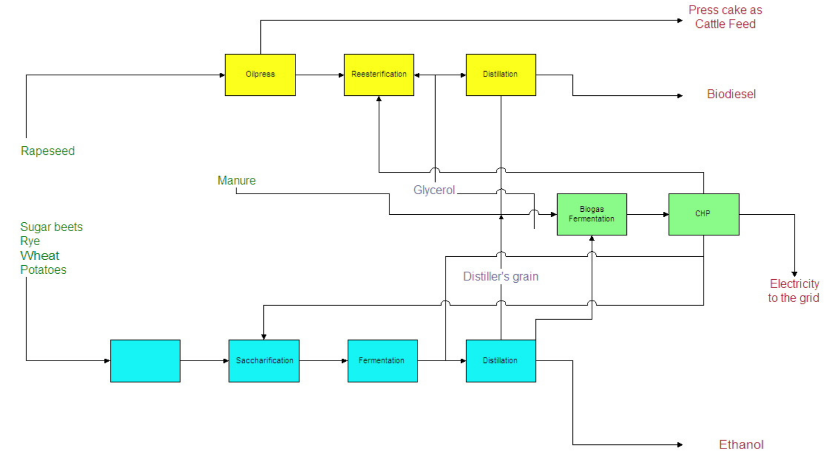


Figure 6: KVG Schleswig

Inspirated by the different developments in scientific discussions as well as in reality around us, we start to simulate biorefineries with conventional software tools, like SuperPro Designer, ChemCAD, and in future with ASPEN and Umberto, in order to integrate different processes of biomass conversion and optimize them to become most profitable. The kind of simulation allows to make go-nogo decisions, sensitivity studies to identify weak process steps, and to develop alternatives. We use commercially avaible and in the engineering community accepted software, in order to use the mighty databases and features within them, to produce results, which may be transparent and acceptable for the engineering community, and last but not least to train our students on that.

It was a success, even if it was negativ result, that we promised the insolvenz of 2B biorefineries in a period they promised profits and all of the world think they will be successful. Later on they concluded based on real data the same reasons as we found out a year before [9].

Our latest project is the simulation of a modularised biorefinery in order to get some information about the dimension of masses and mass and energy balances, complexity and costs and cost structures. Because it is modular, we define core processes one can start with and it may be possible to add the other modules step by step. The main modules are:

- The MiniMill process to convert straw into Cellulose
- Flexiferm to produce fuels, chemical intermediates and solvents dependend markets constraints
- A Biogas plant to convert wet waste streams into Energy (methane)
- A thermochemical gasifier to convert dry solid waste streams into energy (syngas)
- Pretreatment equipment to solubilize sugar beets and potatoes and to reduce the water content in order to make it storable all over the year

The feedstock are cereals, maize silage, sugar beets and potatoes, but also manure different kinds of biowaste from within and from outside the bioreferinery. All of the processes are patentet and at least testet in pilot plants.

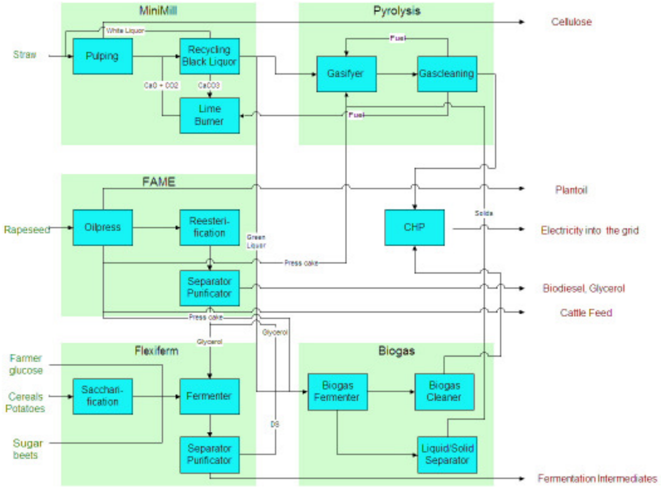


Figure 7: CATS Simulation Concept for a modularised biorefinery

We are in the middle of our work, but as so far one of the amazing results will be, that if the thermochemical procedure will work in practice the biogas process as a source of energy will be omitted, and only be applied as a source of organic acids and alcohols. But that needs some more experience in understanding and control of both, the thermochemical conversion and the biogas process. The future of the biogas process, i.e. the flexible production of diffferent kinds of interesting chemicals dependent only on nutristatisation or chemostatisation respectively, will probably introduce the paradigm change based on biorefineries, because this process might be the most flexible really stable process, caused by its unsterile environment which can be controlled into an ecologic equilibrium.

Conclusion

Biorefineries are evolutionary concepts of integrated biomass conversion processes which open an industrial paradigm change, i.e. conversion of a centralised way of production into a decentralised one, adapting the distributed character of feedstock. The technology is based on flexibel more or less nonsterile fermentations to form basic and intermediate organic chemicals and fuels, which can be integrated into an utilisation cascade for the relevant biomass. These processes can be predesigned and simulated successfully by modern commercially avaible simulation software in order to make go or no go decisions. Caused by its decentralised character biorefineries opens new important sources of income for the farmers and - as a big and fundamentally important financial and administrative challenge - flexibel farmer cooperatives. Nowadays decentralised biorefineries are future projects, at present conventional biomass conversion factories which try to valorise their waste streams are important transition forms.

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"Biorefinery, a long-term solution for side-stream valorisation"

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The large-scale agro-industry is producing a big amount of side-streams which are creating either environmental or economical problems. Bio-refinery might be a longer term solution in solving these problems . However, the economy as well as the technology of a Bio-refinery has to be proven before industry accepts such, most technical driven, solutions. Different options of side-stream valorisation and the hurdles which have to be taken before industry "believes" in Bio-refinery are investigated.

The longer term perspective to survive for the European agro-industry and therefore the European agriculture in general is to invest in full use of their crops, which includes Bio-refinery for side-stream valorisation.

Introduction

The agro-industry like the starch industry, sugar industry, dairy industry, etc. is more and more concentrated to very large-scale operations. In these operations focus is made on the primary product and less on the side products. Over the last decades investments are clearly made in size increase, rationalizing and streamlining the primary operation to reduce the operational and investment costs per ton of product.

Less attention is paid to the side streams which are produced in the processing of agricultural crops. Some exceptions are for example fibers from processing of chicorey into inuline and fructose, potato protein from potato starch production and the use of corn steep liquor for fermentation.

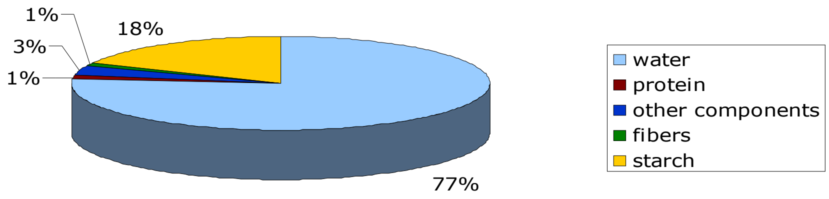
Large scale solutions hardly exist. And in some cases the side streams are either brought back to the land as fertilizer or fed into a waste-water treatment installation.

At various places the “biorefinery” as a solution for side-stream valorization is investigated. So far no real refinery processes are running. This mainly because of the technical but more-over the economical hurdles which are encountered.

Raw materials

Main 'raw materials' for biorefinery are the side-streams from the agro-industry. As an example, in the processing of starch potatoes more than 80% of the crop is non-starch (figure 1).

Figure 1: Composition of a starch potato (by percentage).



As for example a company like Avebe b.a. in The Netherlands processes yearly 600.000 t/y of starch, out of approximately 3 x 10^6 ton of potatoes. In this process the following quantities of side streams have to be handled:

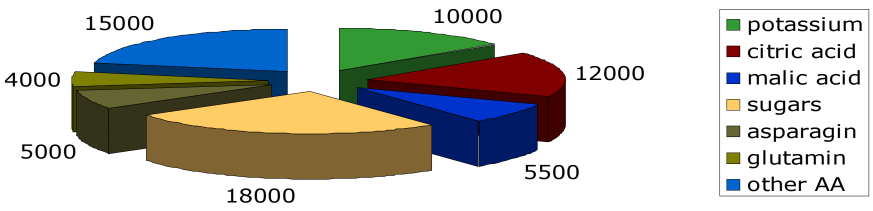
Water	2.300.000	ton/year
Protein	36.000	ton/year
Fibers	39.000	ton/year
Other comp.	99.000	ton/year

Only the evaporation of water takes per year approximately 400.000 t of steam which represents a yearly (energy) cost of 6 M€.

As spreading out of the 'water' fraction is restricted due to environmental rules only in a very limited time period and as in a country like The Netherlands also a large quantity of (pig) manure is produced and spread out over the fields, treatment of such stream leads to a high yearly cost.

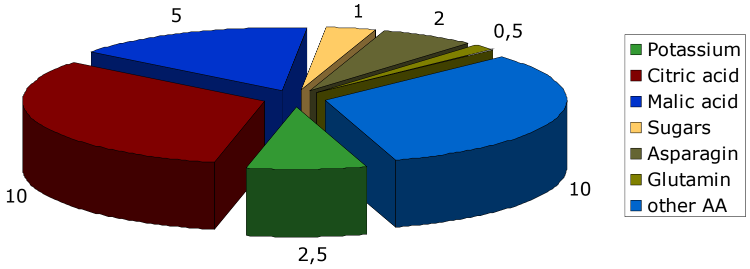
In an economical evaluation made by Avebe, the 'valuable' components making part of the 'other components' have been investigated. The water fraction contains approx. 60.000 t / y dry solids, in which various components are present. The main composition is given by figure 2.

Figure 2: Main non starch / non fiber components in potato juice (by yearly quantities in tonnage ds).



Assuming that these components could be isolated in a (relative) pure form, this stream contains a total value of at least 30 M€, which is divided as given by figure 3.

Figure 3: Market value of the main components (non-starch, non-fiber) from the potato (in M€ / year).



All together this stream has a value of at least 30 M€ / yr.

Looking to the various components application is in different fields, as given in table 1:

Table 1: Application of the different components from potato.

Component	**Application**	**Value (€ / kg)**
Potassium	As K_2SO_4 or KNO_3 as fertilizer	0,20 – 0,40
Citric acid	Feed, food, technical application	0,80 – 1,00
Malic acid	Food application (Ca-malate or malic acid)	1,00 – 2,00
Sugars	Fermentation source	0,15 – 0,30
Asparagin	Food, pharma	2,00 – 10,00
Glutamin	Fermentation source	0,15 – 0,30
Other AA[2]	Food, pharma or yeast extract replacement	5,00 – 12,00

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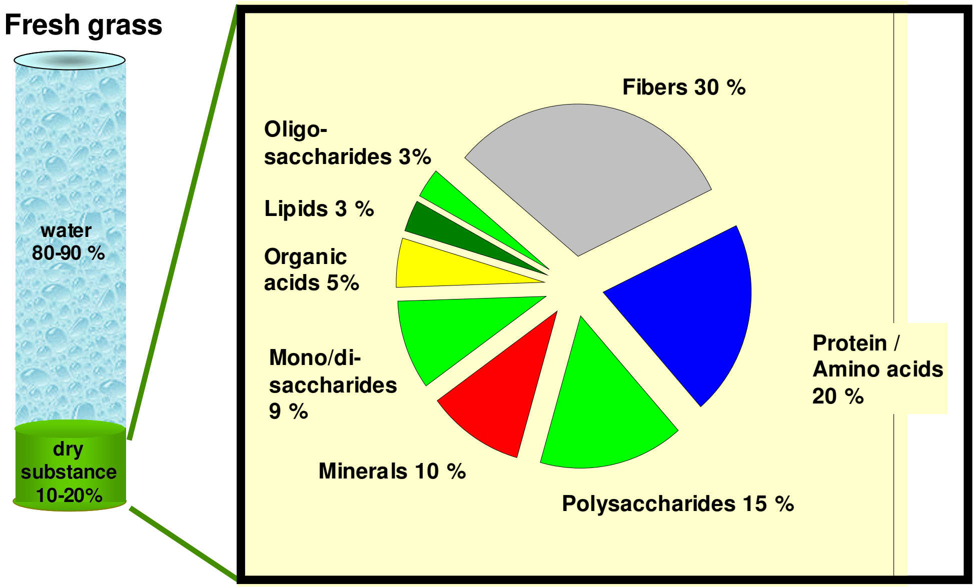
[2] Other amino acids

It is obvious that isolation of these components could be an interesting and attractive case for valorization. However, so far, the potato starch industry has not invested in such a "biorefinery".

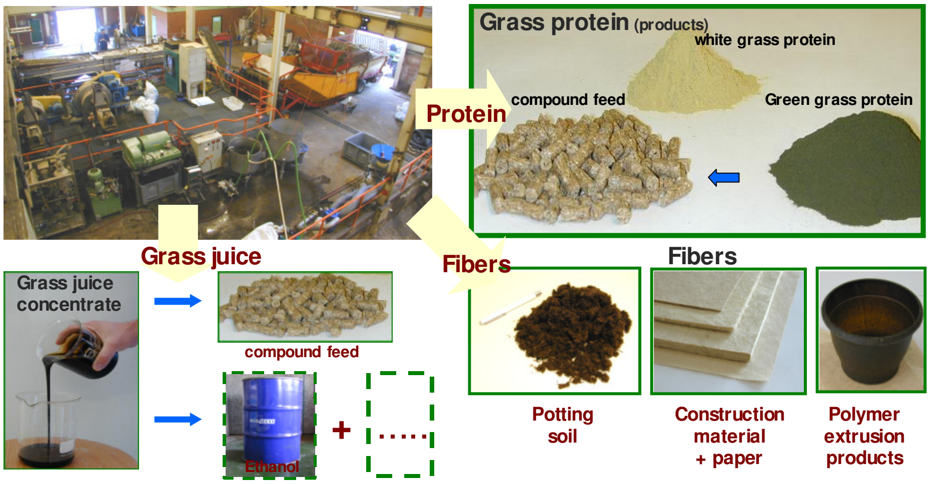
Another raw material which could be investigated for valorization is grass. At this moment grass is grown in massive quantities mainly applied for cattle feed. The grass can be stored using ensilage processes or drying. When grass is dried, in many cases the grass is pressed before drying such to decrease the drying costs. The thus obtained liquid is spread out over the fields for fertilizing purpose, but also the grass liquid contains a high amount of valuable components [1], figure 4.

Figure 4: Composition of grass.



In a consortium in which different governmental bodies, institutes and industry co-operated, the feasibility of a biorefinery process for treatment of grass has been investigated, figure 5.

Figure 5: Biorefinery of grass.



For this process a pilot facility was build, and kept into operation for several years. However, mainly due to financial problems, this process was not realized at real scale.

Available technologies

In order to isolate the various components different technologies could be applied. In order to judge the feasibility it is important to know the investment level and operational costs, but especially also the technological feasibility. In case a new technology is applied, this will involve a risk which the traditional industry is not likely to take.

A limited overview of applicable technologies for biorefinery is given by table 2.

Table 2: Available technologies for side-stream valorization.

Technology	Applicability	Demonstrated	Cost	Earnings
Separation				
Ion-exchange	KNO_3	Pilot	Medium	Medium
Chromatography	Isolation of sugars	Large-scale	High	High
Membrane separation	Isolation of proteins	Large-scale	High	Medium
Crystallization	K_2SO_4	Large-scale	Low	Low
Filtration	Isolation of proteins	Large-scale	Medium	Low
Electrodialysis	Isolation of cations / anions	Pilot	High	Medium
Conversion				
Burning	Combination with high ds	Large-scale	Low	No
Anaerobic digestion	Full treatment of liquid	Large-scale	Medium	No
Anaerobic fermentation	Lactic, propane-diol	Pilot	Medium	Medium
Aerobic fermentation	Lysine, glutamic	Large-scale	High	Medium
Enzymatic conversion	Only for pre-purified streams	Pilot	High	Medium
Isolation				
Chromatography	Isolation of specific components	Pilot	High	High
Membrane chromatography	Isolation of specific components	Laboratory	High	High
Affinity chromatography	Isolation of specific components	Laboratory	High (very)	High
Bipolar electrodialysis	Isolation of specific cations/anions	Pilot	High	Medium/high
Selective membranes	Isolation of proteins	Pilot	High	High

None of these technologies will bring in one step "the" solution for side-product valorization. This means that a biorefinery has to be a combination of technologies.

Economics

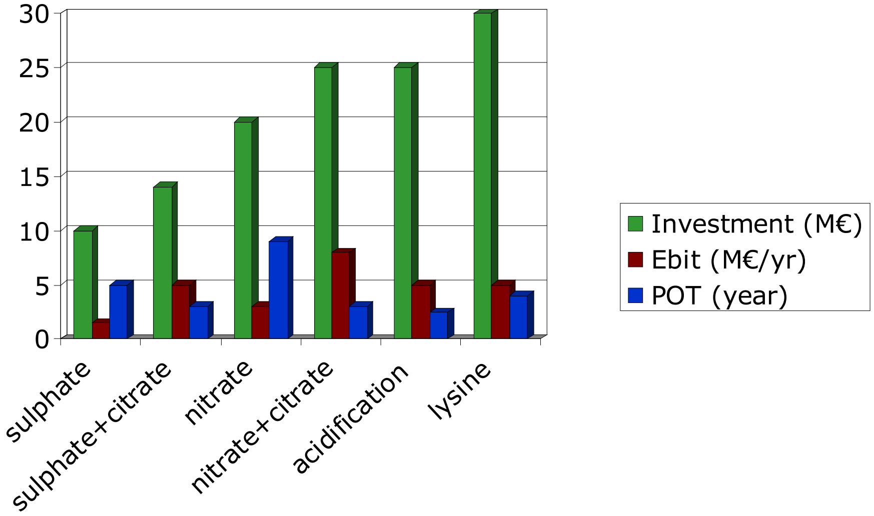
As mentioned, only the application of a combination of technologies will justify the eventual investment in a "biorefinery".

In case of the treatment of potato fruit juice (the main side stream of potato starch production), various options and combinations can be investigated and an economic feasibility can be done:

1. production of K_2SO_4 by means of crystallization
2. production of K_2SO_4 by means of crystallization and crystallization of Ca-citrate
3. production of KNO_3 by means of ion-exchange
4. production of KNO_3 by means of ion-exchange and crystallization of Ca-citrate
5. production of KNO_3 by means of ion-exchange and acidification
6. fermentation of lysine

Figure 6 gives a rough estimate of the economy of different options. In all cases, the present operation has been valued as zero, although costs are involved as well.

Figure 6: Economics of side stream valorization of potato juice.



Except for the crystallization of K_2SO_4 which is an evaporative crystallization (applied for vinasse treatment of ethanol production), the investments are in the range of 15 – 30 M€ to treat the full amount of potato juice produced. Down-sizing makes no sense as the investments are highly sensitive for the scale of economy. The most attractive operation (based on financial analysis) would be the acidification of the juice, followed by KNO_3 production and potential isolation of (some) amino acids. Disadvantage is the high complexity of such process and the risks in the market.

Market

Finally the market will determine the decision of a potential investment in a biorefinery process. In case of a biorefinery different products have to be “put on the market”. Difficulty is that it either concerns new products or products which have to be replaced. In such case the price is an important driving factor.

As an example the market for potassium nitrate, a higher grade fertilizer can be mentioned. Total world market is 1,2 – 1,5 Mton/year. Prices are in the ranger of 200 – 300 US$/ton. A biorefinery based on potato juice will deliver (only) 30.000 t/yr, as such not disturbing the world market. However, the producer has to prove the purity and the applicability of the product in the market as the production source is fully different from the presently produced material (based on chemical production from mining sources). The market is dominated by a few large chemical companies. Even putting a small amount in the market involves a serious risk in price, market introduction time and costs.

For products for food or eventually pharmaceutical application, the risk is even higher.

Conclusion

Valorization of side-stream is technically and even economical feasible if different unit operation are integrated. These unit operations and processes are available. However, various, large hurdles have to be taken:

- high investments needed
- risk of acceptance of the products in the market
- long development time
- *convincing the conservative agricultural industry*

The last point is maybe the most difficult hurdle to be taken. The EC support of the agricultural industry will further decline. This is an additional stimulation for the industry to invest in side stream valorization in order to survive.

An alternative scenario is that the agricultural process industry will "move" to either Eastern Europe (Ukraïne, Russia), due to less restrictions and larger agricultural area's or even to the Far East. In such case the agriculture in Western Europe will step by step disappear.

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Manure Based Bioethanol and Biogas Co-production

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1 INTRODUCTION

Bio-fuels such as bio-ethanol and biogas are emerging on the European market as new green fuels. Because these fuels are renewable and CO_2-neutrale they help to reduce emission of carbon dioxide.

Bio-ethanol is today mainly produced from molasses and starch, but new technologies offer a way to utilize sugars from lignocellulose (*e.g.* straw and wood) in production of bio-ethanol. Apart from cellulose (40%), hemicellulose is a main sugar component (25-35%) in lignocellulosic materials. However, these carbohydrates are closely bound together with lignin in the plant cell wall. Pre-treatment of the lignocellulose is necessary in order to open the structure and make carbohydrates susceptible to enzymatic hydrolysis and fermentation. Successful aqueous pre-treatment methods such as wet-oxidation and steam explosion have been developed [1], [2].

In Denmark a pilot scale pre-treatment plant (1 ton/h) has been established, and the developments of cheaper enzymes [3] and microorganisms capable of utilising both C-6 and C-5 sugars [4], means that we are close to having a feasible process. In Denmark, approximately 6 mill tons of straw is produced each year, of this a large portion is used in farming as fodder, animal bedding and soil improvement, 1.15 mill tons is used for energy production (this will be increased by 200,000 ton in the next coming years), which leaves us with approximately 1,4 mill tons of excess straw. This amount of straw could be converted to approximately 400,000 tons ethanol, which could substitute 20% of the transport fuel used in a year in Denmark.

Biogas is like bioethanol CO_2 neutral energy. In Denmark there are 20 big biogas plants receiving manure from approximately 100 farms, and 35 single-farm biogas units [5]. These 55 units treat approximately 1,3 mill. tones of manure from farm animals each year. Which means that approximately 3 percent of the manure produced from farm animals in Denmark is used for biogas production. The Danish government has a goal that in 30 years half of the manure produced in Denmark should be used for biogas production [5]. Beside manure biogas plants also treats approximately 200,000 ton/year of organic waste from industry, wastewater treatment and households.

Today, both fresh manure and digested manure are used as fertilisers in the fields. The most significant differences on fresh manure and digested manure is that [5]:

- Digested manure is a mixture of manure and organic waste
- Part of the organic matter in the manure has been used
- Digested manure has a higher pH
- Digested manure has a less obnoxious smell when being spread on the fields
- Digested manure has a slightly higher content of some nutrients than fresh manure (due to addition of waste) (Table 1).

Table 1 Comparison of fresh cattle manure and digested manure [5].

	DM (%)	Total N (kg/ton)	NH_4-N (kg/ton)	Phosphorus (kg/ton)	Potassium (kg/ton)	pH
Cattle manure	9.3	3.2	1.6	0.7	2.5	6.7
Digested manure	8.5	3.2	1.9	0.9	2.8	7.4

Biomass for energy and fertiliser

When producing bio-ethanol from biomass (starch and lignocellulosic materials) it is very important to think in the concept of a bio-refinery, where every part of the biomass is utilised and where nutrients are returned to the fields. This will enhance the feasibility of the process, and recycling of nutrients will prevent mining the farmlands.

In order to convert lignocellulosic material to bio-ethanol in a wet-oxidation process water is needed. The idea presented at hand is to use anaerobically digested (AD) manure as a water source in the wet-oxidation process. This offers several advantages:

- AD manure is a cheap water source for use in wet oxidation of straw
- AD manure act as N-source for the microorganism during ethanol fermentation
- Wet oxidation of AD manure diminish obnoxious odour and hydrolyse fibres
- Residue from the fermentation process is very well suited for use as a mineral-rich fertiliser.

To day AD manure is spread on the fields and table 1 shows the composition with slightly higher contents of N, P and K compared to undigested manure. However, the loss of nitrogen due to evaporation of ammonia is increased, because the higher pH leads to conversion of NH_4 to NH_3. If we instead used the AD manure for bio-ethanol production, the nitrogen would partially be taken up by the microbial biomass, and the residue from the bio-ethanol fermentation could then be used as fertiliser containing nutrients from manure, microbial biomass, and straw. During such fermentation pH will decrease to around 4 preventing NH_3 evaporation.

Both macro-and micro-minerals needs to be returned to the soil, otherwise we will end up cultivating crops and plants, that have low nutritional value. The fermentation residue from bio-ethanol production from straw and manure contains macro- and micro minerals both from the manure and from the straw in significant amounts, and it is very suitable for use as a fertiliser (Fig 1). Preferably, the biomass used for this purpose should be annual crops such as straw and corn stover, due to the fact that these crops contain valuable elements to be used for plant growth in contract to *eg.* wood materials that contain very little amounts of inorganic elements. In Denmark we use primarily nitrogen-phosphorus-potassium-fertilisers. But the intensive monocropping of the farmland is mining the soil of important micronutrients such as selenium, magnesium, copper, manganese, ion and zinc. Fertilising the soil with large amounts of phosphate furthermore leads to a decrease in availability of some of the micronutrients by binding of the minerals in a form, which cannot be taken up by the plants. Besides minerals the soil also needs to be enriched with organic matter (humus). Measurements have shown, that the soil becomes difficult to cultivate, when organic carbon becomes less than 1% [6]. It is well known that regularly chancing the type of crop grown in a field has a positive influence on the organic matter of the soil and also incorporation of straw in the fields has a positive effect. The fermentation broth contains significant amounts of carbon both from biomass, fibres and lignin, which end up as humic substances after decomposition.

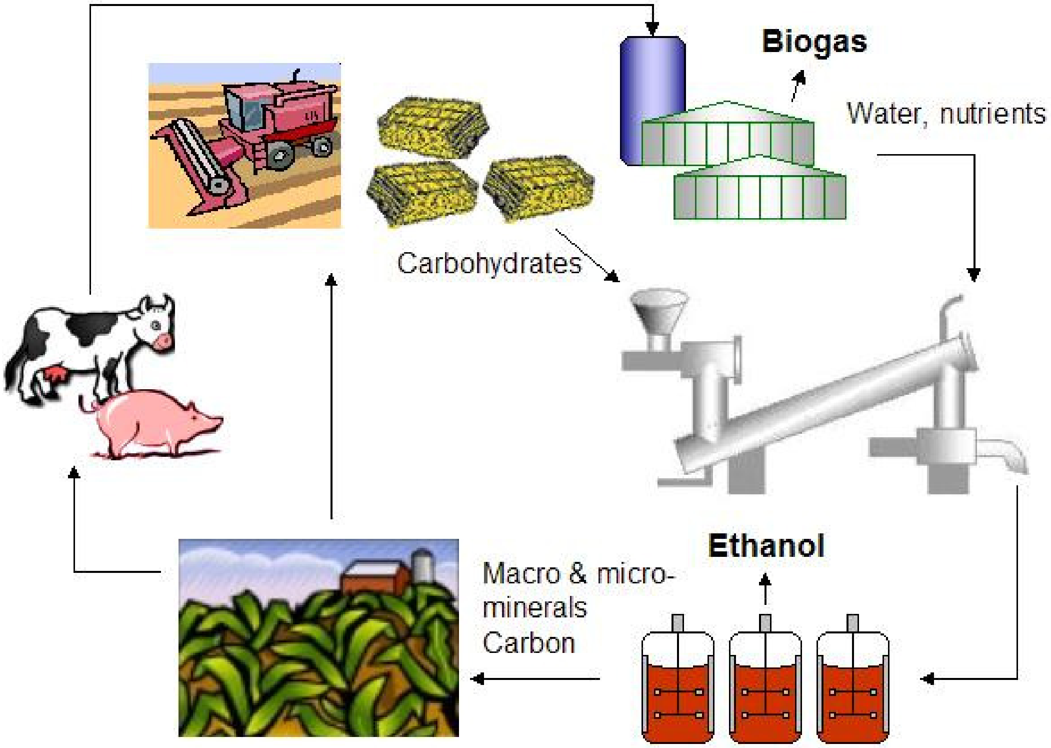

Figure 1 Concept of using straw and anaerobically digested manure for bioethanol production at the same time producing a nutrient rich fertiliser for farmland.

According to economical evaluations of producing ethanol from lignocellulosic materials, the second most costly operation of the process is the SSF (simultaneous saccharification and fermentation) step, accounting for approximately 28% of the total [7], [8]. One way to minimise the cost of SSF is by minimising the addition of the water, nutrients and elements during the fermentation. The dual aim of this study was to test the possibilities of substitution of water and nutrients needed for ethanol fermentation with pre-treated AD manure, and to demonstrate that a major part of the important macro and micro elements in the raw materials remain in the solid fraction after fermentation, and that this as a result could be used as a fertiliser for plants.

2 MATERIALS AND METHODS

2.1 RAW MATERIAL

Corn stover (Zea Mays L.)

Corn stover was grown and harvested in south Hungary in the fall of 2003 following the harvest of the mature crop. The raw material were air-dried to an average 94% dry matter (DM) content then milled to a 2 mm particle size. The grinded materials were stored in paper bags at room temperature.

Wheat straw

Wheat straw (Triticum aestivum L.) was grown and harvested after a drying period in Denmark during summer 2003. The straw was cut into 1-6 cm pieces on the field by a New Holland FX375 forage harvester and stored in containers at ambient temperature. The dry matter content was 92-100%. The straw was milled to a 2 mm particle size and stored in paper bags at room temperature.

Manure

The liquid manure (containing 5% DM) was collected from a biogas plant (Denmark). It was collected after degasification and it was kept in a well-closed 20 L plastic container in an outside storage room at temperature from 0-20°C.

2.2 WET OXIDATION EXPERIMENTS

Biomass was wet oxidised in a 2-L loop autoclave constructed at the Risø National Laboratory (Bjerre et al. 1996). 60 g biomasses (DM) was mixed with 1 L of water and 2 g sodium carbonate followed by addition of oxygen (12 bar) to the remaining gas volume. The applied chemicals were added before closing the autoclave and applying oxygen pressure. The gas-liquid mass transfer was accomplished by mixing with a pumping wheel. Due to the excellent heat-transfer conditions, the heating and cooling times were very short (about 2 min), which made the pretreatment much more controllable and reproducible. Thereby an excellent heat transfer was maintained, which resulted in 3 min heating-up time and 1 min cooling-down time.

Pre-treatment of manure

AD manure was pre-treated in the 2-L loop autoclave. Pre-treatments were performed at different severity conditions: 120ºC for 20 min (sterilisation), 160ºC for 15 min, and 195ºC for 10 min. The three different conditions were tested with and without addition of oxygen. All trials were performed in duplicate. The pre-treated manure was colleted and stored frozen at 2ºC.

Pre-treatment of wheat straw

Wheat straw was pre-treated in a pilot plant (100 kg/h) located at Fynsværket, Odense (IBUS) [9]. It was pre-treated by hydrothermal treatment (no addition of oxygen) at 190ºC, residence time of 6 minutes, and 40% DM in the reactor. The pre-treated straw was dried in a climate cabinet at 20°C and 65% relative humidity before analysis and use in SSF.

Wet oxidation of corn stover with and without AD manure addition

Based on the results of our optimization experiments on corn stover [10] the optimal condition of wet oxidation was: 15 min, 195°C at 12 bar oxygen pressure using 2 g/L sodium carbonate addition. These parameters were kept constant, but 20% of the water was replaced for AD manure before wet oxidation. After the pretreatment, each sample was separated into a liquid and a solid fraction, and both fractions were analyzed. The filter cakes were dried in a climate cabinet at 20°C and 65% relative humidity and the filtrates were stored frozen (-20°C) for further analysis and use in SSF.

2.3 SUGARS AND LIGNIN IN RAW MATERIAL AND IN THE SOLID RESIDUE FROM WET OXIDATION

The compositions of the raw materials and the solid fraction obtained after pretreatment were analyzed using strong acid hydrolysis method by Kaar [11]. The cellulose and the hemicellulose content were calculated from the concentration of monosaccharides (glucose, xylose and arabinose) quantified by HPLC with refracting index detection. Conversion factor for dehydration on polymerisation to cellulose was 162/180 for glucose and to arabinoxylan was 132/150 for xylose and arabinose. The residue was dried and weighed and reported as Klason lignin.

The ash content was determined by placing approximately 0.5 g sample in a tarred crucible that was ignited at 550ºC for 3 hours, cooled in a desiccator, and weighed.

2.4 SUGARS IN THE FILTRATE FROM WET OXIDATION

The sugar-content in the WO filtrate was measured after acidic hydrolysis of the polysaccharides with 4% (w/w) H_2SO_4 at 121°C for 10 min. The monosaccharide components were detected also refractometrically by HPLC.

2.5 ENZYMATIC CONVERTIBILITY OF BIOMASS TO FERMENTABLE SUGARS

The pretreated, solid materials were enzymatically hydrolyzed to determine the efficiency of cellulose conversion. The hydrolysis of the wet oxidised fibrous fraction was performed at 50°C for 48 hours, using 0.2 M sodium acetate buffer (pH 4.8). The applied cellulase enzyme loading (Cellubrix) was 25 FPU/g DM and the substrate concentration was 2% (DM).

The concentrations of glucose, xylose, cellobiose and arabinose following hydrolysis were measured by HPLC. The percentage of cellulose enzymatically converted to glucose (ECC) was calculated as a quotient of liberated glucose (g) during the enzymatic hydrolysis and weight of cellulose (g) before enzymatic hydrolysis.

2.6 SIMULTANEOUS SACCHARIFICATION AND FERMENTATION (SSF)

Fermentation of the WO solids and filtrates was performed to determine the efficiency of the WO pre-treatment for bio-ethanol production from the cellulose fraction of corn stover. The conversion of the cellulose into ethanol was achieved by means of two steps: enzymatic pre-hydrolysis of cellulose (and hemicellulose) to sugar monomers and fermentation by Saccharomyces cerevisiae to ethanol at a theoretical yield of 0.51 g ethanol/g glucose.

Pre-hydrolysis (liquefaction) and SSF was performed in shaking flask containing 5% DM solid, fibrous fraction in a pH adjusted (pH 4.8) filtrate, originated from the same pretreatment. Pre-hydrolysis of the WO solids was performed at 50°C for 24 h at an enzyme loading of 15 FPU/g DM, using Cellubrix. After liquefaction, the fermentation flasks were supplemented with a second batch of enzymes (Cellubrix) at an enzyme loading of 15 FPU/g DM and inoculated with 0.2 g/L yeast. The flasks were sealed with a yeast lock filled with glycerol and incubated at 30°C for 5 days. Neither minerals, nor nutrients or vitamins were added during fermentation.

The cellulose to ethanol conversion was monitored by CO2 loss, as determined by weighing the flasks at regular intervals. The ethanol yield during fermentation was calculated by multiplication of the molar ratio of EtOH/CO2 (= 1.045) with the CO2 loss. The final ethanol concentration was also determined by HPLC analysis and the calculation of ethanol yield was based on these results.

2.7 ANALYSIS OF ELEMENTS IN RAW AND TREATED MATERIALS

Dried, solid fibre samples was digested in a microwave oven using a mixture of 65% HNO_3 and 40% HF. The digested samples were diluted with water and following analysed by Varian Vista AX -ICP AES (optical emission spectrometry with inductively coupled plasma) using argon gas as carrier gas. The plasma temperature was 7000ºC at which temperature most elements emit light of characteristic wavelengths, which can be measured and used to determine the concentration a by light-sensitive detector at 167-785 nm.

3 RESULTS AND DISCUSSION

3.1 SEPARATELY PRE-TREATED AD MANURE AND WHEAT STRAW

AD manure was pre-treated at different severity conditions (120ºC, 20 min - 160ºC, 15 min and 195ºC, 10 min) with and without addition of oxygen. It was observed that when pre-treating the AD manure with oxygen (wet-oxidation) the obnoxious odour was reduced or eliminated, and a right liquid was obtained. pH after pre-treatment ranged from 8.4 in the mildest conditions to 7.8 in the most severe conditions (195oC). After pre-treatment the concentration of sugars significantly increased from 0.15 g/L in untreated manure to 2.5g/L in wet oxidised manure (195ºC) caused by solubilization of hemicellulose sugars in the solids of AD manure (consisting of mainly undigested straw) (Fig 2).

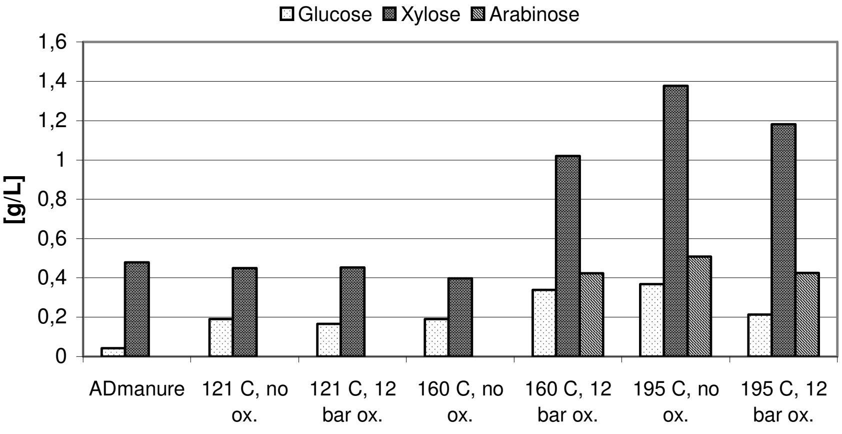

Figure 2 Sugar content in AD manure and pre-treated AD manure.

The pre-treated manure was used in SSF experiments with wheat straw (pre-treated in a pilot plant pre-treatment reactor (100 kg/h)) as carbohydrate source. In all experiments, a rapid ethanol fermentation was observed. There was no significant difference between the manure pre-treated at the different temperatures, however a slightly higher ethanol yield was found in experiments with manure pre-treated at low severity (Fig 3A). SSF of pre-treated wheat straw was compared to SSF performed in water (with added urea) (Fig 3B), and no difference in the fermentations was observed.

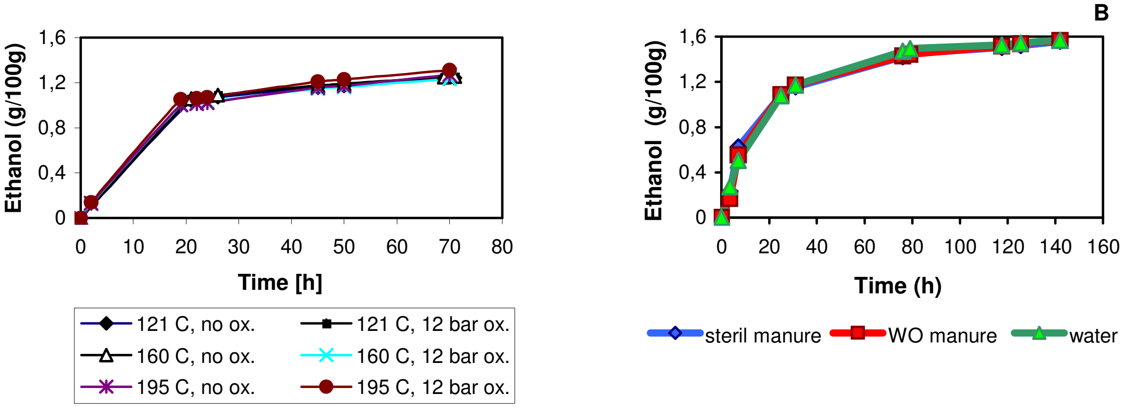

Figure 3 A: SSF of AD manure pre-treated at different conditions (120ºC, 20 min - 160ºC, 15 min and 195ºC, 10 min) with pre-treated straw as carbohydrate source. B: Comparison of pre-treated AD manure and water (with added urea) as fermentation liquid in SSF of pre-treated wheat straw.

From these experiments it can be concluded that pre-treated AD manure can substitute water supplied with nutrients in SSF of lignocelllulosic materials when pretreated separatly, and that sterilisation of the manure is sufficient to obtain a suitable fermentation liquid. However, a very bad odour was observed after SSF in manure not pre-treated with oxygen, so the best way to prepare AD manure for used in SSF was 120ºC, 20 min with 12-bar oxygen.

3.2 MANURE AND CORN STOVER PRE-TREATED IN ONE STEP

AD manure and corn stover was pre-treated by wet-oxidation in one step (Fig 4). In this experiments different concentration of manure was added to the corn stover before wet-oxidation. AD manure seems to have a slightly negative effect on the enzymatic hydrolysis of the corn stover when adding more than 20%. However when substituting all water with AD manure, the total glucose yield only decreases by around 10%.

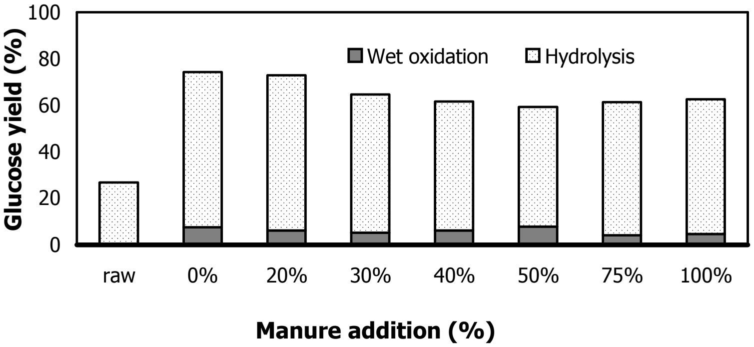

Figure 4 Glucose yield in pre-treatment of AD manure and corn stover in one step (195°C, 15 min, 12 bar O_2, 2g/l Na_2CO_3).

SSF of corn stover pre-treated with 20% of AD manure was compared to SSF of corn stover pre-treated in water (Fig 5). A lower ethanol yield was obtained in the experiment with the corn stover pre-treated with 20% AD manure due to the lower convertibility of this material.

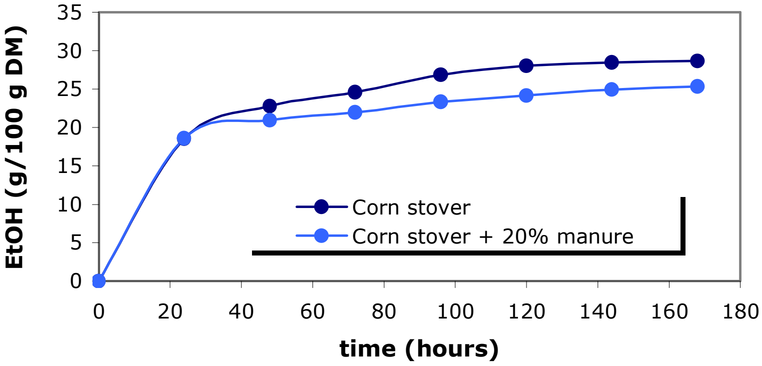

Figure 5 SSF of corn stover pre-treated with 20% of AD manure and corn stover pre-treated in water.

Wet oxidation parameters were not optimised in these trials, but trials were done with and without oxygen (not shown), and oxygen showed a positive effect on the yields. As a result it is expected that the glucose yields shown in figure 4 and 5 could be improved by optimisation of temperature, reaction time, oxygen pressure and maybe catalyst addition.

3.3 NUTRIENTS

The main goal of this experiment was to follow the circle of different important elements during wet oxidation and also in the subsequent fermentation. The ash content of biomasses was determined before and after pre-treatment (Fig 6), and the composition of the ash was determined (Table 2).

Analysis of the nutrients from the whole process

Concentration of macro- and microelements in the raw material as well as in the solid and liquid phase after wet oxidation and also after SSF were analysed as it is shown in Figure 6.

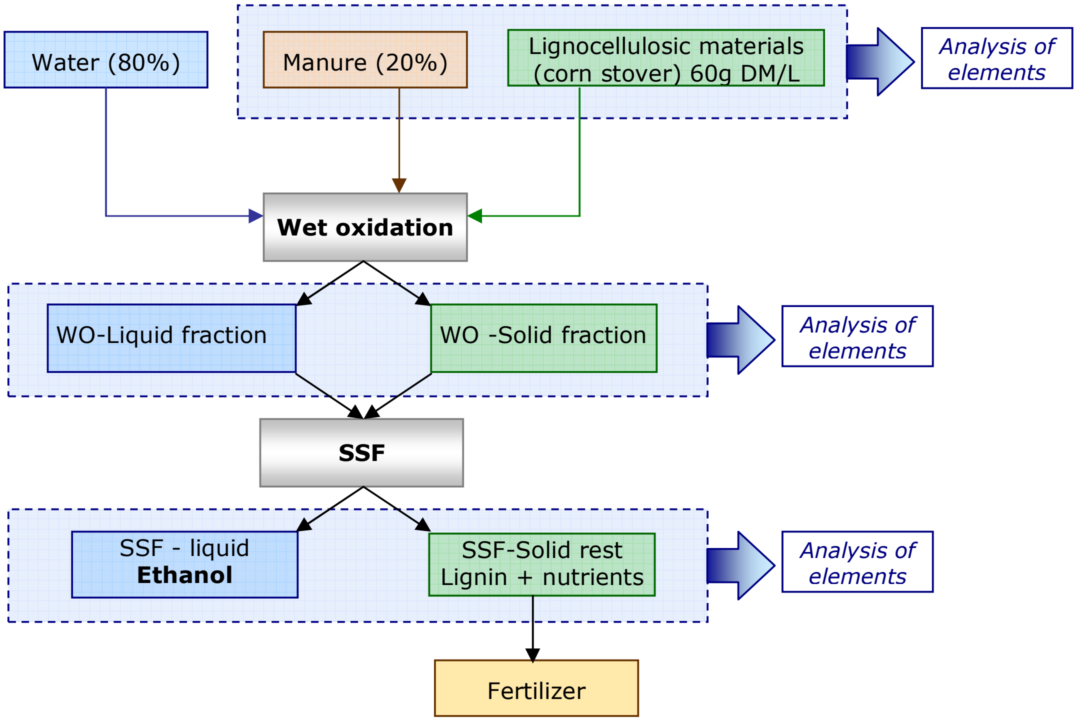

Figure 6 Selected fractions for nutrient analysis.

In general, the contents of elements in corn stover and in wheat straw are quite similar, but corn stover contains slightly higher amount of nearly all elements and its content of phosphor, iron, magnesium and calcium content are significantly higher than in wheat straw. However, wheat straw contains significantly more potassium, barium and zinc (Table 2).

Table 2 The amounts (ppm = mg/kg) of different elements during wet oxidation and fermentation of wet corn stover. During wet oxidation 6% dry matter was used and 20% of the water was substituted for manure.

	Raw materials			**After WO**			**After SSF**			
	Manure ppm	corn stover ppm	Wheat straw	WO-CS solid ppm	WO-CS liquid ppm	WO-straw ppm	SSF-solid ppm	SSF-solid (%)	SSF-liquid ppm	SSF-liquid (%)
Ash (%)	**39.8**	**9.5**	**5.4**	**8.7**		**4.2**				
P	61940	67987	503	101247	72979	398	41788	17.2	86747	89.6
Si	18405	10743	6820	12266	11180	5287	26543	63.3	3374	29.6
K	62507	5388	7928	2628	21222	2600	6098	14.1	11904	81.5
Ca	52547	4805	3883	10682	10664	4156	17700	47.7	6865	52.6
Mg	6809	2811	523	1809	5049	650	1931	16.4	3338	79.9
Al	6593	609	41	2484	364	54	4244	90.7	58	6.3
Fe	3560	366	43	1572	68	318	2172	82.1	83	7.8
Na	56538	194	112	1600	12544	129	11520	47.9	6473	81.5
Mn	288	51	32	98	65	22	114	40.5	59	55.4
Sr	369	45	19	108	95	22	102	34.6	73	67.3
Ti	207	35	3	120	1	4	178	89.2	2	2.5
Zn	902	30	51	180	106	9	215	45.6	77	45.0
Cu	202	22	3	86	10	2	117	75.9	10	16.3
Ba	106	9	45	36	8	79	47	65.4	7	27.0

Compared to the herbaceous materials dry manure contains even more, (in some cases ten times more) essential nutrients. Manure has an ash content of approximately 40% (of the dry matter) (Fig 7), which is very rich in phosphor (6.1% of the DM), potassium (6.2% of DM), calcium (5.2% of the DM) and sodium (5.6%). Although manure has a relative high magnesium and iron content (0.6%), it also contains many different microelements (Mn, Zn, Cu, Sr) at the concentration of 0.01-0.1%, thereby representing a potential nutrient and minerals source for fermentation (Table 2).

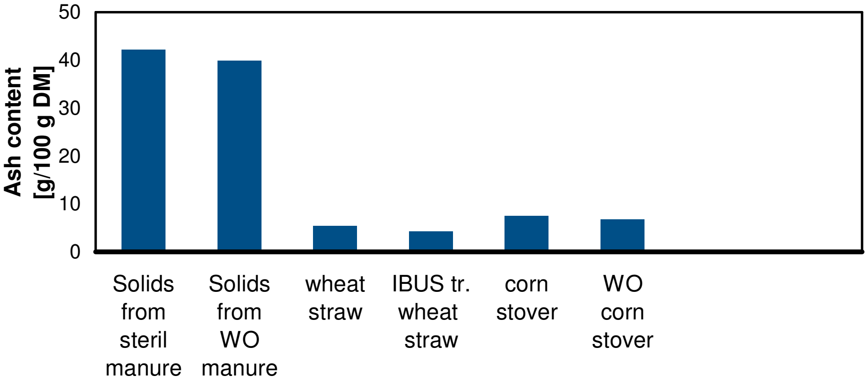

Figure 7 Ash content in raw and pre-treated materials

The amount of water-soluble salts and elements, like potassium, magnesium, sodium and phosphor decreased considerably in the solid fraction after fermentation. Approximately 80% of the initial amount of these elements can be found in the liquid phase after SSF. Although the amount of these water soluble elements are low in the SSF solid, but it is higher than in the WO-solid indicating, that *Baker's yeast* is able to utilise some of these components from the liquid (*e.g.* potassium) and so transfer these from the liquid to the solid phase (Table 2). Majority of the non water-soluble elements, mainly different metals remains in the solid fraction, *e.g.* 82 % of the initial amount of iron and 76% of the cobber can be detected in the SSF-solid. However, half of the original zinc and manganese, which play central roles in many enzymatic reactions, remains also in the SSF-solid (Table 2).

Conclusion

AD manure can serve as water and nutrient resource during fermentation of agriculture waste products like wheat straw and corn stover. Most sugars were obtained when treating manure and biomass separately. Valuable elements present in these fermentation feedstocks (constituting up to 40% of the solid in AD manure) are used both during fermentation and during crop cultivation when recycled to the fields.

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Application of high-voltage plasma and cavitation technologies for production of liquid humic products

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1. Introduction

Two types of high technologies intended for production of liquid humic products are developed.

The first one is the high-voltage plasma technology based on utilization of different interconnected nonlinear dynamic effects and physical phenomena. Plasma filament with high temperature, powerful shock waves, pulse electromagnetic and X-radiations, ultrasound, turbulization of flows occur in a fluid under high-voltage discharge [1]. These factors give rise to productive extraction with particularly pronounced sterilization effect. Three types of high-voltage plasma installations have been designed and tested at the Firm “Latinvent”: the device for activation of chemical reactions, the installation for processing of organic raw materials and the installation for cleaning of pipes from internal deposits [2].

Fig. 1. Electro-sparking chemical reactor

Such physical factors as intensive shock waves, plasma, cavitation and X-radiation simultaneously act on chemical reagents in the electro-sparking reactor designed (Fig. 1). Thanks to this the reactor can be successfully used in different applications including high-effective extraction and coagulation of components from organic materials, sterilization of potable water, acceleration of chemical reactions and synthesis of new compounds.

Fig. 2. Installation for processing of organic raw materials

Installation intended for processing of peat, medicinal herbs, seaweeds, fruits, vegetables, dairy produce, sawdust, pine needles and other organic materials is shown in Fig. 2. Installations of middle and high capacity can be obtained by increasing of the numbers of mini-modulus used. Rapid dismounting of the mini-plant and its carriage by road is possible. Mounting the mini-plant and its start-up in the new location place may be carried out in 4-6 hours.

High-voltage plasma installation “Mole” intended for cleaning of pipes from internal deposits is shown in Fig. 3.

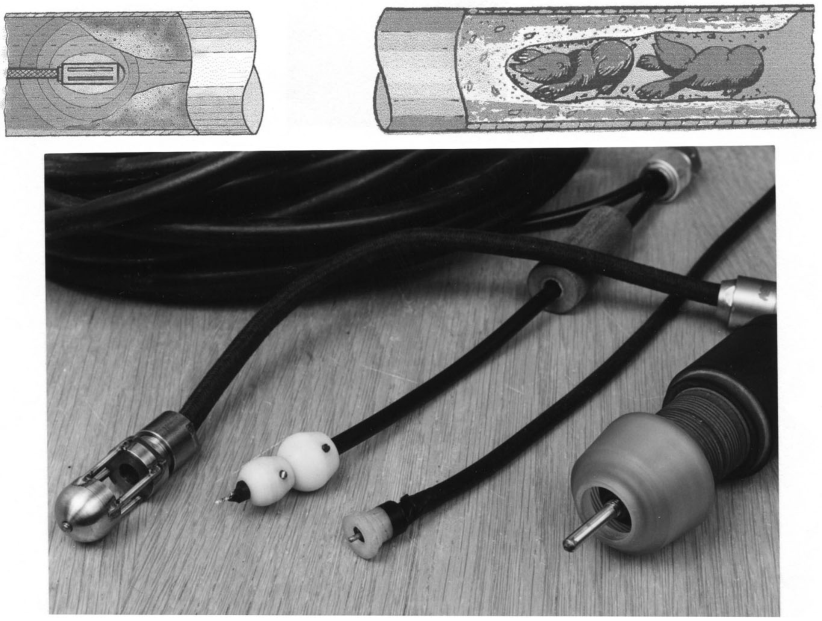

Fig. 3. Installation for cleaning of pipes from internal deposits

The second proposed technology is based on cavitation extraction, which belongs to high-tech procedures. Cavitation is a specific method for energy concentration in collapsed bubbles. This method is one of the strong multifactor tools for chemical and physical manipulation with solid particles dispersed in liquid media. Cavitation is accompanied with appearance of water hammer (up to 100 MPa), shock waves, intensive vortex formation and ultrasound radiation. This technology gives an opportunity to obtain the following products: liquid humic fertilizers; mixed feed with natural organic fillers; extracts from medicine grasses, etc.

Examples of practical application of these technologies for manufacturing of liquid humic products are considered in this paper.

2. High-voltage plasma installation for production of artificial manure

At present there is a great demand for organic fertilizers due to the intensive development of non-polluting agriculture. One of the most effective fertilizers is horse manure. For its production the following means and conditions are necessary: a pasture in the summer and hay in the winter, a paddock and automation facilities for submission of feeds and water, means of cleaning of manure and bunkers for its storage during 4 - 6 months, veterinary and other maintenance. Demerits of the natural way of horse manure production lie in its low productivity (the horse makes about 3 - 4 kg of manure in a day), as well in insufficient sterility and unpleasant smell of final product.

Inventor L.A.Yutkin proposed to use a high-voltage plasma method for production of artificial manure [3]. These activities have been continued in Scientific and Production Firm "Latinvent".

The installation (Fig. 4) consists of the belt conveyer 1 carrying a peat mix 2, the metering hopper 3, the first high-voltage plasma bioreactor 4, the transfer pump 5, the second bioreactor 6, system of pipelines with cocks. The electric part contains the programming block 7, the surge current generator 8 of high voltage, the first (9) and the second (10) groups of electrodes, connecting power cables 11.

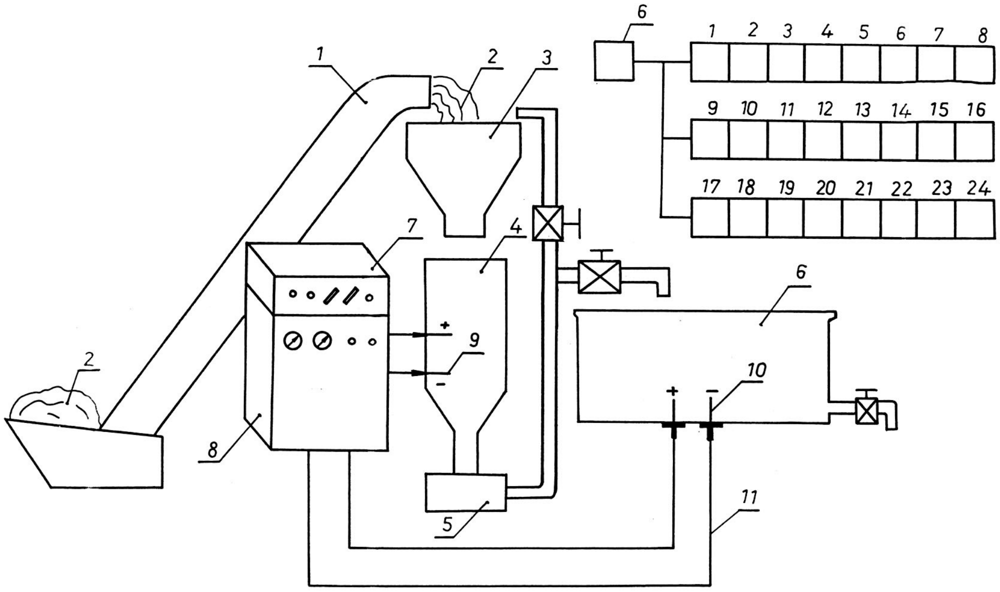

Fig. 4. Block diagram of the installation for production of artificial manure

The peat mix 2 with the aid of the belt conveyer 1 is transported to the metering hopper 3 and then it comes into the first bioreactor 4. The transfer pump 5 fills a bioreactor 4 with water. Operating mode of the generator 8 is set up with the aid of programming device 7, and then output voltage of generator is applied to the first group of electrodes 9.

After processing during a certain time the peat pulp is pumped over in the second bioreactor 6. In this reactor secondary processing of pulp in other regimes of high-voltage discharge is performed. Thanks to this the ammonia nitrogen content of mix is increased in 1,4 - 4,5 times. Then, after 10 - 15 days of storage, the content of NH_4 in the bioreactor 6 grows in 10 - 15 times (at the expense of bacteriological explosion).

The bioreactor 6 consists of 24 sections (in Fig. 4 sections are numbered). In each section the daily dose of product enters. Therefore bioreactor 6 is fully filled for 24 days. Then daily taking out of a ready product from sections 1, 2, 3, etc begins. Ready fertilizer is directly transported to a vehicle of the consumer or to a packing line. Standard means of loading, unloading and packing are used.

Advantages of the proposed technology and produced artificial fertilizer are as follows [4]:

- Ecologically harmless technology (the infinitesimal content of nitrates);
- High sterility (harmful microbes are destroyed by high-voltage discharge);
- More high output of product from the area of one horse stall (3 x 2 м), than at a natural way of its production (approximately in 400 times);
- Full absence of a smell.

The processed peat can be used for coating of seeds, manufacturing of heat insulation plates, micro hotbeds and nutritious briquettes as well for production of liquid top-dressing, chimney fuel and in other purposes.

3. Results of agricultural experiments

Yield capacity of different plants cultivated in a mix of ground (50%) and usual peat (50%) was compared with their productivity in a mix «ground - processed peat ».

Results of hotbed experiments were the following. In the case of the processed peat using the green weight of oats has increased by 140%, and height of plants has become 1.7-2.1 times bigger. The bean crop has come to 140%, the mass of potato tubers has increased by 110% and the green weight of barley has increased by 365%. Such rapid growth of plants may be explained by the arising of vegetative hormones in the peat mix after its processing (together with increasing content of nitrogen and other microelements). These hormones essentially stimulate the growth of plants and facilitate the increase of nutritives and vitamins content in products. For example, the content of starch in potato tubers increases by 20%, but vitamin C - by 45 - 60%. Besides, the use of the processed peat has made it possible to improve appreciably the phytosanitary conditions in a hothouse ground and to deodorize a hothouse atmosphere (thanks to bactericidal properties of the high-voltage plasma discharge). The most effect from the application of the processed peat can be achieved in the case of hotbed cultivation of expensive production (e.g., flowers, vegetables, mushrooms, etc.).

It is experimentally proved, that processed peat is a dispersed nutritious medium with good gluing ability. Therefore such peat pulp can be used as good compound for seeds coating. The porous shell of such coat facilitates the ingress of moisture into the seed. As the result of coating it is possible to unify the sizes of seeds of different crops and thanks to this to sow seeds into the ground with the same standard instruments, to lower normal value of sowing and to abolish a very laborious operation of shoots thinning. In accordance with the experiments, coating has given the rise of carrot crop by 26%, but beetroot and mangel-wurzel crops - by 14% and 29% correspondingly.

Besides, according to experimental data, 1 kg of the processed peat gives twice as large gain of yield capacity than 1 kg of horse manure.

4. Application of high-voltage plasma technology in other fields

4.1. Pharmaceutical manufacture

Making of fine suspensions (up to colloid condition) of synthetic and natural resin used for preparation of medicines is possible. Solutions of low-soluble and almost insoluble substances with the concentration, which considerably exceeds a natural limit of solubility, can be received, too.

Significant acceleration of extraction of some substances from vegetative and animal raw material is achieved: sea-buckthorn oil, pine-needles, marrow, grape pips. For example, the amount of citisin extracted under high-voltage plasma processing from vegetative raw material during 1 minute is the same as extracted from it during 51 minutes in the case of fast mixing.

Glaucin has been extracted during 2 minutes, but santonin - during 5 minutes. The quantitative output of active substances from calendula flowers, leaves of bushes, valerian herb or seaweed can reach about 88 - 95% (this value is sufficiently higher than can provide familiar methods of extraction).

Reduction of extraction time of fragrant substances (ambergris, coriander, iris) is observed: for animal raw material - from 30 days up to 40 - 60 minutes; for vegetative raw material - from 14 hours up to 1.5 - 2 hours. Extracts with qualitative smell and full-blooded composition have been produced.

It was possible to combine grating operations of dried cherry fruits and hawthorn with their extraction. A sterilized nutritious crop intended for rapid cultivation of various kinds of bacteria is extracted from peat.

Application of high-voltage plasma technology has made it possible to reduce the mature time of perfumes, colognes and other perfumery liquids (in a course of experiments the mature time is reduced from 20 days up to 3 hours).

4.2. Stock-breeding

4.2.1. Production of a forage and fodder additives to animals and birds from plants with the strong casing

Nowadays there is a heightened interest to application of a straw as rough power forage in agriculture of many countries. Due to high rigidity and big content of cellulose, and also owing to the low content of nutritive, animals cannot eat a straw in great amounts. The daily diets containing big amounts of straw do not provide high producing of livestock, because the digestibility of straw of winter rye makes only 40 - 42%. More than half of used straw fodder is not digested by animals. For this reason the nutritiousness of straw is estimated as low and usually it lies within the limits from 0.2 up to 0.3 fodder units.

High-voltage plasma processing destroys the strong lignin-cellulose capsule of a plant and gives off nutritive from it. For example, after plant's processing the content of crude fat increases by 10 - 20%, mass content of soluble and reducing sugars - by 73%, but level of a crude protein - by 5 - 6%. Digestibility of forage reaches 70 - 80%. Seaweeds, rough herbs (reed), prickles, branches, pine-needles, leaves and other organic waste products may be used instead of straw, too.

The forage prepared in such a way is completely disinfected, becomes non-polluting and can be stored during a long time without losing the nutritious properties. The processed pine-needles are the perfect vitamin additive.

4.2.2. Manufacture of protein from nutrient yeast

Fermentative yeasty cells are not well digested in a stomach of animals and birds. In some cases they can cause pathogenic processes in guts. High-voltage plasma processing of yeast is a worth-while method for production of the endocellular yeasty protein causing fast growth of animals.

4.2.3. Production of fodder additives from sludge of sewage works

Natural silt is inexhaustible source of forages containing useful albuminous, mineral and vitamin additives. Processed sludge is a worth-while fodder additive. Processing of sludge includes its clearing of mechanical impurity and further high-voltage plasma treatment in special regimes providing sterility and nutritiousness of the received forage.

4.2.4. Processing of fish garbage

During fish processing a plenty (up to 20 - 30%) of quickly rotting waste products turns out. High-voltage plasma processing makes it possible to transform these wastes into a homogeneous sterile pulp which is a good food for coypu.

4.2.5. Production of watering water with increased content of nitrogen

High-voltage plasma processing causes the increase of nitrogen content in water and provides its sterilization. The processed water can be used both for plants watering and for animals feeding.

4.2.6. Increase of fertilizing properties of soil in field conditions

As is known, silty soils are the most fertile ones. These soils show high degree of dispersion (total surface area of particles in 1 kg of soil is about 23000 cm^2). High-voltage plasma processing of soil (for example, in places of trees planting) can sufficiently increase its dispersitivity, and thanks to this the processed soil becomes much better than silt.

4.3. The food industry

Now such aromatic substances as fragrant pepper, bay-leaf, cardamom and others are added in foodstuff as a powder. Powdery spices are strongly polluted with micro flora. Sterilization of spices is complicated, because volatile essential oils evaporate during this process. Therefore in production of sausage products special extracts, free of micro flora, are used. These extracts are much cheaper than powdery spices, and 1 kg of an extract replaces 30 kg of natural fragrant pepper. Besides, emulsion is more uniformly distributed in mass of a product.

High-voltage plasma processing makes it possible to increase the efficiency of some other technologies used in food industry:

- Production of true fatty emulsions for inclusion in a force-meat (in order to fix moisture better).
- Homogenization of ground canned food from strawberries, black currants, tomatoes and apples, carrots. Products have more high quality indexes. The best preservation of the aroma inherent in fresh berries is shown.
- Extraction of bitter stuff from hop. High-voltage plasma treatment of raw material expedites the extraction process in 2.5 - 3 times (in comparison with thermal processing). Besides, application of the proposed technology makes it possible to save up to 20% of raw material.
- Making of emulsions for sugar biscuits (usually about 10 - 15% of sugar remains in an insoluble condition).
- Homogenization of chocolate paste.
- Dispersion of quicklime in beet sugar manufacture.

5. Cavitation technology for production of humic substances

Investigations directed on the design of different types of cavitation devices are carried out in the Scientific and Production Firm "Latinvent" since 1991.

At first cavitation station for fuel's emulsification has been developed. Integration of these stations into the heat generation process (boiler houses in Madona and Rezekne cities, Latvia) has made it possible to reduce considerably the fuel consumption and effluents of harmful gases [5]. The principle of action of station consists in realization of a toroidal vortex inside which intensive cavitation occurs. However, processing of organic plant substances at this station was inefficient.

Therefore at the second stage of research the acoustic station has been developed. The operation principle of this station is based on excitation of plate vibrations in a fluid flow under the action of the Carman vortex trail. At this station it was possible to mix well various low-viscous organic substances (water-petrol emulsions, diesel fuel - water emulsions, emulsions for greasing of concrete forms). Main demerits of this device lie in fast clogging of narrow nozzle holes and frequent break-downs of a vibrating plate.

On the next stage of improvement of cavitation devices a rotor station was designed. At the certain speed of disk rotation the boundary fluid layer becomes turbulent, i.e. consisting of set of vortexes. Inside each vortex cavitation arises. Well dispersed “water – peat” emulsions have been produced on rotor station. Under the flowing out of such emulsion and its further drying, very thin and strong sheet is formed. However, rotor station effectively operates only at high speed of rotation or in the case of sufficiently large rotor diameter. Besides, careful dynamic balancing of a rotor, and also maintenance of compulsory liquid cooling are necessary.

The cavitation station of shock action is structurally simpler. Cavitation arises in the limited area under the impact of a resonant jet with a special barrier. Productivity of station depends on a jet's speed, distance between nozzle and a barrier, shape of a barrier and nozzle, temperatures of a liquid, relationship between water and crushing fibrous organic material. Lack of this station lies in difficulty of selection of the pump which would pump over mixes with the high content of organic substances under the high pressure on an output.

Each of developed and tested cavitation stations had its specific field of practical application. By the use of these stations carrots, needles, sawdust, peat and other substances were subjected to cavitation processing [6].

Since 1993 cavitation technologies were developed together with SIA "Stalkers". But in 2002 investigations have been transferred on SIA “Intellectual Resources” (Ventspils) and have concentrated on processing of peat. The special pumps providing circulation of a peat pulp (peat - water volume relationship is as 4:6) have been developed. Besides, original hydrodynamic flowing cavitation device and auxiliaries have been designed. Thanks to this experimental emulsification station for production of humic substances (Fig. 5) was produced. Main technical data of the station are as follows:

- power consumption 5 kW;
- weight 90 kg;
- occupied area 3 m^2;
- total productivity 200 l/h.

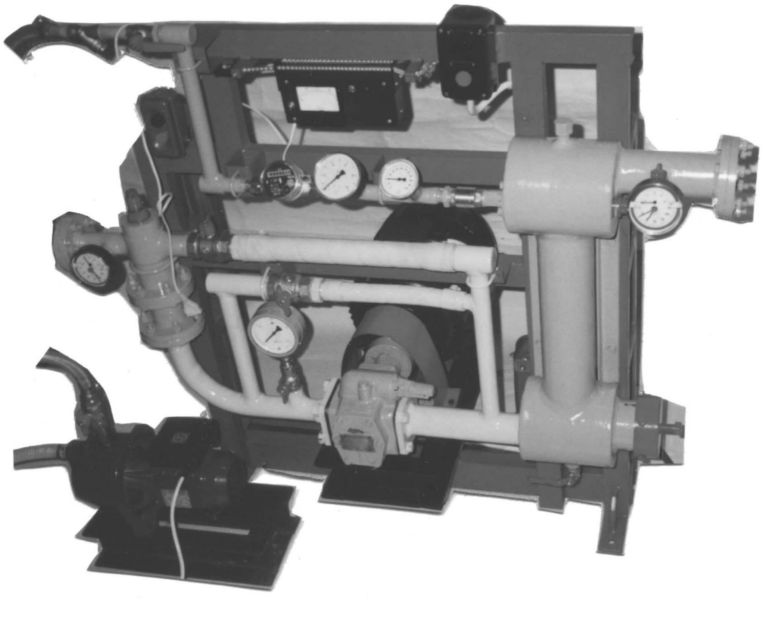

Fig. 5. Experimental emulsification station for production of humic substances

Biological testing of produced humic liquid has been performed during 2003 - 2004 by Dr. agr. L. Borovko (Institute of Crop-growing, Skriveri, Latvia). Influence of humic substances on yield capacity of spring raps has been studied.

The results of research show, that processing of raps seeds with a 0.01 % humic solution facilitates its field germinating power on 10 - 26%. The increase of raps crop was about 340-740 kg/ha (depending on year of experiment). It is characterized with essential difference coefficient $\gamma_{0,05}$ = 110 – 360 kg/ha (in comparison with the control made without application of humic substances).

Application of humic substances has positively affected on quality of a crop. For example, the crude fat content of summer raps' seeds is increased on 0.53 – 2.14% that assures a gain in output of crude fat on 172 - 340 kg/ha.

Economic calculations were made in assumption, that the price of raps seeds is 0.24 EUR/kg (the price of biological product was accepted higher on 30% than the average purchase price 0.185 EUR/kg). In this case application of humic substances for processing of raps seeds is economically justified (the net profit is about 68.20 – 150.67 EUR/ha).

In author’s opinion, application of the proposed high-voltage plasma and cavitation technologies can give good results in production of bioethanol, grass juice, etc. Persons and firms are invited to cooperation both in sale of finished products and in organizing of joint production.

Acknowledgment
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Large scale fermentation processes, utilisation of grass juice to produce lysine to the animal feeding sector.

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Introduction

The green crop drying industry in Denmark uses Italian ryegrass, clover, and alfalfa as raw materials for production of fodder pellets. The green crops are harvested and transported to the green crop drying plant, where it is subjected to a wet separation resulting in a press cake and a juice. Pressing of the green crop prior to drying reduces energy consumption during drying.

Most of the factories in Denmark use a low energy drying process, where the green biomass is heated by steam and pressed in a screw press. A smaller part of the brown juice is concentrated by means of evaporation and the concentrate led back to the press cake before drying, whereas the bigger part is a waste stream, which can be used as fertilizer in the growing season (Fig. 1).

Approximately 200,000 m^3 of brown juice is produced in Denmark each year. [4]

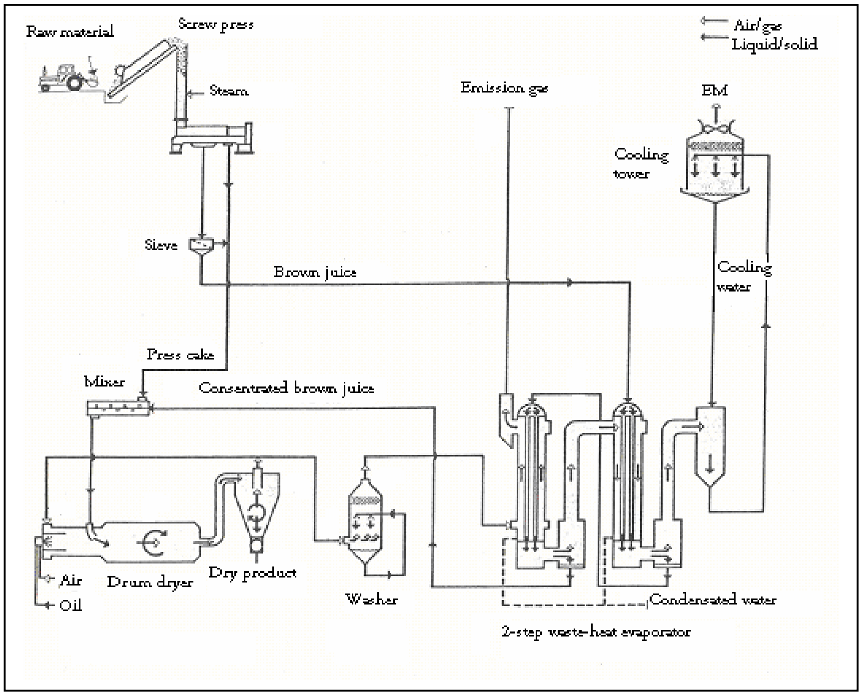

Figure 1. Flow sheet of the low energy drying process with wet separation and use of waste heat evaporator [4].

In Denmark there is a ban on applying grass juice and other organic waste materials as a fertiliser from October 1st to February 1st.

Plant juice produced in the period after October 1st therefore has to be stored until the spring because of legislations or be used for other purposes. Storage in cisterns and large lagoons are difficult, because natural and uncontrolled fermentation processes will soon take place and spoil the brown juice. It was therefore of great interest to find an alternative solution for the brown juice.

The green biorefinery

Typically brown juice has a dry matter content of 4 to 8% and it contains nutrients such as carbohydrates, organic acids, vitamins, and minerals, which make it suitable as substrate for microbial fermentation.

Our first idea was to change the green crop dying plant to a green biorefinery, where different raw materials were used and different products produced.

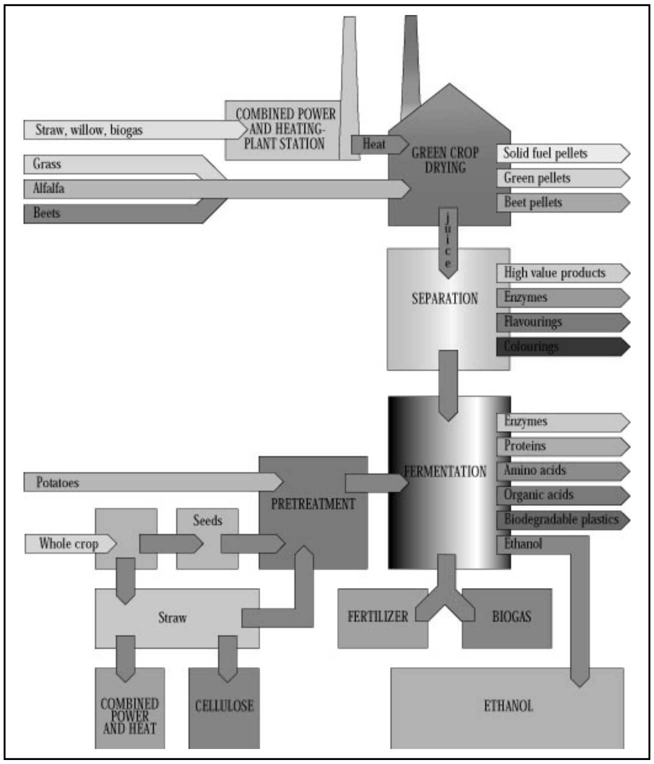

Figure 2. The principles of the green biorefinery [3]

In the green biorefinery, described jointly by the University of Southern Denmark and AgroFerm A/S, different crops can be converted by means of mechanical and biotechnological methods (e.g. fermentation) into useful materials such as food and feed products and additives, as well as fermentation medium to be used in the production of organic chemical compounds, materials and bio-energy [3].

Brown juice as fermentation medium

A process has been developed in which brown juice is converted to a basic, universal fermentation medium by lactic acid fermentation. By subjecting brown juice to lactic acid fermentation available carbohydrate in the juice is converted to lactic acid, which has an inhibitory effect on microbial growth thereby converting the juice into a stable and storable medium. This medium can be used as fermentation medium for the production of useful fermentation products such as organic acids, amino acids, enzymes, proteins and peptides, when complemented with an extra carbohydrate resource and inoculated with specific microbial strains. [1, 2]

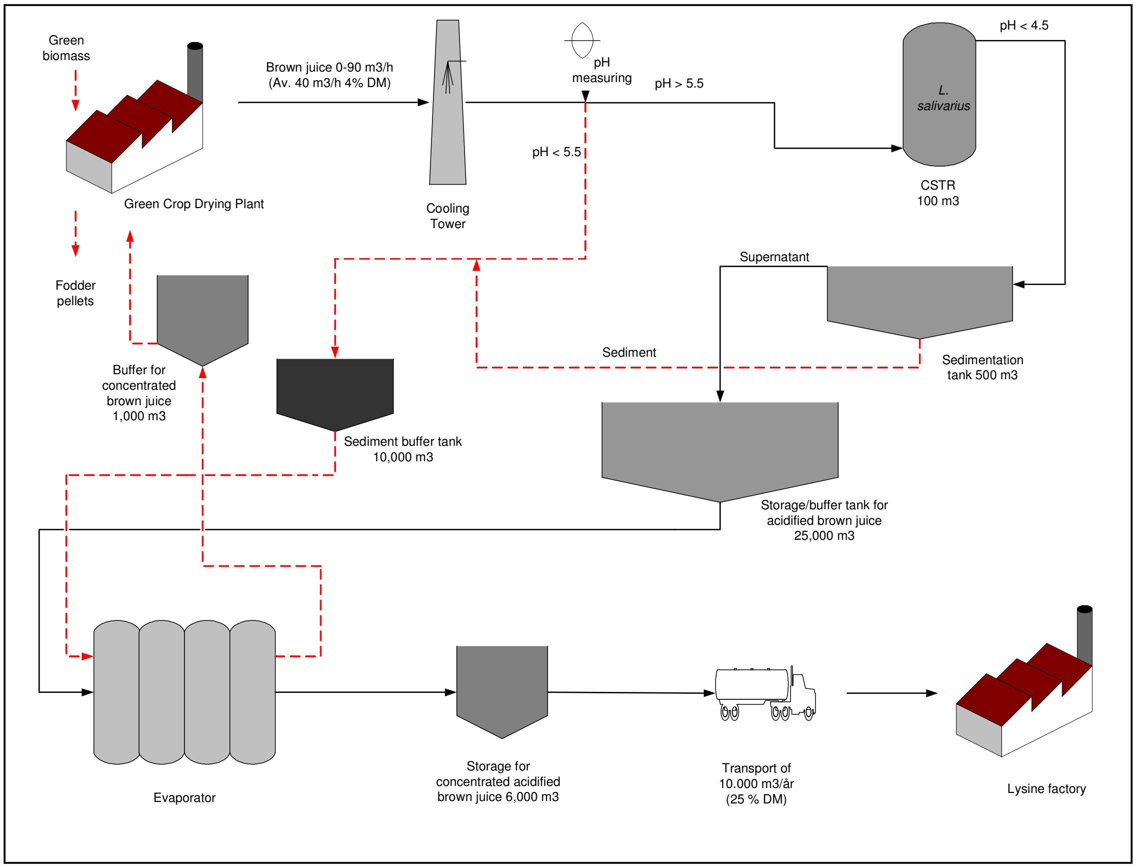

Figure 3. Brown juice from a green crop drying plant is cooled to fermentation temperature, 40-45°C and on the basis of pH measuring split up into two directions: 1. pH > 5.5: the brown juice is led to lactic acid fermentation in a 100 m^3 CSTR inoculated with *Lactobacillus salivarius*. The acidified brown juice (pH < 4.5) is led to a sedimentation tank, from where supernatant is led to a storage/buffer tank before evaporation to 25% DM. The sediment is led to a sediment buffer tank. The concentrated acidified brown juice is stored until transport to the lysine factory.

2. pH < 5.5: the brown juice is led to the sediment buffer tank, where also the sediment from the sedimentation tank is led. After evaporation, the concentrated brown juice is used in the production of fodder pellets in the drying plant. [6]

On the basis of chemical analyses of the juice and laboratory as well as large pilot scale fermentation experiments, a plant for production of 10,000 tons of acidified, concentrated (25 % DM) brown juice a year has been designed. It will be possible to supply an L-lysine factory with stabilized high quality brown juice all year round and produce about 100,000 tons of liquid lysine feed concentrate a year.

The acidified brown juice can be produced almost without costs (or at a very low cost ≈ 0.1 DDK/kg)for the green crop drying industry, when taking into account that the green crop industry has expenses amounting to 2.000.000 DDK/year for disposal of the brown juice. The lysine factory benefits from this process by buying a low price medium for the fermentation process instead of more expensive traditionally used fermentation media such as corn steep liquor. [5]

The lysine fermentation plant

The lactic acid fermented, concentrated brown juice can be stored in big lagoons in the winter period and be used as basis for production of L-lysine using Corynebacterium glutamicum as producer organism.

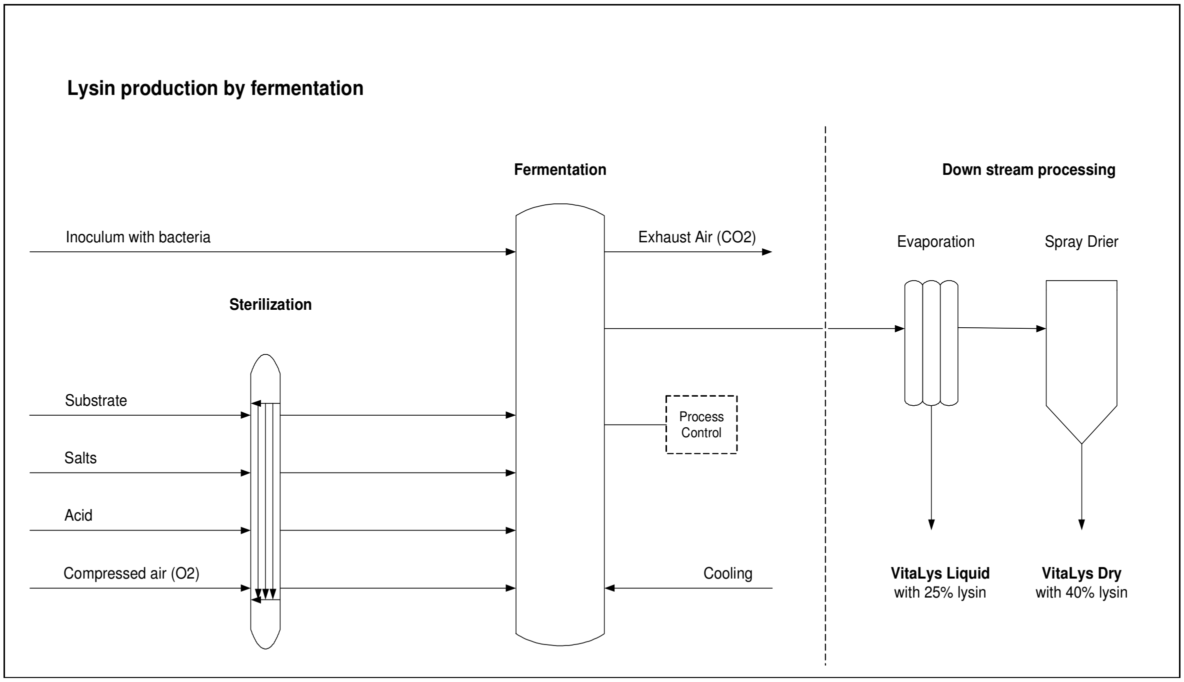

Figure 4. Concept of production of lysine feed concentrate based on brown juice.

The idea in the concept of using stabilized brown juice as fermentation medium in the production of lysine is that a waste liquid is utilized and a useful product produced without producing new waste materials and by using low energy recourses in the down stream processing.

The brown juice is analysed and necessary minerals and vitamins added. This complex media is sterilized in a continuous sterilizer and added a sterilized solutions of carbon source, such as sucrose or molasses and nitrogen sources, such as ammonia and ammonium sulphate solution.

After the fermentation process, which can a be fed batch or continuous fermentation process, the whole broth is pH adjusted by sulphuric acid to pH 4 and evaporated to a dry matter content of about 60 %. The final concentration of lysine in the product will be about 25 %.

One green crop drying factory producing 50,000 tons of fodder pellets a year has enough brown juice to supply a 20-30.000 tons L-lysine factory with fermentation medium. First step in the production chain is the lactic acid fermentation of the fresh brown juice in the green pellet factory. The next step is production of a liquid lysine feed concentrate at a fermentation plant using brown juice as growth medium.

The AgroFerm factory is now situated in Esbjerg not far away from the green crop drying plants and close to harbor and highways. The production started in August 2004.

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Hydrogen from food residues

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Abstract

Biogas processes are gaining position as a major tool to handle organic wastes, such as food residues, producing methane. Such anaerobic digester processes may also be used to produce hydrogen, but only a limited number of laboratory tests have yet confirmed this option. The potential for H_2 production in biogas reactors is investigated. The analysis is based on experimental data from the literature and combined with mathematical modeling. Modeling and simulations is performed using the "Anaerobic digestion model", ADM1, implemented in Aquasim. The goal is to find out how much of the total biogas potential from a given organic waste can be harvested as hydrogen. Evaluating to what extent the ADM1 model is an adequate tool to simulate such processes and to suggest modifications needed for ADM1 to be capable of adequately simulate H_2 production in biogas reactors is also a purpose of this study. It is concluded that ~24 % of the biogas potential (as energy) can be recovered as hydrogen, at the most. The potential depends on the composition of the waste treated with carbohydrates as the favored substrate for hydrogen production. The effluent from hydrogen production fermentors is well suited for methane production and the total energy yield from such a two-step process is higher than the yield from conventional methane production based on the same waste and process retention times. Digester processes adapted for such purposes are discussed.

Introduction

Hydrogen is produced through various biological processes in biogas plants, but it is also removed by H_2 consuming bacteria, yielding methane. Inhibiting the hydrogen consumption is a strategy to harvest hydrogen from anaerobic digestion, which has been demonstrated in several published lab scale experiments. These results need to be generalized in order to evaluate the potential for full-scale hydrogen production in anaerobic digesters. Ideally these lab scale results are generalized through a mechanistic mathematical model. If successful, such a model can also be used to design efficient full-scale bio-hydrogen fermentors. It is hypothesized in this study that the Anaerobic digestion model 1 (ADM1) (Batstone *et al.*, 2002) can fulfill this purpose, but might require some modifications. Some known and potentially relevant processes with respect to hydrogen production occurring in anaerobic digesters are not included in ADM1 to avoid unnecessary complexity. Some such processes are incorporate into the model to simulate bio-hydrogen production more accurately (Peiris *et al.,* 2005).

Simulations of bio-hydrogen production using the ADM1 with the suggested modifications compared to published experimental studies (Bai *et al.*, 2004; Yu *et al.* 2002) are presented to demonstrate the models ability to mimic the observed bio-hydrogen production processes. The model is then used to evaluate schemes for full-scale bio-hydrogen production based on various substrates such as typically found in food residues.

Theory

Suggested modification to ADM1

Biological hydrogen production is comprised of an extracellular disintegration step, an extracellular hydrolysis step, acidogenesis and acetogenesis. These processes have a number of parallel reactions (Figure 8). The ADM1 model addresses most of these processes and is therefore used as basis for bio-hydrogen production modeling. Modifications proposed (Peiris *et al.*, 2005) are explained here.

Zheng *et al.* (2004) showed that biological hydrogen production depends on the operating pH. Chen *et al.* (2002) and Yu *et al.* (2002) also observed the roles of pH in production of bio-hydrogen. Computation of realistic pH values is therefore very important in a mathematical model used to simulate biological hydrogen production.

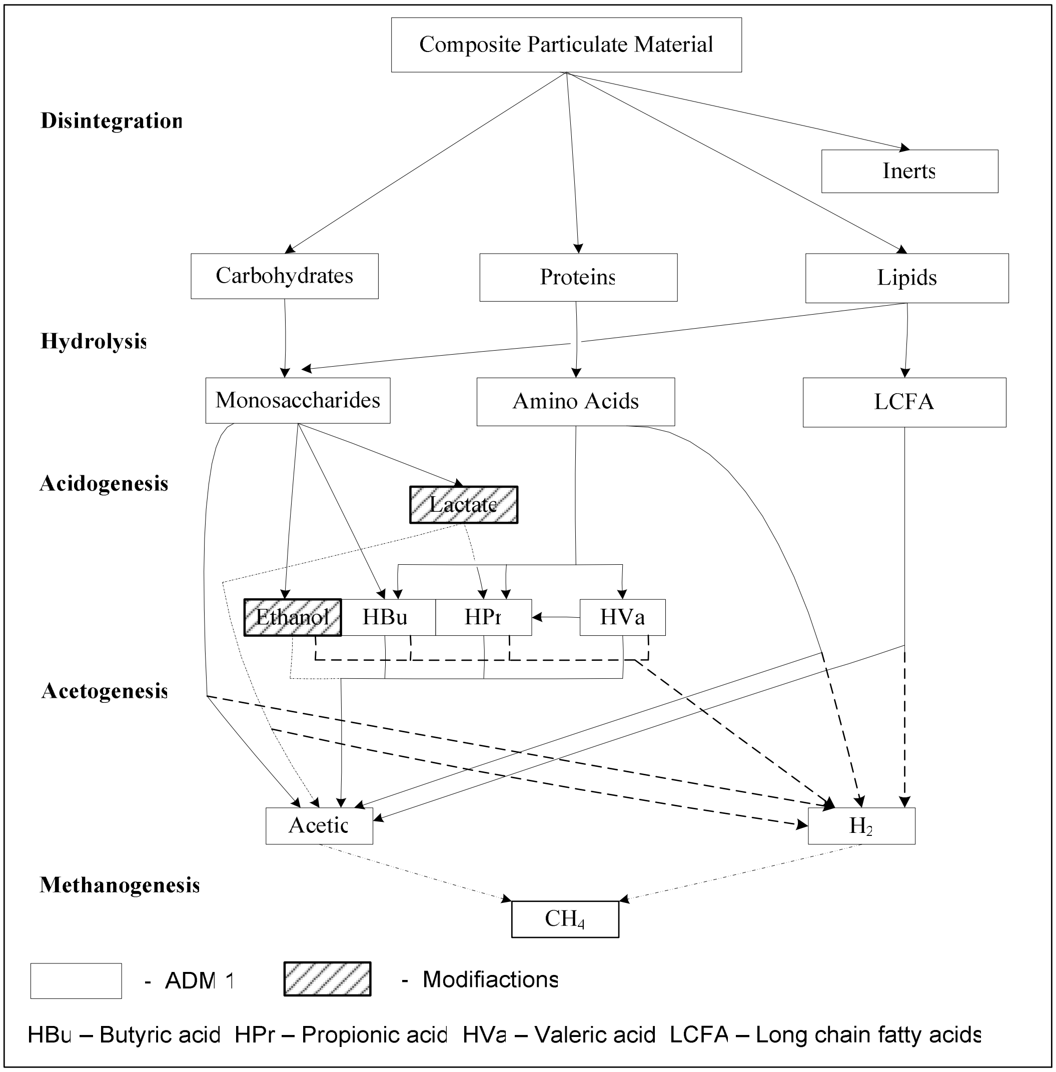

Figure 8 Diagram describing COD flux for an anaerobic particulate composite degradation in the ADM1 with the proposed inclusion of ethanol and lactate as intermediate products.

Lactate and ethanol, two key intermediate products in the anaerobic digestion processes are excluded from the ADM1 model due to their insignificant impact on methanogenic and low-loaded systems. Lactic acid has, however, a relatively low pK_a (3.08), which has strong effect on pH values. Even though the pK_a value of ethanol is comparatively larger and hence the effect on pH values is lower, it is desirable to include both lactate and ethanol in the model to achieve accurate pH predictions. Inclusion of ethanol in the model should also make the bio-hydrogen process simulations more accurate, as ethanol has been observed as a by-product in most of the reported bio-hydrogen experiments.

Lactate has been implemented as an intermediate by Costello *et al.* (1991a) and Romli *et al.* (1995) in their models. Skiadas *et al.* (2000) later introduced and validated a model with results from batch experiments. A structural anaerobic model developed by Batstone *et al.* (2000) for degradation of complex wastewater, also has lactate as an intermediate. Lactate is consistently implemented of in all these models.

Ethanol is produced as an alternative to acetate at low pH (pH<5.0; Ren *et al.*, 1997). A model including degradation of glucose to ethanol and other intermediates of its acidogenic degradation (butyrate, propionate and acetate) has been developed by Kalyuzhnyi *et al.* (1997). References to models including degradation of glucose to ethanol via lactate have not been found and it is therefore assumed that the glucose is directly degraded to ethanol. Figure 1 illustrates how the above-mentioned lactate and ethanol processes are included in the ADM1.

Acidogenesis from monosaccharides

According to Figure 1, certain portions of the monosaccharides are degraded via lactate. Unlike in ADM1, propionate is not directly produced from monosaccharide degradation in the proposed modified version. Propionate is assumed produced by acidogenesis of lactate. Ethanol is also included as an intermediate, directly produced by acidogenesis of monosaccharides. The stoichiometry of the acidogenesis reactions from monosaccharide (glucose; glucose [hexose] is used as the model monomer) are presented in Table 1.

Table 1 Products from glucose degradation

	Products	Reaction	Ref.
1	Lactate	$C_6H_{12}O_6 \longrightarrow 2CH_3CHOHCOOH$	1,2,3
2	Ethanol	$C_6H_{12}O_6 \longrightarrow 2CH_3CH_2OH + 2CO_2$	1
3	Butyrate	$C_6H_{12}O_6 \longrightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2$	1,2
4	Acetate	$C_6H_{12}O_6 + 2H_2O \longrightarrow 2CH_3COOH + 2CO_2 + 4H_2$	1,2,3

References cited: 1. Batstone *et al.* (2002), 2. Costello *et al.* (1991a) and 3. Skiadas *et al.* (2000).

The lactate is subsequently degraded to propionate and acetate. Stoichiometric reactions of lactate acidogenesis are presented in Table 2.

Table 2 Products from lactate degradation

	Products	Reaction	Ref
1	Propionate	$CH_3CHOHCOOH + H_2 \longrightarrow CH_3CH_2COOH + H_2O$	1,2
2	Acetate and propionate	$2CH_3CH_2COOH \longrightarrow 3CH_3CHOHCOOH + CH_3COOH + H_2O + CO_2$	
3	Acetate	$CH_3CHOHCOOH + H_2O \longrightarrow CH_3COOH + CO_2 + 2H_2$	1,2

References cited: 1. Costello et al., (1991a) and 2. Skiadas et al., (2000).

Reaction 1 in Table 2, which is the uncoupled reaction of lactate to propionate, has been used by Costello *et al.* (1991a) and Skiadas *et al.* (2000) in their models. Reaction 2 is however chosen in place of reaction 1 due to the facts that no organism producing propionate only has been cultured and sourcing electron from elemental hydrogen is thermodynamically unfavorable except at high H_2 partial pressure (Batstone *et al.*, 2002). This argument is consistent with the reaction proposed by ADM1 for propionate production from glucose (Batstone *et al.*, 2002).

Stoichiometric coefficients for uptake of monosaccharides and lactate can be calculated by balancing of elements, and assuming that fermentation proceeds by the reactions outlined in Table 1 and 2.

Methods

ADM1 is modified according to Theory and used to predict hydrogen yield for various feeds and operating conditions in a proposed biogas production scheme.

Lactate and ethanol are included in ADM1 by the addition of four extra state variables; two for soluble lactate and ethanol and two for lactate degrading and ethanol degrading organisms. Two processes for uptake of lactate and ethanol and two processes for decay of lactate and ethanol degrading organisms were included. Lactate and ethanol uptake rates were assumed to follow simple Monod kinetics with inhibition factors to account for pH inhibition and inhibition due to lack of inorganic nitrogen. A none-competitive inhibition factor to account for hydrogen inhibition was also included in the ethanol uptake process. First order rate equations were used to model the decay processes of lactate and ethanol degrading organisms.

The model was implemented in Aquasim 2.0 (Reichert, 1998) as a variable volume mixed-liquid compartment and a gas compartment linked by a diffusive gas link. Biochemical and acid-base equilibrium processes were implemented in the form of differential equations [DE] and implicit algebraic equations [AE], respectively. Two acid-base equilibrium processes were included to model lactate and ethanol acid-base effects. pH control was simulated by acidic and caustic control mechanisms by means of regulating cations (S_{cat+}) and anions (S_{An-}) in the liquid compartment.

The kinetic and stoichiometric parameters used in the simulations are the recommended values for biogas reactors from the ADM1 (Batstone *et al.*, 2002). The kinetic parameters relevant to lactate and ethanol were taken from other references (for lactate: Costello *et al.*, 1991b and Skiadas *et al.*, 2000, for ethanol: Kalyuzhnyi *et al.*, 1997). No parameter estimations or adjustments were made to fit the model to the bio-hydrogen production data.

Bio-hydrogen production is achieved by eliminating the hydrogen-consuming microorganisms, simulated by setting the initial concentrations of the methanogens to zero.

Results and discussion

Some of the simulations of bio-hydrogen experiments used to evaluate the modified ADM1 model's abilities (Peiris et al., 2005), are presented first. Simulations of proposed hydrogen producing biogas process scheme are then discussed.

Model evaluations

Bai *et al.* (2004) investigated the roles played by carbohydrate and protein in hydrogen fermentation using multiple substrates containing different ratios of glucose and peptone. Simulated and experimental results of cell growth and hydrogen production on feeds consisting of different ratios of carbohydrate and protein are presented as cell growth and hydrogen yield through batch processes in Figure **9** and **Fejl! Henvisningskilde ikke fundet.**. The highest hydrogen and biomass yields were observed at a carbohydrate/protein ratio of ~3/2 in both simulations and experiments. Simulated results and experimental results show a similar trend over different ratios of substrates with a best fit at the 3/2 ratio. Measured and simulated final pH in batch reactors, following hydrogen fermentation, are also quite consistent (results not shown).

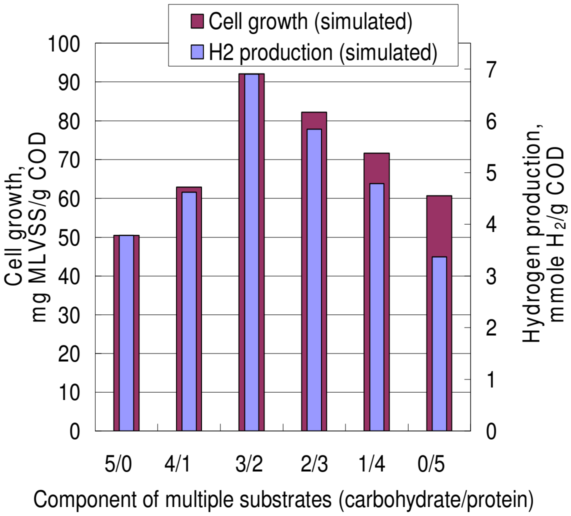

Figure 9 Simulated cell growth and hydrogen production on feeds consisting of carbohydrates (5/0) and protein (0/5) and multiple carbohydrates to protein ratios (4/1, 3/2, 2/3, 1/4) in between. All experiments had the same total quantity of substrates, 5 g-COD/L.

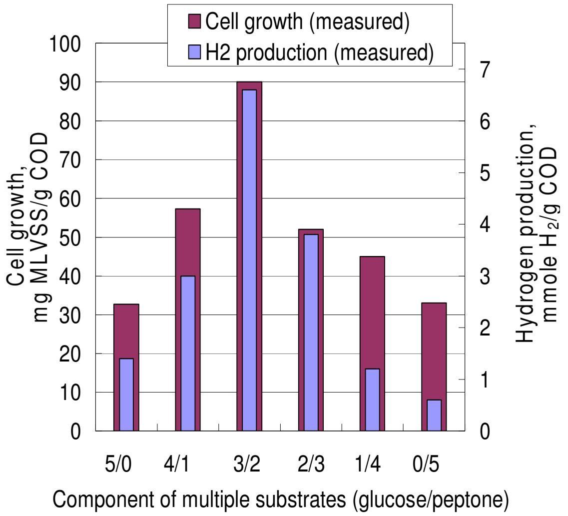

Figure 3 Measured cell growth and hydrogen production on feeds consisting of glucose (5/0) and peptone (0/5) and multiple glucose to peptone ratios (4/1, 3/2, 2/3, 1/4) in between. All experiments had the same total quantity of substrates, 5 g-COD/L.

Yu *et al*. (2002) demonstrated continuous production of hydrogen from the anaerobic acidogenesis of a high strength rice winery wastewater and examined the individual effects of hydraulic retention time (HRT), pH and temperature on hydrogen production

Simulated results of the influence of operating parameters (HRT, pH and temperature) on bio-hydrogen production followed the similar trends as those measured in general. Variations of partial pressure (kPa), hydrogen production rate (l/g-VSS.d) and H_2 yield (mole-H_2/ mole-hexose) with respect to HRT resulted from the simulations are consistent with experimental results (Figure 10). Variation of the same variables with respect to pH and temperature were however less consistent with the experimental results (Figure 11 and **Figure 12**). These correlation deficiencies suggest that model is not capable of handling some of the phenomena in bio-hydrogen production.

The fractions of monosaccharide that degrade to various fermentation products (propionate, butyrate, acetate, lactate, etc.) vary depending on hydrogen concentration, pH, temperature, volatile fatty acid (VFA) and ethanol concentrations. No regulating mechanism to handle this phenomenon is however included in ADM1 due to lack of knowledge in this area. The fractionation of amino acid on the other hand is not as affected by these variables as the amino acid mix (Batstone, personal communication). The fractional values for monosaccharide degradation used in this study were not subjected to change as functions of hydrogen concentration, pH, temperature, VFA and ethanol concentrations. This appears to be a significant shortcoming of the ADM1, especially when it handles shock loads, changing condition of pH, temperature, VFA, ethanol and hydrogen concentrations. If these fractional values are not corrected with respect to pH and other governing variables mentioned above, the out come would be incorrect VFA levels and hydrogen ion concentrations leading to inaccurate pH values and hence all the other results in the simulations. Depending on these fractional values some pathways of hydrogen production could become more significant than other pathways causing reduction or increase in hydrogen production and cell growth.

The studies of the influence of HRT on bio-hydrogen production were made at constant pH (5.5) and temperature (35 ^{o}C). Simulated and measured VFA mix and ethanol concentration changed slightly with changing HRT except at HRT =2 hours, where the changes were somewhat significant (results are not shown). Therefore fractionation of monosaccharide must have occurred in a set of pathways unchanged or with little changes at all HRT values. Since ADM1 does not have a mechanism to change the fractionation of monosaccharide, it also assumes a specific set of pathways for acidogenesis. This explains why simulated results are quite consistent with experimental results of hydrogen production with respect to HRT. As the pH and temperature change on the other hand, pathways of monosaccharide acidogenesis can be expected to vary, explaining why the simulated results of the influence of pH and temperature on bio-hydrogen production were not that consistent with the experimental results (Figure 11 and **Figure 12**). An additional reason for the difference between simulated and experimental results in the case of changing pH may be that the pH inhibition mechanism in the ADM1 was not tuned well enough to handle this specific case.

Based on the above observations, the ADM1 can be considered to be a good starting point to model bio-hydrogen production. The ADM1 simulated published work by Yu *et al.* (2002) and Bai *et al.* (2004) reasonably well with the modification proposed. Considerable differences between simulated and experimental results are however observed. These differences can be reduced through two alternative approaches:

1. Parameter estimation: The kinetic and stoichiometric parameters used in the simulations were the recommended values for biogas reactors from the ADM1 and were not adjusted for the specific case encountered by Yu *et al.* (2002) and Bai *et al.* (2004). Parameter estimations should make the model simulations fit experimental data better.
2. Proper regulating mechanism to regulate the fractionation of monosaccharide depending on hydrogen concentration, pH, temperature, and VFA and ethanol concentrations, as discussed above, should make the model more robust and reliable by enabling the model to simulate different cases of bio-hydrogen production more accurately.
3.

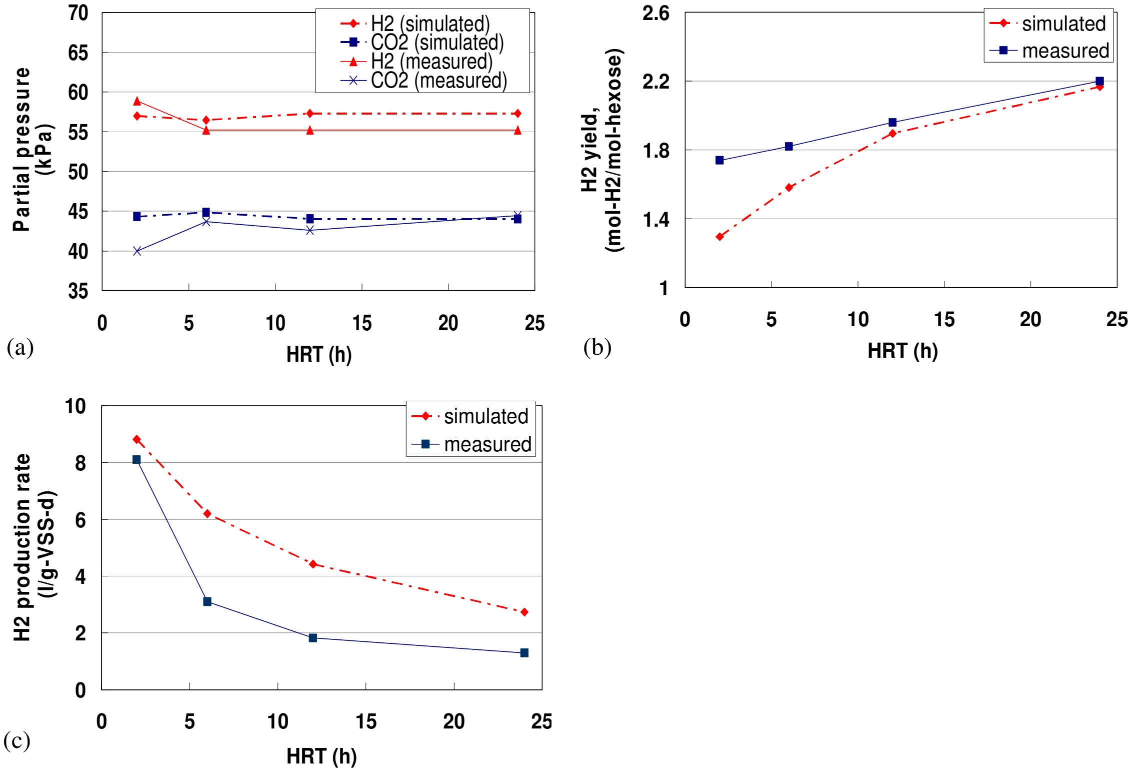

Figure 10 Simulated and measured results of the influence of HRT on the performance of the hydrogen-producing reactor: (a) partial pressure of H_2 and CO_2, (b) hydrogen yield and (c) specific hydrogen production rate. For all cases; pH = 5.5, temperature = 35 ^{o}C and influent loading =34 gCOD/L.

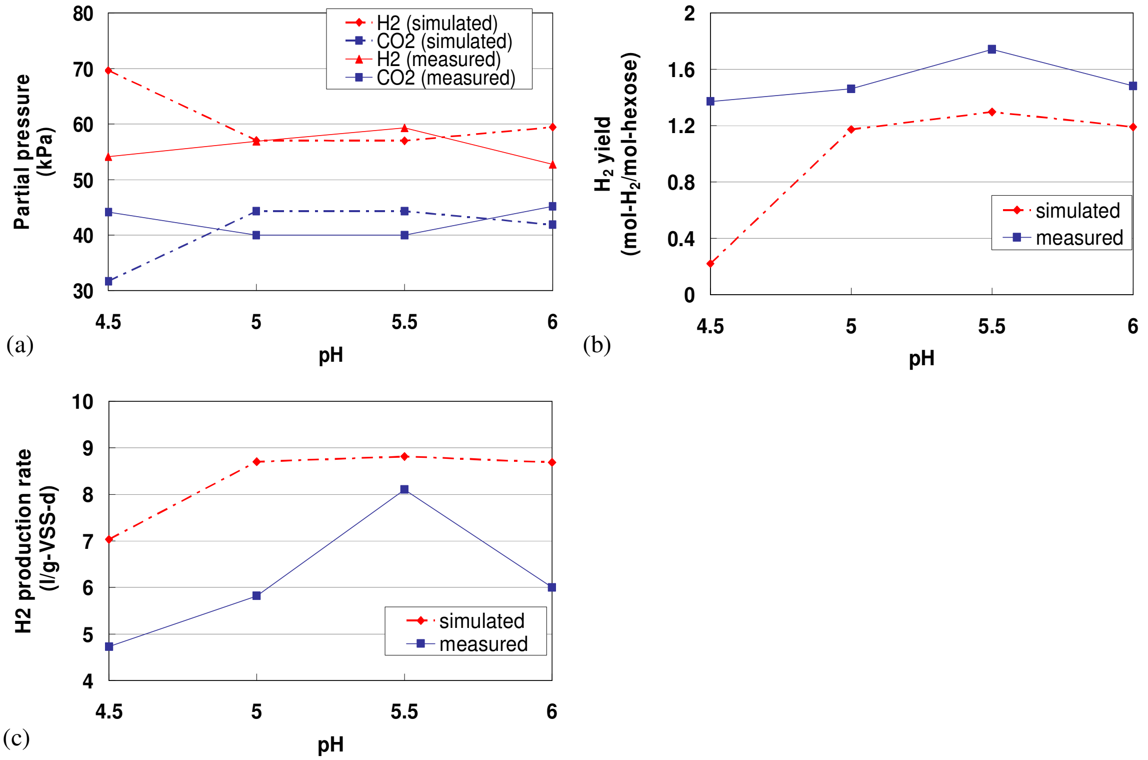

Figure 11 Simulated and measured results of the influence of pH on the performance of the hydrogen-producing reactor: (a) partial pressure of H_2 and CO_2, (b) hydrogen yield and (c) specific hydrogen production rate. For all cases; HRT = 2 hours, temperature = 35 ^{o}C and influent loading =34 gCOD/L.

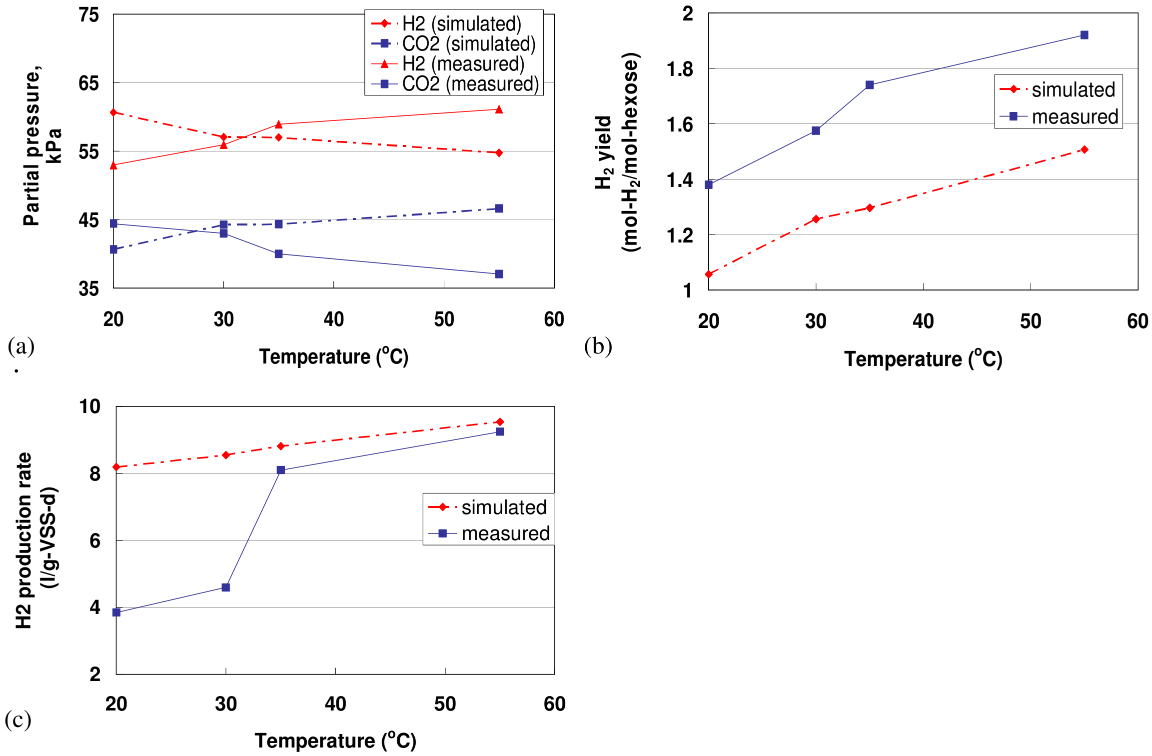

Figure 12 Simulated and measured results of the influence of temperature on the performance of the hydrogen-producing reactor: (a) partial pressure of H_2 and CO_2, (b) hydrogen yield and (c) specific hydrogen production rate. HRT = 2 hours, pH =5.5 and influent loading = 34 gCOD/L

The mechanistic approach of alternative 2 is given priority as it will yield more insight and presumably a more robust model compared to the empirical approach of alternative 1. Extensive further research is, however, needed to devise the required regulating mechanisms.

In general, the ADM1, with the inclusion of lactate and ethanol intermediates, is capable of modelling published bio-hydrogen production processes quite well. Model limitations when pH and temperature change are identified but these shortcomings are assumed not significant for the use of the model in a more general evaluation of bio-hydrogen processes, as presented next.

Process concepts

An evaluation of the bio-hydrogen production potential for various substrate compositions are evaluated through a series of simulations (not presented), showing that carbohydrates are the preferred feed. Lipids also can give relatively high hydrogen yield while proteins are less favourable, due to the degradation pathways. Food residues have varying relative amounts of carbohydrates, lipids and proteins depending on the source, but are frequently fairly low in proteins and therefore quite suitable as feed for hydrogen production. The study, therefore, suggests that it is realistic to design bio-hydrogen production processes based on various food processing residues, especially those with relatively high carbohydrate content.

The highest H_2 yield obtained in the simulations was ~24 % of the total biogas potential (measured as kJ/g-COD). This relative hydrogen yield is limited by thermodynamic constraints, implying that it probably represents an absolute upper limit.

The effluent from a well functioning bio-hydrogen fermentor consists to a large extent of volatile fatty acids and has a composition suitable for further fermentation to methane. A two-step process consisting of a bio-hydrogen production step and a methane production step is therefore proposed (Figure 13). The simulated steady state energy output from such a two-step process is presented in Figure 14. Simulations show that this two-step process has a higher biogas energy yield than a conventional biogas process with the same SRT. The difference is greater at lower SRT than at higher SRT, approaching a ~8 % difference at high SRTs. The ultimate 8 % energy yield increase obtained by the introduction of a bio-hydrogen production step in biogas processes can be explained by the higher energy content of hydrogen compared to methane. The larger energy advantage of the bio-hydrogen step at lower SRT can be explained by the favourable kinetics of the hydrogen producers, suggesting that the hydrogen production step can be obtained in a relatively small reactor volume. Note, however, that the total energy yield is greatest at the highest SRT.

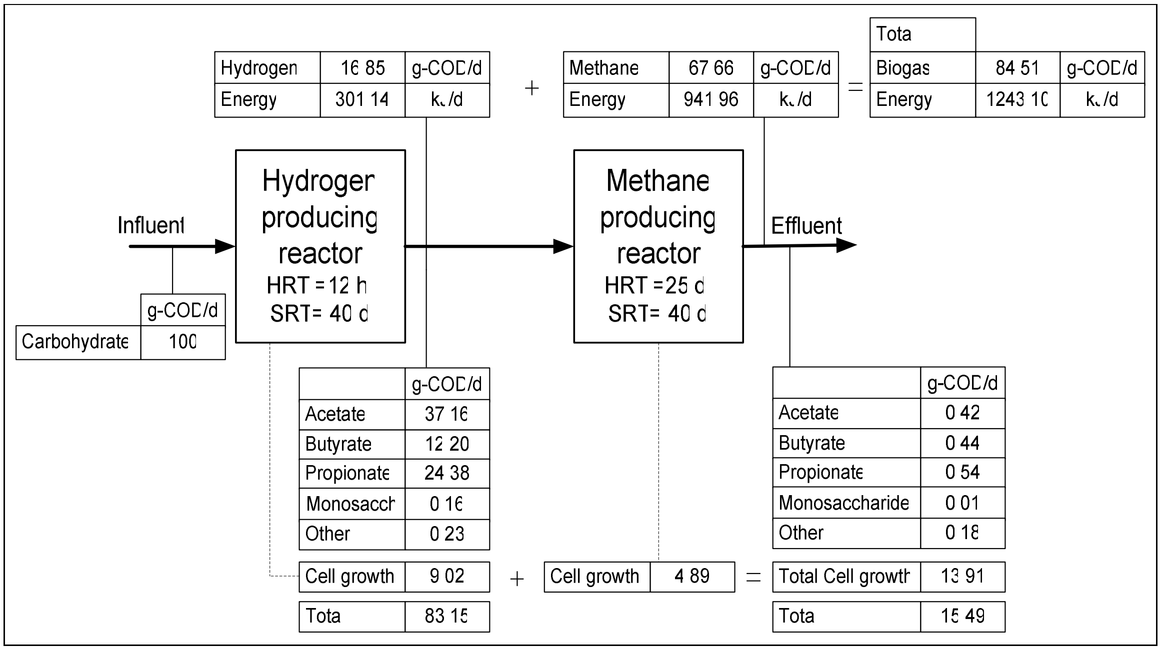

Figure 13 Simulated steady state two-step biogas production process showing concentrations and energy yields for a influent carbohydrate loading of 100 g-COD/d.

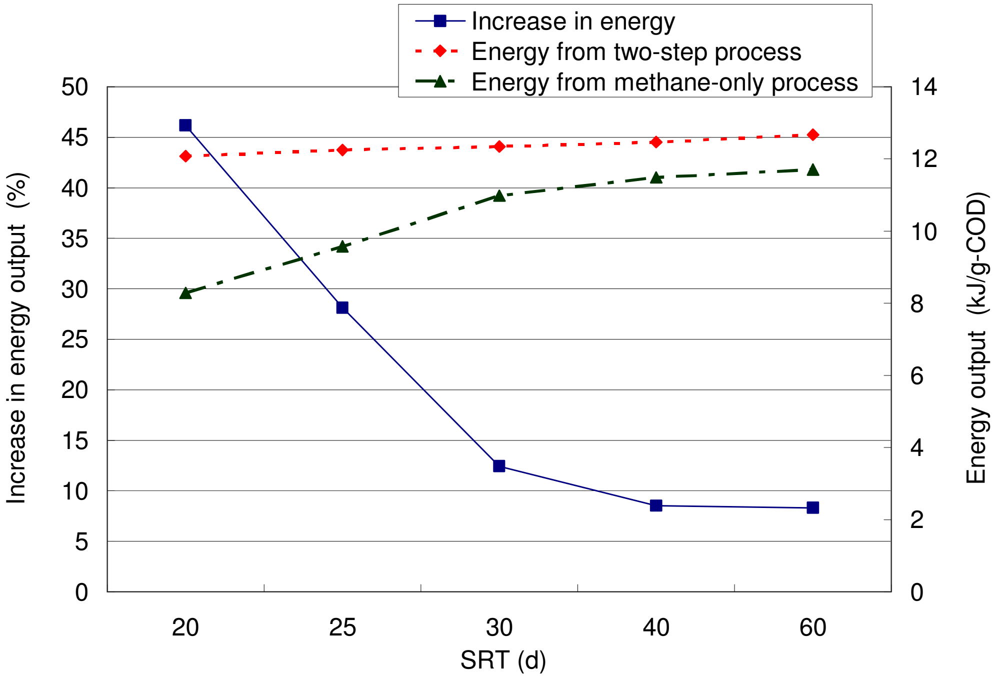

Figure 14 Simulated energy output and relative energy increase in biogas production in a two-step process (hydrogen at first step and methane at the second step) compared to methane-only producing biogas process at various sludge retention times (SRT).

Bio-hydrogen production concepts must include a subsequent methane producing process to be sustainable. Else most of the energy is lost as organic matter dissolved in the effluent. Given a two step process with H_2 and CH_4 production steps as proposed, the methane can be regarded as a relatively low value product used as energy source to run the biogas plant while hydrogen is the high value product to be used for other purposes, such as to run fuel-cells.

Conclusions

- The ADM1, with the inclusion of lactate and ethanol intermediates, is capable of modeling published bio-hydrogen production processes quite well in general and is therefore a suitable tool to evaluate the potential for full-scale bio-hydrogen production in anaerobic fermentors.
- A regulating mechanism to handle monosaccharide fractionation into fermentation products can improve the model's ability to handle pH and temperature changes.
- A two-step digester process with bio-hydrogen production in the first step and methane production in the second is proposed.
- This two-step concept can give a higher energy yield (>8 %, depending operating conditions) than comparable methane only producing systems.
- The maximum relative hydrogen yield is ~24 % and is limited by thermodynamic constraints.
- Carbohydrates are the preferred substrate to obtain high hydrogen yield.

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Utilization of Bioenergy for Decentralized Combined Heat and Power Generation: The MTU Carbonate Fuel Cell HotModule®

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Abstract

The MTU Carbonate Fuel Cell HotModule operated with natural gas is demonstrated meanwhile in approximately 25 field trial plants and reached now a pre-commercial status. It is highly suitable for the utilization of hydrocarboneous gases, such as biogas, sewage gas, coal mine gas, synthesis gases from thermal gasification processes of different waste material. Even lean gases will be converted with high efficiency to electrical power and high exergetic heat. These characteristics recommend the HotModule for applications using the big potential of regenerative and secondary fuels with all their advantages in decentralized consumable energy supply, reduction of dependence on primary energy imports and reduction of greenhouse gas and other contaminants emission. MTU started recently a HotModule fed by methanol from waste material together with BEWAG in Berlin and many experimental work concerning applications with biogas and sewage gas has been performed with promising results.

The MTU Carbonate Fuel Cell HotModule operated with natural gas is demonstrated meanwhile together with our partner Fuel Cell Energy Inc. in approximately 25 field trial plants and reached now a pre-commercial status. The reliable function and operability of this highly integrated carbonate fuel cell system for stationary applications in the 250 kWel range has been shown with these plants. All field tests units started in 2001 and later are still in operation. One of them for more than 25.000 hours, others more than 18.000 hours.

The electrical power of the HotModule is produced in form of direct current, which is transformed into grid compatible AC-energy at the 400 V level by integrated converters. The thermal power of the HotModule will be delivered in form of hot depleted air at a temperature between 400°C and 450°C. This high exergy heat enables a large variety of thermal applications, in particular production of process steam, process heat for industrial purposes. Combined heat and power (CHP) production or trigeneration (power, heat, and cold) are preferred applications.

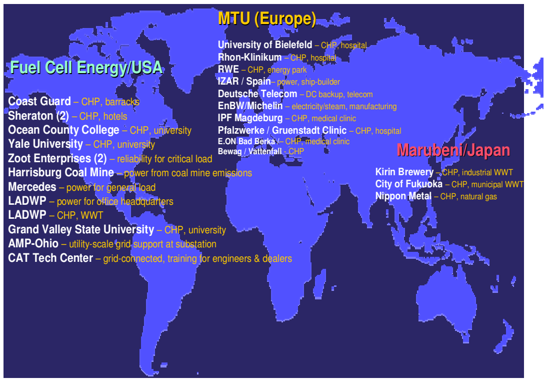
The HotModule can be operated with a big variety of gaseous or gasified fuels and is characterized by low pollutant emissions in combination with excellent electrical and thermal efficiencies. The power/heat ratio is adjustable in a wide range. Many HotModule installations based on natural gas feed are accomplished worldwide and are under operation successfully presently (see fig. 1).

Integration

HotModule at RWE, Essen, Germany

Installation at a Hospital at Bad Berka, Germany

Installation at IZAR, Cartagena, Spain



HotModule Installations worldwide

Methanol HotModule at BEWAG, Berlin, Germany

Fig. 1: The MTU HotModule under construction and in different installations

Utilization of Regenerative and Secondary Fuels with the HotModule

One of the most important activities in reducing greenhouse gas emissions (CO2, CH4, VOCs...) is an efficient stationary production of the consumable energy forms, i. e. power, heat and cooling power. High temperature fuel cells such as Molten Carbonate Fuel Cells (MCFC) are high-efficient electro-chemical generators. When properly installed, they can produce additional high exergetic heat, which can be used due to its high temperature (>400°C) not only for industrial procedures of all kinds but also for production of cooling power via thermal fed cooling systems (absorption chillers, available at the market place).

The application of high temperature fuel cells as a “prime mover” in the translation of the chemical energy content of regenerative and secondary fuels to the consumable energy forms opens a big potential to reduce the dependence in high value primary energy carriers for the production of consumable energy. Additionally, it closes the CO_2 production loop to zero by the fact, that the CO_2 produced in the fuel cell is exactly the same amount, which was necessary to build up the original plant-material, where the regenerative or secondary fuel comes from.

Due to the electrochemical operational principle under contribution of carbondioxide the carbonate fuel cell is not only highly suitable for the utilization of all hydrocarboneous gases, in particular natural gases and synthesis gases, but it is the preferred transformer to electricity of low heating value gases with high amounts of inert components. Even such lean gases will be transformed with a high electrical efficiency (methane containing gases in the range of 50 %, synthesis gases in the range of 42 %). Hydrocarbons, carbonmonoxide, hydrogen are welcome fuels in all composition ratios. Inert gas components, e. g. CO_2, N_2 do not impact the efficiency up to a rate of approximately 50 %, but are welcome for cell cooling purposes, thus reducing the parasitic power demand and increasing the overall plant power efficiency. These characteristics recommend the Fuel Cell HotModule for utilization of secondary fuels, which are fuels from decentralized and regenerative sources, in particular from biomass and waste material, e. g. gases from anaerobic fermentation (biogas, sewage gas, landfill gas, coal mine gas, etc.) and gasified products from wood, paper, waste material, etc.

The combination of systems for biomass or waste material gasification with the MTU Fuel Cell HotModule and adapted thermal fed coolers forms a basic building block for an integrated energy supply system fulfilling the requirements of industry, manufacturing, trade, municipal applications, utilities and possibly the private sector. Manufacturing plants, cold stores, office buildings, computer and telecommunication centers, super markets, sport facilities, residential areas and others will be the future sites of applications.

The decentralized utilization of decentralized available energy sources for production of consumable energy forms has many impacts on the economical and ecological situations by reducing transmission losses, reduced requirements to the infrastructure, reduced emissions of greenhouse gases and pollutants, reduced dependence on primary energy carrier imports with positive impacts to the balance of trade. Last not least decentralized consumable energy production and its decentralized utilization increases employment in rural economies and areas as well as it offers advantages for small and medium enterprises.

State of the art

Until now, biogas/sewage gas is converted into electric energy in conventional CHPs with a relatively low efficiency (max 36 %) and a large quantity of low-temperature process heat. Conventional CHPs in the performance class up to some 100 kW_{el} are mostly based on gas-piston-engines. These engines can be operated with fuel gases containing relatively high amounts of sulphur compounds. 50 to 100 ppmV H_2S are acceptable. Simple methods (air dosing to digester biogas, biological and chemical processes) are used for purifying biogas. But this is not enough for the operation of fuel cells. In this case, the total amount of sulphur in the fuel is limited to 0.1 ppmV. The big challenge results from that fact; it is to find (cost-)effective and reliable methods for treatment and purification of regenerative and secondary gases.

Synergies by using biogas and sewage gas in fuel cells

By bringing the fields of biomass, (bio-)residues, anaerobic digestion and fuel cell technology together, several synergies make such applications attractive:

- Utilization of renewable energy sources (RES) in fuel cell technology – leading to a sustainable cycle by using a CO_2 neutral fuel. Such a fuel enhances the environmental advantage of fuel cell technology. Biogas and sewage gas is renewable energy with a very high potential for greenhouse gas reduction.
- Efficient and clean energy conversion of valuable RES: due to the nature of fuel cells, hardly any emissions are produced while converting biogas into electricity. And this is possible with high electrical efficiencies indicated above.
- High user potential for utilizing the process heat which is released from the MCFC-process: due to the high temperature of the depleted air from the fuel cell system at approx. 400°C, it is possible to use this heat in a broad variety.
- Decentralization of the energy production is an approach for a more secure and stable energy supply. Decentralization is one of the main advantages of RES, as these are in many cases locally available. Biogas plants are to be found usually in the decentralized agricultural sector.
- Anaerobic digestion enables a cost reduction of organic residue disposal and new income for the agricultural sector. Alternative organic waste treatment is usually strongly energy demanding, as is the case of composting. Anaerobic digestion has a higher investment cost as e.g. composting facilities but provides the operator with energy which can be sold to the electrical grid. As organic wastes are usually co-digested in agricultural biogas plants, farmers are enabled to produce more electricity, giving them an additional income possibility.

By involving the agricultural sector also for the production of energy crops for the anaerobic digestion process it is possible to close the nutrient cycle, as the digested organic wastes are used as fertilizer on the farming land. By reducing the use of mineral fertilizers farmers contribute to the environment protection; as such fertilizers are produced with high amounts of energy. The digested substrate in biogas plants can substitute such fertilizers, solving in that way also the question of what to do with these substrates.

Products of the Molten Carbonate Fuel Cell HotModule

- **Electricity**
    - DC for telecommunication and IT
    - AC to grid or to stand alone networks
    - Applications for uninterruptible power supply
    - Premium power
- **Heat**
    - Heat from HotModule is available in form of the depleted air at a temperature level of approximately 400 °C. This high exergetic heat is valuable for industrial production processes as well as for sterilization processes in hospitals, in the food industry, in greenhouse farming. It can also be used in cascades of steam production for electricity generation via steam turbines, medium temperature processes and at the low temperature end for space heating and water heating.
    - Another important heat utilization is the production of cooling energy for air conditioning and food storage facilities by thermal driven cooling systems, e. g. absorption chillers or steam injection chillers. Both temperature levels can be achieved, the air conditioning which needs cold water of 2 to 4 °C as well as the deep temperature storage requirements of -20°C or less.
    - A big advantage of the heat utilization for cooling power production (the “trigeneration”) is the overlapping of the required energy amounts over the year: In summertime much cooling power is required, in winter more space heating. This leads to a thermal full power operation of the HotModule all over the year, where no heat is worthless produced. This decreases the pay back period of such equipment.
- **Depleted air**
    - Beside the heat of the depleted air of which the utilization is described already above, this air is also a worth full effluent: The depleted air consists of nitrogen, a small amount of oxygen, lots of water vapor and a substantial amount of CO2 (in the range of 5 vol%). No contaminants, no toxic ingredients, no other loads.

  - Mixed with fresh air, this depleted air is a most valuable atmosphere for greenhouse farming: Plants need the right temperature, the CO2-contents increase the growing rate of the plants (e. g. tomatoes need an average of 2 vol% of CO2 in atmosphere for optimal growing; CO2-fertilizer) and the high water vapor content saves humidification water.

Potentials of the usable Bioenergies:

- **Biogas:**
  - Only in Germany the number of existent biogas plants in the agricultural sector is presently approximately 1500. The potential for the next ten years in the performance range of 400 to 2000 kW gas output is 4000 plants. In case of a consequent utilization of the gas produced by these plants for Combined Heat and Power Production a contribution of 12% to 15% of consumable energy consumption can be reached. (Meyer-Pitroff, TU Muenchen).
  - Most of agricultural residuals are recycled to the land without any treatment presently. This is similar to the situation 50 years ago concerning the sewage of mankind. It seems to be necessary, to build up a network of biogas plants to treat and gasify at least the big amounts of manure in order to contribute to a clean and healthy environment also in agricultural regions. This would lead to another, more important category of biogas production and utilization.
- **Sewage gas:**
  - The number of biological sewage treatment plants in Europe increases sustainably. A small number is already equipped with low efficiency piston engines to generate electricity. The replacement potential and a new equipment potential is high, since fuel cell systems are reliable and cost effective.
- **Synthesis gases:**
  - As thermal gasification systems are not yet really mature and available at the market, the utilization of synthesis gases is made in some demonstration units only presently. The potential of utilization by fuel cell systems is dependent on the success of the development steps of gasification systems, but if these gasifiers reach a reliable technical status, the potential of biomass and waste material gasification will be somewhat higher in comparison to the biogas potential.
- **Purge gases:**
  - High potentials of purge gases exist in chemical and petrochemical industry. As these gases differ in a wide variety, the technique is not ready yet for a wide spread utilization. There is room for improvement and development, and it is to be taken into consideration, that in industrial processes often purge gases and other combustible residuals are integrated into the processes representing a high utilization.

Biogas projects:

Till now most of the operating HotModules are fuelled by natural gas. In order to achieve a better experience about the operation MCFC-systems under biogas conditions, MTU performed several experimental tests in the lab-scale as well in full HotModule size. The lab-scale experiments were performed in two different research programs. One of them was granted by the EU, in which small lab stacks are operated at different locations with different fuels. The other project was granted by the German Ministry for Agriculture via the Fachagentur für Nachwachsende Rohstoffe, in which a stack was operated on a farm close to Muenchen, Germany. The key points of these projects are listed in the following table 1. The aim of both projects was to establish the process chain from biogas production, biogas cleaning and operating a MCFC-stack with the biogas. The results are rather promising. It was expected, that the gas cleaning units should reduce the concentration of hydrogen sulphide from its original value (approximately 100 – 3.000 ppm) down to the level, which is known from the natural gas operation (< 20 ppm). It seems that all tested gas cleaning units fulfilled this demand. In the national project it was attempted to reduce the lower limiting value down to less than 0,1 ppm. Fig. 2 shows test facilities of the national project.

Table 1: Lab-scale operation of MCFC-stacks fueled with biogas

number of test runs	in total 7 lab stacks at 5 different locations
gas suppliers	Seaborne (Owschlag – DE) agricultural biogas Linz AG (Linz – A) gas from waste water treatment Urbaser (Madrid – E) landfill gas Univ. Nitra (Nitra – SK) agricultural biogas Farmer in Munich area
gas cleaning systems	Seaborne (Owschlag – DE, Fig. 25.1), Profactor (Steyr – A, Fig. 25.2) Different systems designed by Schmack Biogas AG (Burglengenfeld – DE)
test beds and fuel cells	MTU CFC Solutions GmbH (Munich – DE)
scientific support	Studia (Schlierbach – A) Ciemat (Madrid – E) Rent-A-Scientist (Regensburg – DE)
industrial partner	EON AG (Munich – DE)

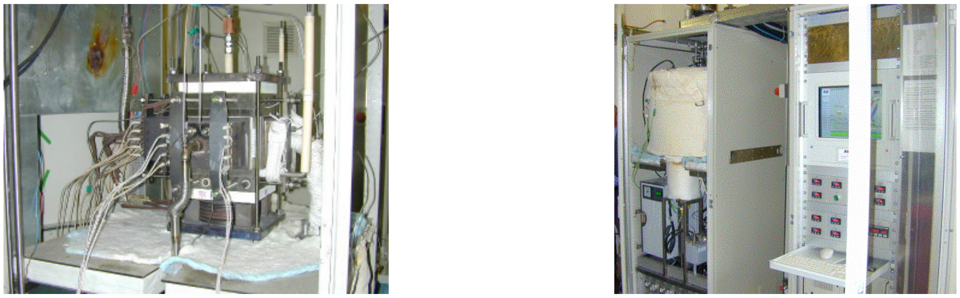


Fig. 2: Lab-scale Stack and Test-Unit which were used during the Biogas-Projects

This is about the level which should be achieved downstream the gas fine cleaning. Here too the available results are rather promising and it seems that there is an option to avoid the gas fine cleaning in future. This means, that the system can be simplified and it consists of only one gas cleaning step between the fermentation process and the fuel cell system. Then the activated carbon filter for the gas fine cleaning, which is rather sensitive towards condensation of the humidity, can be excluded from the system. (unpublished results achieved by Schmack Biogas AG).

The reactivity of ammonia has been determined in lab-scale tests as well as in full-size HotModule tests. Similar results were obtained in both test runs, the added ammonia was decomposing more or less completely while passing through the fuel cell system (unpublished result achieved by MTU CFC Solutions GmbH). During the full-size test (HotModule) ammonia was mixed to the natural gas to reach an inlet concentration of about 5.000 ppm. The NH_3-concentration was monitored at different locations inside the system. It turned out that ammonia was decomposing stepwise in each reforming step. Finally the concentration came down to < 20 ppm (less than 1 % of the initial value). It is assumed that ammonia decomposes in a retro-Haber-Bosch reaction to nitrogen and hydrogen:

$$2\ NH_3 \quad \Leftrightarrow \quad N_2 + 3\ H_2$$

The formed hydrogen can be consumed as fuel in the electrochemical fuel cell reaction. This may also give an explanation to the observation that the decomposition of ammonia was sensitive towards the applied fuel utilization. At lower fuel utilizations, the equilibrium of the decomposition reaction is shifted slightly to the left side of the upper equation, since hydrogen is present in an excess.

Finally, in a different test run the effect of carbon dioxide and nitrogen on the performance of an operating HotModule was examined. Both gases were added to the natural gas in order to simulate two different types of biogas. On the one hand the addition of carbon dioxide should result in a mixture, which is typical for the fermentation process. On the other hand the addition of nitrogen should simulate a gas which is representing the thermal gasification of biomass. An effect of the carbon dioxide addition was expected, since the performance increased slightly. In contrast to the other types of fuel cells carbon dioxide is participating actively in the electrochemical MCFC-reaction (see above). Therefore, it should have the beneficial effect on the overall performance of the HotModule System, which can be seen in the next figure. The amount of carbon dioxide was increased stepwise from more or less pure methane (natural gas) up to a ratio of $CH_4 : CO_2 = 2 : 3$. The average cell potential rose immediately by nearly 7 mV after the first addition. The effect of further CO_2-additions was smaller than the one which was observed during the first step. (See fig. 3)

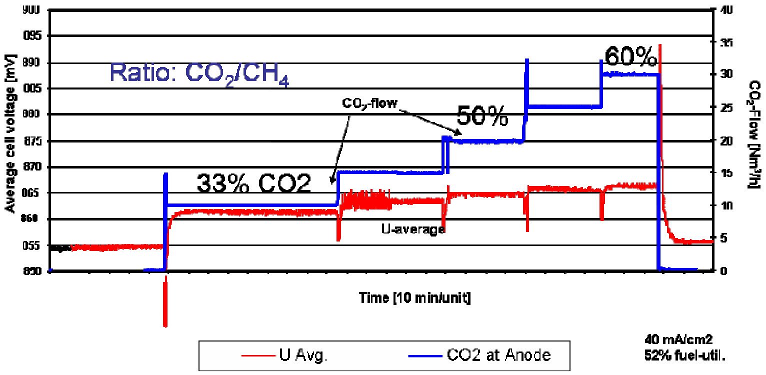


Fig. 3: Effect of CO_2-addition on the performance of a HotModule – simulated biogas operation feeding the stack with CH_4 and CO_2

This experiment was repeated but nitrogen was mixed to the natural gas instead of carbon dioxide. During the auto-thermal gasification of biomass the organic material is oxidized partially by the oxygen of the added air, which is removed completely. The remaining nitrogen then is diluting the formed process gas, which consists mainly of methane, hydrogen, carbon monoxide, carbon dioxide and steam. In order to learn more about the influence of the presence of nitrogen it was mixed stepwise to the natural gas. Surprisingly, the potential of the stack remained unchanged even when the ratio of CH_4 : N_2 increased up to a value of 1 : 2. During the experimental run, the average stack temperature didn't change too (see Fig. 4).

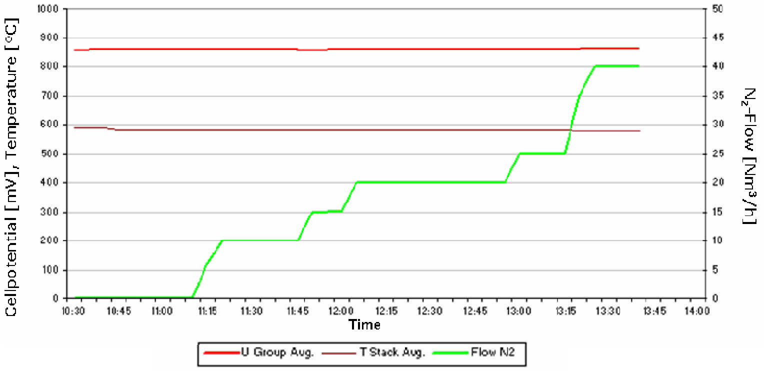


Figure 4: Effect of nitrogen addition to natural gas on the performance of a HotModule system

BEWAG-Methanol-Project:

A HotModule combined heat and power production plant is under operation since September 2004 in Berlin, Germany at BEWAG facilities, which is the local utility company in Berlin (Fig. 5). This modified HotModule is designed for operation with methanol and all possible methanol-natural gas mixtures. As the plant has been started with natural gas for practical reasons the operation with methanol started in January 2005. Its operability with pure methanol and continuously changed mixtures of methanol and natural gas is proven meanwhile. Since these operational conditions were not optimized till now the electrical efficiency varies within the range from 43 to 46 %. By proper optimization of the operational conditions we expect values up to 48% fed by mixtures with a substantial content of methanol. (see Fig. 6)

Fig. 5: The methanol HotModule at BEWAG, Berlin, Germany

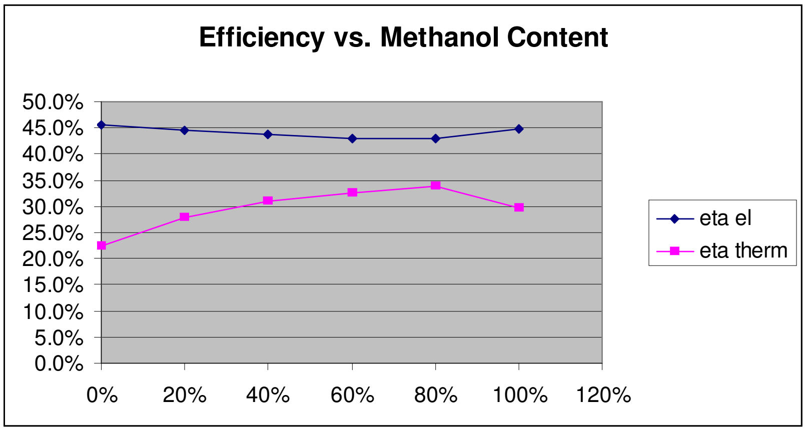


Fig. 6: Electrical efficiency depends on methanol content in feed

Principle is, that the methanol is evaporated in the HUMIHEX together with water upstream a catalytic reformer. Due to the exothermal reforming of the methanol, the reformer is cooled by air in dependence on the methanol concentration in the feed. Till now, the plant operates successfully; measurements for characterizing the plant are under work. The author hopes to be able to present at the conference more details and results of the first experimental session performed at this plant.

Remark: The methanol is produced from plastic waste material at the facilities of SVZ in Schwarze Pumpe near Bitterfeld, Germany. SVZ means: Sekundär-Rohstoff-Verwertungszentrum Schwarze Pumpe. At SVZ, plastic waste is processed in a gasification process together with some lignite to a synthesis gas, which is converted directly to methanol. This plant delivers some megatons of methanol per year. The methanol project is the first application of a HotModule utilizing secondary fuels from waste material.

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The physicist Gerhard Huppmann M. Sc. is working since more than 25 years in the field of energy technologies with a focus on high effective and renewable energy utilizing systems. Since 1989 in the field of carbonate fuel cell systems. Basically he created the design of MTU's Carbonate Fuel Cell HotModule. Head of the group "New Fuel Cell Concepts and Applications" at MTU CFC Solutions GmbH, a subsidary of MTU Friedrichshafen GmbH within the DaimlerChrysler group. The design of the HotModule was awarded for innovations and future applications of natural gas sponsored by the German gas business sector.

Biogas and bioenergy system developments towards bio-refineries
Trends in a central European context

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Introduction

Life on earth depends on the light energy from the sun and on water, thus enabling green plants to synthesize organic polymers like cellulose, starch or sugars from CO_2. The world-wide annual biomass production is estimated to be $1.55 \cdot 10^{11}$ tons. These plant products, respectively by-products and ultimately wastes, can only be recycled through the soil. In the soil, the organic constituents are again mineralized by micro-organisms and subsequently consumed as nutrients by plants (Fig. 1). This natural elemental biomass cycle worked properly for millions of years, until fossil raw materials were "discovered" and fuels were introduced some 150 years ago. As a result, inbalanced CO_2-evolution (greenhouse effect) and waste accumulation (pollution) occurred, together with several other severe global environmental drawbacks like water and soil contamination, shortage in drinking water, depletion of bioresources and stratospheric ozone depletion.

In the following sections it will be demonstrated that anaerobic digestion can play an important role in the treatment and recycling of wastes and their by-products, as well as in energy generation. Furthermore, in the long run it will become an important tool in achieving closed cycle production and sustainable development of a biomass based economy.

Basic production concepts

Conventional processing of raw material typically concentrates on high yields of high quality products. Until recently, by-products and wastes (Fig. 2, A) were not considered harmful, thus being spent to landfills, soils and water courses in huge amounts. Although the implementation and improvement of waste treatment technologies has reduced environmental drawbacks considerably, end of pipe technologies world-wide are still wasting high amounts of raw materials and energy. Stricter environmental legislation and consequently increasing waste treatment and disposal costs are now gradually demanding waste abatement and by-product recovery (Fig. 2, B). Nevertheless, the ultimate goal of waste-free (clean) production (Fig. 2, C), still seems far away from realization. Even biomass based biotechnological production systems cannot be considered waste free. But wastes and by-products deriving from biomass principally allow a save recycling and a closing of nutrient cycles.

Biomass or biomass derived wastes and by-products can be used manifoldly (Fig. 3). Direct energetic use (combustion, upgrading), direct use as fodder or direct reclamation of valuable contents (carbohydrates, proteins, fat, fibres) is frequently practised successfully. Biotechnological upgrading to food, biochemicals and feed stuffs has principally been proofed successful. Introduction of microbial proteins, biosolvents, bioalcohol, organic acids, biosurfactants, biopesticides etc., depends on economic market preconditions, getting more likely with increasing costs of fossil raw material- and energy.

Among the existing waste treatment and by-product recovery processes, anaerobic digestion has a unique, integrative potential. It can act simultaneously as a waste treatment and waste recovery process (Fig. 4).

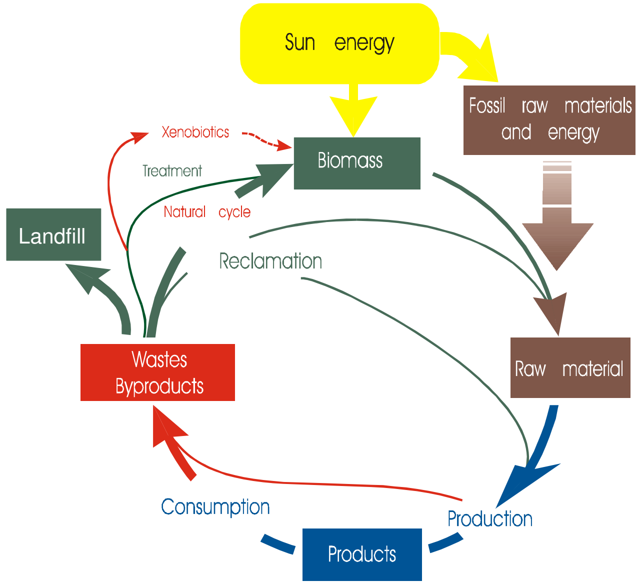

Fig. 1: Biomass and fossil raw materials cycles

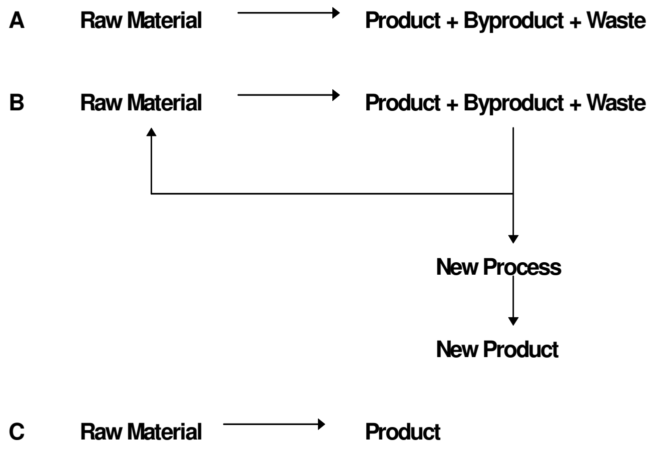

Fig. 2: Conventional (end of pipe) production system (A), By-product- and waste recovery (B) and Clean production systems (C)

Waste stabilisation an biogas recovery

Anaerobic digestion (AD) originally has been introduced as a waste stabilisation process. Due to more stringent European landfill requirements (EC, 1999), reduction obligations for green house gas emissions (Kyoto protocol) and increased hygienic requirements (ABP, 2002), AD still has increasing importance as a waste treatment alternative. It not only provides pollution prevention, but also allows for energy-, compost-, respectively nutrient recovery. As the technology continues to mature, AD is becoming a key method for both waste reduction as well as recovery of a renewable energy and other valuable co-products.

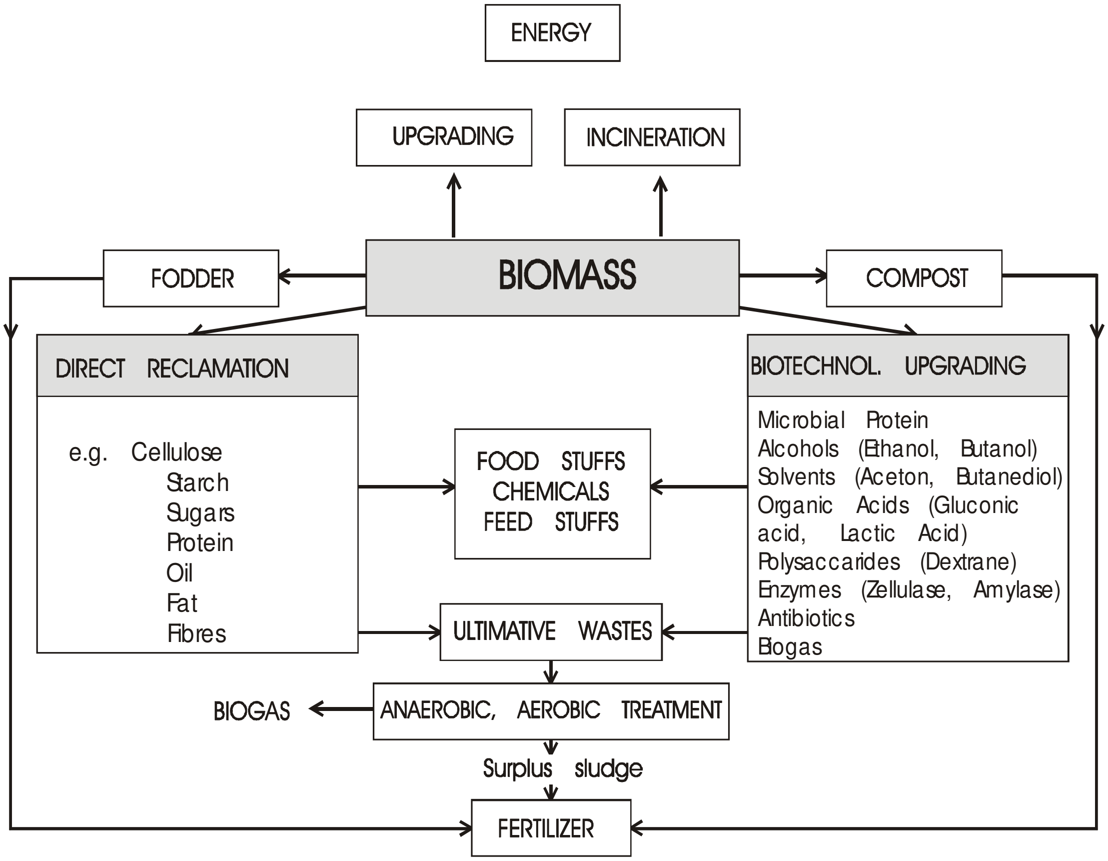

Fig. 3: Different usage of biomass and biomass derived wastes and by-products

World-wide, several hundreds of large scale municipal AD plants are in operation and many more installations are under construction or planned. Most plants treat municipal solid waste (MSW), or source separated municipal solid waste (SSMSW). Many plants additionally use different organic industrial wastes and by-products. The total annually installed capacity of anaerobic municipal bio-waste treatment is estimated to be more than five million tonnes. The use of AD for sewage sludge stabilisation is state of the art. Many sewage sludge digesters frequently use free digester capacity for the codigestion of various biogenic waste materials.

Furthermore, the application of AD as a (pre-) treatment step for industrial wastewater is still increasing. To the point, there are more than 2,500 industrial applications in operation or under construction throughout the world. Over 30 types of industries have been identified having wastes and wastewaters amenable for anaerobic treatment, including processors of beverages, chemicals, food, meat, milk, pulp & paper and pharmaceuticals, among others.

Finally, numerous small and medium scale agricultural (partly commercial) AD plants started operations during the last decade. While co-digestion of agricultural by-products, industrial- and municipal wastes was the primary goal of such installations, recently energy recovery became the prime objective of most agricultural installations. Actually more than 2,000 agricultural digesters in Germany and nearly 200 plants in Austria are in operation. Main substrates are manure and „energy crops“, but in some more commercial plants, a variety of biogenic wastes is used for co-digestion. The free capacity in agricultural- respectively commercial digesters for additional bio-waste treatment is low. Such plants now concentrate on „Green energy“ production, using renewable plant biomass. Recent Austrian legislation (Anonymous, 2002) guarantees high electricity feed in tariffs for pure “energy crop” digestion plants. Dependent on the plant size, between 0.123-0.165 € / KWh are being paid. Co-substrates are restricted to agricultural by-products. If other wastes are used, electricity tariffs will be reduced by 25 %. As a rough estimation, not more than 10-20 % of the overall digester capacity (152,000 m^3) are currently used for the co-digestion of waste.Austria is among the leading countries in bio-treatment of wastes with a long tradition in source separation. About 45 % of the household- and comparable commercial wastes are source separated. In 1999, about 478,000 tonnes of source separated municipal biowaste were collected (Anonymous, 2001). Furthermore 60,000 t of food leftovers, 1,000 t of fat scraper contents, 20,000 t of market wastes, 300,000 t of grass cuttings, 620,000 t of garden- & park wastes and 200,000 t of cemetery wastes have been reported. Roughly 1/3 of the latter wastes can be considered amenable for anaerobic treatment. From the resulting 371,000 tonnes approximately 50 % should actually be available.

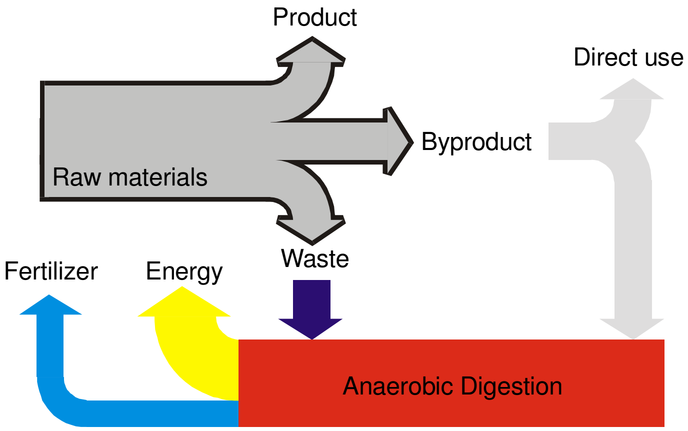

Fig. 4: Integration of Anaerobic Digestion in biomass based by-product- and waste recovery

Industrial bio-wastes come up to nearly 7,000,000 t (in 2001) of which less than 1/5 can be considered amenable for AD. Roughly 1/10 of this mass, or 590,000 t, could be made available for anaerobic treatment. In sum, available municipal- (185,500 t) and commercial / industrial wastes (593,000 t) result in an overall mass of 778,500 tonnes / year available for AD.

In 2001, 526 treatment plants (mainly composting) with a total capacity of 1.1 million tonnes were available for bio-treatment (including composting and anaerobic treatment). From the 478,000 t of municipal biowaste collected source separated, about 454,000 t remained for bio-treatment (24,000 t contaminants separated), finally resulting in 159,000 t of compost.

Concerning anaerobic treatment, some 140 sewage sludge digesters, 200 agricultural (partly commercial) AD plants, about 25 industrial waste pre-treatment plants and 4 municipal biowaste treatment plants are in operation (Tab. 1). The respective estimated total digester volumes are 210,000 m^3 (sewage sludge digesters), 152,000 m^3 (agricultural / commercial digesters), 25,000 m^3 (industrial waste pretreatment) and 8,000 m^3 (municipal biowaste digesters). The resulting waste treatment capacity (based on volatile solids) is 307,000 t / year (sewage sludge), 111,000 t / year (agricultural / commercial digesters), 36,500 t / year (industrial waste) and 12,500 t / year (municipal biowaste). Some 156 million m^3 biogas (corresponding to about 1,000 GWh / year) are recovered from these installations. Furthermore 123 million m^3 of landfill gas (corresponding to 737 GWh / year) are collected from some 31 landfills.

It has been estimated that, sewage sludge digesters offer free digester capacities between 15 and 30 %. Theoretically 46,000 – 92,000 tonnes of wastes (dry matter) could undergo co-digestion in existing sewage sludge digesters. As can be seen from practical experience, for several reasons not more than roughly 1/10 of this capacity are actually used.

Tab. 1: Sources of Biogas and estimated annual production in Austria 2005

Source	**Plants**	**Biogas (Mio m^3 per year)**	**Energy (GWh / year)**	**% of total**
Landfills	31 Sanitary landfills	123	737	44.1
Sewage sludge	140 Sludge Digesters	77	460	27.6
Agriculture	200 Biogas- & Co-Fermentation Plants	55	330	19.7
Industrial waste-water / -waste	25 Anaerobic waste-water pretreatm. plants	18	109	6.45
Biowaste	4 Municipal Biowaste Digestion Plants	6	37.5	2.15
TOTAL		**279**	**1,673**	**100**

Biogas from energy crop digestion

The energetic use of biomass for heating is well established in Austria. Roughly 25 % of the overall energy demand is provided from renewable resources (including hydropower). Compared to biomass combustion (ca. 30 % of renewable energy), bio-transformation, i.e. biogas and bio-ethanol, has little (< 1 % of renewable energy), but increasing significance.

Although the net energy balance favours direct combustion processes or synthetic fuels (Synfuel) from dry biomass sources (Tab. 2), bio-transformation can be advantageously applied with high water containing crops, e.g. sugar beets, potatoes or maize. Energy crop digestion can solve the problem of agricultural overproduction, it can make use of fallow land and set aside land and hence provide a new income possibility for farmers. By replacing fossil fuels, the greenhouse gas emissions (CO_2) can be reduced accordingly. The net energy balance of optimised energy crop digestion, i.e. the output / input ratio, can be in the range of 3 - 6. As can be seen from table 2, the recovery of bio-ethanol from crops yields much less net energy. Under European climate agricultural conditions, the output / input ratio with ethanol from maize is not higher than 1.3 and can even range below 1 under unfavourable conditions. Only alcohol from sugarcane provides high output / input ratios of 7, provided that the thermal energy from combustion of the residual bagasse is considered. Even plant oil- and bio-diesel production results in lower output / input ratios than energy crop digestion.

In principle, the AD process is very flexible and numerous crops can be used as single raw materials or as mixtures with manure and other co-substrates. As can be seen from table 3 most crops used for AD show similar biogas yields of 0.4 - 0.5 m^3 / kg organic dry matter (VSS).

The crop yield per hectare varies considerably with the plant, variety, climate conditions etc. and hence has substantial influence on the overall energy yield of crop digestion. Under optimum conditions the overall energy yield can be as high as 100-200 GJ / ha.

Tab. 2: Energy input / output ratio of different transformation processes

Process / Crop	Energy yield (GJ / ha)	Energy input (GJ / ha)	Net energy yield (GJ / ha)	Output/Input ratio
Combustion/Firewood$^{1)}$	252	12	240	21
Synfuel$^{2)}$	86 – 104.5	10.7 – 13	75.3 –91.5	8.04
Ethanol / Sugar beet	140	152	-12	0.92
Ethanol / Wheet	53	72.5	-19.5	0.73
Ethanol / Maize	64	49	15	1.3
Ethanol / Sugar cane	134	18.5	115.5	7.2
Biogas$^{3)}$	138 – 168.5	24.65 – 56.75	111.75 – 113.35	2.97 – 5.6
Plant oil	55.5	16.5	39	3.35
Biodiesel$^{4)}$	54	-1.5 –24.5	29.5 –54	2.21

$^{1)}$ KTBL – Arbeitspapier 235 "Energieversorgung und Landwirtschaft" (1996);. $^{2)}$ Fischer Tropsch synthesis
$^{3)}$ Thermal process energy demand included / excluded; $^{4)}$ Energy content of glycerine included

Most AD plants use maize as energy crop. Compared to other alternative crops e.g. clover, sunflower, sugar beet, rape, rye etc., maize delivers high biomass- and biogas (energy) yields at reasonable low production costs (Tab. 3).

According to the equated electricity feed in tariffs, decreasing between 0.165 - 0.123 € / KWh with increasing plant capacity, a tendency to medium sized plants (i.e. 500 KW electrical power) could be observed. A characteristic mass balance of a 500 KW energy crop AD plant can be seen in figure 5. The 3,850 m^3 digester converts 9,000 m^3 silage and 5,500 t liquid piggery manure to 1,840,000 m^3 biogas (55 % CH_4) per year. The biogas is converted to 3,718 MWh / year electricity and 1,600 MWh / year heat can be sold to the local grid. The digestion residue (8,600 t / year) is recycled to arable farm land.

Due to the resulting favourable economic conditions, the number of energy crop AD plants has more than doubled in the last two years (Tab. 4). It can be expected that numerous new plants will go into service before the final deadline for eco tariffs by June 2006. All plants operating within this deadline will receive guaranteed feed in tariffs for 13 years.

It has been estimated that by 2030 roughly 25 % of the EU overall energy demand could be supplied by energy crops (Anonymous, 2004). Not more than 25 % of the actual agricultural arable land, i.e. 33.8 million hectares, would be required for the cultivation of energy crops. The same estimations show that even by-products from agriculture and forestry could supply roughly 10 % of the EU overall energy demand.

Tab. 3: Biomass-, biogas- and energy yields of different energy crops

(Biogas yields from own results; Salter, 2004; Amon et al, 2003; Reinhold and Noack, 1956)

	Maize	Alfalfa	Rye	Triticale	Sugar beet	Sun-flower	Rape
Fresh mass (t / ha)	30-50		30-40	≈ 30	40-70$^{1)}$ 30-50$^{2)}$	30-50	20-35
Dry mass (t TS / ha)	9-15	10-11	4-5	≈ 6	15$^{1)}$ 7.5$^{2)}$	6-8	2.5-4
Biogas yield$^{3)}$ (m^3 / kg VSS)	0.4-0.5	0.44	0.45	0.45	0.76$^{1)}$ 0.5$^{2)}$	0.45	0.45
Biogas yield$^{3)}$ (m^3 / ha)	4,050 to 6,750	3,960 to 4,360	1,620 to 2,025	2,430	10,260$^{1)}$ 3,375$^{2)}$	2,430 to3,240	1,010 to 1,620
Energy yield (GJ / ha)	87-145	85-94	35-43	52	220$^{1)}$ 72$^{2)}$	52-70	22-35

1) Beet; 2) Leaves; 3) CH_4-content 50-55%

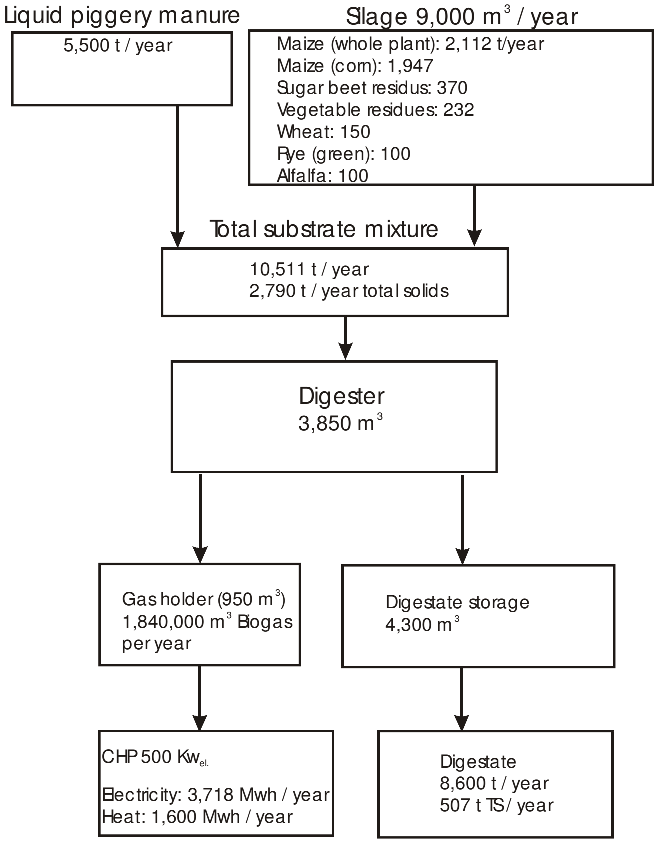

Fig. 5: Mass flow in a representative energy crop AD plant

Tab. 4: Recent development and forecast of agricultural biogas plants in Austria

Year	2001	2002	2003	2004	2005	2006	2007
Number of plants	86	110	119	171	196	>250	**?**
$KW_{el.}$ total	4,100	7,500	8,100	34,100	46,600	>73,600	**?**

Integrated biogas recovery

Biorefinery is considered to be a “Bridge between Agriculture and Chemistry”. Process integration into biorefinery offers in a first step the advantageous possibility of high value product recovery from valuable biomass raw materials. As indicated earlier, anaerobic digestion is well suited for process integration, efficiently using by-products and wastes from various production processes in a second step. As shown in figure 6, biomass raw materials (e.g. grass, corn, sugar beet) and agrobased by-products (e.g. brewery waste, potato sap, whey, glycerol, sugar wastes), can be used for organic acid fermentations. Anaerobic digestion is consequently applied for fermentation by-product- and waste recovery (biogas, fertiliser) in a second step. Single process steps have been successfully demonstrated in laboratory- and pilot scale investigations (Danner et al 1998a, 1998b; Danner et al 2002; Thomasser et al, 2002; Neureiter et al, 2004).

Using membrane bioreactors for lactic acid fermentation with *Lactobacillus sp.* on pure substrates (whey, extracts), as well as mixed culture fermentations (silage) on biomass, the products can be recovered at high yields, using electrodialysis or supercritical fluid extraction (Danner et al 2000; Madzingaidzo et al, 2002). The remaining fermentation residues are fed to the anaerobic digestion process.

Based on grass yields of 50 $t.ha^{-1}$ (21 % TS), a yield of 33 $t.ha^{-1}$ silage (30 % TS) can be obtained (Fig. 6). The fermentation liquid can be converted to 0,44 $t.ha^{-1}$ lactic acid and 103 $GJ.ha^{-1}$ biogas (corresponding to 4.560 m^3). The overall process results in estimated product values of 517 €/ha for lactic acid and 914 €/ha for biogas. Single process steps have been successfully demonstrated in pilot scale (Böchzelt, 2005).

Sanders (2005) recently estimated the mean earnings from biomass with 640 €/ha (as energy electricity, heat), 1,360 €/ha from transport fuel and up to 6,400 €/ha earnings from high value biochemicals. As reported, promising biosynthetic routes from amino acids (1,2-Ethenediamine) and 1,3-propylenglycol (*E. coli*) for bio-based polymers and the huge potential of genetically modified agricultural raw materials as well as GMO`s based bio-processes can be followed.

Biomass based processes should use the advantages of decentralised agricultural production (closed cycles, by-product utilisation, favourable transport logistics). As estimated, 25 % of fossil based chemistry could be replaced through biomass (Sanders, 2005).

As one example, the process integration of lactic acid- and methane fermentation obviously offers promising possibilities for farmers, being faced with overproduction of animals and corn. Biomass- and by-product based lactic acid production for example could be the initial starting route for a decentralised “biorefinery” based on products from agriculture. Decentralised production and implementation of anaerobic digestion guarantees closed cycle operation, simultaneously avoiding high treatment costs for by-products and wastes.

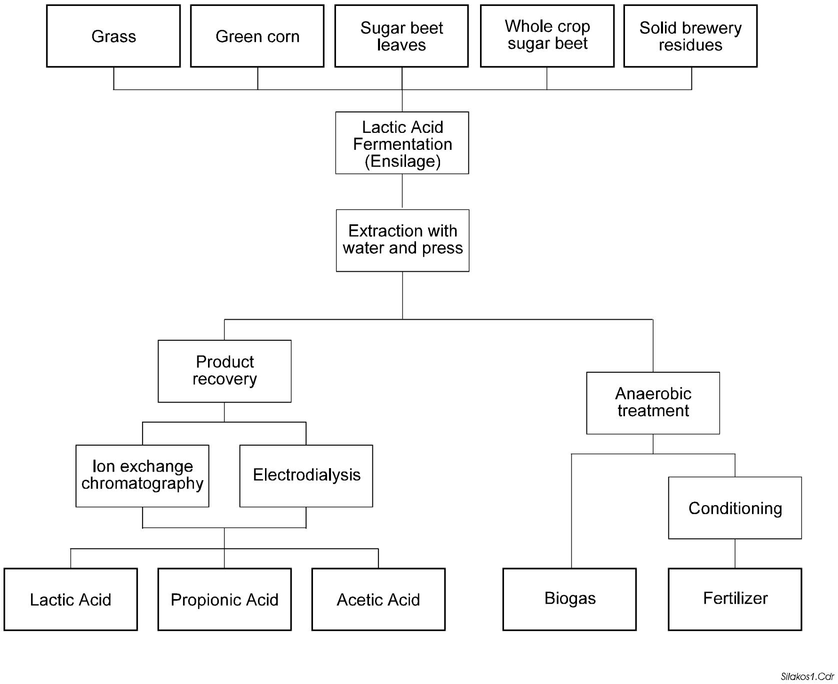

Fig. 6: Process integration with combined organic acid and energy production

Summary

Anaerobic digestion allows multiple advantageous practical applications. As applied for decades, AD can serve as a reliable waste stabilisation process for sewage sludge, organic wastes from industries, municipalities and by-products from agriculture. Compared to other technologies, e.g. combustion, composting, anaerobic digestion in many cases proved to be superior in economic as well as ecological context (Edelmann and Schleiss, 2000; Edelmann et al, 2001)). For this reason waste treatment and –recovery installations of AD are still increasing world-wide.

Recently, more often AD is applied for biogas recovery from renewable biomass (energy crops). A typical plant (3,850 m^3 digester volume) converts 9,000 m^3 of silage and 5,500 t of liquid piggery manure per year to 1,840,000 m^3 of biogas (55 % CH_4). The biogas yields 3,718 MWh / year of electricity and 1,600 MWh / year of heat. It has been estimated, that by 2030 roughly 25 % of the EU overall energy demand could be supplied through energy crops (Anonymous, 2004). Not more than 25 % of the actual agricultural arable land, i.e. 33.8 million hectares, would be required for the cultivation of energy crops.

As proved in several reports, anaerobic digestion can be advantageously integrated into bio-refinery concepts. Provided that the digestate can be recycled as fertiliser to agricultural land, full advantage can be drawn from energy recovery and waste reduction. Concurrently decentralised production offers new possibilities of occupation, income and rural development. Compared to synthetic chemical production processes, ecobalance studies of bio-processes frequently show superior performance. Particularly reduced chemicals-, energy- and water consumption marked out biorefinery processes. As has been estimated, about 25 % of fossil raw material based products can be replaced through biomass based, natural materials.

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Hydrolysis of Biomass for fuel ethanol production

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Summary

Production of fuel ethanol from biomass requires high yields in all conversion steps in order to make it economically feasible. In the last years we have performed several studies on the hydrolysis and fermentation of various forest and agricultural residues in a mini-pilot to improve the overall yield of ethanol and to reduce the energy demand and production cost.

Steam pretreatment, with small addition of acid catalyst, has resulted in sugar yields close to 90% of the theoretical for various types of raw materials, e.g. spruce, salix and corn stover. The simultaneous saccharification and fermentation step, SSF, has been developed and optimized to give high yield of ethanol. For spruce an ethanol yield of about 80% of theoretical based on the composition of the raw material has so far been obtained using a two-stage steam-pretreatment of SO_2 impregnated raw material followed by SSF. Improvements of the SSF step, in the form of high dry matter content, recirculation of process streams and adapted yeast have resulted in ethanol concentrations around 45 g/l leading to substantial reduction in energy demand and production cost.

The process has been further optimised by process integration to further reduce the energy demand. The ethanol production cost was estimated to be around 3.6 SEK/litre ethanol assuming a yearly capacity of 200 000 ton raw material (dry matter).

Introduction

Replacement of gasoline by liquid fuels produced from renewable sources is a high-priority goal in many countries worldwide in order to diminish the green house effect. In order to encourage greater use of biofuels, the EU has adopted a Directive that sets a target of 2% substitution of gasoline and diesel with biofuels in 2005 on an energy basis. In 2010 this percentage should have increased to 5.75%.

One such fuel, which has been found well suited, is ethanol produced from biomass such as agricultural waste and forest residues, which is referred to as bioethanol. Although carbon dioxide is emitted during the combustion of bioethanol the same amount will be assimilated when new biomass is produced. Thus, the total net emissions of carbon dioxide are essentially zero. Bioethanol has also several other advantages;

- It is non-toxic
- it is liquid at room temperature
- can be blended with gasoline and used in most modern spark-ignited combustion engines in concentrations up to 20% without modifications of the engine
- Flexible fuel vehicles can run on pure ethanol, pure gasoline or any blend in between
- It can be produced from sugar, starch and cellulose containing crops and residues

However, to compete with gasoline the production cost must be substantially lowered. The cost of the raw material constitutes one of the major contributions to the total production cost, which makes it necessary to use the cheapest raw materials possible. Lignocellulosic biomass is an abundant and relatively cheap raw material and is the only real option for replacement of a large fraction of the gasoline used today.

Ethanol production from lignocellulose comprises the following main steps: hydrolysis of hemicellulose, hydrolysis of cellulose, fermentation, separation of lignin, recovery and concentration of ethanol and wastewater handling. The enzymatic hydrolysis and fermentation can either be run separately (SHF) or combined into a simultaneous saccharification and fermentation (SSF), which is the configuration shown in Figure 1. SSF has been shown to result in higher ethanol yields than SHF. Some of the most important factors to reduce the cost are: efficient utilisation of the raw material by high ethanol yields, high productivity, high ethanol concentration in the feed to distillation and process integration in order to reduce capital cost and energy demand. A part of the lignin, the remaining part of the biomass, can be burnt to provide heat and electricity for the process and the surplus is sold as a co-product for heat and power application. It is also necessary to minimize the internal energy demand and maximize the production of the solid fuel.

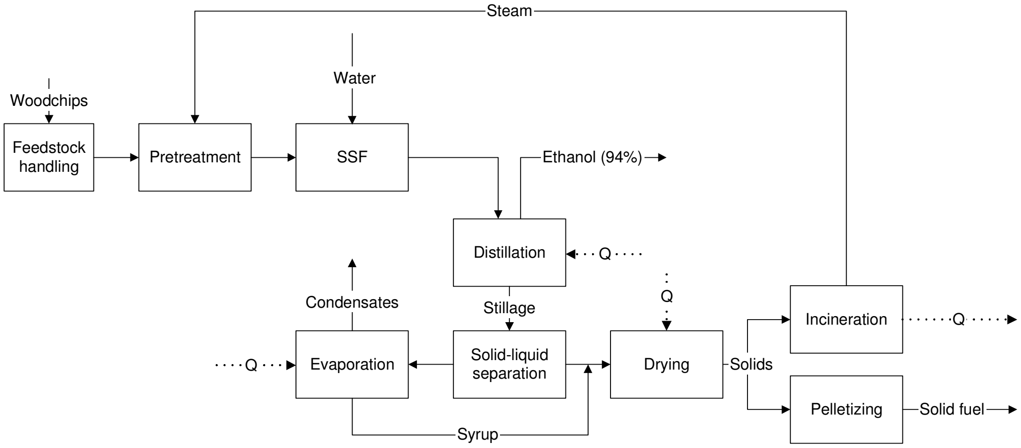

Figure 1 Simplified flowsheet of the base case process.

In Sweden several comprehensive studies have been performed on ethanol production from lignocellulosic materials based on the SSF concept. The studies were performed using a Process Development Unit (PDU) at Lund University comprising all the necessary steps. This presentation will mainly focus on the improvements obtained in the pretreatment and SSF steps in the ethanol production from softwood. The improvements have been assessed by techno-economic evaluation to determine the effect on the ethanol production cost.

Most of the studies were performed on spruce with the composition according to table 1.

Table 1 Range of composition of spruce used in the various studies.

	Range of composition (% of DM)
Glucan	42.3-45.0
Mannan	11.4-15.1
Xylan	5.4-6.6
Galactan	2.0-2.9
Arabinan	1.7-3.2
Lignin	23.5-28.1
Acetyl groups	1.0-1.5
Ash	1.0-2.0
Extractives	2.8-4.7
Water content (%)	50-59

Pretreatment

The enzymatic process is considered to be the most attractive way to degrade cellulose to glucose. However, enzyme-catalysed conversion of cellulose to glucose is very slow unless the biomass has been subjected to pretreatment as native cellulose is well protected by a matrix of hemicellulose and lignin.

Steam pretreatment, often called steam explosion, is one of the most widely used methods for pretreatment of lignocellulosics. The raw material is first chipped and then treated with high-pressure saturated steam. Typical temperatures used are 160-240°C, (corresponding to a pressure of 6-34 bar), for several seconds to a few minutes, after which the pressure is released. During the pretreatment some of the raw material, predominantly hemicellulose, is solubilised and found in the liquid phase as oligomer and monomer sugars. The cellulose, in the solid phase, is then more accessible to enzymatic attack.

Steam pretreatment can be improved by using an acid catalyst, such as H_2SO_4 or SO_2. The acid increases the recovery of hemicellulosic sugars, and also improves the enzymatic hydrolysis of the solid residue. The use of an acid catalyst in steam pretreatment results in an action similar to chemical pretreatment with acid, but with less liquid. It is especially important to use an acid catalyst for softwood, since the hemicellulose in softwood contains less acetylated groups and autohydrolysis cannot occur to the same extent as in hardwood.

Steam pretreatment is the pretreatment method for hydrolysis and enzymatic digestibility improvement that is closest to commercialisation. It has been widely tested on pilot scale, for example, in the Iotech Pilot Plant (Canada), the Souston pilot plant (France) and in the pilot plant in Örnsköldsvik (Sweden) and is used in a Demonstration scale ethanol plant at Iogen (Canada).

Several studies of one step and two-step steam pretreatment of spruce, assessed by enzymatic hydrolysis at standard conditions, showed that the highest sugar yields were achieved for two-step pretreatment with either SO_2 impregnation or H_2SO_4 impregnation in both steps, whereas material treated with H_2SO4 in the first step and SO_2 in the second did not result in a high overall yield. The optimal conditions are shown in Table 2.

Table 2 Optimized pretreatment conditions for softwood in one- and two-stage procedure.

	Impregnator	
	H_2SO_4	**SO_2**
Step1		
Catalyst	0.5%	3%
Temperature (°C)	180	190
Time (min)	10	2
Step 2		
Catalyst	1%	3%
Temperature (°C)	210	210
Time (min)	2	5
One-step pretreatment		
Catalyst		2.5%
Temperature (°C)		215
Time (min)		5

For pretreatment with SO_2 impregnation in both steps the maximum overall sugar yield was 82% and was obtained for pretreatment conditions of 190°C for 2 minutes and 220°C for 5 minutes. Pretreatment conditions of 180°C for 10 minutes with 0.5% H_2SO_4 and 200°C for 2 minutes with 2% H_2SO_4 resulted in an overall sugar yield of 77%. However, several different pretreatment conditions resulted in yields in the same range. The sugar yields obtained with two-step steam pretreatment was higher than those previously achieved with one-step steam pretreatment, using similar conditions in the assay with enzymatic hydrolysis

During the pretreatment the sugars released from the hemicellulose can be subjected to thermal degradation to furans and lignin can be partially hydrolysed. These degradation products can be inhibitory in the downstream processes, mainly fermentation but to some extent also enzymatic hydrolysis. It is therefore important to choose conditions that do not generate toxic hydrolysates. Impregnation with dilute H_2SO_4 followed by pretreatment at high combined severity (that is high temperature and/or high residence time) resulted in materials that were not fermentable. Impregnation with SO_2, however, was successful in creating fermentable materials for all investigated pretreatment severities.

Two other materials for which the pretreatment has been optimised recently are salix and corn stover. For salix the highest glucose yield, based on the theoretical glucan content in the raw material, was 92 %. This was obtained for pretreatment at 200ºC for 8 minutes after impregnation with 0.5 % H_2SO_4. The maximum glucose yield was similar to that obtained when steam pretreatment was performed with non- and SO_2-impregnated *Salix* chips. However, the maximum xylose yield, 86 %, obtained for pretreatment at 190ºC for 4 minutes after impregnation with 0.5 % H_2SO_4, was higher than that obtained using SO_2 or non-impregnated material. The overall yield of sugars was 55.6 g glucose + xylose per 100 g dry raw material, corresponding to about 88 % of the theoretical based on the content in the raw material.

Pretreatment of SO_2 impregnated corn stover, with a dry matter content of 40 %, at 200ºC for 5 minutes resulted in a glucose yield of 92 % of the theoretical and a xylose yield of 66 %. The maximum xylose yield was 84 % obtained with pretreatment at 190ºC for 5 min. At these conditions the glucose yield was 90 %.

Enzymatic hydrolysis and fermentation vs simultaneous saccharification and fermentation. Enzymatic hydrolysis can be designed in different ways. Following the pretreatment, enzymatic hydrolysis and fermentation can be run separately, as separate hydrolysis and fermentation (SHF) or simultaneously, as simultaneous saccharification and fermentation (SSF). The advantage of performing enzymatic hydrolysis and fermentation separately is that both steps can be performed at optimal pH and temperature, e.g. enzymatic hydrolysis at 45-50°C at pH 4.8 and fermentation at 30°C at pH 5.5. However, one great disadvantage of SHF is the end-product inhibition of the enzymes. The released glucose and cellobiose inhibit further hydrolysis by the enzymes. This makes it difficult to reach high ethanol concentrations prior to distillation, which results in high energy demand in the distillation. In SSF the glucose is immediately consumed by the fermenting organism, which removes the end product inhibition and makes it possible to reach high ethanol concentrations. The ethanol produced can also act as an inhibitor in the enzymatic hydrolysis, but not to the same extent as cellobiose or glucose. One more disadvantage of SSF is the problem of recycling the yeast. In SSF the yeast will be mixed with the solid residue after fermentation, mainly consisting of lignin, and is thus difficult to recycle. Recycling of yeast is much easier in the SHF case, where fermentation is performed without the lignin residue

The following results are based on enzymatic hydrolysis, performed with a cellulase activity of 15 FPU/g WIS (using a mixture of Celluclast 1.5L and Novozyme 188, both kindly donated by Novozymes A/S, Bagsværd, Denmark) and fermentation with 5 g/l of Saccharomyces cerevisiae (ordinary baker's yeast), which ferments hexoses to ethanol. In SSF a compromise must be reached regarding the pH and the temperature, which in this work was 37°C and pH 5.0. The yield of sugar and ethanol was determined in a process development unit, where the pretreatment was performed in a 10-L reactor and simultaneous saccharification and fermentation (SSF) or enzymatic hydrolysis (EH) were performed in 30-L reactors. EH and SSF of the whole slurry after the second pretreatment step were performed, at a concentration of 5% water insoluble solids (WIS), to determine the yield of sugars and ethanol. The liquid after the first pretreatment step was also fermented.

Figure 2 shows the overall ethanol and sugar yields, as % of theoretical based on the raw material composition, obtained with SSF and SHF of spruce pretreated at optimal conditions in two-steps. When SSF and EH were performed at the same dry matter content and enzymatic activity, the ethanol yield in SSF exceeded the sugar yield in EH in both pretreatment cases. Thus SSF is a much better process alternative if the yield is of main priority. Comparison of the acid catalyst used showed higher yields for the SO_2-case in both SSF and EH. The overall ethanol yield in the SSF alternative for the SO_2-case reached 81% of the theoretical, i.e. 357 litres per metric ton dry raw material.

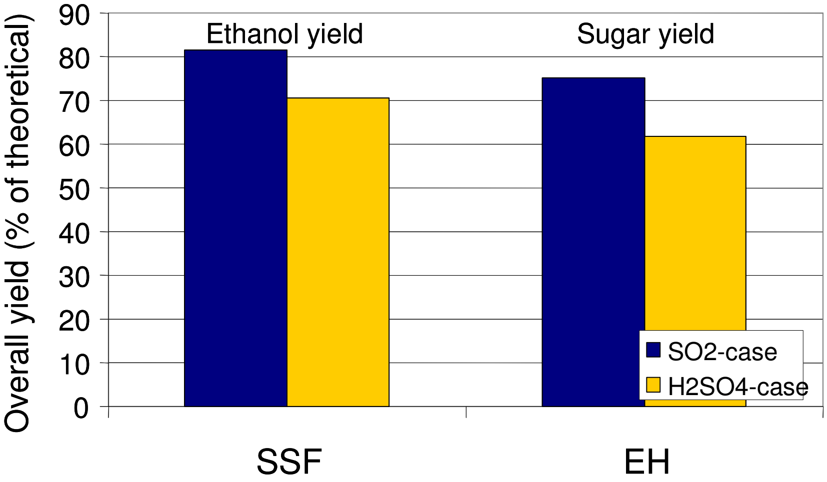

Figure 2 Overall yields obtained with two-step pretreatment of spruce

Also SSF of both salix and corn stover pretreated at optimal conditions using bakers yeast resulted in high ethanol yields. With salix an overall ethanol yield around 84 %, based on the total glucan and mannan content in the raw material was obtained, using 7 % WIS. SSF on pretreated SO_2 impregnated corn stover, with a higher dry matter content, showed that the concentration of water insoluble substances in SSF could be increased from 5 % to 10 % without the ethanol yield being affected. The ethanol yield was around 70 % of the theoretical. It was also shown that the amount of yeast used in the SSF could be decreased from 5 g/L to 2 g/L without any effect at all on the ethanol yield and only minor decrease of the productivity. The use of yeast cultivated on the pretreatment hydrolysate at these conditions did nott improve the ethanol yield and only slightly improved the productivity at the beginning of the SSF.

Economy

All experimental data obtained in the process development unit has been used to perform technical and economic evaluation of various process alternatives. The whole process, from wood to ethanol as well as the production of solid fuel has been evaluated. The approach has been to establish a base case, which has been used as a reference when evaluating alternative process configurations and to study the influence of various process parameters. The base case configurations is for a production unit with a capacity of 200 000 tons of dry raw material (spruce). The simulated process (Figure 1) consists of the following process steps: pretreatment, SSF, distillation, dewatering of solids, evaporation, drying, pellet- and steam production. In the economic evaluation a feedstock handling area and an off-site area are included as well.

The overall ethanol yield for the SSF process was 70% of the theoretical based on the glucan, mannan and galactan in the raw material, based on a one-stage pretreatment. In the SHF process the yield was estimated to be 62%. In the base case both SSF and SHF were performed at 5% WIS.

According to the data used in the evaluation, use of the SSF process results in a lower ethanol production cost, see Table 3. The production costs were estimated to 4.81 and 5.32 SEK/l for the SSF and SHF base cases, respectively. The main reasons for the cost for the SHF process being higher are the capital cost being higher and the overall ethanol yield being lower. If SHF can be improved, (without additional costs) to reach the same ethanol yield as the SSF process, its production cost would be lower than SSF. A significant cost reduction could also be achieved if the residence time in the enzymatic hydrolysis step could be shortened without affecting the ethanol yield. At a residence time of around 30 h, compared to the base case value of 96 h, the production cost is the same as the SSF base case. However, both a higher yield and a shorter residence time would require higher enzyme loadings or a more efficient enzyme cocktail.

Table 3 Effect of improvements in SSF on the production cost

Cost (SEK/L)	SSF-5%	SHF-5%	SSF*-8%
Wood	1.36	1.57	1.36
Enzymes	0.70	0.48	0.70
Yeast	0.50	0.00	0.16
By-products	-0.08	-0.08	-0.62
Other chemicals and utilities	0.35	0.43	0.27
Labour, Maintenance, insurance	0.59	0.84	0.53
Capital	1.39	2.08	1.18
Total	**4.81**	**5.32**	**3.58**

* Improvements including 8% non-soluble solid material, recirculation of process stream after distillation (26%) and reduction of yeast load to 2 g/l

The income from the solid fuel is crucial to the economics of both the SSF and the SHF process. Since the base cases investigated require large amount of energy, the production of solid fuel they provide is low. Experiments have shown that it is possible to reduce the addition of fresh water either by running the process at a higher concentration of non-soluble solid material (WIS) or by recycling of the process streams both alternatives with a considerable reduction in the cost of ethanol. Figure 3 shows the effect of increased WIS up to 8%. Recent SSF-runs have actually been performed with up to 12% WIS. This results in ethanol concentrations around 4.5 wt-%, which reduces the energy demand in the distillation and evaporation steps considerably leading to a larger amount of lignin co-product for sale.

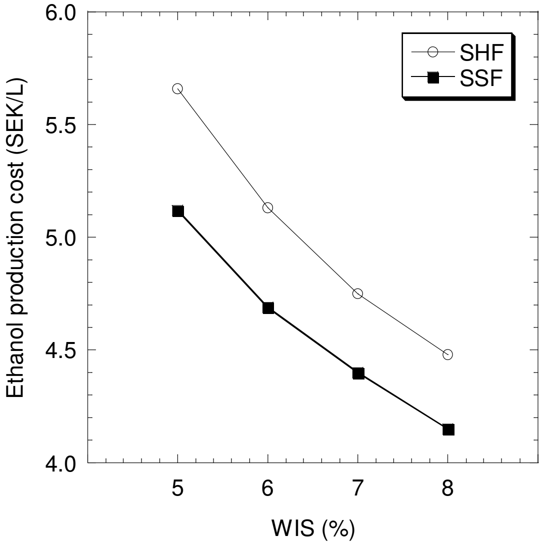

Figure 3 Influence of WIS in SHF and SSF on the ethanol production cost

A major drawback of the SSF process is the addition of yeast required. The residue slurry leaving the SSF step contains, along with the yeast, other solids such as lignin and cellulose. Recirculation is thus very difficult to perform, although if it could be performed it would reduce the production cost significantly. Another option is, of course, to lower the concentration of yeast. This can be done by using adapted yeast to overcome possible inhibition from the sugar and lignin degradation products present in the hydrolysate. This is especially important at high WIS concentration as the concentration of inhibitors is increased proportionally to the increase in WIS. The performance of adapted yeast is shown in Figure 4, where yeast cultivated on the hydrolysate from the pretreatment shows a much better performance than normal baker yeast. The maximum ethanol concentration is reached already after 24 hours and is higher than that obtained with normal bakers yeast after 72 hours.

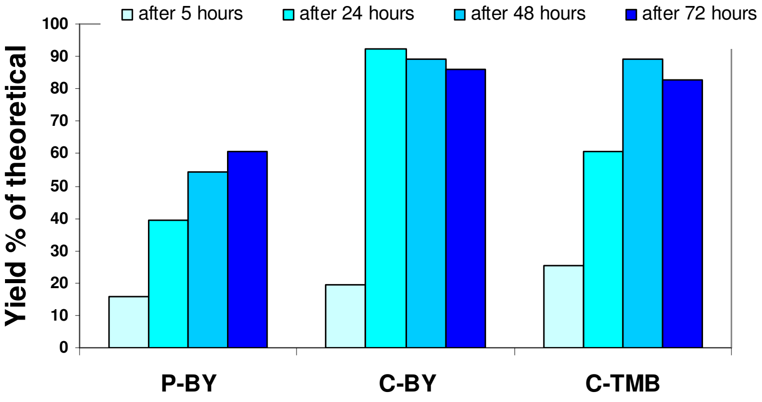

Figure 4 Ethanol yield in SSF with 8% WIS (pretreated softwood) using various yeasts
P-BY = normal package yeast (bakers yeast)
C-BY bakers yeast cultivated on hydrolysate from pretreatment
C-TMB TMB3000 cultivated on hydrolysis

The cumulative effect of the most promising alternatives was evaluated for the SSF process. The effect of a combination of higher concentration of non-soluble solid material, the recycling of process streams and lower concentration of yeast was investigated. A realistic case would be a process involving at least 8% non-soluble solid material and 26% recycling of the stillage stream, which together with a 50% reduction in the yeast requirement would result in an ethanol production cost of 3.58 SEK/l, see Table 3. This is a decrease with 26% compared with the SSF base case.

Conclusions

Steam pretreatment, with small addition of SO_2 or H_2SO_4, has been shown to be a very effective pretreatment method, prior to enzymatic hydrolysis or SSF. It has resulted in overall sugar yields around 90% of theoretical for several raw materials, e.g. spruce, salix and corn stover. For spruce, an overall ethanol yield around 80% of the theoretical has been achieved. Steam pretreatment results also in high solids content, which makes it possible to reach high ethanol concentrations in the SSF. Future challenges are to run at even higher WIS concentrations in SSF with lower dosages of enzymes and yeast.

The results have to be verified in the Swedish fully integrated pilot plant, with a capacity of 2 ton raw material per day, which has been taken into operation in the middle of Sweden by Etek – Ethanol Technology Corp. This will provide detailed data for scale up to a full scale production unit.

Integrated biomass utilisation system

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Abstract

Modern waste-fired and biomass-fired power plants have low electrical efficiency compared to power plants using fossil fuels. The low electrical efficiency is mainly due to the increased corrosion risk caused by alkali chlorides. Hydrothermal pre-treatment of the primary ligno-cellulosic biomass can reduce this problem.

The leachate from the hydrothermal extraction process has a high content of alkali chlorides and organic compounds, which can be used for ethanol production using a thermophilic bacillus strain. The remaining fibre fraction can be hydrolysed enzymatically and fermented by yeast to ethanol. The ethanol will be suitable for utilisation in the transportation sector in a cost effective and environmentally sound way. The lignin containing presscake can be dried and co-fired with coal in power plants with advanced steam data without corrosion risks.

Elsam is the project coordinator in a large EU project (contract no. ENK6-CT-2002-00650) with the aim of demonstrating this new technology in a bench-scale plant and a pilot plant with a capacity of 1 t/h. The project also comprises a detailed design and feasibility study of a full-scale plant with a total capacity of 450,000 t/y of biomass. The total project budget is approx 13.6 million Euro of which the European Commission funds 6.5 million Euro. The project partners are: the British tmo Biotec, and the four Danish companies Sicco, RVAU, Risø, and Elsam.

The production of liquid fuels - methanol, and as mentioned here - ethanol, is the basis of Elsam's VEnzin vision from 2004). With the VEnzin vision, Elsam's line of products, viz electricity and district heating, now also includes liquid fuels based on renewables.

In the past two and a half years, Elsam has been the project coordinator of a large EU-project with the aim of demonstrating a new technology for producing fuel ethanol from agricultural residues and household waste. In the course of the project, a pre-treatment reactor with a capacity of 100 kg/h of straw has been designed, built and operated for some 250 hours, and a pilot plant with the capacity of 1 t/h has been designed and built. Valuable design and operational experience from the 100 kg/h facility have been incorporated in the design of the pilot plant. In 2002, when the project

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was initiated, the primary task was to extract alkali metals and C5 sugars (hemicellulose) from straw. The reduced alkali content in the straw improves the combustion properties, making co-combustion more feasible, and the C5 sugars were intended for fermentation with special micro organisms producing ethanol. A number of technological advances have changed the overall process, incorporating ethanol production from the cellulose fraction as well. With these achievements, ethanol yields of approximately 200 kg per ton of straw can be achieved.

100 kg/h pilot plant

In 2003, the first pilot plant with 100 kg/h capacity was constructed and brought into operation.

More than 250 hours of operation with the small pilot plant have given Elsam a lot of valuable operation and design experience, and through varying the operational parameters in cooperation with the scientists from RISØ and RVAU, a much better picture of the processes has been achieved. A large number of samples of both the solid fraction and the liquid fraction has been analysed by the researchers for sugar yield, fermentability and potential ethanol yield.

On the mechanical side, Elsam has gained valuable experience with the design of the equipment, and this knowledge has been put into the design of the 1000 kg/h plant. Some of the most important findings are:

- The design of the valves in the particle pumps is critical for the operation of the plant

- The (standard) valves installed in the 100 kg/h unit can be kept in operation in shorter periods at a time (app 1 day), but will not be suitable for continuous operation.

- Different types of valves are needed for the different positions in the process.

- Several new valves have been designed for the 1000 kg/h plant.

- The first reactor was constructed for pressure up to 40 bar, but a process optimum is achieved at a lower pressure.

- The original system for internal recirculation of water/hydrolysate has been modified for the 1000 kg/h reactor.

- With a good recirculation in the system, trials have shown that it is possible to wash out more than 60% of the hemicellulose in the straw.

- A very good pretreatment process has been achieved with the potential of high yields of ethanol.

Trials with household waste

Lightly sorted household waste has been tested in the pilot plant under cold conditions, in order to investigate the mechanical function of the equipment with household waste. The preliminary test showed that the chosen fractions could be transported through the pressurised reactor. No samples were taken out for analysis.

The first ethanol

Preliminary trials with enzymatic hydrolysis and fermentation (including SSF) have already produced the first amounts of ethanol, both at Risø and at Fynsværket.

1000 kg/h pre-treatment plant

In the autumn of 2004 the first equipment was delivered to the site for the 1000 kg/h pilot plant, and in April 2005, the last component was installed. The 1000 kg/h pilot plant includes the following components:

Weighing table for registration of the straw input.
Feeding table with a capacity of 6 bales.
De-baler
Stone trap
Straw cutter
3-stage reactor comprising a soaking reactor (will be operated at 80°C), a new reactor designed for operation at 25 bar/200°C and the reactor from the 100 kg/h pilot plant, which has been modified in order to increase the capacity to 1000 kg/h.

In May and June 2005, the installation will be completed with electrical installations, piping, steam supply etc, and the plant will be put into operation. The first experimental data is expected in August/September 2005.

Fermentation unit

In order to optimise and develop the fermentation process in an industrial scale, a fermentation facility is installed in connection with the pre-treatment facility. The facility includes fermentors of various sizes (5 l, 50 l, 100 l). The combination of fermentors can be used for batch-, fed batch- and cascade fermentation and C6 fermentation followed by C5 fermentation. The facility also includes mobile feeding tanks, control system, and a 500 l reactor for hydrolysis. The 500 l reactor will be specially designed for liquefaction and enzymatic hydrolysis of the fibre fraction and can also be used for fermentation. Finally, equipment for continuous ethanol recovery will be added.

The primary objective of the hydrolysis and fermentation facility is to demonstrate the complete process from straw to ethanol in an industrial scale. For example, the hydrolysis process cannot be fully demonstrated for straw in laboratory scale due to the physical properties of straw. In this facility, it will be possible to investigate hydrolysis of straw (and other pretreated biomass) in a realistic scale.

It will also be possible to asses the suitability of all combinations of pretreated biomass, extracted liquid and different types of micro organisms (yeast, thermophile organisms, fungi) for the IBUS process.

The size of the fermentation units allows for production of ample amounts of biofuel (residual cellulose and lignin) for large-scale (co)-firing trials.

Feasibility study

From the beginning of the project, a detailed feasibility study with a complete model of mass and energy flows has been elaborated. In the course of the project, the feasibility study has provided the design team with valuable information about optimisation of the process and equipment in order to improve the overall feasibility of the concept.

Based on the experimental data, the mass balances have shown, that 200 kg of ethanol can be produced from 1000 kg straw, under the condition that micro organisms, which can produce ethanol from C5 sugar are available.

Detailed energy balances of the process have demonstrated that approximately 55% of the total energy content in the straw remains in the fibre fraction and will be converted to energy (heat and electricity) in the power plant. This in turn will provide enough energy for the complete pre-treatment, hydrolysis, fermentation, distillation and drying of ethanol – in fact, a surplus of electricity produced from co-firing the fibre fraction in the power plant can be exported to the grid. Of the total energy content in the straw, 34% will be converted to ethanol, and 17% will be sold as electricity from the power plant.

Integrated Biomass Utilisation

An essential part of the system is the integration with other facilities:

- Ethanol production from conventional sources (grain, corn etc).

- Power plant supplying low value steam for the IBUS process and converting the lignin fraction to useful energy (heat and electricity).

Plans for an ethanol production facility based on grain and situated at one of Elsam's power plants are being made, and detailed feasibility studies have been carried out demonstrating a considerable economic benefit in integrating ethanol production with the power plant. The plant will convert 320,000 t/y of grain to 100,000 t/y of ethanol.

Included in the planning of the grain to ethanol plant are all necessary preparations for adding a straw based ethanol production facility to the grain based facility. The plant will convert 150,000 t/y of straw to 30,000 t/y of ethanol.

The overall aim is to demonstrate the IBUS system in full scale.

Information and Communication Technology

In order to promote implementation of the technology, an Information and Communication Technology (ICT) system is being developed. The ICT system consists of three parts:

A public website with general information about the project. The website has been established and is updated on a regular basis. The website is located at http://www.ibusystem.info.

A website for potential end-users of the technology. It will be possible for potential users to give input data concerning local conditions (prices for biomass, steam, power, site conditions etc) and receive output from the system concerning the feasibility of establishing an ethanol plant under the given conditions. Modified versions of the models from the feasibility study will form the basis of the ICT system, and a user interface designed by Elsam will be used for exchanging data with potential end-users via the website.

A project web with exclusive access for the project participants has been established, and more than 200 documents have been uploaded to the website.

In addition to the ICT system, the results from the project have been published in a number of scientific papers from Risø, RVAU, Sicco and Elsam. Furthermore, a significant number of students from various educational institutions have made projects in connection with the pilot plant.

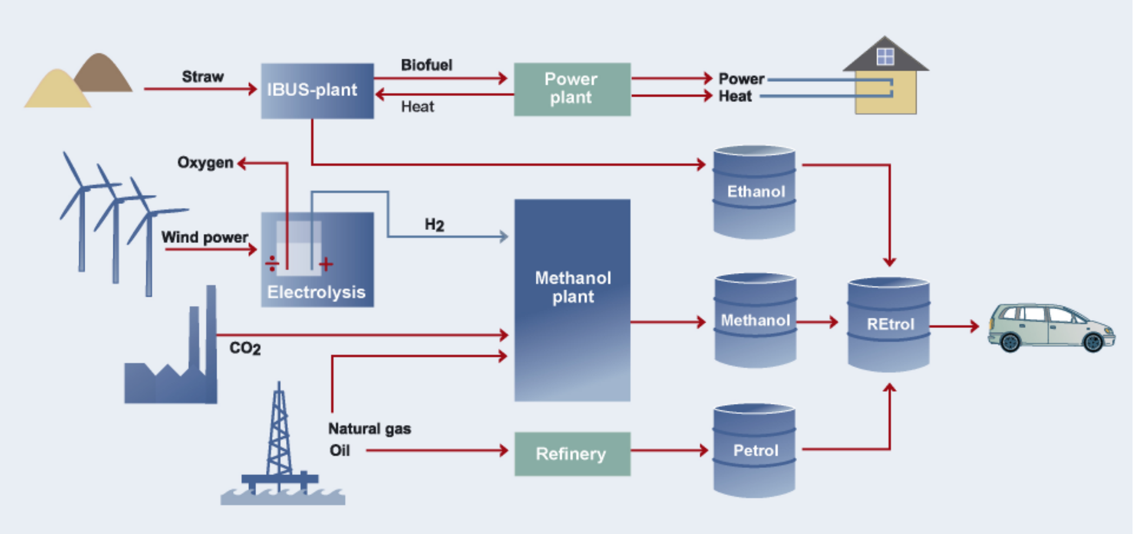
Future work

The following work is planned for the remaining 12 months of the project:

- optimisation of the pre-treatment process for straw
- trials with other raw materials (bagasse, corn stover, palm oil residues)
- development of a system for receiving and handling whole-grain bales
- long term continuous operation of the 1000 kg/h plant (30 days)
- optimisation of the hydrolysation and fermentation process
- development of equipment for handling (drying) the lignin fraction, and determination of the combustion properties
- improving the quality of input to the feasibility study based on trial results
- completion of the ICT system.

From Petrol to REtrol

The IBUS project is a part of Elsam's overall vision for the Danish energy sector. The vision is named VEnzin and aims to combine the existing supply system for electricity and heat (power plants, wind turbines, waste-to-energy plants) with production of liquid fuels (ethanol and methanol), which can be blended with gasoline, and utilise the existing distribution system and existing vehicle technology. Ethanol and methanol will be produced from renewable sources, ethanol from straw and other biomass, and methanol from hydrogen produced with electrolysis driven by surplus wind turbine power. The new fuel, which is a blend of gasoline, ethanol and methanol is called REtrol, and the share of fuel in the blend, which has been produced from renewable energy can be increased when the economic situation allows it (as the conversion technologies are improved, the gasoline price goes up, or the politicians request it). Learn more about the VEnzin vision at http://www.elsam.com.



Bio-ethanol production in the region of Southern Denmark – SFL, Tønder bio-ethanol project

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Introduction

The production of bio fuels is increasing rapidly all over the world. In the US, bio-ethanol has been used for many years based on corn and bio-ethanol has been produced on sugar canes in Mexico and Brazil.

Today, no plants in Denmark produce bio-ethanol, but there is one existing, ongoing plant producing bio-diesel (RME, rapeseed methyl ester) at Emmelev Mølle on Funen, Denmark.

Basically, the production costs of bio-ethanol and bio-diesel are higher than those of equivalent products based on oil. Thus, there is a need for reducing the fuel taxes in order to render an industrial production of these products feasible and attractive to the industry.

At present, there is no such tax reduction in Denmark but an EU directive has been presented, urging the national governments all over Europe to take appropriate measures in order to bring bio-ethanol and bio-diesel on the market aiming at a share of 5-6% of the fuel supply by 2010.

Today the Danish government has taken measures to investigate the potential of reducing the tax on bio-fuels and we expect that there will be some incentives in the year to come.

Basic principles of bio-ethanol production

The basic principles of producing bio-ethanol are to utilise the starch content in crops by means of enzymes which convert the starch into sugar. Afterwards, a simple fermentation of the sugar produces a slurry with an ethanol content of about 10-12%. After the fermentation, the liquid is distilled and the ethanol is purified. The remaining part, mainly containing proteins, is sold as a feedstuff directly to the farmers following a simple de-watering, or it is dried to a more stable foodstuff which can be stored for extended periods.

The raw material for bio-ethanol production can be various kinds of cereals, sugar beets, sugar cane or even whey, which is a surplus product in the cheese production. The content of starch in the raw material is quite essential and the content of dry matter to be pumped into the digesters limits the amount of alcohol to be produced in each batch. As the subsequent distillation is rather costly it is necessary to maximize the content of ethanol in the fermentation.

Alternative raw materials

During the past 10-15 years, extensive research has been carried out in order to utilize other types of raw material such as straw, wood chips, paper and organic household waste. It is however difficult to open the straw and take out the starch, but processes using wet oxidation or thermal cracking have been investigated.

Small pilot plants have been set up, but the technology has not yet reached an appropriate result which enables the industry to utilise the process at an industrial scale with financial results comparable to the traditional methods.

Feasibility study of bio-ethanol production in Denmark

In 2004, the farmer's association Sønderjysk Landboforening in Southern Jutland and COWI carried out a feasibility study regarding full-scale industrial production of bio-ethanol to be located in the southern part of Jutland. The production capacity of this plant is estimated to 150,000 m^3 per year, mainly based on wheat or other cereals. The by-products will be foodstuffs, very rich in protein, in the magnitude of 140,000 tons per year.

The main characteristics of the process and its equipment, together with the final results of the financial calculations are listed in the slides following this introduction.

Future potentials

As mentioned above, there is an ongoing research towards the possibilities of utilizing straw and other raw materials for the bio-ethanol production. Enzyme researchers have obtained a lot of improvements but it is still necessary to utilize oxygen or thermal cracking to liberate the starch.

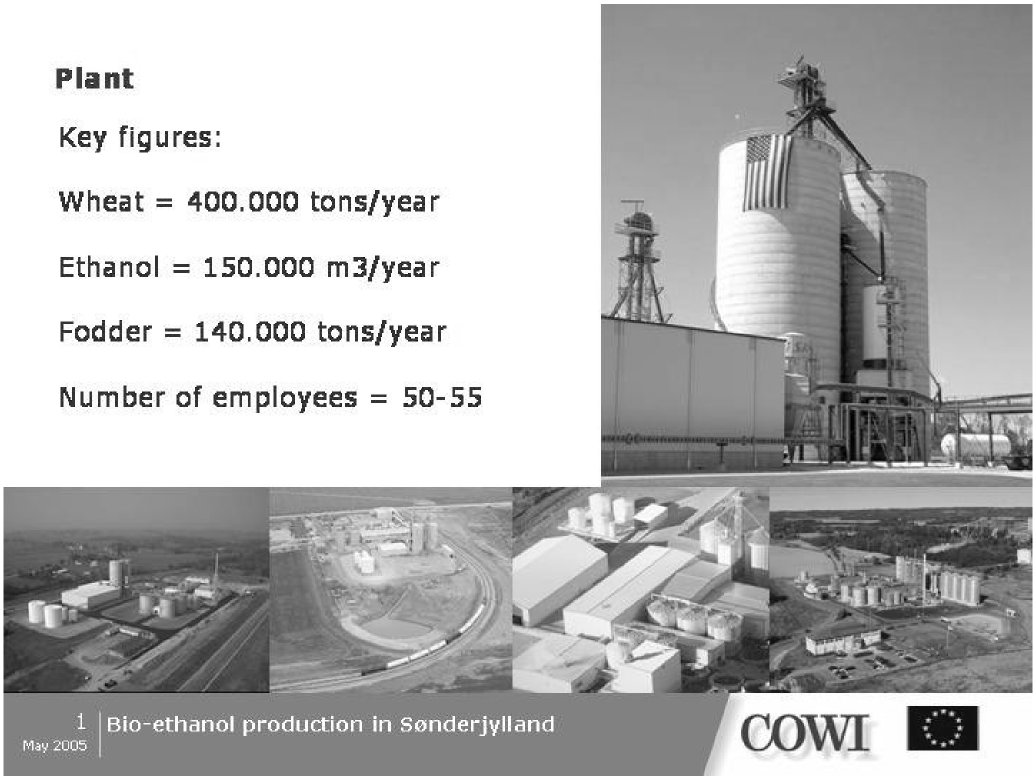
Researchers have also looked at the potential for making a combined process, utilizing bio gas and simultaneous fermentation in order to optimize the overall energy consumption. In some countries deep-shaft processing has been investigated, enabling the process to take place at a very high pressure. During our study, we have looked at the possibility of extracting the protein as the first part of the process and thereby create a simpler second stage, but the capital costs of this process is higher than the traditional process. The efficiency of taking out the protein from the wheat upfront is that the foodstuff will be at a higher cost per ton and it might even be possible to utilize the gluten for human consumption. More research has to be done before the final decision on the concept for this first plant to be established in Denmark.

As mentioned above, the power consumption, especially the steam consumption, of a bio-ethanol plant is very high and measures should be taken in order to minimize the overall energy consumption, for example by means of combined heat and power production with sale of excess heat to a district heating network, for example.

Realisation of the plant

At present we are in dialogue with potential investors for the realisation of the plant in Sønderjylland. We expect that this work will continue over the summer period 2005, awaiting initiatives to be taken by the Government in respect of reducing the fuel tax in the nearest future. It will however be possible to realise a plant in Tønder with export of bio-ethanol to the German market, which is increasing and even demanding more supply. In parallel, we are awaiting the WTO negotiations regarding the future situation for import tax towards agricultural import from the third world. Depending on these negotiations, a production in Europe can be stimulated (if the import tax is maintained) or the consumption of these products can be stopped, considering the much lower production prices in for example Brazil and Mexico.

Below slides present the final results of the financial calculations from the feasibility study of bio-ethanol production in Denmark.



Plant

Key figures:

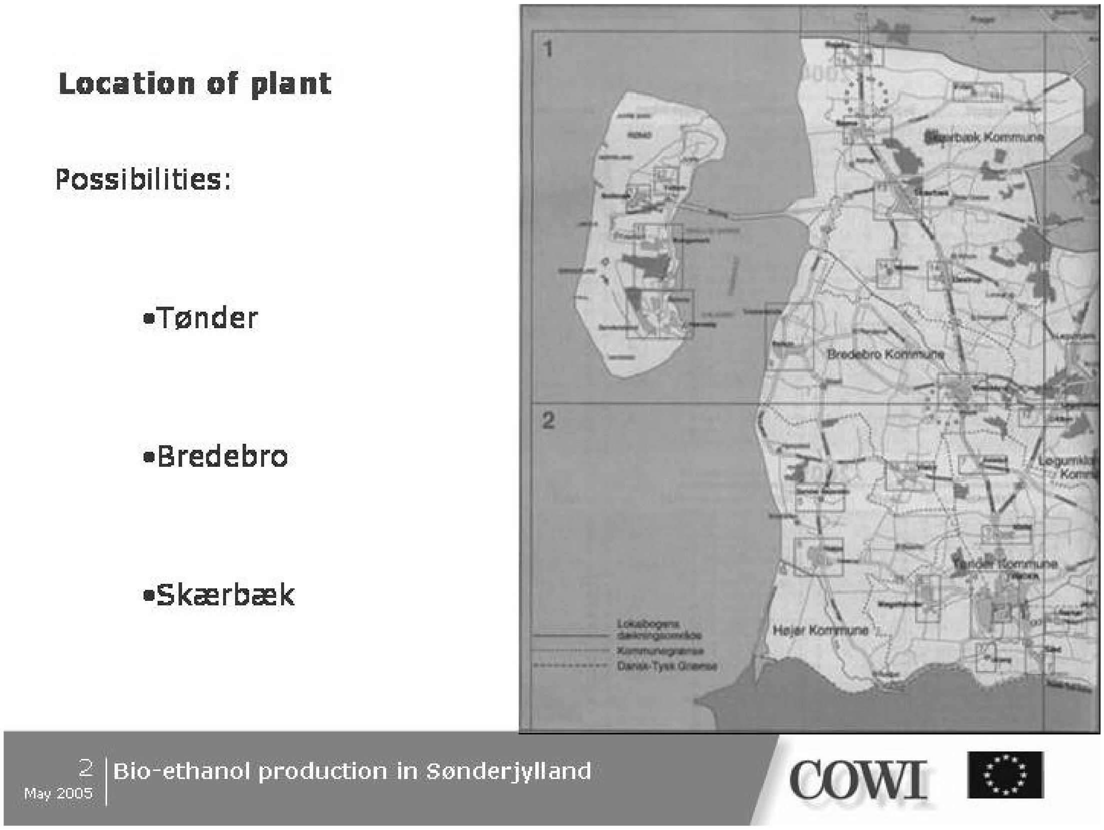
Wheat = 400.000 tons/year

Ethanol = 150.000 m3/year

Fodder = 140.000 tons/year

Number of employees = 50-55

1 May 2005 | Bio-ethanol production in Sønderjylland

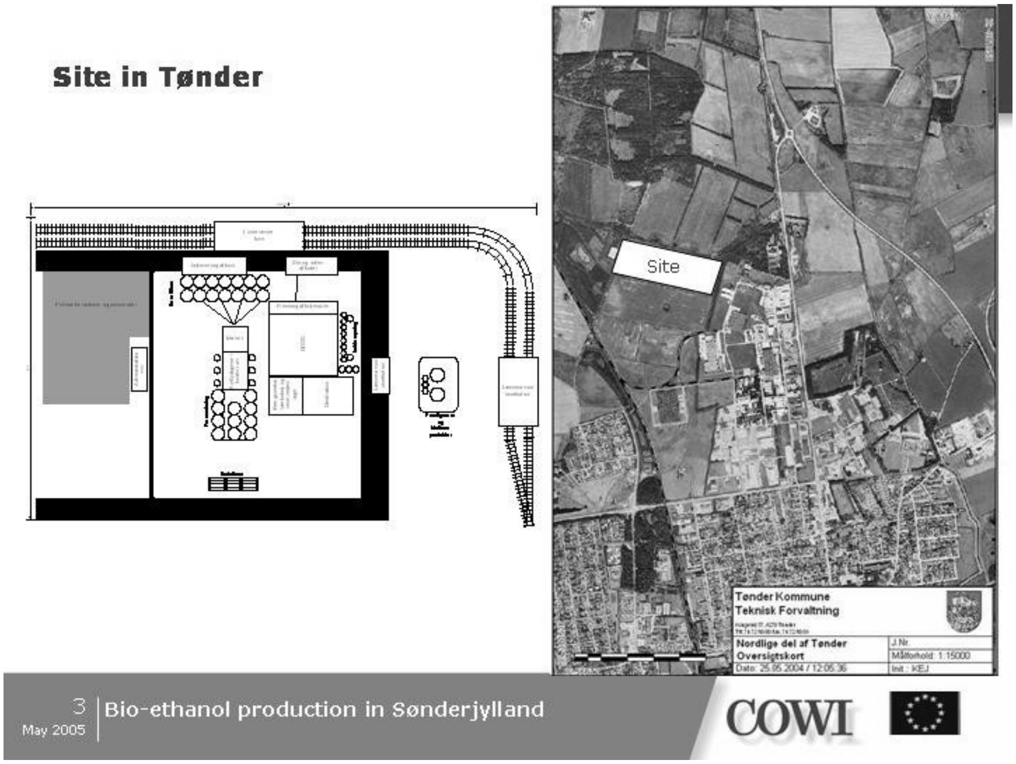


Location of plant

Possibilities:

- Tønder
- Bredebro
- Skærbæk

2 May 2005 | Bio-ethanol production in Sønderjylland

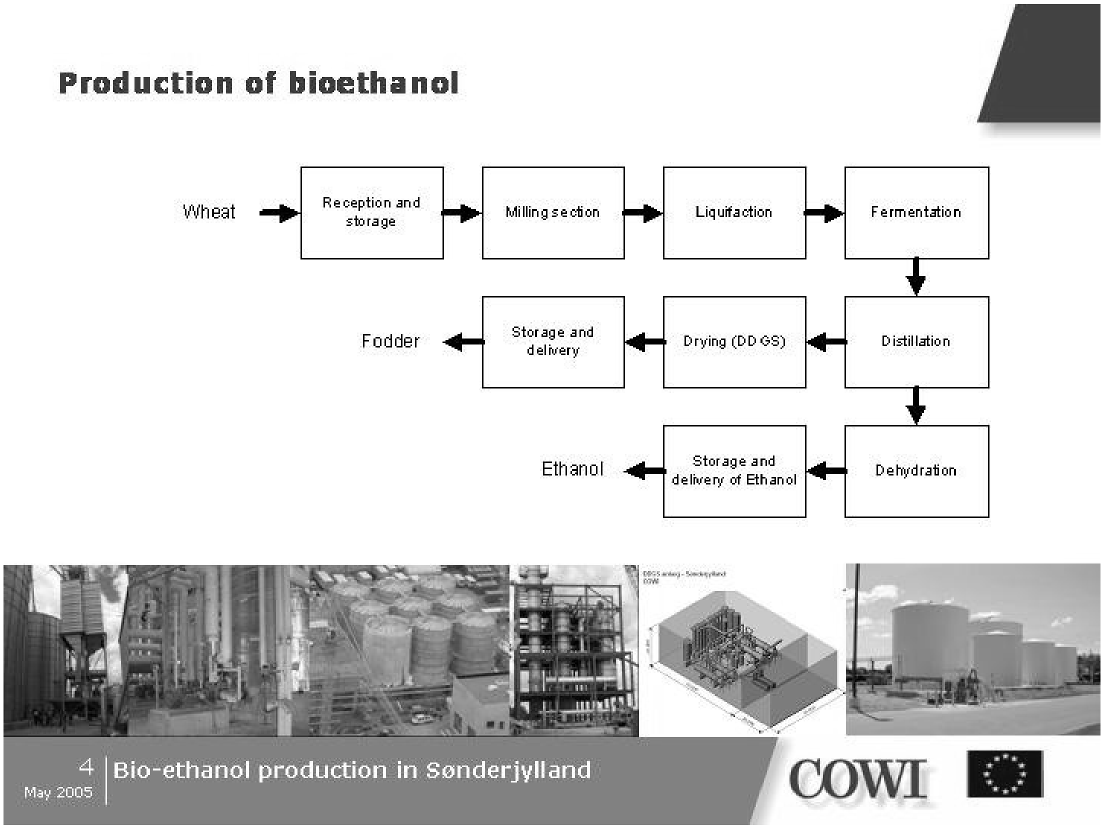


Site in Tønder

3
May 2005

Bio-ethanol production in Sønderjylland

COWI



Production of bioethanol

Wheat → Reception and storage → Milling section → Liquifaction → Fermentation → Distillation

Distillation → Drying (DDGS) → Storage and delivery → Fodder

Distillation → Dehydration → Storage and delivery of Ethanol → Ethanol

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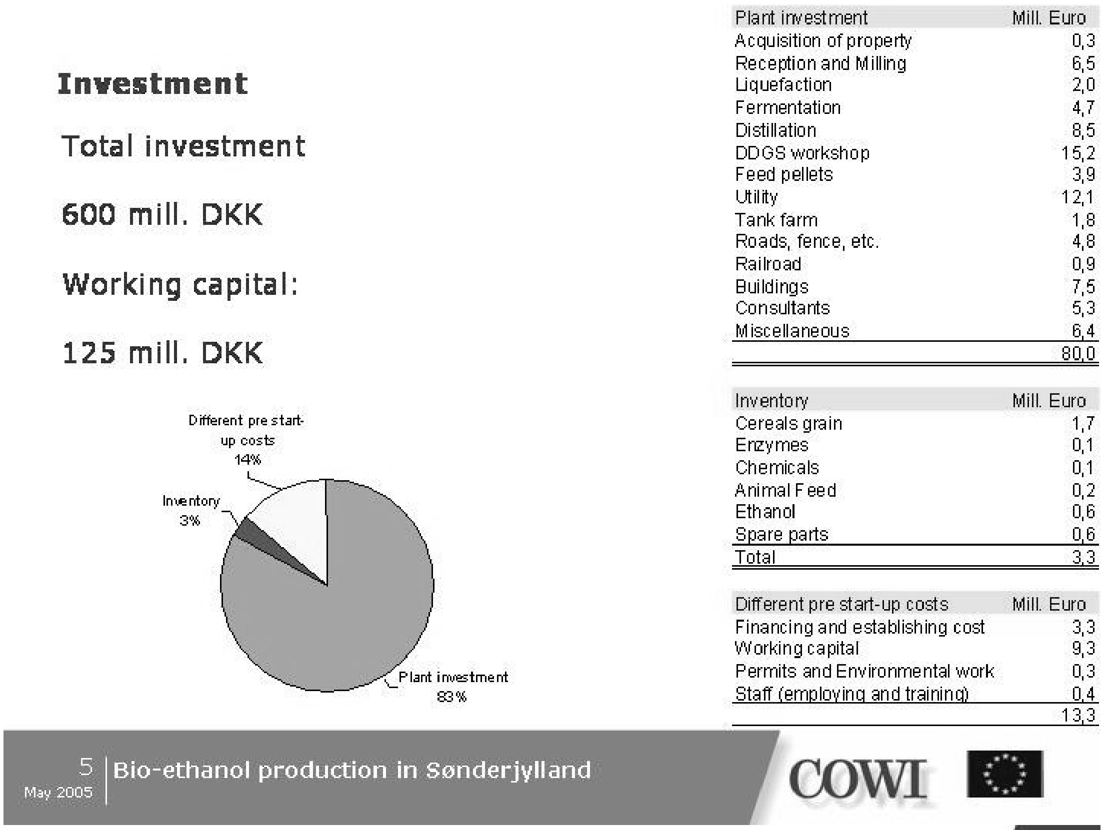
May 2005

Bio-ethanol production in Sønderjylland

COWI



Investment

Total investment

600 mill. DKK

Working capital:

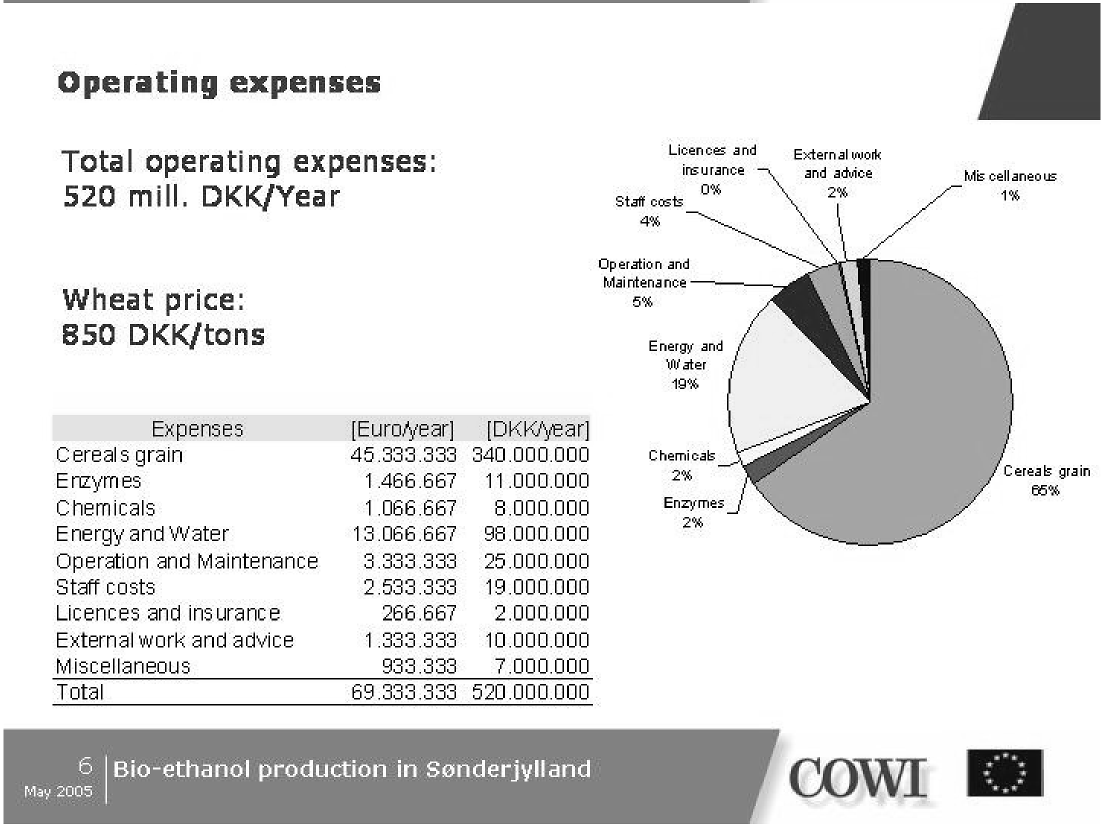
125 mill. DKK

Plant investment	Mill. Euro
Acquisition of property	0,3
Reception and Milling	6,5
Liquefaction	2,0
Fermentation	4,7
Distillation	8,5
DDGS workshop	15,2
Feed pellets	3,9
Utility	12,1
Tank farm	1,8
Roads, fence, etc.	4,8
Railroad	0,9
Buildings	7,5
Consultants	5,3
Miscellaneous	6,4
	80,0

Inventory	Mill. Euro
Cereals grain	1,7
Enzymes	0,1
Chemicals	0,1
Animal Feed	0,2
Ethanol	0,6
Spare parts	0,6
Total	3,3

Different pre start-up costs	Mill. Euro
Financing and establishing cost	3,3
Working capital	9,3
Permits and Environmental work	0,3
Staff (employing and training)	0,4
	13,3

5 May 2005 | Bio-ethanol production in Sønderjylland



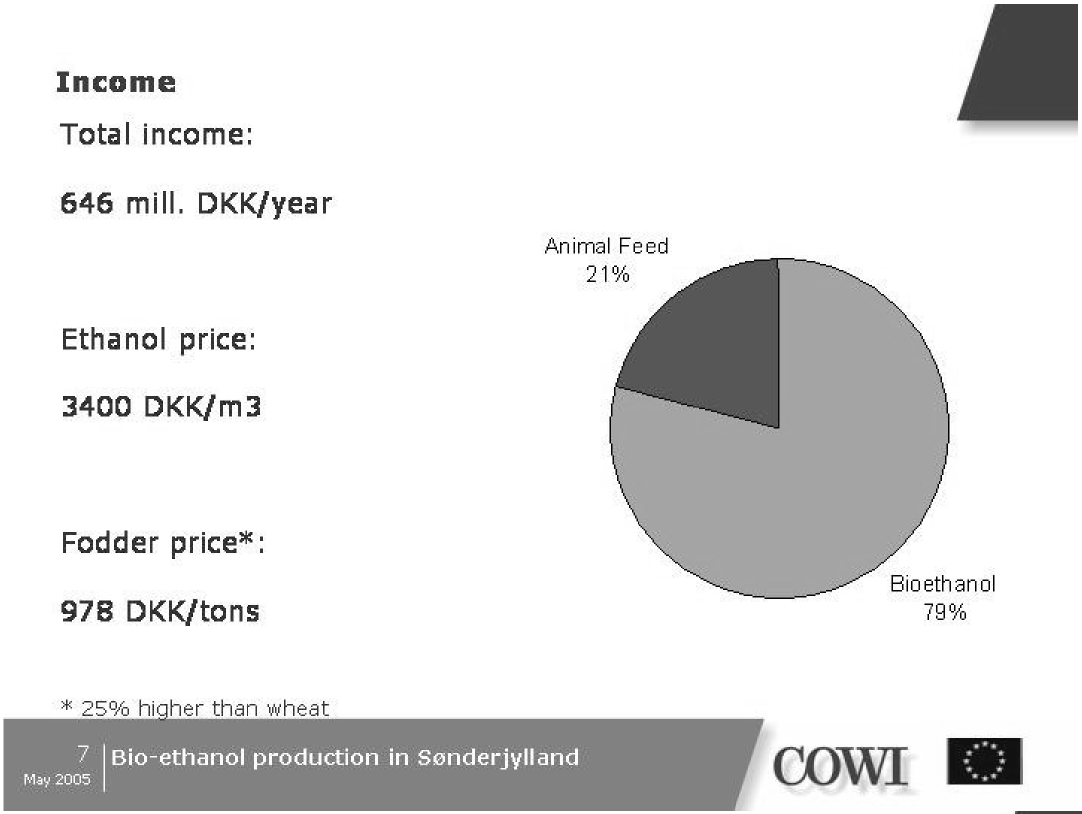
Operating expenses

Total operating expenses:
520 mill. DKK/Year

Wheat price:
850 DKK/tons

Expenses	[Euro/year]	[DKK/year]
Cereals grain	45.333.333	340.000.000
Enzymes	1.466.667	11.000.000
Chemicals	1.066.667	8.000.000
Energy and Water	13.066.667	98.000.000
Operation and Maintenance	3.333.333	25.000.000
Staff costs	2.533.333	19.000.000
Licences and insurance	266.667	2.000.000
External work and advice	1.333.333	10.000.000
Miscellaneous	933.333	7.000.000
Total	69.333.333	520.000.000

6 May 2005 | Bio-ethanol production in Sønderjylland



Income

Total income:

646 mill. DKK/year

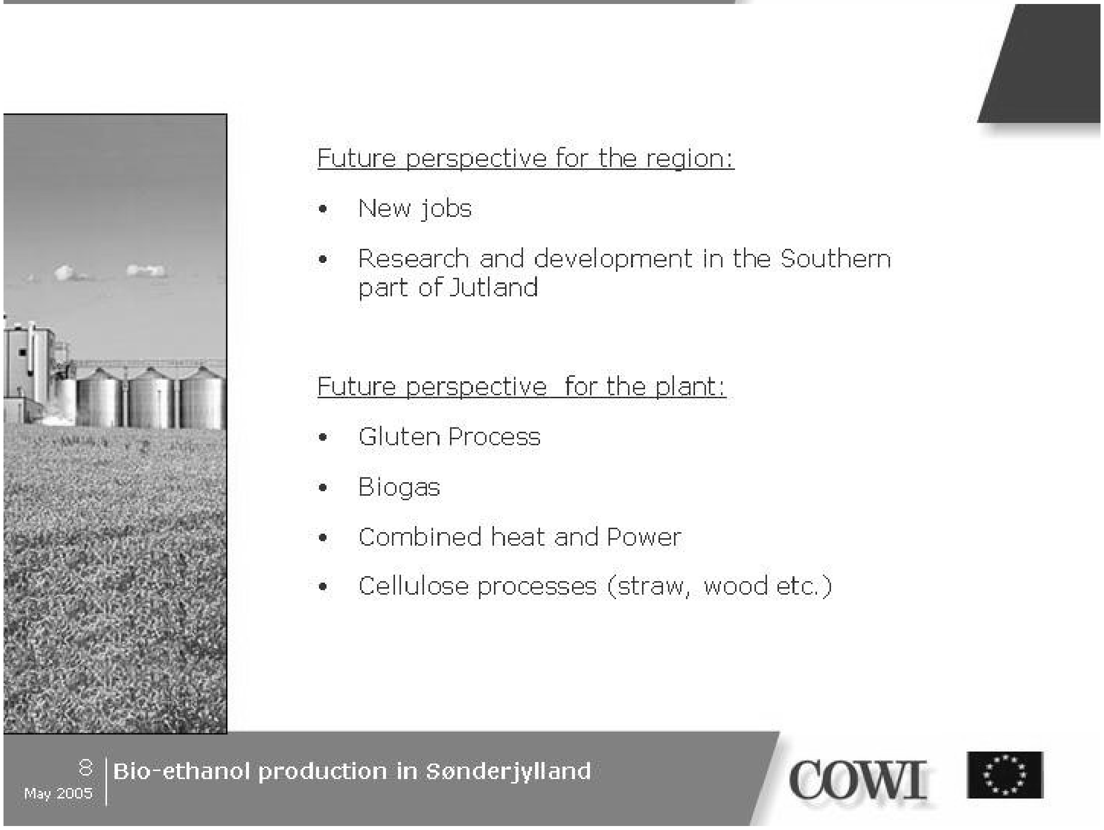
Ethanol price:

3400 DKK/m3

Fodder price*:

978 DKK/tons

* 25% higher than wheat



Future perspective for the region:

- New jobs
- Research and development in the Southern part of Jutland

Future perspective for the plant:

- Gluten Process
- Biogas
- Combined heat and Power
- Cellulose processes (straw, wood etc.)

Biogas

- **Biogas (Thin stillage)**
- **Biogas (Whole stillage)**
- **Potential:**

50-80 mio. Nm^3/year

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May 2005
Bio-ethanol production in Sønderjylland
COWI

Realisation and construction

Step 1)	Ownership – a group of investors or company takes over the project.
Step 2)	Additional analyses: -Process design -Plant design -Location -Sales agreements
Step 3)	Financial construction of company
Step 4)	Official approval
Step 5)	Design, tender and construction

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Bio-ethanol production in Sønderjylland
COWI

Sampling in Practice: a TOS Toolbox of Unit Operations

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Abstract

A basic knowledge of the Theory of Sampling (TOS) and a small set of sampling unit operations is all the practical sampler needs to ensure *representativeness* of samples extracted from all kinds of lots, including biotechnical systems: production batches, barrels, sub-division in the laboratory, sampling in nature and in the field (environmental sampling, forestry, geology, biology), from raw materials or manufactory processes etc. We here give a brief introduction to the Fundamental Sampling Principle (FSP) and eight Sampling Unit Operations (SUO). Respecting FSP and invoking only the necessary SUO's (problem-dependent in the specific practical situation) is the only prerequisite needed for eliminating all sampling bias and simultaneously minimizing sampling variance. No reliable analytical results can be produced unless the entire sampling_and_analysis process corresponds with TOS.

Introduction

Scientists, engineers and process operators spend a significant amount of time, money and efforts on optimizing and validating process and product analytical procedures and methods, purportedly to ensure optimal quality of the analytical results. But what if it is stated that very nearly always other errors arise that are in the order of 10, 100 or even 1000 times larger than the analytical error? It is in fact fully documented over more than 50 years that all primary, secondary and tertiary sampling of heterogeneous materials indeed produces errors of this magnitude [Gy, Pitard]. The Theory of Sampling (TOS) is more than 50 years old but is still little known and/or heeded in both industry and academe.

Although alarming the situation is not at all hopeless; there are many ways of getting such sampling errors in control. But nothing is for free – the dominating sampling errors cannot be reduced and/or eliminated without doing the necessary work, indeed knowing what constitutes the work needed is half the game. There are no possibilities for correcting or making up for flawed sampling, but this is unfortunately not well known: "bias-corrections" or "sampling robustness" and similarly unfortunately cannot remedy erroneous sampling. Representative sampling is eminently doable however, only it does not come about by itself. A minimum of TOS knowledge is necessary.

Proper sampling takes place on many scales, from primary sampling in the field/process to the smallest sub-samplings with a spatula from sample vials in the laboratory of the order of only micrograms, because all materials are inherently heterogeneous. Sampling of heterogeneous materials will always result in sampling errors (sampling variances), because any two samples extracted as close to each other as physically possible will necessarily still make for different analytical results, precisely because one cannot sample the same volume twice, and because there will always exist a local, residual heterogeneity at the scale of the sampling tool volume.

It is simultaneously equally important to realise that *all* sampling procedures and stages by themselves will generate their own unavoidable errors.

In this contribution we present a number of simple tools (conceptual as well as practical) for optimal sampling in practise. After intensive studies of the Theory of Sampling (TOS), developed by the French scientist Pierre Gy, we have formulated the salient aspects of TOS in a small number of simple "Sampling Unit Operations" (SUO) that cover all aspects of practical sampling, ranging from simple procedures such as mixing to more complex heterogeneity characterizations and variographic experiments. Of these unit operations some are intuitive and easy to perform while others are more labour intensive and perhaps not obvious to untutored minds. We here present only the necessary minimum of theoretical understanding of the principles of TOS, without which the system of SUO would degenerate to rote learning.

This presentation first gives a short introduction to material heterogeneity, an introduction to the Fundamental Sampling Principle (FSP), and a description of the seven basic Sampling Unit Operations (SUO).Additionally we must also refer to the extensive general literature on sampling [Gy, Pitard, Minkkinen, Smith, Esbensen & Minkkinen].

Heterogeneity

The basis for understanding all practical sampling starts with the material to be sampled; in particular we need to be able to describe the phenomenon of heterogeneity. Any material is heterogeneous at *some* level with regard to *some* of its parameters. Even a so-called 100% pure particulate chemical substance to be used in high-cost laboratory experiments is not homogeneous: If we keep on magnifying the scale of an "observation module", we will at some point observe differences in particle size, shape and composition.

But the question for practical sampling rather is whether the material is "sufficiently homogenized" at all scales from the original lot down to scale of the sampling tool volume (which we use for the actual sampling from the lot). In order to address this issue competently we need to understand the following minimum of the concepts of heterogeneity.

A material must be described by two different kinds of heterogeneity: Constitutional Heterogeneity (CH) and Distributional Heterogeneity (DH). Constitutional heterogeneity, CH, describes the differences in composition, shape, density etc. between the smallest individual and separable constituents of the lot: the *fragments*. Thus CH is concerned with the heterogeneity *between* these fundamental units at the smallest scale level of interest. Distributional heterogeneity, DH, then further describes the part of the overall heterogeneity stemming from spatial distributions at a higher scale level, i.e. the scale representing the set of so-called *observation modules*, which in practise corresponds to a sample volume. Thus DH deals with the intermediate to full lot scale heterogeneity aspects stemming from the spatial distribution of the entire set of *virtual samples* together making up the entire lot. It is in fact equal to the heterogeneity contributions *between* these sample-size units of observation at the intermediate scale.

The generic term for a potential sample volume to be selected is an "increment".

CH can be affected (reduced) only by processes that alter the physical composition or appearance of the individual particles (crushing, comminution etc.), whereas DH can be affected (reduced) by mixing, blending and other, similar means of homogenization.

Further, in-depth heterogeneity theory can be found in the extensive primary sampling literature [Gy, Pitard, Smith, Esbensen & Minkkinen].

The fundamental sampling principle (FSP)

The master governing rule for all sampling is the Fundamental Sampling Principle (FSP), which can be stated:

***Any* virtual increment of the lot *must* have a non-zero**
and *equal* probability of being materialised in the final sample

Respecting the fundamental sampling principle (FSP) ensures *probabilistic sampling*. Any deviation from FSP leads to "incorrect sampling" which will result in an unavoidable sampling bias. Imagine a stockpile of material to be sampled, characterised by a significant grain-size distribution. A normal procedure would be grapping a few increments here and there from the surface (the readily available parts of the lot) or at the most within a reasonably accessible depth. This is clearly non-probabilistic sampling and since there are very many parts of the lot (all the interior parts as well as the bottom of the pile) which in this scenario with certainly has a zero probability of being sampled, there is no way the sample can be representative of the whole lot.

Sampling unit operations

In order to perform correct sampling in practice, always respecting the principles of TOS, we only have to know about seven *basic* sampling unit operations (SUO) pertaining to normal sampling of 0-D lots and one in addition, specifically related to the special case of sampling 1-D lots (definition of lot dimensionality given below). All these unit operations will be explained in detail below.

1. Structurally correct sampling is the *only* safeguard against sampling bias
2. Mandatory heterogeneity characterization of all 0-D lots
3. Homogenization, mixing, blending
4. Composite sampling
5. Representative mass reduction
6. Particle size reduction (comminution or crushing)
7. Lot dimensionality transformation (3D or 2D → 1-D or 0-D)
8. Variographic characterisation (1-D lot heterogeneity characterization)

Armed with these tools anybody can perform correct sampling, all it takes is a little practical work, which will be repaid generously from the significantly more reliable analytical results.

Structurally correct sampling

If handed a particular sample, there is no way of telling whether it is *representative* or not from any type pf inspection or characterisation of the sample itself – not even by the most refined and expensive analytical techniques in the world, neither by any kind of statistical analysis.

Representativeness can only be ensured by performing structurally correct sampling, i.e. representative samples result from a representative sampling process. The focus should consequently always be on the sampling *process*. It is outside the scope of the present paper to deal completely with all the principles of structurally correct sampling, but a brief introduction will suffice.

There is a fundamental difference between accurate and precise sampling. Precise sampling means that a number of replicated samples will display a low standard deviation, or variance, between them. Accurate sampling means that the replicated samples, regardless of their precision, on average will allow an estimate (the mean) that is closely coincident with the true mean (grade/concentration) of the lot. In other words an accurate sampling process does not posses a significant systematic sampling bias! Performing “structurally correct” sampling then means that all sources of bias have been eliminated from the sampling process. What are these sources of bias? According to the extensive analysis of heterogeneity and sampling in TOS, there exist only three sources:

1. Increment Delineation Error (IDE)
2. Increment Extraction Error (IEE)
3. Increment Preparation Error (IPE)

These errors are jointly named Incorrect Sampling Errors (ISE), as they all result from incorrect sampling. A highly appealing fact about ISE is that they can ultimately be eliminated completely by careful considerations and efforts during the design, maintenance and use of the sampling procedures and equipment; this often involves a significant amount of work though.

Ad 1) To be structurally correct, a sample must be correctly delineated, meaning that it must cover an entire dimension of the sampled material with parallel sides so that no part of a cross section is represented in higher or lower proportions than any other. This is best illustrated graphically (fig 1), which should be viewed as a *generic* illustration covering both conveyor belts, pipe-lines etc:

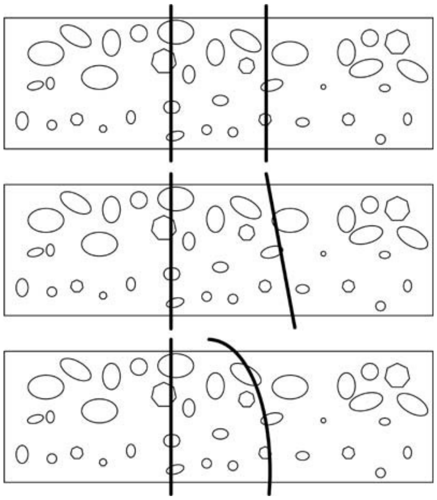

Figure 1. Examples of correct (top) and incorrect increment delineation (middle and bottom). A correctly delineated increment must have fixed parallel sides to ensure equal representation of the whole width of the lot.

In the figure one should imagine that the lot is actually moving on a conveyor belt or in a pipe-line and consequently that only a small portion of the (horizontal) total lot is shown – please notice the stratified distribution of large and small particles emphasizing the need of parallel sides.

Ad 2) Subsequent to correct delineation it is important that this material is actually the only material extracted. If the geometric delineation “cuts” some particles, they must either enter the sample or be rejected according to the so-called centre of gravity rule. This rule simply states that any particle having its centre of gravity inside the increment should in fact end up in the final sample and vice versa. Even appearing as a triviality this indeed has great importance in the physical design of cutting devices, valves and other sampling devices [Gy, Pitard]. This is particularly important if the cutting device is physically *moving* across the process stream. This matter gains in importance in direct proportion to the actual particle size distribution of the material, and forms a distinct non-trivial challenge concerning bio-slurries and similar materials.

Ad 3) The Increment Preparation Error is the only error that is non-statistical in its nature. It consist of a number of potential errors that all occur *after* extraction of the increment or sample. Some examples are:

- Loss/gain of water/moisture due to evaporation/condensation
- Unintentional loss of sample material related to materials handling etc.
- Loss of fines, or addition of fines, due to dust
- Contamination from storage devices, equipment-induced cross-contamination

These errors must be avoided by careful supervision, thorough education of employees and by showing the greatest responsibility towards the sampling procedure. Common for all these errors are that they are the *only* sources of systematic sampling bias, and therefore *must* be eliminated (or at the very least thoroughly minimized).

Sampling is nearly always a multistage process consisting of primary-, secondary-, and perhaps tertiary sampling stages. It is important that errors at all levels are eliminated. What are the relative error levels at the different stages?

Heterogeneity characterization

In order to describe quantitatively the constitution of the material to be sampled, we can quantify the heterogeneity in a given lot either empirically (experimentally), or by a model of the typical behaviour of heterogeneous materials (via simplifying real-world estimation of a few salient physical mixture characteristics).

It is always recommended, before design of any sampling procedure, that sufficient efforts are spent on an initial heterogeneity characterization of the material to be sampled. In terms of time and money this is always considered to be expensive, but the alternative, which is uncontrolled biased samples and unnecessarily large erroneous analytical results, is always much worse - not only from a scientific point of view but especially also from the economics surrounding the decisions which are to be taken based on flawed information!

An empirical heterogeneity characterisation is always carried out by a multi-stage replication experiment, designed to yield an estimate of the variation at the relevant different scale-levels of interest. An absolute minimum would be two replicates at all levels (fig. 2), which can only be supported under the strong assumption that all sampling errors at all levels are normally distributed – a questionable assumption by itself oftentimes; however up to some 10 replications is highly recommended. It really does not pay to save the expenditures at this stage of sampling. From experiences with practical application of TOS, we have reached the conclusion that what is needed is far from a prohibitive large number of total replicates – always less than 42 (and many times even less is sufficient). This number of replicates, N^{replic}, needed in order to reach completely reliable estimates of the relative magnitudes for all sampling stages must be distributed over all the relevant (problem-dependent) sampling + analysis stages, for example PSE: 12; SSE: 12; TSE 12; TAE: 6 replicates. Contrast with figure 2.

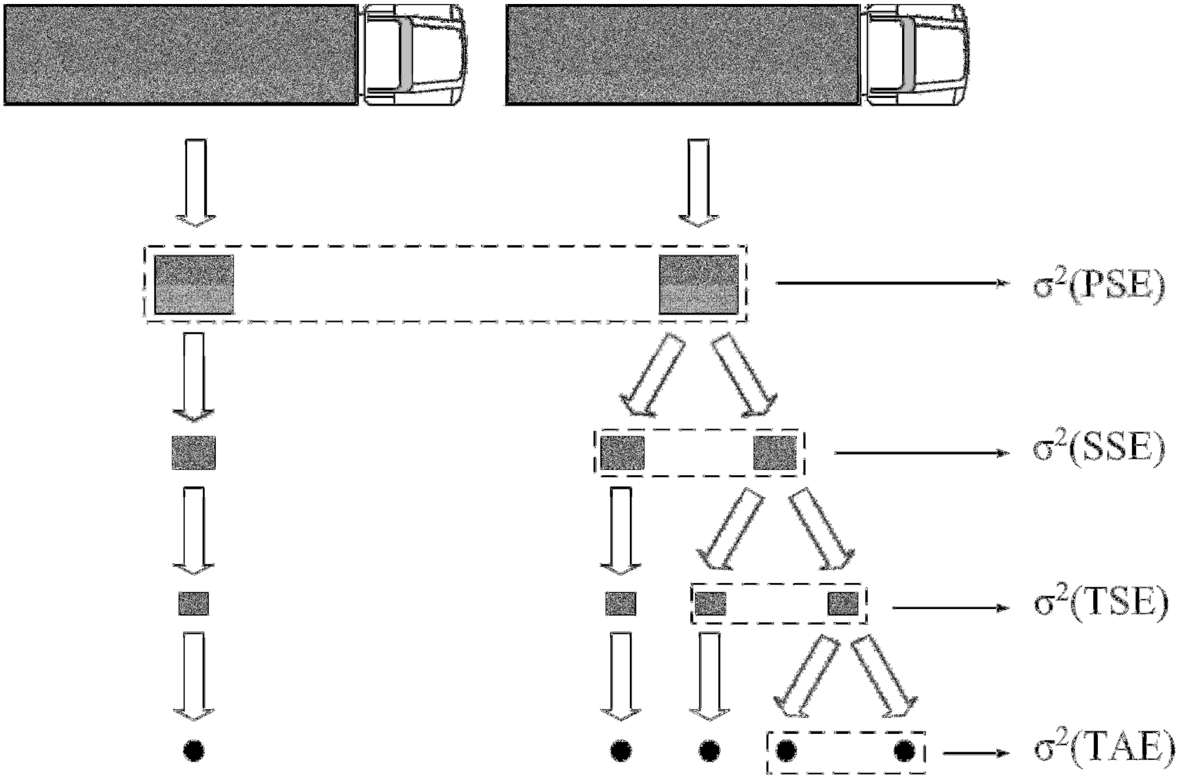

Figure 2. The absolute minimum layout of an experimental design yielding an estimate of the effective errors at different sampling stage levels. Two replications is the ultimate minimum number under strong normality assumptions; however many more replicates, up to 10-12, must in general be recommended. Black dots represent analysis. PSE (Primary Sampling Error); SSE (Secondary Sampling Error); TSE (Tertiary Sampling Error); TAE (Total Analytical Error).

The summation of all errors is termed the Global Estimation Error (GEE) and this is estimated directly as the variance of the uppermost level (replicated primary samplings).

By carefully performing the multi-stage replication experiment as laid out in figure 2, either following the maximum or the minimum layout, one can successively subtract the lower error estimates from the higher, in a bottom-up procedure. The errors can be tested statistically by an F-test if needed, telling whether a particular level of variance is significantly different from the preceding levels or from zero. It will be appreciated how this empirical scheme yields the absolutely most reliable sampling error estimates, because *all* the empirical sampling -, sample preparation - as well as all the analytical procedures are involved. They all contribute to the aggregate errors precisely because of the bottom-up configuration of "ordinary", only replicated samplings delineated. Since there are only empirical errors involved, and since their reliability will be in direct proportion to (square root of) the number of replicates decided upon, this empirical heterogeneity characterisation procedure is greatly popular by all practical samplers: it is easy to understand and is extremely simple to implement.

Another way of getting information on the lot heterogeneity would be using the "Gy's formula", which derives from the theoretical apparatus of TOS. This simplified formula is designed to give a reliable estimate of the order of magnitude of the *factor of invariant heterogeneity* (which is a material's characteristic irrespective of the total mass present), also called the Heterogeneity Invariant (IH_L), or the variation of the Fundamental Sampling Error (FSE), the error dependent on the material itself that can never be eliminated. Application of this formula requires knowledge of the essential physical properties of the material to be sampled, which is sometimes easy at hand, while at other times not so easily available. A simplified expression of "Gy's formula" reads:

$$\sigma^2(\mathrm{FSE}) = \frac{C \cdot d^3}{M_S}$$

where:

C is the sampling constant (actually consisting of four sub-constants, App. 1)
d is the top particle size (upper 95 % average grain size diameter)
M_S is the sample mass

This central formula is rich with information on how to do practical sampling. Once you know three of the four factors involved one can of course very easily calculate the remaining one (more on this in section 4.6 below).

Homogenization, mixing and blending

In order to minimize contributions to the sampling error by segregation and grouping, we should *always* homogenize the material to be sampled prior to increment extractions. The only allowable exception to this rule is the primary sampling, where this is not always possible for purely practical reasons – but then *composite sampling* comes to the fore with the greatest emphasis, see further below. Sampling effects by segregation and grouping of the lot material is described by TOS as contributing to the Grouping and Segregation Error (GSE). GSE, along with the fundamental sampling error (FSE), make up the "Correct Sampling Errors" (CSE) which can never be fully eliminated, only minimized, by following the guidelines prescribed by TOS. GSE has two contributing parts, as the name suggest, one related to segregation and the other to "grouping". This latter term may not be obvious to the reader, but it simply means contributions to the error stemming from the fact that neighbouring particles often bear *some* compositional resemblance to a higher degree than what concerns particles farther away (spatial auto-correlation). Thus simultaneous extraction of more than one particle (a necessary effect of using a sampling tool usually with a volume pertaining to many particles) means more of rather similar particles in the increment. After all has been done with regard to homogenisation, this contribution from grouping can only be further minimized by reducing the size of the extracted increments. In fact it will be totally eliminated if fragments are extracted one at a time, independently, but this is of course very often (completely) impossible in practice.

Heterogeneity contributions from segregation (most often vertical segregation, due to the effect of gravity) can be effectively minimized by homogenization.

Composite sampling

This sampling unit operation is very closely related to mixing (or homogenization), since it also works on minimizing the contribution to the overall error from GSE. As indicated by the delineations in the above section, it will be appreciated how combined extraction (composite sampling) of many small(er) increments, which are subsequently combined to add up to form the final sample, instead of e.g. extracting just one large increment with the same total mass, M_S, will minimize the contribution from grouping and segregation. This is always the case, and one can also intuitively understand the value of extracting material from many areas/sub-volumes in the lot instead of just one. It is recommended to perform composite sampling whenever at all possible. It is particularly noteworthy that even if this will result in "too-large" primary sample masses, this is no real excuse for not complying with this SUO, as any "over-mass" can if fact always be easily reduced to appropriate size, using the very powerful subsequent SUO: representative mass reduction.

Representative mass reduction

When sub-sampling any sample (i.e. reduce the mass of primary, secondary etc. samples), it is of great importance that this procedure is carried out in strict accord with TOS principles; this is in fact the guarantee that SUO No.s 3 & 4 can be effective.

In 2002, a large experimental survey of 17 current devices and methods for reduction of sample mass was carried out (2 kg of a tri-component mixture was reduced to 100 or 125 g respectively). A summary of the central results are shown in figure 3 below, where it is clearly observed that the correct choice of device has tremendous effect on the reliability of the final sample mass. The ordinate axis in figure 3 describes this "representativeness" of the method/device - the smaller the numeric values of this attribute, the better the method. Representativeness is in TOS defined so as to contain measures of both accuracy and precision; it is thus a powerful measure to evaluate and compare such methods. The entire mass reduction reliability survey, together with all pertinent TOS interpretations etc. can be found in [Petersen et al.].

In the figure are summed representativiness contributions from three, very different *types* of constituent elements, representing three different concentration levels: 89.9 %, 10.0 % and 0.1 % by weight, so as to produce information on the mass reduction variations of both abundant elements (90% and 10 % levels) as well as at a typical trace element level (0.1 %, or 1000 ppm).

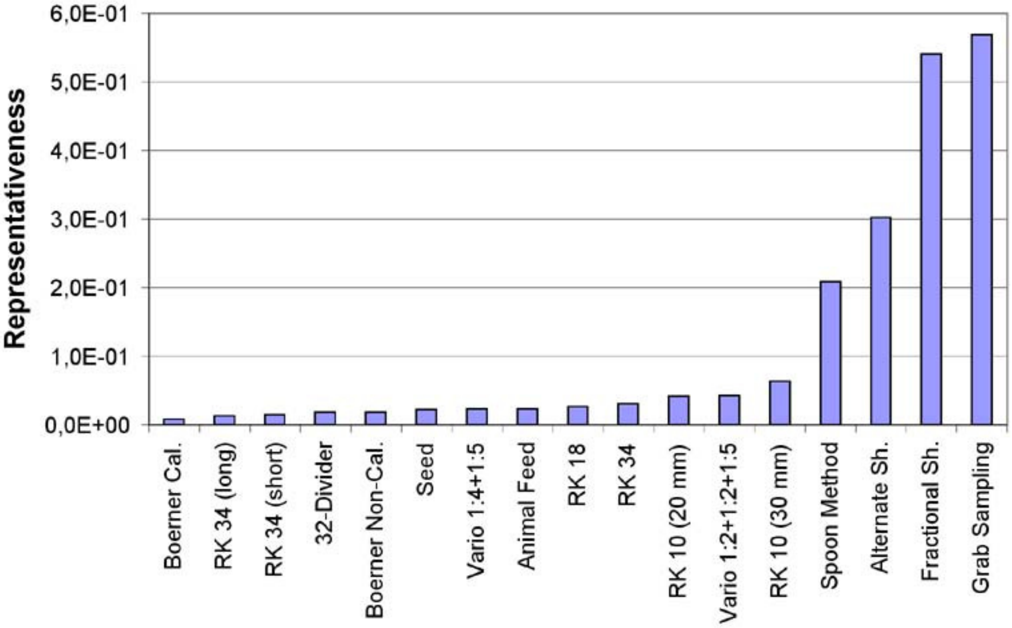

Figure 3. Summary evaluation of 17 widely used methods for mass reduction. A low value on the comparison ordinate axis indicates better representativeness. The representativeness is proportional to the effective total sampling error. Note in particular that the world's most often used sampling technique – grab sampling – is actually the world's poorest performer (further comments in text).

The methods and devices are fully described elsewhere and we here only outline that ordinary *grab sampling* (: scooping some material out from an easily accessible part of the lot) is the overall worst performer of all mass reduction techniques, as witnessed by an extremely high value of representativeness. By way of contrast, the principle of *riffle splitting* [Pitard, Gy, Petersen et. al.] and its directly equivalents, called *rotational dividers*, all perform very well and are recommended for use in most situations. A word of caution is appropriate here as the choice of device in these categories also has immense influence on the quality of the final results. The following rules-of-thumb are relevant:

- The higher the number of splitting-chutes (or: rotational sectors) the better
- Chute width must be a minimum 3 times the top particle size
- "Correct usage" is vital (all chutes must be used and fed *evenly*)

Particle size reduction

When all other SUO have been invoked etc. but the effective total sampling error is still too high, the only way to minimize the remaining Fundamental Sampling Error (FSE) is to *comminute,* or to crush, the material particles so as to reduce the average particle size. This is evident from Gy's formula (see above):

$$\sigma^2(\mathrm{FSE}) = \frac{C \cdot d^3}{M_S} \qquad \text{or} \qquad d^3 = \frac{\sigma^2(\mathrm{FSE}) \cdot M_S}{C}$$

The particle size is seen to contribute to the error by its third exponent, so it is evident that reducing the particle size greatly reduces the fundamental sampling error. It is also observed that increasing the sample size (M_S) results in a reduced error as well. But since there will always be a maximum physical limit to the size of samples that can be brought back from the field or process, at times there may be no other option than to reduce the particle size.

The formula can naturally also be rearranged to yield the sample size needed to have a certain error if the particle size is given, or to provide the necessary particle size if sample size and error is fixed.

Lot dimensionality transformation

According to TOS it is only possible to sample 0-D and 1-D bodies completely correctly. The reader may easily imagine the nature of various 1-D, 2-D and 3-D objects, which correspond to the physical shape of many practical lots. If one dimension is negligible in size compared to the other two, we are essentially dealing with a 2-D object, and if two dimensions are negligible in this sense, we are effectively dealing with a 1-D object. 0-D objects are at first a little harder to understand, as these objects have had this name assigned to them primarily because they are made up of a set of units (virtual increments/samples) without internal correlation. Many 0-D objects in this TOS-meaning, in fact physically corresponds to 3-D objects, but since they display no significant internal spatial autocorrelations they can be viewed and sampled corresponding to the 0-D paradigm. For this lot type, the potential sampling units are not "fixed" in space and in fact they often can be - or have been - mixed prior to being laid up. Since TOS only deals with sampling of 0-D and 1-D objects one should always consider the possibility of reducing the lot dimensionality prior to sampling. An example will illustrate this:

A huge stockpile (fig. 4) is to be sampled for analytical purposes. In general it is obviously impossible to sample such a large and unmoveable stockpile correctly (according to the fundamental sampling principle) without some extreme manipulation (digging to the centre and the bottom etc.) – and this is clearly not possible in practise. But this does not mean that it is impossible to sample the stockpile correctly and representatively, however!

Figure 4. A large stockpile is for all practical purposes impossible to sample directly in any correct way without enormous, in practise prohibitive, amounts of time and effort. But no stockpile was ever born into this physical form directly however – on the contrary: it was certainly laid up *incrementally*, witness the various conveyor belts present. This simple fact opens up for another approach to completely correct and representative sampling! The example shown here is in point of fact *scale-invariant*, i.e. this pile can be envisaged at practically all scales.

The solution: When the lot material arrives it is transported via a conveyor belt and laid up in the stockpile by a stacker/reclaiming device (also a conveyor belt). Sampling directly from the conveyor belt, cmp. Fig. 1, or even better at a transfer point between two conveyor belts (both a 1-D material stream) is by far always the easiest sampling solution. There are two principal ways to go about this in practise, called the *stopped belt sampling* method (fig. 5) and by use of a so-called automated *cross-stream sampler* (fig. 6). Both will ensure complete, structurally correct sampling, since they both result in correctly delineated and ditto extracted increments with parallel sides etc. The automated approach (the cross-stream sampler) is in fact used extensively in very many industrial sectors where bulk materials handling is on the agenda.

Figure 5. ***Stopped belt sampling*** **results in structurally correct samples. Correct increment delineation and extraction is ensured in the above situation by using a device with fixed, parallel sides and a brush to extract all the fines along the bottom etc.**

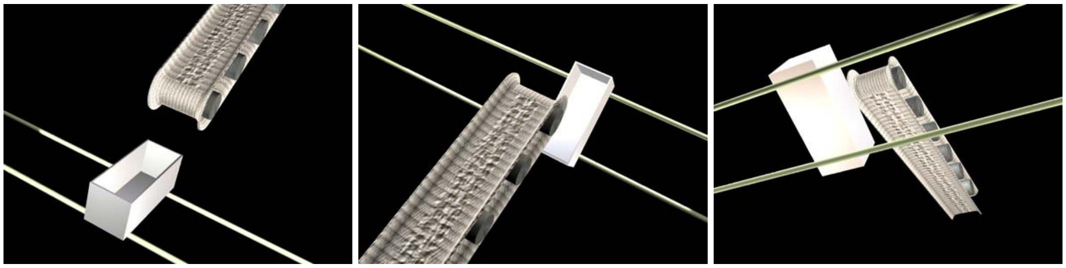

Figure 6. An automated *cross-stream sampler* seen from above-front (left) and above-rear (middle) and below (right). The sample box (white) is moving from side to side – with a *constant* speed of maximum 0.6 m/s (TOS) - and so crosses the stream (fully) twice to collect two increments, combined into one sample, delineated correctly with parallel sides etc. This illustrates an archetype correct sampling device for particulate materials.

Discussion and conclusions

We have briefly illustrated a number of the most central aspects of practical 0-D sampling according to TOS. As a minimum level of understanding, it is critically important that anybody responsible for practical sampling is at least acquainted with the fundamental sampling principle and is familiar with all the seven basic sampling unit operations. The fundamental requirements first of all stipulates to do everything concerning the sampling process *correctly*, and <u>always</u> to obey FSP. After this we only need invoking the relevant SUO's in the sampling practice as the specific situations call for. Structurally correct sampling will eliminate any sampling bias and also help minimizing the effect of the other sampling errors. TOS is the only *modus operandi* that will result in reliable analytical results. There are no shortcuts to this goal, contrary to many myths, like the presence of a "constant sampling bias".

Even though presented above in largely a particulate matter scenario, it is easy to translate TOS' general principles e.g. to also cover typical biotechnological systems etc.

Conclusions:

- Only FSP ensures probabilistic sampling.
- Only structurally correct sampling ensures non-biased samples, i.e. elimination of the incorrect sampling errors IDE, IEE and IPE.
- Initial characterization of the lot heterogeneity provides information on optimal sample size/mass, sampling strategy and at which sampling stages most effort should be put into optimizing the sampling procedure.
- Homogenization reduces the error contribution from segregation (part of GSE) and should always be carried out when possible – between all samplings and sub-samplings.
- Composite sampling reduces the error contribution from grouping (part of GSE). A larger number of smaller increments reduce sampling errors very effectively.
- Choice of correct device/method for mass reduction critically minimizes loss of representativeness from this procedure, and can in many cases reduce the time (and hence money) spent on laborious manual methods that does nothing more than decrease the reliability of the final reduced sample masses (with regard to the lot representativeness).
- Comminution reduces the fundamental sampling error (FSE) and is often a worthwhile effort, since a reduction in average particle size influences the sampling variance to the third exponent.
- Lot dimensionality transformation (from 3 or 2-D to 1 or 0-D) brings many sampling problems directly into the practical TOS realm.

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TENIRS - NIR analysis of heterogeneous bioslurries

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Introduction

Biomass conversion processes often involve the handling of complex heterogenous bioslurries, e.g. biogas production, which is based on slurries consisting of liquid manure, organic waste and/or plant silages. In this context on-line sensor systems are needed as analytical tools to improve the understanding of the underlying complex processes, but also as a control tool in the plant. TENIRS – transflexive embedded near infrared sensor – is an approach that fulfils most requirements of lab-scale applications (stand-alone NIR measurement prototype). Beyond lab applications it has also the capability of a process analytical technique (PAT) in biomass conversion plants.

TENIRS was developed in the context of a pig fattening project, funded by the German Federal Ministry of Research and Education. Goal of the project was to develop a sensor based feeding control system that integrates not only feed and animal growth data, but also changes of the manure. Properties of the manure are directly related to digestion and feed conversion. The manure sensor was supposed to allow an on-line monitoring of the manure with little restrictions in volume and number of samples and it was also aimed to analyse the manure as representative as possible. NIR spectroscopy, combined with chemometric tools, fulfilled best the basic specifications for an on-line sensor. Many applications in agriculture, pharmaceutical and chemical industries have proved the power of NIRS as a tool for qualitative and quantitative analysis of organic compounds. Based on a standard NIR spectrometer (Zeiss CORONA 45 NIR, spectral range 960 – 1600 nm)) a flow through measuring cell had to be developed and was constructed at the Institute for Agricultural Process Engineering at the University of Kiel, Germany. With respect to future application the complete system was named TENIRS.

The feasibility of measuring dry matter (DM), organic dry matter (ODM), nitrogen (N) and ammonium-N (NH_4-N) in liquid hog manure using TENIRS in a flow-through measuring mode was tested and is used as main analytical tool within the fattening project. Results of the TENIRS prototype testing are presented here.

Materials and methods

As most bioslurries, liquid manure is a complex multiphase system that roughly can be described as suspension with a liquid and a solid phase. Spectral analyses of liquids are usually performed by measuring the transmission through a sample with a defined path-length, whereas for solid samples the diffuse reflectance can be used (Fig. 1). For bioslurries both principles are unified in the transflection mode, which combines reflection and transmission in one setup. The incident beam of the measuring head is transmitted through the sample and then scattered back from a reflector. It is recorded similar to the diffuse reflection of the particles. In this way, liquid and particulate properties of a sample can be recorded simultaneously. For samples with low dry matter content, where transmission dominates, it is necessary to limit the path length of the measuring cell [1].

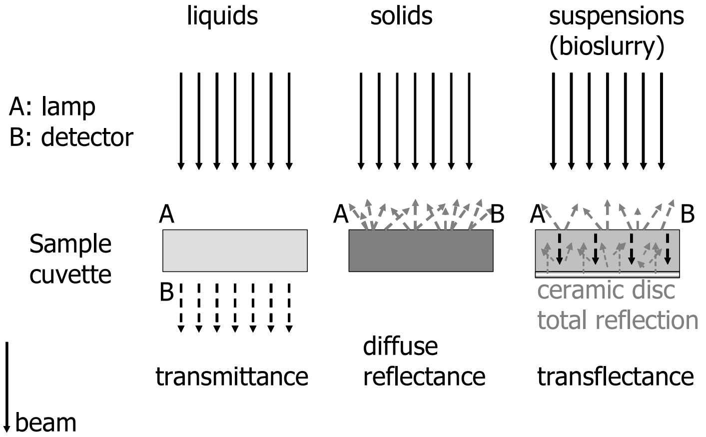

Figure 1. Spectroscopic principles

Measuring cell

The measuring cell is built of polyoxymethylen (POM). POM is a thermoplastic material with very good mechanical, chemical and thermal properties. It is acid-proof, has a low co-efficient of friction and shows good resistance to wear.

Figure 2 depicts the internal layout of the measuring cell that is attached to the measuring head of the spectrometer. The liquid manure sample flows through the measuring cell in a layer of 3mm between two glass plates (silicate) and is irradiated with near-infrared light. The cell is backed with a ceramic disc opposite the measuring head, along with the light source and the diode-array detector.

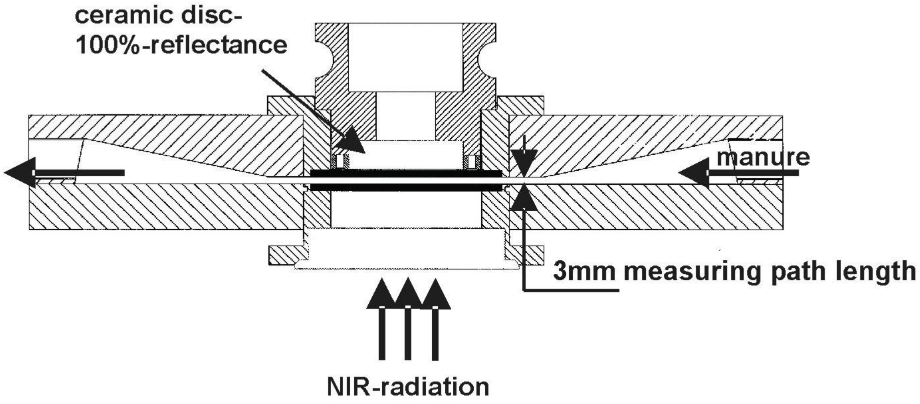

Figure 2. Flow-through measuring cell

The hydrodynamic design of the measuring cell (Fig. 3) intends to provide a uniformly distributed flow across the measuring window. When entering the measuring cell, the cross section of the flow changes. To avoid separation within the manure, three built-in pins cause a turbulence zone that generates remixing. In that way an evenly distributed stream across the entire measuring surface is assured.

To avoid clogging, the maximum sizes of particles within the manure have to be smaller than 3 mm. Hog manure usually fulfills this requirement without pretreatment. In the case of slurries with larger particles it is necessary to macerate the sample prior to the measurement with this cell. Future generations of TENIRS will be either equipped with an integrated macerator or with a thicker sample layer at the measuring window.

The measuring head of the spectrometer is protected from contamination, since it is attached to the glass plate of the measuring cell. The cleanliness of the glass in the cell has to be checked in regular intervals and cleaned as needed. Cleaning apparatuses are integrated into the system. Periodic referencing of the spectrometer must be carried out anyways, which implies a clean optical path.

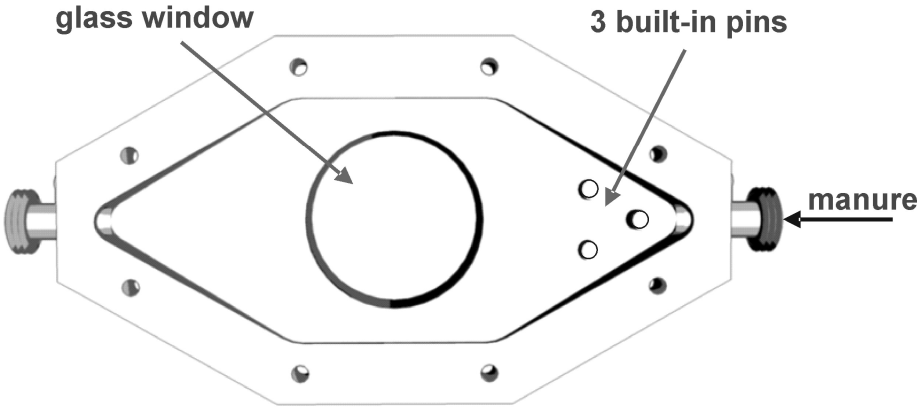

Figure 3. Flow-through measuring cell, interior view.

TENIRS-Prototype

Based on the measuring cell described above, a stand-alone prototype for an operating NIR-measuring system has been constructed and tested (Figure 4).

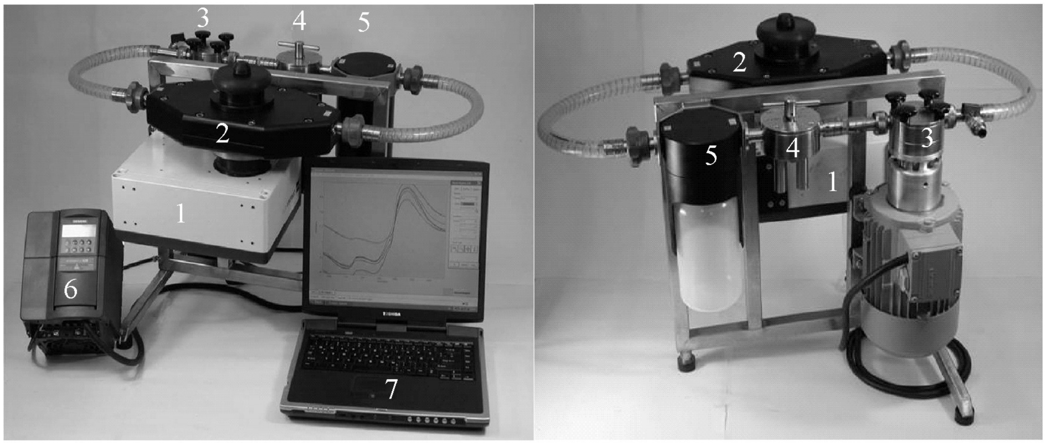

Figure 4. TENIRS stand-alone prototype (front and back view)

The tested prototype consists of a spectrometer (1) ZEISS CORONA 45 NIR, a measuring cell (2), an electric pump (3), a multi-way valve (4), a sample compartment unit with a 1 l sample bottle (5), a frequency inverter (6) and a PC (7).

The pump conveys the liquid manure with constant velocity in the closed system loop. The first cycles are used for homogenization. After the attached sample has reached a homogeneous state, the scanning procedure of the spectrometer can be started while the manure still flows through the cell. Spectral data is recorded with the control computer. Valves for water and compressed air allow for the cleaning of the system (Figure 5).

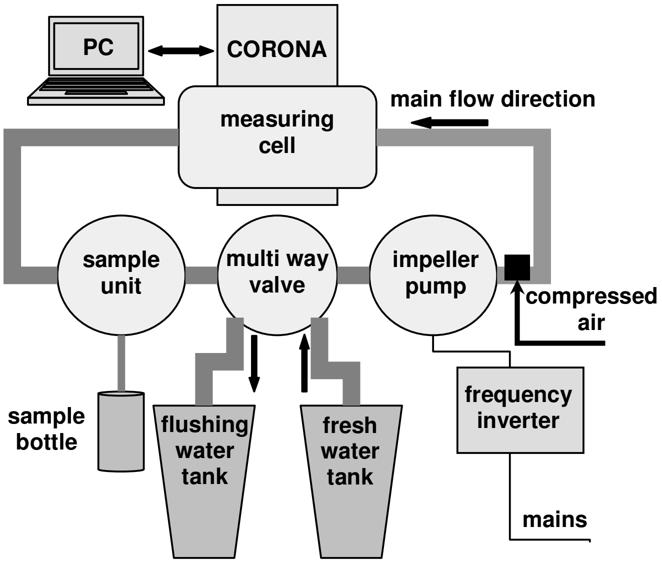

Figure 5. Functional block diagram of the TENIRS-prototype

Samples

One hundred and twenty eight (128) representative manure samples were collected from 24 pig pens during a fattening trial on a commercial farm. From each pen, 3 sample bottles (1l) were collected and scanned with the NIR-Prototype. After scanning, the samples were immediately frozen and stored at -18°C until reference analysis in the laboratory. Measurement and sample handling was carried out in a standardized procedure to avoid uncontrolled environmental effects and changes in the sample between spectral scanning and lab analyses. Reference analyses were performed by a certified laboratory for total nitrogen (N), ammonium nitrogen (NH_4^+-N), dry matter (DM) and organic dry matter (ODM).

Calibration Procedure

The possibility of using NIR to perform rapid analyses and to predict constituents in unknown samples highly depends on the accuracy of reference data and the quality of the calibration used. Calibrations were developed with The Unscrambler/Camo Process AS/Norway, using principal component analyses (PCA) and partial least squares regressions (PLS). Calibration that showed the highest R^2 and lowest SEP (standard error of prediction) between NIR-predicted and chemically measured values were selected as the best [2]. The calibration procedure was repeated for each constituent.

Results

Composition of Samples

Results of the reference analysis for the 128 manure samples are listed in Table 1. Values for total N ranged from 0.59 % to 1.17 % in the original sample. The NH_4^+-N-content varied from 0.40 % to 0.68 %, for DM from 4.37 % to 15.04 %, and for ODM from 3.16 % to 11.88 %. The mean coefficient of variation (CV %) was highest for ODM, with 21.15 %. Mean CVs for total N were 13.29%, for NH_4-N 12.02 % and for DM 15.69 %.

Table 1. Average chemical composition of the 128 liquid hog manure samples.

Constituent	Mean	Range	SD-mean	CV %-mean
Total N %	0.75	0.59-1.17	0.098	13.29
NH_4-N %	0.50	0.40-0.68	0.060	12.02
DM %	7.51	4.37-15.04	1.179	15.69
ODM %	5.87	3.16-11.88	1.242	21.15

Estimates of the laboratory's precision in analyzing the hog manure were made by calculating SD and CV for each sample. The coefficients of variation ranged from 0.01% to 12% for total N, from 0.03% to 8.55% for NH_4^+-N, from 0.02% to 14.83% for DM, and from 0.003% to 14.88% for ODM. The samples with CVs higher than 5 % were not used for calibration and were kept out from the data set.

Calibration and validation procedure

The measured and predicted data were matched in calibrations by means of PLS1 procedures. In this algorithm, calibrations were developed for each constituent individually. Outliers were identified by viewing plots of scores for each constituent in the Unscrambler software. From the data set for NH_4^+-N, 11 were removed and for total N 4 samples were identified and deleted as outliers. Outliers were not identified for DM and ODM constituents. The calibrations were thereby developed (Figure 6).

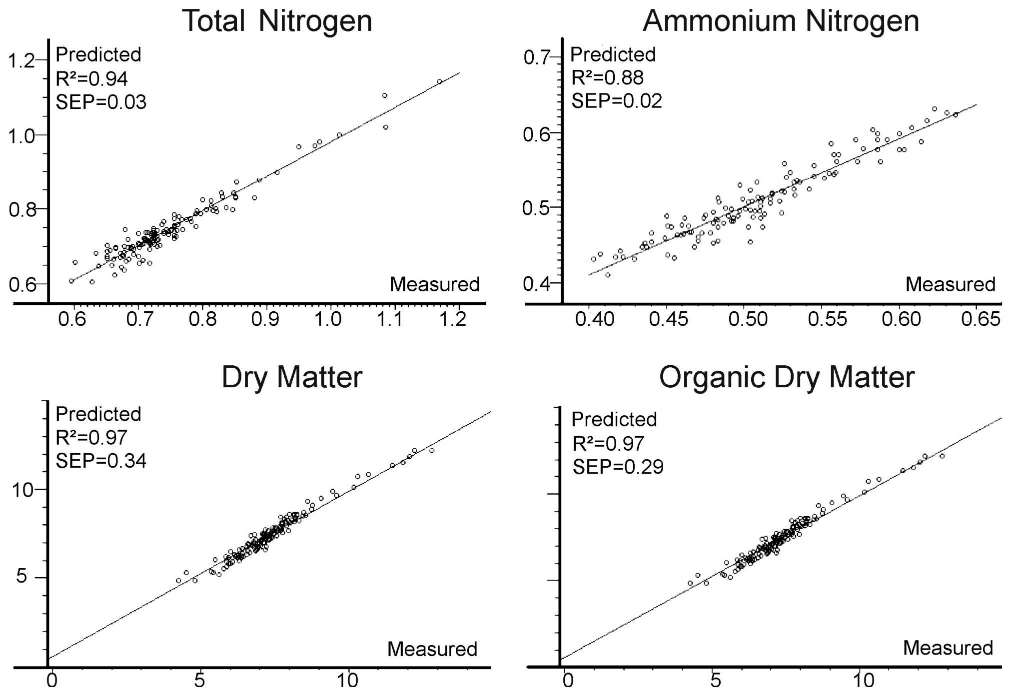

Figure 6. Linear regression relationships for total nitrogen, ammonium nitrogen, dry matter and organic dry matter.

The quality of the calibration was estimated using two types of validations. The first was based on a leave one-out cross validation. The results are shown in Table 2.

Table 2. Partial least squares regression results using 1-out cross validation

	Calibration						1-out cross validation				
Constituent	n*	PC**	r^2	SEC***	Slope	Bias	PC	R^2	SEP	Slope	Bias
Total N %	124	12	0.97	0.021	0.94	$4.84 \cdot 10^{-8}$	12	0.94	0.027	0.95	$7.39 \cdot 10^{-5}$
NH_4^+-N %	117	13	0.89	0.017	0.89	$6.54 \cdot 10^{-7}$	13	0.88	0.024	0.83	$9.79 \cdot 10^{-5}$
DM %	128	8	0.98	0.287	0.96	$8.56 \cdot 10^{-8}$	8	0.97	0.340	0.94	0.0078
ODM %	128	8	0.97	0.249	0.95	$2.88 \cdot 10^{-7}$	8	0.97	0.295	0.93	0.0080

*n = number of samples
**PC = number of principal components
***SEC = standard error of calibration

The second method was carried out using a test-set validation with random selection of a calibration set and test set from the basic data set. The calibration for ammonium nitrogen was tested using 71 samples for calibration and 46 test samples. Total nitrogen, dry matter and organic dry matter were also tested using 77 calibration samples and 51 test samples. The result of PLS regression using test set validation are presented in Table 4.

Table 4. Partial least squares regression results using test-set validation

	Calibration						Test-set validation					
Constituent	**n**	**PC**	**r^2**	**SEC**	**Slope**	**Bias**	**n**	**PC**	**R^2**	**SEP**	**Slope**	**Bias**
Total N %	77	10	0.95	0.023	0.91	$2.86 \cdot 10^{-8}$	51	10	0.94	0.032	0.89	0.0053
NH_4^+-N %	71	11	0.93	0.019	0.87	$1.28 \cdot 10^{-6}$	46	11	0.88	0.024	0.88	0.0007
DM %	77	8	0.98	0.304	0.96	$1.25 \cdot 10^{-6}$	51	8	0.97	0.276	1.03	0.0999
ODM %	77	8	0.98	0.239	0.96	$9.50 \cdot 10^{-7}$	51	8	0.97	0.264	0.99	0.0097

The R^2 between NIRS predicted concentrations, and the concentrations determined by chemical analysis using 1-out cross validation and test-set validation were for total N 0.95, for NH_4^+-N 0.89, for DM and ODM 0.97. SEP for all constituents ranged from 0.024 for NH_4^+-N to 0.34 for DM for 1-out cross validation and was almost identical for test-set validation. The smaller the SEP, the closer the estimate is likely to be the actual value of the dependent variable. Using the SEP to calculate the ratio of range/SEP for each constituent gives a good indication of the model strength in predicting accuracy. A large range/SEP (>8) indicates good predictability of quantitative data [3]. The ratios of range/SEP for N, NH_4^+-N, DM and ODM are 8, 12, 39 and 33, respectively.

Discussion

Even though bioslurryies, here pig manure, are quite heterogeneous it was possible to develop satisfying calibration models for the tested constituents. The high values of principal components (PC > 8) demonstrate the complexity of the calculated models. In this study it could be demonstrated that NIRS calibrations for total and ammonium nitrogen, as well as for dry matter and organic dry matter, can be developed and used to determine the composition of bioslurries. Further constituents have to be tested.

The comparison of these results with the results of similar studies with static NIRS measurements illustrate that flow-through NIRS-measurements of liquid manure are more precise and accurate [4], [5] and [6]. This is especially important for heterogeneous samples with a high tendency to sedimentation. For pig manure, but also for bioslurries with low dry matter content this could easily lead to erroneous measurements, if measured in a static way.

Another factor in accuracy of measurement is the sample volume. The flow-through cell used in this study works on a sample volume of 1 l, which allows a higher representativeness of the measurement. The flow through cell can also be used as a bypass measuring system that is attached to a main line. In that way it is fully suited as process analytical technology, that gives continuous information about the process and can be integrated into control loops of a plant.

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Membrane Technologies in Biorefining Processes

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Abstract

Uncontrolled degradation of organic waste leads to the loss of valuable nutrients to the aquatic environment, causing problems such as algea growth. It is also a major source of greenhouse gases, such as methane and carbon dioxide which needs to be reduced. Controlled Anaerobic Digestion (AD) designed to entrap the nutrients and the produced biogas is considered the best solution to this problem. Wet organic waste treatment by AD is rapidly gaining dominance as the preferred solution for waste treatment in EU and the rest of the world. The current AD technology has, however, not been significantly upgraded and improved for decades [1,2]. Today's systems are overwhelmingly "process-by-design" batch (or fed-batch) solutions, with very limited means for process monitoring and control. These systems have to be fed complex mixtures of variable feed-stock compositions, which invariably entails a serious end-product uncertainty, e.g. unwanted decrease in bio-gas yields, unstable production, adverse organic fertiliser and mineralised end-product characteristics, which is unacceptable as these are meant for re-use. Their value and contribution to sustainable development depends on their quality and reliability.

Recent research has demonstrated that there is a significant enhancement potential in this field [3-6]. It has also been demonstrated that there is a need for enhancement measures both in large industrial scale treatment plants as well as for small-scale AD-systems. Typical large-scale systems are plants to handle food waste, sludge and industrial wastes in larger cities. Improved treatment of these systems will benefit from ongoing research on integrated monitoring systems such as emerging sensing methods (electronic tongue (ET) facilities, Near-InfraRed spectroscopy (NIR), Image Analysis (as Angle Measure Technique, AMT), to measure key inorganic and organic substances and intrinsic system states. Novel membrane separation technologies integrated at several critical process steps may be used as means of avoiding unfavourable interferences and fouling, thus enabling robust long-term process control.

In the current presentation focus will be on the potential use of integrated membrane separation for an AD biorefining process.

1. GENERAL ABOUT THE BIOREFINING PROCESS

For concentrated wastewater the membrane bioreactor has been successfully applied at some plants in full scale. A good overview of the state of the art and potential was given by van Dijk and Roncken back in 1997 [7]. It should be pointed out that a bioreactor combined with membrane filtration and a membrane biofilter is not the same type of process, but they are both referred to as membrane bioreactors (MBR). When a bioreactor is not an active part of the membrane treatment, it may be necessary to disinfect the membrane with respect to microorganisms on a regular basis.

Membranes used for liquid sludge separation demand prevention of fouling in order to maintain flux and long-life durability of the membrane. This means active control of pre-treatment and washing routines, as of the pH of the solution [8-12]. Fouling will take place in the bioreactor, and needs to be controlled; although for a bioprocess fouling may have both positive and negative effects (see paragraph on fouling below).

A proposed system for an AD biorefining process is shown in figure 1. The process consists of two reactors, and in this case recirculation is applied in the process optimisation. Membranes may be integrated at several places in the system for various purposes:

1) To stimulate desirable biological conversions, small amounts of oxygen may be introduced through a membrane in a systematic manner at fixed locations in the bio-reactor. This intermittent oxygenation can potentially give real-time information about the anaerobic biological conversion process rates, e.g. through oxygen utilisation rate measurements
2) An in-line membrane module (potentially a dense polymeric membrane) may be used for extraction of ammonia (as NH_3 or NH_4^+) – in the figure indicated as a loop
3) For recovery and upgrading of biogas, various membrane materials may be used. Several different types are recommended; polymeric materials, carbon membranes or mixed matrix membranes

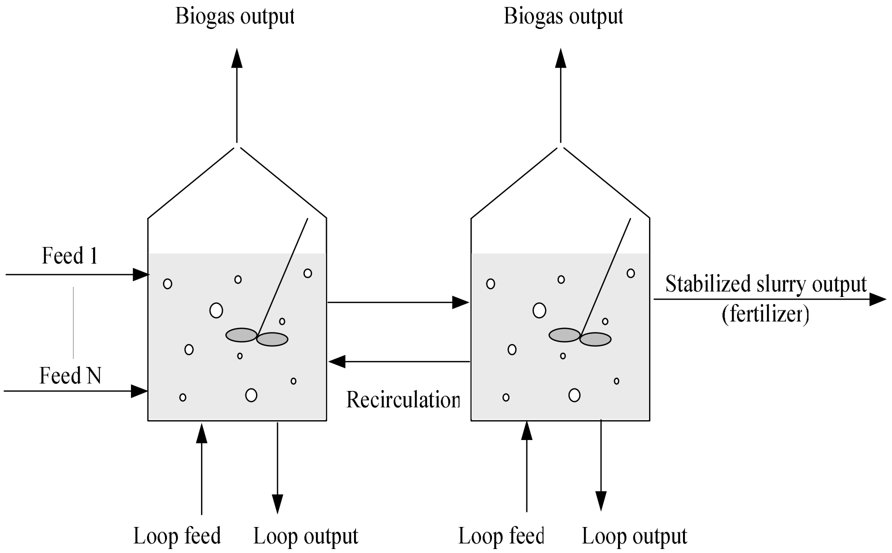

Figure 1 Schematic presentation of a proposed enhanced anaerobic digestion process (Bakke-04).

2 MEMBRANES FOR BIOREFINING PROCESSES

The main objective of the current presentation is to evaluate the three different types of membrane separations mentioned above when applied in a biorefining process, and discuss potential problems related to their use.

2.1 Membranes for oxygen supply

A membrane system where there is gas on one side and liquid on the other side is usually called a membrane contactor. The membrane module may be designed as flat sheets or hollow fibres. The membrane contactor will not take active part in the transport, but will act more as a barrier between the gas and liquid phase. If a microporous membrane is used, the oxygen must be supplied at a pressure governed by LaPlace equation (See figure 2 for a schematic illustration of the principle behind LaPlace):

$$r_p = \frac{2\gamma}{\Delta P}\cos\theta$$

where r_p= pore radius, γ= surface tension, ΔP = min. transmembrane pressure, θ = contact angle

Using a micro-porous membrane may be very efficient, but there will always be the possibility of having liquid leakage into the gas side if the process is not well controlled unless a hydrophobic material is being used. It is obvious that only by careful control and evaluation of data can this process be optimised. The microporous membrane may sometimes be covered by a thin film of dense rubbery material, like silicon rubber, this will reduce chance of having liquid break-through, but will represent an additional resistance to the gas transport (now by solution-diffusion) through the membrane. With a biofilm on the other side of the membrane, the oxygen must be carefully controlled. There will always be the possibility of having back diffusion of NH_3, CO_2 and some CH_4 into the membrane which is supplying oxygen – this may be an advantage or disadvantage depending on how the process is set up. In Figure 3 a commercially available membrane bioreactor (the Kubota reactor) where air is introduced through a diffuser is shown. The membrane module may easily be of different construction; for instance like a coil put into the reactor.

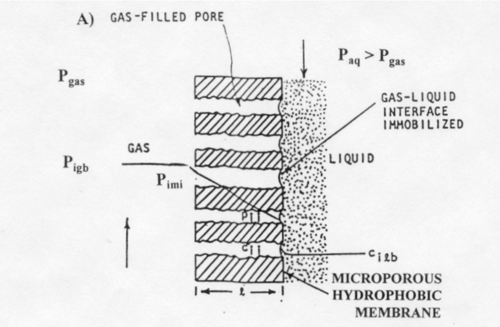

Figure 2: Schematic illustration of the Basic mechanism for a contactor [13]

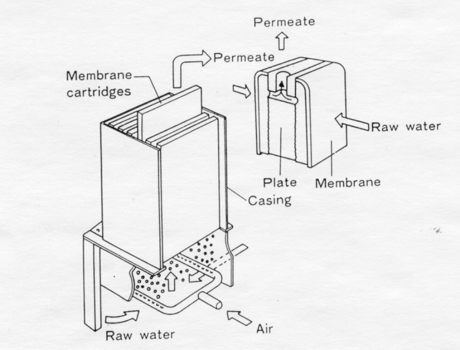

Figure 3: A schematic diagram of the Kubota membrane bioreactor [14]

2.2 Membranes for extraction of NH_3 or NH_4^+

Depending on the pH control of the process, the ammonium will be present as gas (NH_3) or dissolved NH_4^+, to various extent (at pH 7.8 about 5% will be present as NH_3 [15]). Theoretically the ammonia gas may be extracted by using stripping gas (like a contactor), vacuum (like pervaporation) or by acid stripping (liquid/liquid system). A simple rubbery membrane can be used (i.e. silicon membranes) through which the gas will be transported basically according to a solution diffusion mechanism. The problem will however be that along with the ammonia, gases like CO_2 and CH_4 will also permeate. This may cause loss of valuable biogas, and should be avoided. This indicates that the best solution may be to use some kind of acid stripping where the other volatile gases will not react with the stripping solution. The principle of the gas-membrane based ammonia removal is illustrated in figure 4.

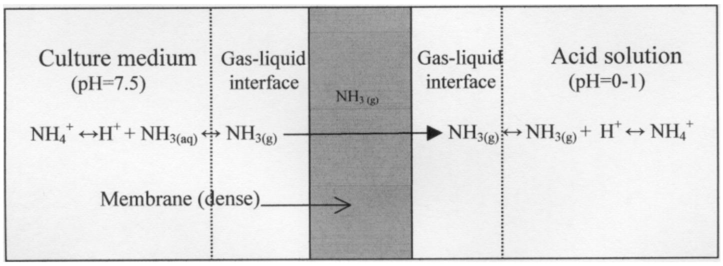

Figure 4: Schematic illustration of gas membrane based ammonia removal [15]

2.3 Membranes for upgrading of biogas

Sweden was one of the countries that broadly developed biogas as energy source after the energy crisis in the 1970s, and is today the leading nation when it comes to biogas as vehicle fuel. There are more than twenty plants in Sweden for upgrading this renewable gas to fuel quality. Norway got the first biogas powered vehicle in 2001, while in Denmark the biogas is mainly being burnt to produce energy; very little is used for vehicle fuel. Pretreatment of the biogas is different depending on the usage. Biogas upgraded to fuel quality, has the most strict quality demands, and for this purpose membrane separation may be useful to consider.

Corrosive components (water vapour and sulphur) and energy diluting gases (mostly carbon dioxide) must be removed to obtain high quality CH_4. Gas separation membranes are effective upgrading units. Polymer membranes have been commercially available for some decades, and new efficient polymeric materials with facilitated enhanced transport are under development. Microporous carbon constitutes a membrane material with better separation performance than polymers, but suffers currently from high costs. The mechanisms governing the separation of the gas components are very different for these two types of material.

The main components in biogas are methane (CH_4) and carbon dioxide (CO_2) arising from various anaerobic processes. Different trade names are landfill gas, sewer gas, manure gas, and the composition of the biogas will be different depending on the source, digestion time and process conditions. The most difficult process is extracting CH_4 from landfills where there is also uncontrolled amount of air leaking into the system. The most challenging membrane separation is separation of N_2 and CH_4 as these two gases have very much similar physico-chemical properties.

Rautenbach and Welsch [16] evaluated different usage of biogas. Upgrading to pipeline quality gives the highest portion of exportable energy, and a medium range energy demand for the energy production (10%). In this case, the upgrading was carried out with a membrane process, figure 5.

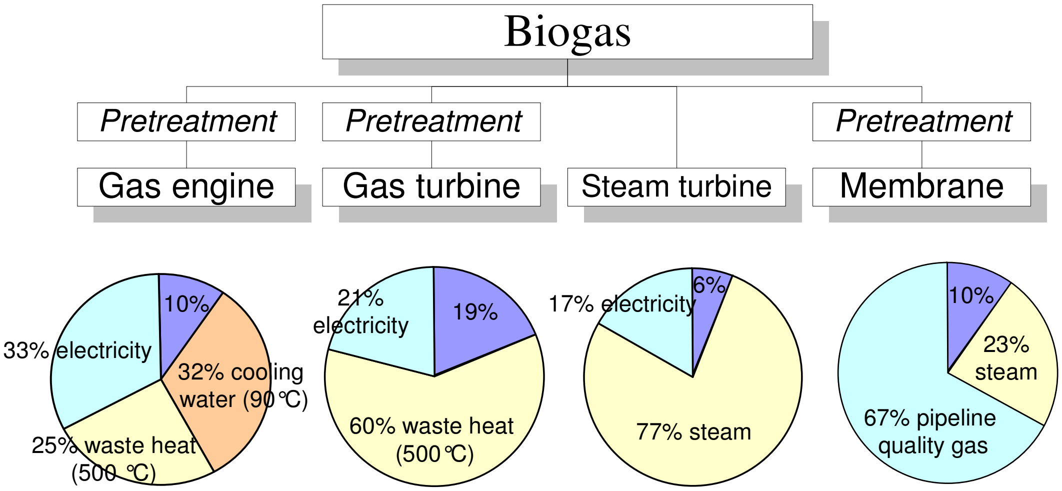

Figure 5: Evaluation of different biogas applications (dark regions show energy production requirement). After Rautenbach and Welsch [16]

3. CHALLENGES RELATED TO USE OF MEMBRANE SEPARATION

3.1 Fouling – membranes for liquid separation

The fouling is essentially a heterotrophilic biofilm developing on the membrane surface or in the pores. It is a key issue to investigate and quantify how this deposit influences the membrane flux. While fouling usually have negative effect on the membrane flux, it is expected that for oxygen the flux will be enhanced, while the methane flux (the other way) is reduced [17], thus improving the overall process performance. How the fouling will affect the transport of NH_3 and CO_2 will depend on the type of membrane material being used. Fouling caused by other compounds in the solution may need to be controlled – several methods are recommended [18-21]. Challenges related to fouling will be briefly discussed in the presentation

3.2 Durability of membrane material

It is crucial that the membrane material will not degrade when exposed to the gases and liquids in a bioprocess, but will have a long-life steady performance. Fundamental knowledge about the process as well as how certain components may degrade the material is therefore important, as well as having good quality washing routines.

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BioFuel Region – a successful example on how to bring people into a sustainable future

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BioFuel Region

BioFuel Region is the propelling force in a long-term process where regional co-operation is used to implement the development and introduction of renewable fuel, which is based on biomass from forests, fields and recycling. For the most part, the counties of Västernorrland and Västerbotten make up the region. The vision for BioFuel Region (BFR) is that we are going to be self sufficient in transport fuels in 2030 and a world-leading region in the area of cellulose-based biofuel that will be in the forefront of the acquisition of knowledge about biofuel, as well as being a leader in the development of technology, production and utilization of biofuel.

BioFuel Region's strategy is to promote and lead development by mobilizing, committing and activating as many potential developmental forces as possible in each respective region. BFR began in 2003 and at the present time there are about 25 stakeholders that represent municipalities, county councils, county administrations, federal authorities and private enterprises.

Work is organized in relatively independent groups, which are closely connected within different areas of the biofuel developmental chain, that is to say raw materials, production, distribution, vehicles, laws and regulations, and consumer information. The work groups in question are as follows: Adult education and commitment, School, Research and development, the Public sector, Development of filling stations, Raw material issues, Industrial development, and Long-term financing. In total, there are approximately 150 people participating in the work groups. The motivating forces behind BioFuel Region are the key problems of climate and energy supply. As part of the EU's work, these questions were addressed in a directive in May 2003 of the European Parliament that declared that 2 % of all gasoline and diesel fuel in the transport sector shall be replaced by the year 2005. This percentage shall be increased each year so that by the year 2010 it will total 6 %. This means that the volume will increase 10-fold in seven years. A system and technology will have to be developed that is more sustainable than that which exists at present, not to mention supplying facilities that produce the 20 billion litres annually that will be needed in Europe alone up to 2010—and even more in the future. BioFuel Region has a great potential of being a winner since we can capitalize on our knowledge and experience.

Many things that are going to be implemented in BFR are activities that the municipalities and the other stakeholders are required to achieve in their normal environmental work. However, through co-operation, exchanges will be greater and the image of the region as a global model will become even clearer and more focused from an international perspective.

During the first project period 2003 to 2006, it is calculated that BFR will have a budget of 4 million Euro for process work that aims at preparing the foundation for the future. This amount is the equivalent of approximately two pro mille of the amount spent on gasoline and diesel fuel in the region, which is to say 1,8 billion Euro during the project period.

Activities in the region

In Sweden as in many other countries ethanol is the most spread alternative to gasoline and diesel. Sweden has more then 400 busses running on neat ethanol, about 14 000 Ford FFV running on e85 and almost every car running on gasoline runs on e5. The region has been the base for the development buses was introduced in 1986, Flexifuelcars in 1994 and low blending, e10 at that time in 1997.

The activities have been based on the insight that this could lead to a regional development based on the tradition of sawmills and pulp production. It is interesting to find that new fields for the forest by products are needed at the time that we have to change to renewable, sustainable fuels in the transport sector.

Activities in Schools like project tasks in the Colleges have inspired young people to find out more and do very interesting reports and in some cases motor modifications.

In the communities the task group has reached free parking for the “environmental cars” and also supporting rules for public purchase of fuels and ecocars. The distribution is very important to get people to really fill the car with ethanol and not run on gasoline. There are about 10 refuelling stations in the region.

A lot of work has been done in the region together with scientists in Sweden, Europe and North America, to develop the process for ethanol from cellulose

Softwood is the feedstock with the biggest potential in Sweden for ethanol production. Softwood residues from harvesting or from sawmills and other wood based production units can be used. Hard wood residues and cultivated energy crops could also be interesting feed stocks in Sweden, when pentoses can be fermented in industrial environment. In Sweden cultivated energy crops mainly means salix (willow) and reed canary grass.

Ethanol production in a stand alone unit, based on cellulose raw material is hard to motivate today due to high costs and low energy output. About ten different feasibility studies have been made in Sweden by BioAlcohol Fuel Foundation integrating ethanol production with municipality power plants, sawmills, pulp mills, wood pellets plants etc.

The development of ethanol production from cellulose raw material has been going on for 20 to 25 years at the Universities in Sweden and other countries. Several process alternatives for hydrolysis of cellulose materials have been evaluated. Diluted acid in two steps and a third enzyme step seems to be the most suitable for softwood to get high yields of ethanol.

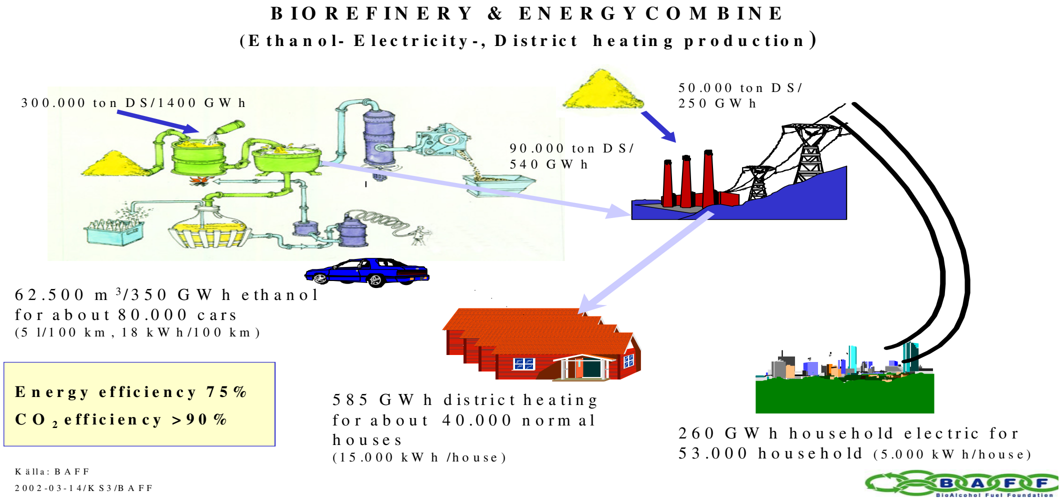
For hardwood and straw probably just one step of diluted acid completed with one enzyme step is necessary.

Based on results from the bench scale unit at the technical university of Lund the next step in the development was to build a pilot plant for verifying and optimising process and technology and further development.

Bioenergy combines

Regional energy companies are the most committed stakeholders in ethanol development in Sweden at the moment. They have a vision to give energy support to the inhabitants in all fields, electricity, district heating, and fuel for transport. This could be described in the following figure, representing a medium-sized municipality in Sweden with about 60 000 inhabitants.

Figure 1



Sweden have about 35 municipal electric and power plants producing totally 5 TWh_e/year and 15 TWh_w/year. By combining these power plants with ethanol production facilities bioenergy combines are created.

A bioenergy combine with a capacity of 60 000 000 liters ethanol/year is what we can call a ”normal-sized” Swedish plant. In this case roughly most of the energy demand in the municipality for transport, heating of buildings and small and medium sized enterprises are supported from the combine excluding bigger industry. Energy saving can increase the share even more.

The same result can be reached with an ethanol plant in combination with a sawmill, including a dryer for board and deal or a plant for upgrading biofuels to pellets.

Pilot plant

To develop the technology for ethanol production from soft wood residues, some regional energy companies formed, seven years ago, a new company, called Etek EtanolTeknik (EthanolTechnology) which has made the process design of the pilot plant or Process Development Unit (PDU) that was erected in mid 2004. Etek was also responsible for the construction and the operation of the plant.

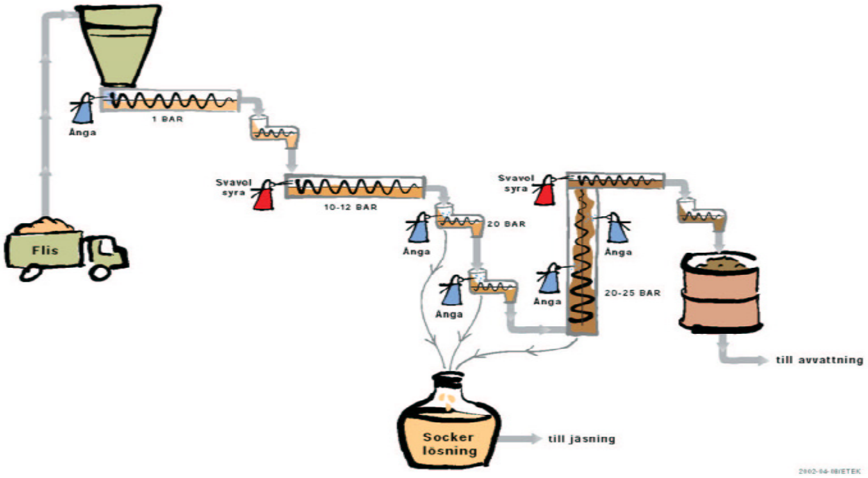
The plant will be linked to the three Universities in the region and other Swedish Universities like Lund and Chalmers.

Location for the pilot plant is in Ornskoldsvik in the northern part of Sweden, close to an existing sulphite pulp ethanol plant.

The plant have a capacity in feedstock input of about 2 tons of dry substance/day. With the expected yield the production of ethanol will be 400-500 litres /day. The plant is basically designed for development of the continues diluted acid hydrolysis process in two steps with a third step for enzymatic hydrolysis and for softwood residues as cellulose material.

The second step in the reactor is a countercurrent reactor which has a good potential to increase the yield and reduce the amount of byproducts. The reactor has basically the same design as the reactor at NREL, Golden, Co, US. (Figure 2)

Figure 2. Schematic design of the reactor



As catalyst for the hydrolysis diluted sulphuric acid or sulfur dioxide will be used.

The second step, the countercurrent reactor, can be replaced or changed to a co current reactor.

The pilot plant will be a complete industrial plant with all unit operations like hydrolysis, dewatering, fermentation, distillation and recycling of process streams.

The plant is operated 24 hours per day in periods of 3 to 4 weeks to get long time effect on deposits and build up of circulating byproducts. It will be operated by personnel from the existing sulfite pulp ethanol plant.

The products from the pilot plant will not be sold on the market. The energy content in the ethanol, lignin and residues will be used in the industries lying close and for further development.

The plant was inaugurated by the Swedish Prime Minister Goran Persson in May 2004 and taken into operation in the end of year 2004. To verify the process and technology and to get more accurate design data for production plants it is needed to operate and evaluate the pilot plant for about two years before the design of a full scale demonstration plant.

Production plant

In a bioenergy combine with ethanol production some of the hemicellulose and cellulose are not converted to ethanol but solved in the process water and evaporated to a liquid fuel residue, comparable with syrup or spent liquor. This residue is burned in the boiler and could in some applications correspond to the total energy need in the plant.

Most of the lignin remains as a solid product after the process. The lignin is used as a fuel in bioenergy combines, sold as an additive in wood based biofuel pellets or as a biofuel for special purposes. The lignin fuel is very suitable for gas turbines and as an incineration additive, because it has low alkali content and high energy value, 6,2 MWh/odt. In the future it may also be a raw material for “green” chemicals.

Based on the design data for the pilot plant Etek also has made a study of a production plant in combination with an existing combined heat, power and wood biofuel pellets plant in the north of Sweden. The production of ethanol was set to 75 000 000 liters a year. The investment costs for the production plant was calculated to about 120 million Euro.

In the economic evaluation, the byproducts have big influence as can be seen in figure 4.

Figure 4. Production costs for ethanol from cellulose

	US$ / litre ethanol
Raw material	0.20
Energy	0.15
Chemicals	0,05
Credit by products	-0.15
Production costs	0,05
Capital costs	0.15
Total	**0.45**

Financing of the pilot plant

Both the basic design of the pilot plant, the study of a full scale production plant and the investment in the pilot plant has been financially supported by the Swedish National Energy Administration, regional EU-funds, local governments and private and regional energy companies. The investment costs in the pilot plant is about 16 million Euro and the annual running cost about 1-2 million Euro depending on the research program. An existing infrastructure at the sulphite pulp ethanol plant of a value of 6 million Euro will also be used.

Further development

Regarding the production technology, different feed stocks like hardwood and annual crops like straw and reed canary grass will further on also be tested in the pilot plant.

The pilot plant will be open for cooperation with partners all over Europe and may be other countries.

In the region big efforts will be taken to inform, motivate and activate the inhabitant to use biofuels like Ethanol and Biodiesel. New target groups will be in the spot for the task groups in different activities like the taxi drivers, driver schools, car mechanicals, car dealers

Acknowledgments

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Production of Biofuels with the Danish BioRefinery Concept

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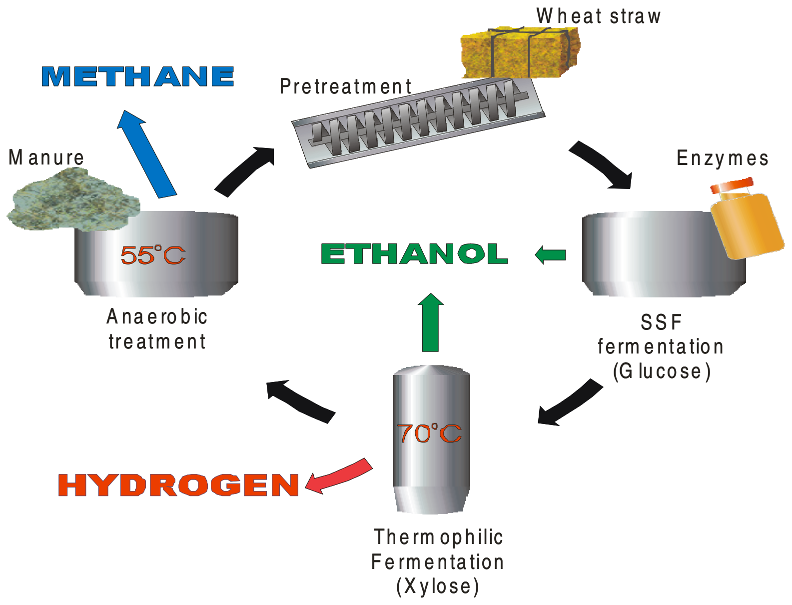
Abstract

The Danish BioRefinery Concept is constructed to address the major barriers for bioethanol production from lignocellulosic materials: the overall process outline has been defined to yield the maximum amount of biofuels per unit of raw material and increasing the process benefit by utilization of the residues for further energy conversion and by-product refining. The main product is Bioethanol for use as an alternative transportation fuel and emphasis has been on optimizing ethanol production. The supply and efficient conversion of the raw material is the major economical burden of bioethanol production and full and optimized use of the raw material is the key to future success. Production of other biofuels such as methane and hydrogen and other valuable by-products from the parts of the biomass not suitable for ethanol production will add full value to the overall process benefit. It will further exploit an environmentally friendly way of producing bioethanol where recirculation and environmental reuse of all streams produced in the process can be encountered. This is in contrast to most other process schemes for bioethanol production based on combustion technology, which will involve polluting steps giving rise to toxic waste or will produce a polluting effluent demanding large amount of energy for evaporation and further disposal. The basic ideas of producing biogas along with bioethanol and then to recycle the process water, or part of the process water within the process (the Danish BioRefinery concept), are patented. A combination of these innovative ideas along with the best available technologies has ensured an economical feasibility with a competitive advantage compared to outside competitors. The development of the optimized process of bioethanol production from lignocellulosic biomass can be integrated into a conventional bioethanol production based on starch.

The Danish BioRefinery Concept consist of the following process steps:

- Pre-treatment
- Hydrolysis
- Fermentation
- Waste water treatment with anaerobic digestion



An example of a Danish Biorefinery using Wheat Straw and Manure for the production of Bioethanol, Biogas (methane), and Biohydrogen

Pre treatment

Ethanol production from lignocellulosic biomass has to include a pre-treatment more intensive than those used in processing sugar and starch-rich biomass in order to release the sugar compounds contained in the biomass. Agricultural residues like wheat straw or other types of biomass derived from plant material contain lignin, which is constructed to resist microbial attack and to add strength to the plant. Pre-treatments are used to open the biomass by degrading the lignocellulosic structure and by partially hydrolysing the substrate. Current pre-treatment methods, however, contribute to 30-40% of the total costs of bioethanol production from lignocellulosic biomass. The National Renewable Energy Laboratories (NREL) estimates that in a Nth generation plant (mature technology) feedstock handling and pre-treatment would account for approximately 20% of the total ethanol production costs.

DTU and the Norwegian company Cambi has worked intensively for the last years on development of a pretreatment method aiming at high biomass concentrations and resulting in high recovery of sugars from the biomass. The new pretreatment process, ***Wet explosion (WE)*** is a combination of steam-explosion and wet oxidation, applying both the addition of oxygen and pressure release in the pre-treatment. The optimal combination of process parameters such as temperature (180-200°C), pressure (12 – 30 bar), amount of oxygen addition, and residence time (2-15 min) has been tested. The newly developed method uses no chemicals and all results show that the method will be efficient and cost effective for opening of biomass material. A patent application has been filed on the new pretreatment method, and all calculations shows this method to be superior compared to any other process on the market when it comes to sugar yield and cost.

Hydrolysis

The hydrolysate released from the pre-treatment is typically treated with enzymes in order to break down cellulose and hemicellulose into hexoses and pentoses that are then further fermented to ethanol. Enzyme production costs are, however, generally high, so that the search for new enzymes with high efficiency that can be produced at low costs is the key to overcome the bottleneck of this process step. Another possible way to reduce treatment costs is to implement recycle loops in order to feed back washed out enzymes into the vessel of enzymatic hydrolysis. The hydrolysis step will be together with the yeast fermentation of glycose, SSF fermentation (simultaneous saccharofication and fermentation). The Danish Biorefinery Concept makes use of on-site enzyme production significantly reducing cost for enzyme production.

Fermentation

Fermentation by *Saccharomyces cerevisiae*

Biomass or agricultural residues consist of the polymers cellulose, hemicellulose, pectin, protein and lignin. Of the carbohydrate monomers xylose is second most abundant after glucose. Because the raw material cost is >50% of the overall cost of the ethanol process, fermentation of xylose is needed to improve the yield over raw material and lower the production cost of ethanol. Many biomasses and agricultural wastes contains xylose, in the order of 10-40% of the total carbohydrates. Co-fermentation of xylose and glucose is therefore a crucial step forward in reduction the cost of ethanol production from lignocellulosic raw materials.

The baker's yeast *Saccharomyces cerevisiae* is a desired process organism for fuel ethanol production due to its extensive use in current large-scale industrial ethanol production processes. Also the excellent ethanol productivity, and tolerance towards ethanol and the inhibitors found in biomass hydrolysates has been one of the important reasons for using this organism even though its natural xylose utilisation capability is, however, poor. Fermentation will often be done in batch culture due to the problems with contamination with other microbes.

A pentose and hexose fermenting thermophilic microorganism HY10 is used to ferment the residual sugars in the hydrolysate left after yeast fermentation. The thermophilic microorganism is able to grow under the harsh conditions provided by the hydrolysate, it ferments pentose sugars efficiently and produces mainly ethanol. Furthermore, it grows up to temperatures of 75°C, which is close to the temperature needed for distillation of ethanol from the reactor. Operation of the fermentation process at thermophilic conditions counteracts other bacterial contamination, which is generally a problem for mesophilic yeast fermentation.

To optimize the feasibility of the bioethanol production process the thermophilic fermentation is conducted in an immobilised reactor system. The immobilization of the fermenting organism inside the reactor brings an array of important traits to the fermentation process like increased ethanol tolerance, high substrate conversions and decreased sensitivity towards process imbalances.

Waste water treatment

In the effluent from bioethanol production will still be a large part of the organics after bioethanol production- namely the part, which is not composed of carbohydrates. Anaerobic digestion (AD) has been used for a long time as treatment of organic waste streams with a high concentration of organic matter. The benefit of the anaerobic treatment is the stabilization of the waste, the high reduction of organic matter and the production of methane, which can be used as energy source. This gives, in contrast to aerobic waste treatment, an overall positive energy balance of the waste treatment process. The income from the methane produced after bioethanol production compose a value corresponding to a lowering of the ethanol production price with 34%.

The effluent from the fermentation step of bioethanol production contains lignin derived degradation products primarily generated during the physical-chemical pre-treatment. These aromatic compounds are generally difficult to degrade under anaerobic conditions. Furthermore, a repeated reuse of the process water has the potential of causing build up of these fermentation inhibitors. It is therefore important to achieve an anaerobic purification technology, which is able to remove these compounds from the process water. Experiments in our laboratory have shown that all problematic organic components can be removed in the anaerobic step. The low hydraulic retention times and the organic removal is of great importance looking at the overall process feasibility.

The Danish Biorefinery is now ready for implementation in pilot and demonstration scale.

The biogas programme in Denmark 1998-2001

Johannes Christensen & Jens Bo Holm-Nielsen

The special biogas programme being implemented now and until the end of 2001 is intended as a contribution towards the realisation of plans of action in respect of energy conservation, the reuse of waste, and the improvement of the water environment. The programme focuses on, among other things, operating economy, biogas from domestic waste and the improved distribution and utilization of farmyard manure. It is also designed to create more movement in the establishment of new biogas installations.

Since 1987, the Danish Ministry of Food, Agriculture and Fisheries and the Danish Ministry of the Environment and Energy have jointly financed a development and demonstration programme. Support for research and development has also been forthcoming from the Energy Research Programme and the Development Programme for Renewable Energy. Biogas technology has since developed significantly in Denmark, helped along the way by government energy plans, by more specific biogas plans of action and the above-mentioned R&D programmes. Many different institutions, companies and individuals have made contributions to the results achieved. It has been teamwork in which the interests of energy conservation, the environment, industry, and agriculture have become united. There is need to continue the work by improving the function and efficiency of biogas plants, and create improved economic and organisational framework conditions to further the establishment of new installations in accordance with the plans outlined in the government's energy plan - Energy 21. At the moment, the wider adoption of biogas installations has stagnated, especially where new centralized biogas installations are concerned. Instead, new farm biogas plants are being installed in connection with large-scale pig farming. From a production point of view, actual progress is quite good and will accelerate in the coming years. There will still be a possibility of expanding the recovery of landfill gas and the production of biogas based on domestic and industrial waste. However, by far the largest potential can be found in farmyard manure and slurry based biogas plants and therefore this area is of special significance for the development of the biogas industry.

Main objective

It was decided to progress the special cross-ministerial biogas programme during the period 1998-2001. The advisory Biogas Group was given the responsibility of implementing the programme, which consists of a number of follow-up, development and information activities undertaken by different institutions primarily within sector research and The Agricultural Council of Denmark. The total budget for the period is DKK 12 million. The government therefore continues to give significant support to the biogas area for research and development work, and in the form of support for installation investments. In addition, there is a special electricity subsidy and indirect support in the form of tax exemptions in connection with the consumption of heat generated from biomass. Without these support measures no renewable energy sources would be capable of economic survival. Behind this state support is the desire to see biogas technology contributing to the realisation of some of the main objectives of society.

There are three part-objectives:

1. Achieving the objectives laid down in Energy 21, where in the long term 35 percent of energy supplies will come from renewable sources. An annual 20 PJ of this energy is to come from biogas, corresponding to an eightfold increase in relation to the 1998 biogas production. The whole of the biogas area is included, but the main effort will be directed towards installations based on the digestion of farm manure.

2. Helping to increase the reuse of organic domestic waste, of waste water sludge and other suitable types of waste. The objective of the plan of action for waste - Waste 21 - is to use 100,000 tons of organic domestic waste in biogas installations during the year 2004. In the longer term, the objective is 350-400,000 tons.

3. Clarifying the extent to which different types of biogas installation are able to contribute to the fulfillment of the requirements of agriculture in the utilisation of livestock manure in relation to Water Environment Plan II. Action Plan II for the development of organic agriculture points to biogas installations as a means of ensuring the recycling of nutrients from organic waste - a central issue in being able to convert a major part of agriculture to organic production. In addition to the three main objectives named above there are also possibilities of providing more jobs and increasing exports. Export activities are in progress but these must be further supported, primarily through well-functioning reference installations on the home market.

Areas of activity

State research and development activities must be coordinated with the development carried out by companies who operate in the market. Biogas plant is by no means a new technology, but one that to a certain extent has made a breakthrough, commercially and in terms of development. The public sector must therefore concentrate on what the various players on the market cannot themselves undertake. Significant parts of the technological development of the plant itself can be more appropriately left to the companies who supply the equipment, for it is this they have to sell and compete on. The programme covers a number of more general conditions in relation to the social economic function of biogas installations when seen from the point of view of energy supply and the environment, but there the division of labour is not clear-cut. Agriculture, the district heating sector and public authorities must also make a contribution if biogas installations are to be further developed and adopted more widely. Finally, the more fundamental parts of process and technological development will need state funding. This article focuses on some of the more essential activities included in the Biomass Programme 1998-2001. The programme is quite flexible in its approach, which means that tasks which subsequently emerge can also be included on the agenda.

Economic analyses

The economic follow-up programme and the collation of operating experience gained from both farmscale and centralised biogas installations are in progress, thus the way the production and operating economy of established plant are developing is under good control. Economic analyses and model calculations are being carried out in this connection in order to illustrate the significance of cost reductions, billing, different plant concepts, etc. The purpose here is to provide a basis for the various decision makers involved. There is also need for information that can be used for administrative and political purposes. The recently adopted reform of the policy on electricity supply in Denmark means that the billing rules for biogas installations will have to be scrutinised more closely before the end of 2003. The economic development will of course determine the rate at which wider adoption takes place, which types of plants appear, which financing and organizational models become dominant. Large variations in earnings can be anticipated and risk evaluation takes on a special significance. The economic consequences for farmers and authorities, and the possible supplementary treatment of the degassed manure are expected to become factors of more importance. On the municipal side it is essential to be able to evaluate the economic patterns arising from domestic waste and sludge treatment taken together livestock manure and its relation to biogas installations. The programme is intended to initiate the development of better methods and the compilation of enhanced databases for analysing the social and environmental-economic consequences of biogas installations.

More gas from manure

The results of research suggest among other things that through comminution around 20% more gas from manure can be obtained than is possible today. If this does show itself as a practical possibility at not too high a cost, it will have much impact on biogas economics. Work is being carried out on upscaling the experiments with a view to demonstrating the practical possibilities. The aim is to transfer the results to both existing and future plants, provided of course that the system does prove to be economically advantageous. The programme is also aimed at increasing knowledge on winning gas from livestock manure, including the possibility of being able to predetermine the gas potential. In practice there are large variations, because of feed, collection and storage methods for example. For this reason, investigations have been started to shed more light on these conditions.

Integrated waste treatment

The programme will help improve and clarify the technology, economy, and the organisational conditions surrounding the use of domestic waste and sludge in agriculturally-based biogas installations through goal-oriented technological development and the establishment of new demonstration plants. Considerable experience in this area has already been gained, but more work is necessary, specifically on the sorting of domestic waste - primarily with the object of avoiding plastics, and with techniques for separating plastics that cannot be avoided. The development work itself is to be undertaken by municipalities, the waste disposal sector and plant suppliers. The primary role of biogas programme activities will be to document results achieved and operating experience in a form that creates a decision-making basis for future integrated waste treatment.

In the same connection there must be closer analysis of the role biogas installations can play in the recirculation of nutrients as a factor in the more widespread adoption of organic agriculture and horticulture. Domestic waste and sludge are what can be called “problem products” in the sense that they might contain substances which burden the environment. Steps must also be taken to ensure that no germs can be present to spread disease. Investigation and analysis are needed in both areas and the programme is designed to help the process. Further investigation must be devoted to the significance of biogas installations in connection with the prevention of contagious disease among livestock.

Distribution and use of nutrients

Centralised biogas plants provide good possibilities for the redistribution and better utilisation of nutrients in livestock manure and waste. The Biogas Programme 1998-2001 develops and further documents these possibilities in the light of the now stricter requirements of Water Environment Plan II. This work is aimed especially at:

- The preparation of a nitrogen report on untreated and degassed manure in order to quantify the effect on washing out and nitrogen loss including that which occurs when transferring the manure from stable to field using different spreading strategies.

- The preparation of a follow-up programme for nutrient transformation by using separation plant in connection with biogas installations, with special focus on the phosphorus burden on agricultural soil.

- The possibilities of using the potential of improved nitrogen utilisation of degassed manure seen in the light of legislation which reduces permissible amounts of nitrogen fertiliser. The motivation of farmers in taking part in the wider use of centralised biogas plants largely depends on what can be documented and demonstrated, i.e. they must be shown that there are marked practical and economic advantages in treating farmyard manure in this way.

Information

The information and dissemination activities will be continued and adapted to the needs of the Danish biogas sector, the authorities, and decision-makers in general - in an international setting.

Regular seminars will be held for operations managers at which specific facets of management will be discussed and at which there will be opportunities to exchange experience. There will also be regular seminars on the economic side for managers and chairmen of centralised biogas installations. Here such matters as operating economy, financing, maintenance strategies and plant improvements will be discussed. Information is also being issued through articles in “Dansk Bioenergi”. Detailed background reports from various other areas of activity are also being issued.

The promotion of new installations

The reform of the policy on electricity supply in Denmark, adopted on 3 March 1999, to a certain extent clarified future billing rules for biogas-based electricity and heat. Experience from already established centralised biogas installations shows that normally it is very time-consuming to plan and finance an installation. The planning time can often be 2-3 years. Authority requirements have gradually increased in significance concurrently with the sector becoming an important factor in energy supply. Therefore a proposal under consideration is to create a team of experienced board members from established installations to advise new initiators so that they avoid the obvious traps in setting up new projects. Some existing installations, even quite new ones, have suffered from technical defects that have led to many difficulties. An appeal must be made here to suppliers and consultants to make sure that the quality of installations prevents the teething troubles that give rise to a poor reputation, and uncertainty on the part of future owners. The biogas programme will continue to include the offer of detailed technical assistance and the discussion of new installation projects with a group of experienced managers and technicians for the purpose of establishing quality assurance and the transfer of experience.

The interest of farmers in taking the initiative and accepting the responsibility for centralised biogas installation is less clear than it was 5-10 years ago. It was then advantageous for farmers to provide the required manure storage capacity in a centralized biogas installation. This capacity has now been created, but new requirements concerning the agricultural environment again direct the interest of farmers to phosphorus distribution, increased nitrogen utilisation in cultivation, and less emission and odour from pig production and manure spreading. However, biogas installations still offer a number of advantages which up to now have perhaps not been made sufficiently visible, but which are so good that they would at least stimulate the desire of farmers to become suppliers to biogas installations. Others can assume the responsibility for establishing and operating them. “Others” in this context might be already established biogas companies who would benefit from being able to expand. Initiatives might also come from equipment suppliers or from waste disposal companies perhaps in cooperation with a financing institution. Common to the new organisation models is that from now on satisfactory economic conditions can be created, to the extent that money can be earned from biogas. The main objective of the biogas programme is thus to contribute to the greatest extent possible in ensuring that such a commercial foundation can be created.

Description of Ribe Biogas Plant

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Ribe Biogas Plant was built in 1989-90 and started operating in 1990. The plant is owned by Ribe Biogas Ltd. The owners are the slurry supplying farmers, a food processing company that supplies organic waste to the plant, the regional power company and two investment companies. The aim of Ribe Biogas Ltd. is to establish and operate a biogas plant and to develop and promote biogas production technologies.

The biogas plant contributes to solving some major environmental and agricultural problems in the area, related to handling, storage and redistribution of animal manure, and brings some economic advantages for the farmers.

The plant receives cattle, pig, poultry and mink slurry from 69 livestock farms. The slurry is mixed and co-digested with intestinal content from abattoirs, digestible fatty organic wastes from food and fish processing industries and from medicinal industry and with sludge from poultry abattoir. The digestion temperature is 53 ºC (termophilic). A minimum guaranteed retention time of 4 hours at 53 ºC ensures efficient sanitation of digested biomass.

The digested biomass is returned to the slurry suppliers as a pathogen free, nutritionally declared, liquid fertiliser. The surplus is sold to about 72 crop farmers in the area. 25 decentralised storage tanks for the digested biomass, with a total capacity of 50,000 m^3, are shared by the slurry suppliers. The storage tanks are placed close to the fields where the fertiliser is to be applied. This has significantly reduced the cost and time consumption for transport and has enlarged the application area for digested biomass. The tanks were constructed with a 40 % investment grant from the Ministry of Agriculture.

The biogas is piped via a low pressure transmission system to the new CHP-plant at Ribe. The plant supplies the city of Ribe with electricity and heat, and was established in 1996/97, to replace three earlier coal-fired CHP- units. The gas engine is fuelled with a mixture of biogas and natural gas (dual-fuel). The biogas fuel has first priority.

Main data

Animal manure	352 tons /day
Alternative biomass	68 tons / day
Biogas production	4.8 mill. Nm3/year
Digester capacity (3 x 1745m3)	5235 m3
Process temperature (thermophilic)	53 ºC
Sanitation	MGRT 4 hours at 53 ºC
Gas storage capacity	1000 m3
Utilisation of biogas	Gas engine, CHP-generation
Biomass transport vehicle	Three vacuum tankers 2x20 m3 +1x 30 m3
Average transport distance	11 km
Investment cost (incl. storage capacity)	45.3 mill. DKK
Government grant	12.9 mill. DKK
EEC-grant	4.8 mill. DKK
Contractor	Krüger Ltd.
Operation start-up	1990

More interesting plant descriptions can be downloaded from the web: www.sdu.dk/bio.

BIOENERGY DEVELOPMENT IN UKRAINE: STATE OF THE ART AND PERSPECTIVES

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ABSTRACT: The paper presents data on biomass potential in Ukraine. Present state of bioenergy development and future targets are analyzed. Examples of successful implementation of biomass-to-energy projects and their economic indicators are given. The strategy of bioenergy development in Ukraine is developed. Total energy potential of biomass in Ukraine is estimated at 12.3 mtoe (9% of the total primary energy consumption). The most promising technologies are analyzed.

1 INTRODUCTION

Ukraine is a country with a lack of domestic energy sources. Own extraction of fossil fuels in the country is about 56 mill toe while primary energy consumption (PEC) is 140 mill toe.

2 PRESENT STATE OF BIOENERGY DEVELOPMENT

29 PJ (only heat) is produced from biomass in Ukraine (0.5% of total PEC) mainly from wood residues.

Fig 1: CHP biogas plant 160 kW_e+300 kW_{th} at farm Agro-Oven (15 thous. pigs), Ukraine. Design of BTG, the Netherlands.

Table 1: Modern bioenergy projects implemented in Ukraine

Place of implementation	Type and capacity of equipment	Invest-ments, thous. $	Pay-back period, years
Plywood factory Odek-Ukraine	Wood fired boiler 5 MW	430	1.8
Malin Timber Enterprise	Wood fired boiler 1.5 MW	215	3.2
Agricultural farm “DiM”	straw fired boiler 980 kW	100	4.7
Farm Agro-Oven (15 thous. pigs)	CHP biogas plant 160 kW_e+300 kW_{th}	413	8.1
Lugansk landfill (plan)	LFG power plant 1.5 MW_e	1395	3.9

3 ENERGY POTENTIAL OF BIOMASS

Table 2: Energy potential of biomass in Ukraine (2001)

Type of biomass	Energy potential, mill toe/y (moderate)	Energy potential, mill toe/y (optimistic)
Cereal crops/ straw:	2.54	3.9
Maize / stems, ears	0.83	1.70
Sunflower/ stems, husk	1.62	1.60
Manure/ biogas	1.1	1.13
Sewage gas	-	0.16
Landfill gas	0.21	1.12
Wood wastes	1.1	1.4
Fuel from MSW	-	1.3
TOTAL	**7.42**	**12.3**

*) W - mass moisture content

Fig. 2: 5 MW wood fired boiler at veneer plant Odek-Ukraine. Design of KARA, the Netherlands.

4 STATE TARGETS

According to draft version of “Energy Strategy of Ukraine till 2030” targeted utilization of RES is 6.6 mtoe (4.7% of PEC) in 2010 and 24.6 mtoe (17.5% of PEC) in 2030. Corresponding figures for biomass are 1.9 mtoe (1.35% of PEC) and 6.5 mtoe (4.6% of PEC).

5 STRATEGY OF BIOENERGY DEVELOPMENT IN UKRAINE

Table 3 summarizes data on the equipment that may be installed in Ukraine under the realization of developed strategy.

Fig. 3: 980 kW straw fired boiler in Kyiv oblast. Design of PASSAT, Denmark.

6 CONCLUSIONS

Ukraine has rather big potential of biomass available for energy production. Biomass can cover up to 9% of the total PEC.

If elaborated strategy is realized, total installed capacity will come to 9071 MW_{th} and 415 MW_e. It would result in the replacement of 4.7 mill toe/year and reduction of CO_2 emission at rate of 34 mill t/year.

Table 3: Bioenergy equipment that can be installed within the implementation of proposed conception

Type of equipment	Capacity of market, units	Installed capacity,		Operation time, h/year	Replacement of fossil fuels, mtoe/year	CO_2 reduction, mill t/year	Invest-ments, mill US $
		MW_{th}	MW_e				
Wood-fired DH plants, 1-10 MW_{th}	250	500	---	4400	0.21	0.49	38
Industrial wood-fired boilers, 0.1-5 MW_{th}	250	250	---	8000	0.19	0.45	25
Wood-fired CHP plants, 1-10 MW_e	1	10	5	8000	0.014	0.05	5
Domestic wood-fired boilers, 10-50 kW_{th}	53000	1590	---	4400	0.67	1.57	80
Farm straw-fired boilers, 0.1-1 MW_{th}	15900	3180	---	4400	1.34	3.14	254
Straw-fired DH plants, 1-10 MW_{th}	1400	2800	---	4400	1.18	2.76	280
Straw-fired CHP plants, 1-10 MW_e	1	10	5	8000	0.014	0.05	8
Large-scale biogas plants	2903*)	711	325	8000	0.93	22.36	290
Small-scale LFG power plants	90	20	80	8000	0.17	3.26	48
TOTAL	**73795**	**9071**	**415**		**4.7**	**34.13**	**1027**

*) including 2478 plants on cattle farms, 295 plants on pig-breeding farms, 130 plants at poultry factories.

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