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green oil from wet waste

EUDP Project Report – Phase 1

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1 Preface

This report covers the main results obtained in project ***Demonstration of sustainable biooil production using CatLiq technology – phase 1***. The project was supported by EUDP, having the project number 64009-0030. The partners in project are Vattenfall A/S (industrial partner) and Ålborg University (Institutional partner). The project was stated on August 1st 2009, and ended on September 1st 2010. The total project costs were estimated to DKK 20,035,000.- and the maximum subsidy from EUDP was DKK 9,378,000,-. The overall cost of the project has during the course of the project exceeded the original estimated project costs, and all funds from EUDP have been depleted.

2 Executive summary

The project ***Demonstration of sustainable biooil production using CatLiq technology – phase 1***, reached all the milestones originally set up for the project. Manure fibers were identified as the key feedstock for the plant, and a large support for the demonstration plant was experienced from the Nordjylland region, both politically and from local industrial organizations. The project resulted in a basic design for the Demonstration plant based on the selected feeds for the demonstration plant, where new and innovative solutions have been implemented hereby obtaining maximum synergies between a CatLiq plant and a Heat and Power plant. A cost estimate for the Demonstration plant was generated based on the basic design and quotations from selected equipment suppliers.

A substantial amount of work was done to optimize pretreatment and processing conditions, and the main conclusions from the experimental work can be summarized as follows:

- The results obtained with manure fibers exceed the expectations and targets originally set up for the project and new processing technologies have been tested and validated during the cause of the project.
- More than 691 hours of operation on feed and 141 mass- and energy balance measurements have been achieved by SCF in the CatLiq pilot plant in the period August 2009 – June 2010 as part of the EUDP project (Contract no. 64009-0030) entitled “Demonstration of sustainable bio oil production using CatLiq technology”.
- A loborotor? cut system was installed in the CatLiq pilot plant primo 2010 improving the pretreatment considerably
- Pump tests at Feluwa demonstrated that a 20% dry matter manure solution of manure fibers could be pumped
- In June 2010 it was demonstrated that manure fiber solutions with a dry matter content of 22 wt % could be processed in the pilot plant of SCF using a different type of feed pump.
- A MVR unit dedicated for the recovery and recycling both organics and homogenous catalyst from the effluent water phase was installed in the autumn of 2009. The recirculation of the MVR concentrate further increases the processability of the feed and has shown to have a positive effect on oil characteristics and plant economics.
- Energy recoveries in the oil phase during a 50 hours test exceeds 90 %. Similar results have been obtained for other relevant input streams and mixtures.
- Currently, processing of manure fibers result in oil with a high ash content. In order to reduce the ash content of the oil, further processing is required. Extraction of the oil with ethanol has proven to be an applicable solution, but also results in an oil loss of 5-10 %. Hence, a conservative estimate is that the net energy recovery of the feed energy in the oil phase is more than 80 %using manure as raw material.

The findings and conclusions of project have been supported by a substantial amount of documentation by SCF, where the most important documents are have been listed in Appendix A.

3 Project description

Demonstration of sustainable bio oil production using CatLiq® technology, hereinafter called "Demonstration project", is a collaboration between SCF, Vattenfall, and AAU. Purpose is evaluation, design, construction and start-up of a CatLiq® demonstration plant. The core technology in the demonstration project is SCF's patented CatLiq® technology, through which it is possible to convert wet biomass to a bio oil having a volumetric energy density comparable to that of fossil oil. CatLiq® technology and its flexibility with regards to choice of biomass has already been demonstrated in SCF's continuous pilot plant in Copenhagen. Besides the production of bio oil, the purpose of the CatLiq® demonstration plant is to prove that the technology is scalable. This demonstration step is required before an industrial implementation of the technology is possible. SCF's contribution to the project will be CatLiq® technology, IPR rights, R&D resources and know-how. Vattenfall will contribute through its detailed knowledge about heat and power generation, energy integration, focus on bio fuels, and ability to use the bio oil produced in its own power plants. AAU will contribute with expert knowledge and sparring within plant design and energy efficiency. Furthermore, the Agrorådet, Vrejlev Møllegård (supply of manure), Randers Energi and Dansk Fjernvarme are participating in the Demonstration project as subcontractors.

The partners agree that the unique features of this project are:

- Collaboration between three (3) key players within the area "energy", all three with expert knowledge on their specific fields. Joint developments between these three partners should ensure synergetic effects in the project
- Novel thinking within the field bio energy through application of the front edge CatLiq® technology using low value feeds such as de-watered manure
- A clear and well defined value chain throughout the project as both feed suppliers (Vrejlev Møllegard among others) and end-user of the bio oil are participating in the project
- Design and implementation of new and innovative process equipment(s)

3.1 Work packages

Phase one of the demonstration project is composed of 7 working packages. These cover the main issues to be dealt with during the project, and provide the basis of decision for the project partners on whether or not to continue with the Demonstration project. The working packages are as follows:

WP0: Project Management, headed by SCF

WP1: Demonstration project development, headed by Vattenfall. Focus on feedstock available for the demonstration plant, location and financing

WP2: Pilot plant testing and optimization, headed by SCF. Testing of feedstock and process optimization

WP3: Alternative alkali sources & utilization of mineral product, headed by SCF. Alternative alkalis sources and utilization of mineral product from CatLiq

WP4: Basic engineering, headed by SCF. Basic design of the demonstration plant

WP5: Feasibility study, headed by Vattenfall

WP6: Dissemination, headed by SCF

The essential reports generated in connection with the different work packages are listed in Appendix A.

3.2 Project management

The project was managed by a project group, composed of members from each project participant. A steering committee of three persons was also set in place to secure, that the project being developed would stay in line with strategic targets set. Finally, the project management was supported by a stakeholder committee, being represented by respectively feed suppliers (Rådet for Agroindustri), and potential users of CatLiq oil or customers for a CatLiq plant (Dansk Fjernvarme and Randers Energi).

4 Value proposition of CatLiq

The CatLiq technology is able to convert wet low- or no value organic waste into a bio oil, this way opening a new and flexible window of storable liquid fuels that can be used for the production of green heat and power or further upgrading in a refinery to produce transportation fuels. Conventionally, biomass such as wood and straw is burned either pure or co-combusted with fossil fuels such as coal or fuel oil to generate power. In both cases, process conditions in the boiler have to be under control to avoid fouling and corrosion. Furthermore, the steam temperature will suffer with increasing biomass content which results in a lower power output. When biomass is combusted, water in the biomass is evaporated prior to the gasification of the biomass. Besides consuming energy for the evaporation of water, the resulting water vapor phase also increases the loading on exhaust channels and emission control systems.

Wet organic waste streams have a low heating value can be converted in the CatLiq process producing a raw bio crude that can be burned in a traditional oil or coal furnace to produce heat and power. Following its origin, the bio crude is considered as CO_2 neutral and can substitute heavy fuel oil on a 1:1 basis. In other words, liquid high energetic fossil fuels can be substituted with CatLiq bio oil without a resulting loss in output from the power plant. Furthermore, the bio oil can be stored and transported making it a flexible green fuel that can be used in time and place where most value can be generated.

5 Market potential of CatLiq® technology

From an energy perspective, CatLiq bio oil should be considered as a substitute for fossil fuels such as coal, oil, and gas. Together with green technologies like wind power, solar power and 2nd

generation bio ethanol and bio diesel, CatLiq bio oil is expected to continue with the substitution of CO_2 deriving fossil fuels. Alternatively, the CatLiq technology can be used as a smart waste destruction unit which besides solving a waste problem also generates a useable and storable energy product.

5.1 Energy utilities

Energy utilities are seen as a key focus market. This means, that the initial fossil product to substitute should be heavy fuel oil, characterized by its coal black color and high viscosity. The drivers for the utilization of CatLiq oil are the mandates for renewable energy and general wishes to reduce CO_2 emission as e.g. communicated by Vattenfall. Increasing the production of green heat and power will increase the demand for typical biomass feedstock such as wood and straw, in the end impacting the cost price for the biomass feed. This means that new technologies to produce bio energy using other feed stock than conventionally used today will be required. Furthermore, bio oil from CatLiq can support irregular energy sources such as wind and solar due to the oils storability.

In Denmark, 13 PJ of different substitutable forms of mineral oil was used in central power plants, central heat and power plants, combined heat and power plants, district heating plants, private electricity production and private district heating units. This is equivalent to more than 350,000 tons of CatLiq bio oil. For comparison, the total contribution in Denmark from wind power was 25.8 PJ and the contribution from straw, wood and pellets hereof was 32.1 PJ. The market potential for CatLiq bio oil is hence significant in Denmark. On a global scale there are more than 143,000 power plants according to UDI World Electrical power on Plant Database, indicating a huge market potential for Catliq bio oil.

5.2 Waste management

Waste management is also an important market segment for CatLiq. The market can be split into three groups which are sludge from waste water treatment (municipal), Industrial waste & residue, and Municipal waste (domestic).

5.2.1 Sludge

Waste water treatment facilities that generate sludge with organics. CatLiq is considered as an alternative to drying and incineration of sludge. The benefits compared to the conventional processing will be reduced total processing cost and lower investment cost.

5.2.2 Industrial waste and residues

Industrial sectors such as agriculture (e.g. manure), food processing industry (residues from food processing/production), producers of 1^{st} generation bio fuels. Common for all is that CatLiq will improve sustainability and provide added value to co- and waste products. This will improve the overall utilization of resources and increase income.

5.2.3 Domestic waste

Companies handling municipal waste in the local community. An alternative path to utilize the energy in our domestic waste compared to conventional incineration, composting or bio gas production.

5.3 Transportation fuel

The market for liquid transportation fuels is today immense and is growing continuously. International mandates and other requirements encourage producers of transportation fuels to use bio fuels. EU has set the target of 10% bio fuels (on energy basis) as of 2020 forcing the transportation fuel producers to seek the greenest bio fuel possible produced at lowest cost possible.

6 Technology description

CatLiq is a novel 2nd generation thermal process developed by SCF Technologies. The process is able to convert a wide range of both wet and dry biomass' and residuals into a stable bio crude oil characterized by its high energy density reaching levels close to fossil oil on volumetric basis. The CatLiq process resembles the earths' natural geothermal process whereby organic material is converted into fossil fuels under high heat and pressure conditions over millions of years. In the presence of appropriate catalyst and process conditions that same process occurs in less than half an hour in the CatLiq process. In Figure 6.1, as simple illustration of the CatLiq process is given.

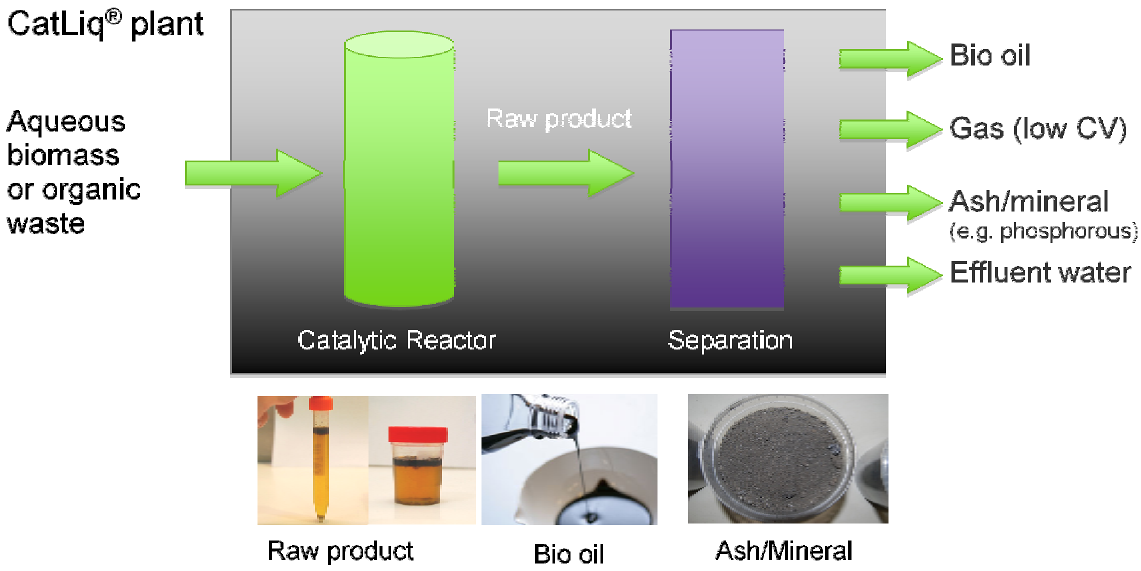

Figure 6.1: Simple overview of the CatLiq process

The organic material is converted into a bio crude in the presence of water and a proprietary combination of homogeneous and heterogeneous catalyst at high pressure (250 bars) and temperature (≤ 370^{o}C). Under these conditions water is very reactive and breaks down the organic fraction of the feed into smaller and more saturated molecules which then are reformed into bio crude, a gas phase, and a water phase containing organics. The process is very flexible and is well suited for waste streams such as sewage sludge, partly dewatered manure, fruit- and food residues etc. Furthermore, it is perfectly possible to mix different feeds in the CatLiq process this way increasing its flexibility in use considerably.

The bio crude typically has a calorific value of 35 – 37 MJ/kg on dry ash free basis (dab) which combined with a density typically between 1.0 - 1.1 g/ml results in a calorific value on volumetric basis very close to a crude oil.

The CatLiq process has been under development since the late nineties, starting under the umbrella of FLS Miljø. The basic process was demonstrated in respectively a 1 kg per hour laboratory scale unit and in a 100 kg/h pilot plant. Following this, SCF has built and operates a 20 kg/hour continuous pilot plant in Herlev, Copehagen..

6.1 Greenhouse gas savings

In the attempt to reduce CO_2 emission and reduce dependency on fossil fuels alternatives to the well know fossils fuels are sought, both for heat and power generation and for transportation fuels. A key point when evaluating a sustainable technology like CatLiq is its CO_2 reduction potential – an important parameter alongside with investment costs (CapEX) and operating costs (OpEX).

As waste streams are in focus for CatLiq, the CO_2 footprint from the feed itself is typically low to zero meaning that the major CO_2 contribution originates from the heat and power demand of the process. Other smaller CO_2 contributions will come from the catalysts and chemicals used in the process and possibly deposition cost for the ash fraction from the CatLiq system. Transportation of the feed to the Catliq plant should eventually be considered depending upon the current use of the waste stream today and the distance from the plant. In case the feed already today is transported, e.g. to a waste incineration plant, or the distance from the waste producer to the CatLiq plant is less than 50 km, the CO_2 contribution from transportation can be omitted.

For every liter of fossil fuel substituted by a liter of CatLiq bio oil the atmosphere will be saved from 2.8 kg CO_2 otherwise discharged to the atmosphere. To calculate the CO_2 reduction potential of using CatLiq bio oil, many other contributions should be considered. Following assumptions have been made in the greenhouse gas (GHG) saving in the calculation:

- No GHG emission from pig manure, i.e. nothing from transportation and production
- The CatLiq plant is integrated with NJV
- Waste water from CatLiq is used in FGD plant of NJV
- Exhaust gas from CatLiq process is combusted in Unit 3 of NJV
- CatLiq oil will be used to substitute fuel oil used by NJV

Using these assumptions, the net GHG saving is between 60-70% depending upon the oil production from the CatLiq plant – see Appendix B for more details.

One has to be careful when comparing these numbers with other numbers communicated in the literature for other substrates. The numbers used here do not take any positive contributions from the feed itself into account. In the case of manure fibers, a positive contribution from saved emissions of methane and N_2O otherwise generated if the fibers e.g. were spread out on farmland is often included in the calculations.

7 Pilot plant description

The Catliq pilot plant was put into operation in January 2007, and since the inauguration more than 2500 hours of operation on different input streams have been achieved. More than 20 different input streams have been tested, and many others have been tested in SCF's laboratory scale units. A comprehensive list of input streams tested is given in appendix 2.

The CatLiq pilot plant has a nominal capacity of 30 kg/h wet feed, but is typically operating with a feed flow in the range 10-20 kg/h as some limitations exist with respect to combinations of temperatures and residence times achievable.

The CatLiq pilot plant is typically operated with one or two shifts from Tuesday to Thursday and maintained hot by circulating water during night.

A flow diagram of the pilot plant is shown in Figure 7.1

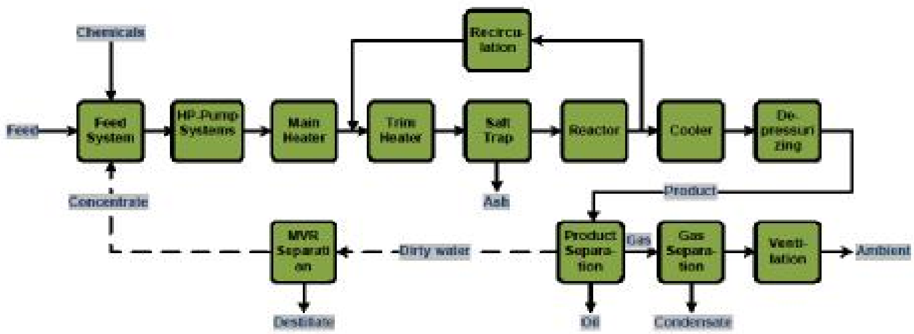

Figure 7.1: Process diagram for SCF pilot plant

8 Location and integration of demonstration plant

A key deliverable of the demonstration project was to identify the optimal location for the demonstration plant and generate the argumentation for this decision. The outcome of this work is that the optimal location of the demonstration plant is on NJV where a significant integration with the power plant is possible, see Figure 8.1.

8.1 Nordjyllandsværket selected as site

There are considerable ongoing efforts in Northern Jutland trying to promote sustainable energy technologies creating political goodwill for this type of project. Furthermore, Northern Jutland is a key farming area of Denmark generating substantial amounts of biomass waste products, which are well suited for the CatLiq process. To avoid important CO_2 emission from transportation of the waste products and the oil produced, the plant should hence be located in close proximity to the biomass waste producers and preferably on-site with the consumer of the bio oil produced.

There are no residential areas close to NJV, and there is space available on NJV to build the demonstration plant. Following this, it has been decided that the optimal location for the demonstration plant is north of Unit 2 close to the relevant connections on Unit 3, see Appendix C. This location is preferred due to the extensive integration with NJV, Unit 3 of NJV.

8.2 Integration with Nordjyllandsværket (NJV)

The possibility of integrating the demonstration plant with NJV has been developed intensively leading to several intelligent and sustainable solutions in the concept.

8.2.1 Heating

The heat to the CatLiq plant is provided by superheated steam at 7 bars and 530^{o}C from Unit 3. This solution will lead to the smallest loss of electricity generated from Unit 3, and at the same time minimize the size of the heat exchanger in the CatLiq plant. The integration cost itself is justified by the cost saved for not having to construct a separate burner system generating heat. Excess heat from the CatLiq process, in form of an approximately 150^{o}C fluid stream, is used to preheat boiler feed water for Unit 3 or for district heating.

8.2.2 Exhaust air and gas

The boiler of Unit 3 has a substantial use of primary air. A small part of this air is substituted with air from the CatLiq building covering both the area where biomass waste products are received and the production hall itself (odor). The gas fraction produced by the CatLiq process is utilized as fuel in the boiler hereby increasing the energy efficiency of the CatLiq process

8.2.3 Discharge water

The cleaned excess water from the CatLiq process is not discharged to an external waste water treatment facility, but reused as process water in the flue gas desulphurization (FGD) installation on NJV. This means zero discharge of water from the CatLiq process.

8.2.4 Use of bio oil produced

The bio oil produced is stored and used directly by NJV. Thus there are no logistic transportation costs besides power consumption of pumps. The bio oil will substitute the heavy fuel oil otherwise used by NJV, annually amounting to 8,000 tons per year. Note that the bio oil production from the CatLiq plant will not be able to fully cover this demand due to the size of the demonstration plant.

8.2.5 Control and operations

The control of the CatLiq plant should be done centrally by NJV avoiding cost for a separate control room in the CatLiq plant. Furthermore, NJV already employs skilled personnel having experience with high pressure processes. This should reduce the need for employment of additional process operators to run the demonstration plant.

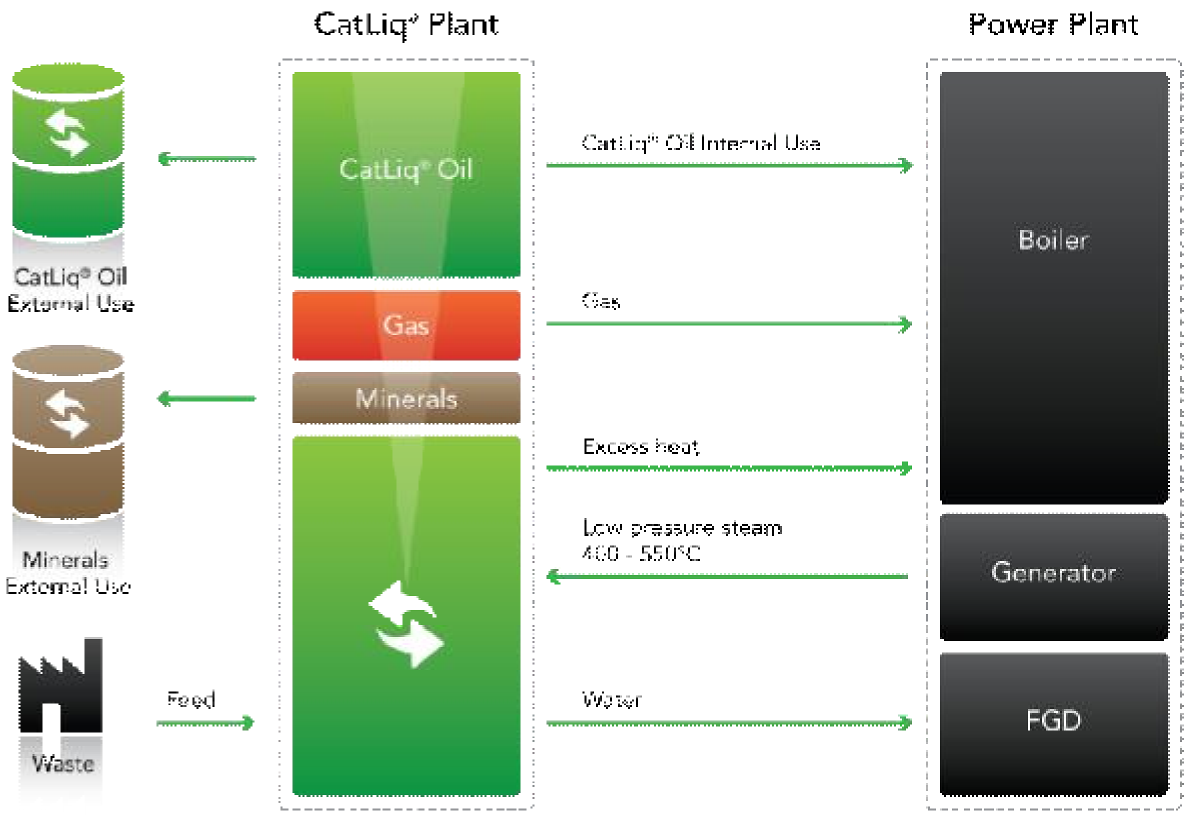

Figure 8.1: Integration of a CatLiq plant in a power plant

9 Raw materials

The CatLiq process is flexible when it comes to input material and not restricted to certain biomass components. Water serves both as catalyst and as reaction medium in the CatLiq process and thus energy for drying of the biomass is not required.

An optimal CatLiq feed should be available in large quantities locally (the CatLiq DEMO plant will be able to convert approximately 10,000 tones of manure fibers per year), have a low/acceptable price, stable supply and a low/medium ash content. In Table 9.1 potentially interesting feeds available in the local area (northern Jutland) are summarized (source: Agrorådet).

Table 9.1: Biomasses available in the local area (source: Agrorådet).

	DM content (%)	Energy content on DM basis (MJ/kg)	Ash content on DM basis (%)	Cost (DKK/ton)	Cost on DM basis (DKK/ton)	Availability (TPY)	Availability, Dry basis (TPY)
Manure fibers after dewatering	35-38	15.5	6	0	0	320,000	112,000
Manure Sludge after dewatering	18-21	21.4	14	0	0	87,000	18,000
Chicken litter	59-61	12.7	14	0 - 300	0 – 491	13,000	8,000
Whey (Perlac®)	7 or 14	15.1	10	82	586	452,400	26,700
Potato pulp	21	15.2	5	98	467	20,000	4,200
Meat and bone meal Category 1	94	13.0	41	- 60	- 64	41,250	43,890
Category 2	94	13.0	41	500	532	33,750	35,900

* DM: Dry matter

9.1 Pig manure and chicken litter

One of the most interesting feeds, abundant in northern Jutland, is manure from pigs. Due to the intensive pig farming combined with regulations limiting the amount of manure that can be spread per hectare, many farms produce a surplus of manure and therefore have problems in increasing their size of livestock. To reduce the amount of manure and improve handling, the solid fraction is separated from the liquid fraction by centrifugation. The liquid fraction, which is rich in nitrogen, is used as fertilizer on the fields. However, the solid fraction is a potential CatLiq feed. The solid fraction itself consists of a straw fraction (approx. 79%) and a sludge fraction (approx. 21%). The fiber fraction is rich in phosphorus and might be used either for biogas production or for co-combustion with straw; however the success has so far been limited. The main biomass components in the two fractions are cellulose, hemicelluloses and

lignin.
Similarly a substantial amount of litter is produced from chicken and egg production. The composition is somewhat different from the fiber fraction from manure in the way that it has a higher protein and fat content and a higher dry matter. The price varies substantially and depends on if the producer has found an alternative use for the litter, for example as a fertilizer.

9.2 Whey and potato pulp

Two by-products from the food industry, which are available in considerable amounts, are whey and potato pulp. However, both have rather low dry matter content and a price on dry matter basis that might be problematic.
Whey that is approved for fodder use is called Perlac® and is available as a 7% and 14% dry matter (DM) solution. The whey that does not fulfill the quality specifications is used for biogas production or in some cases as fodder for pigs. The biomass in whey consists almost exclusively of lactose.

Potato pulp is the residue from starch production and is sold as a fodder. It mainly consists of starch and hemicelluloses.

9.3 Meat and bone meal

Meat and bone meal is another interesting material. All kinds of animal waste are converted into fat plus meat and bone meal. The fat can be used for bio diesel production. The meat and bone meal is divided into two different categories: Category no. 1 is classified as a risk material due to potential content of CJD/BSE-causing prions and is mainly produced from dead animals that are suspected to have suffered from decease as well as dead cud-chewing animals. It is today used as combustion fuel in the cement industry. Approved combustion plants are paid about 60 DKK per ton to handle the Category 1 material. Due to the high temperature of the CatLiq process, potential prions in the material will be destroyed.

Category 2 meat and bone meal is produced from non-herbivores and slaughter house waste and may be used as a fertilizer. It costs up to 500 DKK/ton and thus is a less interesting alternative compared to Category 1. Meat and bone meal mainly consists of protein and fat. The ash content is high.

9.4 Spent brewers grain

Spent brewers grain from is another potential input stream for the demonstration plant, which has been identified in the spring 2010. Spent brewers grains are available from e.g. the Carlsberg breweries in Fredericia in an amount of approximately 50.000 tons/yr at a moisture content of 25-30 %. It has large seasonal variation with a factor of more than 3 between summer and winter as most beers are brewed and consumed in the summer time. It further has a low durability and low value (about zero costs excl. transporting costs), and alternative outlets limited for two reasons:

- The basic uptake and nutrition value for cattle are limited
- Limited need for cattle feed in the summertime

9.5 Dewatered sludge from municipal waste water plants

Sludge from municipal waste water treatment is another potential input stream to CatLiq. This fraction contains organic components, which can be converted into CatLiq bio oil. In Denmark, sludge is typically dewatered and then either incinerated or spread out on farm fields. Due to the composition of sludge (content of heavy metals and other potential health hazardous components) the amount being spread out on farm land is decreasing and the amount being incinerated increases.

10 General observations from tests in the pilot plant

The EUDP tests were initiated in August 2009 and have been an ongoing activity till June 2010. In total more than 140 mass- and energy balances have been established during this period and more than 700 hours operation have been recorded on the pilot plant.

Operation the CatLiq pilot plant on manure based feed has been a development process. Several modifications and general observations have been made. These observations are summarized below.

10.1 Size reduction

The main focus of the testing has been on the fiber fraction of manure as a basis feed for the demonstration plant. The fiber fraction of manure as received has a solid appearance though it has a moisture content of 70-75 %. The particle size of the manure fibers as received is too coarse for the pilot plant, which due to the small dimensions requires downsizing to < 1 mm. The maximum particle size is primarily set by the small dimensions of the contra valves in feed pump in the pilot plant.

At the start of the project no suitable size reduction equipment for manure was available at SCF.
Different types of size reduction equipment were rented and tested during the fall 2009 including a pearl mill, hammer mill, Loborotorcut, Gorator, macerator, and different filtering and sieving units were also tested. Further thermal and chemical pulping techniques have been tested in small scale. Though the latter techniques may have promising perspectives for increasing the dry matter content that can be processed on the longer term, they are not yet ready for implementation in larger scale.

Size reduction of the manure fibers at high dry matter content proved to be a difficult task due to difficulties in pumping the high viscosity manure fibers. Systems are available for size reduction at low dry matter content but this hampers the process performance.

In February 2010 a Loborotorcut system was installed at SCF. This system is used as the first step, and the pearl mill as the last step of pretreatment. The system has significantly increased the capacity for feed preparation.

The size reduction system for the demonstration plant has been designed from experiences at the pilot plant, and described separately in the pretreatment report.

10.2 Feeding manure based input streams

The dry matter content or more precisely the energy content of the feed has been found to impact on the oil yield. A low energy input e.g. following a low dry matter, typically results in a poor energy recovery in the oil phase.

Hence, many efforts have been directed towards operating at as high dry matter content as possible. High dry matter content for a manure based feeds also lead to viscous feeds, which has caused some troubles in the pilot plant.

10.2.1 Mechanical stirring in feed tank

Feeds to the pilot plant are prepared in the batch feeds tanks after size reduction by adding homogeneous catalyst, and a base for pH adjustment (if not the same), and for specific experiments also concentrate from the MVR unit. The stirrers in the feed tanks are designed for stirring of feeds of fluidic nature and not highly viscous feeds. Therefore the stirring of feed tanks may not have been sufficient when operating with highly viscous feeds. In practice this has resulted in some problems in dissolving the homogeneous catalyst in the sludge, and may also have caused some inhomogenity of the feed.

It should be noted that this problem is related to limitations in the current pilot plant design and has been solved in the demo plant design.

10.2.2 Introduction of viscous feed into feed pump

Another limitation of the current feeding system of the CatLiq pilot plant is the introduction of a highly viscous feed to the feed pump. The suction capability of the feed pump is limited and transport of the feed from the feed tank to the pump is performed by pressurizing the feed tank with compressed air to a pressure of about 5.5 bar. Hence, the pressure drop in the pipes and inlet valves to the feed pump determines the maximum viscosity of the feed that can be pumped in the pilot plant.

Again, this problem is related to limitations in the current pilot plant design and has been solved in the demo plant design by inserting a positive pump prior to the feed pump.

10.2.3 Pressure stability during experiments

Frequent stops of the feed pump have periodically been observed when challenging the dry matter content and viscosity of the feed. Often the problem has been solved by diluting the feed with water until stable operation could be achieved.

The result of the above is that the process pressure has sometimes been unstable and on occasions below the critical pressure for shorter periods of time.

The pressure stability has improved significantly over time, but there are experiments which either could not be completed or may have been influenced by pressure instability.

The pressure stability is further discussed below under criteria for data quality and data reduction.

10.3 Co-processing manure fibers with other input streams

A potential way of increasing the processability and/or the dry matter content of feeds based manure fibers is to co-process the manure fibers with other input streams. SCF has previously successfully co-processed e.g. protein rich input streams with input streams having a high ash content and seen synergetic effects from such co-processing.

For this reason, a number of candidate input streams for the demonstration plant have been tested both alone and in co-processing with manure fibers. Whey which is a liquid and therefore is an attractive potential candidate for increasing the dry matter content has been tested along with a number of other potential input streams.

10.4 Oil separation

The manure fibers proved to result in a viscous oil with a density higher than the water phase ("bottom oil") i.e. the oil could not be separated in the disc stack centrifuge as the case is for lighter oils produced in the CatLiq pilot plant (see chapter 12 for more details). Instead the water was decantered off.

A problem arises in this connection as the oil is mixed with the ash fraction and constitutes a thick and viscous bottom phase with high ash content. The fluidity and ash content of the oil makes it difficult to use the oil without further processing, and further makes it difficult to analyze the oil. It has been found that the oil can be extracted with ethanol, whereby an oil fraction with low ash and water content is obtained. The extracted oil was usually used for further analysis.

10.5 MVR unit

As part of the EUDP project, a Mechanical Vapor Recompression (MVR) unit was installed at the pilot plant in October 2009. The purpose of the unit was:

- to recover the homogeneous catalyst
- to clean the water phase for water soluble organics
- to recycle organic components from the water phase

The MVR unit is operated in a batch mode, and the concentrate is recycled by mixing it with the feed. Recycling of the concentrate was found to have a very positive effect on the process performance from an energy recovery point of view as will be further discussed under results (Chapter 11).

10.6 Trim heater temperature

The heating in the CatLiq plant was designed for temperatures of up to 370^{o}C. To investigate the effect of processing at supercritical conditions, extra heatning capacity was installed in the trim heater by the February 2010. Since then maximum temperature in the trim heater has been 390^{o}C.

10.7 Corrosion

No visual signs corrosion or erosion have been observed on any parts of the CatLiq plant during revision and inspections supporting the material choice Inconnel 625.

The depressurization system could have been subject to erosion as the fluid velocities in the capillaries is 10-20 m/s. However, there are no sign of erosion at the capillaries or in other part of the CatLiq pilot plant.

10.8 Fouling

Fouling of pipes and heat exchangers has been observed to be very low during during the course of the project. This is consistent with previous experience from the pilot plant. However, fouling or clogging has been observed at two local positions, which are further described below.

10.9 Clogging of capillaries

The capillaries in the depressurization system are generally working well and stable. However, clogging of the capillaries has been observed. The risk of blocking is increased when feeds having high ash contents and resulting in a so-called heavy is used. Yet the problem with clogging is especially relevant in the pilot plant of SCF due to the very small diameter of the capillary pipes. In the demonstration plant, the capillary pipes will be much larger and following this, no problems are expected with respect to clogging.

11 Pilot plant test

The characteristics of the input streams tested in the CatLiq plant are listed in Table 11.1. In addition to these potential input streams potato pulp and meat & bone meal was also tested to a limited extent. Though the potato pulp had a relatively low dry matter content (14 wt %) it turned out to be very viscous, and resulted in a low oil yield. Hence, potato pulp was skipped in the further experiments.

Meat & bone meal is potentially attractive for mixing with manure as it has a high protein content and a negative market value. Laboratory pre-tests showed that a light fluent top oil could be produced from meat & bone meal.

Chicken litter has also been investigated, but has only been tested in laboratory pretests. It seems to convert similar to manure fibers, and as chicken litter carries a higher market value than manure fibers it has not been tested further in the pilot plant.

Table 11.1: Characteristics of the input streams tested.

	Pig manure - Fiber fraction	*Pig manure - Sludge fraction*	*Whey*	*DDGS*	*Spent Brewers grain*	*Aerobic Sewage sludge (dried)*	*Sludge from industrial waste water cleaning*
Moisture content (AR)	72.0	79.0	85.8	8.7	75.7	7.5	85.0 %
Ash content (AR)	2.5	3.0	1.7	5.02	0.98	38.4	1.0
C, (ASTM D5291), wt% (DAF)	44.6	39.1	38.0	49,2	44.2	44.6	52.9
H (ASTM D5291), wt %(DAF)	5.8	5.1	5.3	6,7	5.9	5.9	8.0
N (ASTM D5291), wt % (DAF)	1.2	1.6	0.5	6,0	7.0	7.0	9.4
S (ASTM D5291), wt % (DAF)	1.2	0.5	0.1	1.0	1.5	1.5	0.4
O (ASTM D5291), wt % (DAF)	47.1	53.7	56.1	36.9	45.9	41.0	29.3
Cl, wt % (DAF)	NA	NA	NA	NA	NA	NA	0.05
HHV (ASTM), MJ/kg	13.8	15.9	14.9	20.9	17.3	13.3	24.8
LHV (ASTM, MJ/kg	12.5	14.8	13.4	16.6	16.1	12.4	23.1
Detailed ash analysis							
K, wt %	0.76	2.2	NA	1.8	NA	0.8	0.52
Na wt %	0.23	NA	NA	0.38	NA	0.1	0.22
Ca, wt %	3.4	NA	NA	0.11	NA	5.8	1.2
Mg wt %	0.26	NA	NA	0.3	NA	0.8	0.19
P, wt %	1.6	3.1	NA	1.2	NA	NA	1.8
S, wt %	1.2	NA	NA	1.5	NA	NA	2.1
Cl wt %	0.31	NA	NA	0.19	NA	NA	0.048
Al, mg/kg sample	130	NA	NA	7.4	NA	15000	240
Si, mg/kg sample	NA	NA	NA	NA	NA	NA	NA
Fe, mg/kg sample	4700	NA	NA	79	NA	21000	430
Cr, mg/kg sample	1.7	NA	NA	0.88	NA	400	14
Ni, mg/kg sample	3.5	NA	NA	0.86	NA	NA	0.86
Cd, mg/kg sample	0.036	NA	NA	0.16	NA	NA	0.02

11.1 Steady state

An experiment on manure fibers was made to establish the time needed to reach steady state conditions. A step change was made from water to feed and the pH and TOC concentration in the water phase was measured as function of time. The result is shown in Figure 11.1.

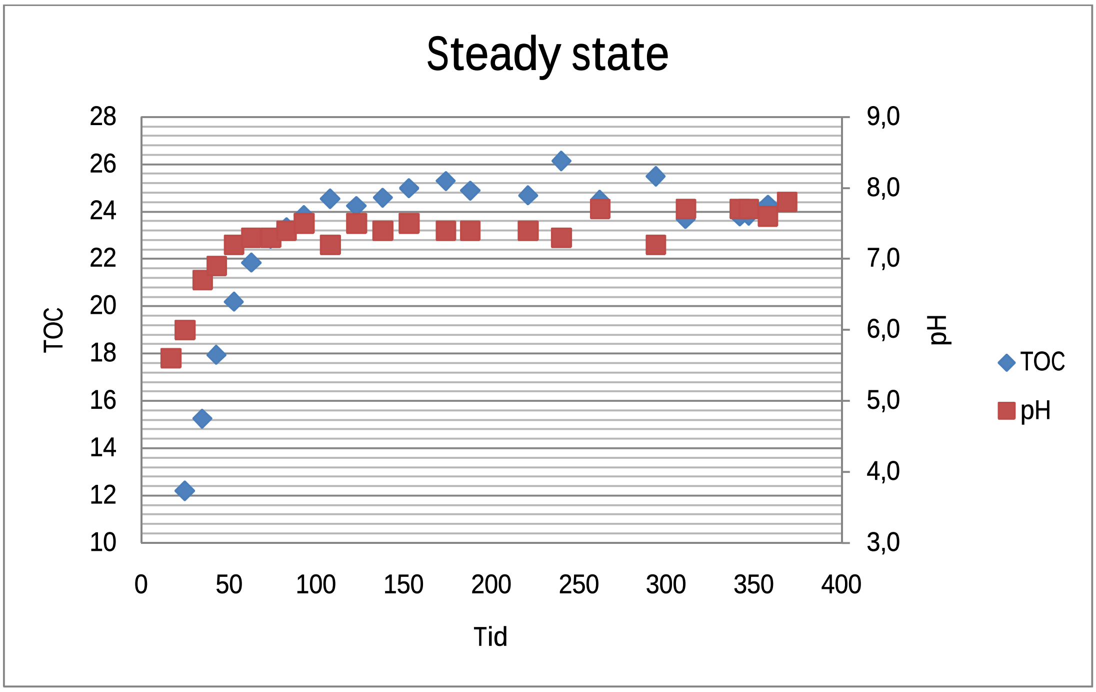

Figure 11.1: Steady state measurement by step change from water to manure based feed.

As seen on Figure 11.1, the time required to reach steady state is 2-3 hours at a flow rate of 11 l/h. Hence, it was decided that no mass balance measurements should be performed before 3 hours of operation.

11.2 Key test parameters and results

Tests in the pilot plant should result in a number or results and measurements. These are:

- Lower heating value (LHV) of sludge (pretreated biomass, ready for use in the pilot plant)
- Dry matter of sludge
- Total mass balance ($Mass_{in}$ – $Mass_{out}$)
- LHV of CatLiq oil on dry ash-free basis (DAF)
- Energy yield in oil
- Energy yield in gas
- Water content of CatLiq oil
- Ash content for CatLiq oil

The recovery of the feed energy in respectively the oil phase (Energy yield in oil) and the gas phase (Energy yield in gas) are of particular importance. In order to calculate this, the energy content in the sludge is a key parameter. For the purpose samples of pretreated feed material (sludge) was often sent to Karlshamn in order to determine the heating value. Especially in the case of manure, variations in the LHV of the pretreated feed were observed despite the manure coming from the same batch.

11.3 Results from test of pure input streams

Experiments with manure fibers have been a key focus area in the test program related to the EUDP project, as this feedstock is available in abundance in Nordjylland and hence is expected to constitute the main feedstock for the Demonstration plant.

Table 11.2: Result from test with manure fibers

Feedstock	Dry matter Wt %	Total MB (%)	LHV of oil (DAF) (MJ/kg)	Energy Yield in oil %	Energy Yield in gas %
Manure	12.8	102.6	35.1	66.6	5.5

As seen from Table 11.2, the total mass balances close to about 100 %, and the average energy recovery in the oil phase is 66%. The heating values of the manure sludge for the individual experiments varied from 10.7 to 17.1 MJ/kg with an average of 13.4 MJ/kg. No significant effects of process parameters (temperature and feel flow) were observed besides a visual improvement of the CatLiq oil phase with increasing temperature.

The other pure input streams tested were manure sludge, dairy waste water sludge, whey, municipal sewage sludge, and DDGS. The results are seen in Table 11.3.

Table 11.3: Key result from tests with other pure feeds. Values are average numbers

Feedstock	Dry Matter (Wt %)	Total MB (%)	LHV of oil (DAF)	Energy recovery in oil (%)	Energy recovery in gas (%)
Manure sludge	15.8	100	35.9	61	3
Dairy sludge	10.5	-	33.9	76	3
Whey	14.8	99	34.3	30	4
Sewage sludge (aerobic)	25.2	100.5	35.2	44	2.8
DDGS	17.2	100	35.7	71	3

As seen from Table 11.3, all feed stock except for whey shows conversion rates, which are comparable to manure. It is further worth noticing that aerobic sewage sludge was processed at a dry matter content of 26 wt % at an ash content of 44 %.

11.4 Mixtures with manure fibers

Experiments with manure fibers mixed with other input streams was performed in order to improve the processability and dry matter content of feeds based on manure fibers and to demonstrate the ability to mix different input streams. The results are seen in Table 11.4

Table 11.4: Key result from test with mixture including manure fibers

Feedstock	Dry Matter (Wt %)	Total MB (%)	LHV of oil (DAF)	Energy recovery in oil (%)	Energy recovery in gas (%)
Manure + dairy sludge	15.8	-	35.4	66	3
Manure + DDGS	10.5	100	35.6	54	3
Manure + whey	14.8	100.3	35.2	45	3.5
Manure + Manure sludge + whey	25.2	101	35.3	43.5	4

As seen from Table 11.4, it was possible to increase the dry matter content of the manure fiber based feed to approximately 20 % by substituting water used for dilution with whey. The low conversion rate seen for whey alone was however also reflected in the mixture manure + whey.

11.5 Addition of concentrate from MVR unit

The MVR unit was operated in a batch mode, where the separated water phase from an experiment was processed in the MVR. The water phase was hereby split into a distillate phase and a concentrate phase

Table 11.5 shows the key results from the experiments with recycled MVR concentrate. It should be noted that the mass- and energy balances are based on the fresh feed input (excl. MVR concentrate) to simulate a continuous process with an internal recirculation loop.

Table 11.5: Key results from test with MVR concentrate

Feedstock incl. MVR	Dry Matter (Wt %)	Total MB (%)	LHV of oil (DAF)	Energy recovery in oil (%)	Energy recovery in gas (%)
Manure	15.8	100	34.6	70	4
Spent brewers grains	10.5	93	35.5	85	-
Manure + spent grains	14.8	99	35.4	77	3
Manure + whey	25.2	100	34.3	77	4.5
DDGS		98	36.1	84.5	4

As seen from Table 11.5 energy yields are improved significantly compared to the results from the experiments without recycling of components from the water phase, see Table 11.2, 11.3 and 11.4. Furthermore, it can also be seen that spent brewers grain represent an attractive feed stock both as a basis input stream or in combination with manure fibers.

It is still too early to conclude if concentrate can be recycled 100 % i.e. if there are any compounds building up over time and thus requiring a bleed-out of the concentrate.

When processing manure and mixtures hereof, the resulting oil product is often rich in ash and salt. In order obtain a ash free oil (ash content < 2wt%), and extraction step has to be performed. This is usually done using a solvent such as ethanol. This additional step will result in an output loss, as not all of the oil will be extracted. However, the energy yield figures in Table 11.2 – 11.5 do not include any losses following the extraction step. It is estimated, that 5-10% of the oil yield will be lost in the extraction step and following this alternatives are currently being investigated.

11.6 50 hours continuous test with manure

Addition of MVR concentrate has proven very interesting and consequently, a. 50 hour test with manure and recycled MVR was performed. The test was done with a feed consisting of pretreated manure mixed with ca. 20 % MVR. The pH was adjusted using ammonia.

The produced oil was thick and heavy and the product could not be centrifuged in a disc stack centrifuge. Hence the oil was a “bottom oil” mixed with salt and ash. The mass of produced oil was estimated by measuring the water content and residue on ignition (ROI) of the “bottom oil” and hereby calculate the amount of dry ash free oil (DAF).

The energy balances were based on the pretreated manure without any additive like MVR or KOH. The energy recovery in oil was calculated as the ratio between incoming energy in the biomass and the energy in the produced dry and ash free oil. The results are presented in Table 11.6.

Table 11.6: Key results from 50 hours test with manure

Mass balance No	Dry matter Manure (Wt%)	Total MB (%)	Mass recovery in oil (%)	Energy recovery in oil (%)
EUDP-60 MB-1	14.50	98%	38%	91%
EUDP-60 MB-2	14.50	85%	35%	85%
EUDP-60 MB-3	14.50	101%	38%	91%
EUDP-60 MB-4	14.40	99%	42%	102%
EUDP-60 MB-5	14.40	101%	37%	90%

The main conclusions from the 50 hour test was that a high energy recovery in the oil phase could be achieved and that manure could be processed over a 50 hour period without processing problems

11.7 High DM manure mixtures

The maximum possible DM of the manure feed (or any other feed) has an important influence on the overall economy of the plant. The higher the possible DM, the higher the oil production from the same plant. For this reason, at lot of work has been dedicated to the development of an optimal pretreatment of manure fibers.

From project start, the Demonstration plant was assumed to be able to process manure mixtures with up to 20% DM. Yet, initially the limitation in the pilot plant of SCF was around 13% DM only. Through dedicated focus on this matter, the pretreatment of the manure was improved drastically, and testruns in the pilot plant were performed with manure mixtures with a DM of up to 22%. This number is impressive considering the very small dimensions of pipes and valves in the pilot plant. The achievement also shows, that the original target of being able to process 20% DM manure in the Demonstration plant is fully achievable and also possible to exceed. This could improve the economy of the Demonstration plant further.

12 Oil quality

CatLiq oil is a liquid fuel with high energy content. It has many similarities with heavy crude oil such as energy content, black color, and smell. The oil is formed under high pressure where oxygen is selectively removed from the biomass, mainly resulting in the by-product CO_2. It is important to note, that this CO_2 is considered CO_2 neutral as it is released from the biomass itself.

There are some differences between fossil fuel oils and CatLiq oils. Whereas fossil oils are oxygen free, water free and have a maximum nitrogen content typically around 2%, CatLiq oils still contains oxygen and nitrogen originating from the biomass and show limited solubility towards water. Traces of other inorganic compounds will also be present in the oil depending upon the feed. The simple logic is that the higher the nitrogen content of the feed, the higher the nitrogen content in the resulting bio oil – the same applies for other inorganic compounds as well.

12.1 Analytical methods

The oil analysis have been carried out either internally or by external laboratories specialized in oil analysis (Karlshamn Kraft in Sweden). The procedures are in line with internationally recognized standards. Elementary composition and ash analysis can be performed by most labs associated to the oil/fuel industry. Density, viscosity, ash content and water content are carried out in-house. Other measurements can be carried out if so is required. The content of Polycyclic Aromatic Compounds (PAH) in the oil can be measured by a combination of extraction with toluene and GC-MSD. The types of analysis performed are seen in Table 12.1.

Table 12.1: Various chemical and physical measurements used to characterize CatLiq oil

Physical	Chemical
Heating Value (external)	Elementary analysis (C, H, O, N, S) (external)
Density (external, SCF)	Composition with GC-MS (external)
Viscosity (external, SCF)	Composition with FTIR (SCF) (Fourier transform infrared spectroscopy)
Ash content (SCF)	Acid number (external)
Water content (SCF)	Stability (external, SCF)
Conradson coke residue (external)	

12.2 Light Oil

The specific chemical composition of the bio oil is different from fossil oil. A summary can be seen in Table 12.2. The typical high content of fatty acids in CatLiq oils results in a relatively high acid number and the ability to dissolve water making it difficult to make a complete dewatering of the bio oil. This might cause corrosion to storage containers and oil tubes and should be considered when choosing the material for storage containers.

A light oil is defined as having a lower density than the water phase making it easy to separate from the water phase in a conventional centrifuge. This type of oil is also named top oil. The ash content in the oil will typically be low, <2% wt. With increasing content of lignocellulosic material, , the viscosity of the oil also increases alongside with the density of the oil. Feeds having a high content of lignin, e.g. manure fibers will result in an oil phase heavier than the water phase

12.3 Heavy oil

When manure is used as feed to the CatLiq process, the resulting bio oil is an oil fraction which is heavier than the water phase. The ash content of this heavy oil is around 20%. It is important to note, that the high ash content is a results of the absence of a hydro cyclone in the pilot plant. Insertion of a hydro cyclone as planned for the Demonstration plant is expected to remove up to 95% of the particles in the fluid and hereby produce a oil fraction which has a very low ash content and consequently lower density.

It is difficult to de-water a heavy oil in a conventional centrifuge resulting in a water content in the oil of around 20%. The ash content of the oil makes it considerably more viscous and heavier than fossil oil, and the water would reduce the effective heat of vaporization during combustion if not removed/reduced beforehand. The ash and water can be reduced to an acceptable level through an extraction step.

The main differences between a light oil and an extracted heavy oil can be seen in Table 12.2

12.4 Analysis of CatLiq oils

The bio oil produced from manure in the pilot plant is not suited for direct burning in smaller plants due to the high content of ash and high viscosity of the oil. Following this, the ash has been extracted from the oil before comparison has been done with DDGS oil (Table 12.2). In this process step, the water content has also been reduced to an acceptable level as can be seen from the table. Note the small difference in density between the DDGS oil and the extracted manure oil – without extraction of ash particles from the manure oil, the density of the oil would be around 1.25 kg/dm^3.

Table 12.2 shows the elementary composition of two different CatLiq bio oils compared to a heavy fuel oil from Shell. A key difference between the fossil fuel and the bio oils is the nitrogen and oxygen content. For the bio oils, the oxygen is mainly represented through carboxylic groups, water, and ethanol in the case of an extracted oil. Yet the higher oxygen content does not seem impact the Conradson number, which indicates that the bio oils are as stable as the fossil heavy fuel oil. The lower heating value of the bio oils is also lower than for the fossil counterpart. On the positive side, the sulfur content of the bio oils is lower than in the heavy fuel oil.

Table 12.2: Properties of two different CatLiq oils and heavy fuel oil (Shell Fuelolie 77)

	DDGS CatLiq oil	Extracted manure CatLiq oil	Heavy fuel oil (Shell 77)
Lower Heating Value (MJ/kg)	35.8	35.1	40.9
C-content (%)	78.3	76.3	87.7
H-content (%)	9.3	8.9	10.7
O-content (%)	5.1	12.0	
N-content (%)	6.4	2.3	
S-content (%)	0.4	0.5	0.9
K-content (%)	0.7	2.6	
Density (kg/dm^3)	1.05	1.02	0.99
Viscosity at 40°C (cP)	499	-	700
Viscosity at 60°C (cP)	116	335	200
Viscosity at 80°C (cP)	39	-	74
Conradson number (%)	13	19	15
Acid number (mg KOH/g)	39	30	

Table 12.3: Effect of washing CatLiq oil from DDGS with water

Value	Unit	Before washing	After washing
Density, 15^{0}C	Kg/m^3	1037	1038
Viscosity, 80^{0}C	mm^2/s	48	59
Water content	% V/V	3.3	3.4
Sulfur	% m/m	0.41	0.41
Ash	% m/m	0.28	0.04
Sodium	mg/kg	30	5
Calcium	mg/kg	16	5
Magnesium	mg/kg	23	6
Phosphorous	mg/kg	672	22
Potassium	mg/kg	489	64
Net heat of combustion	MJ/kg	34.1	34.0

The ethanol extraction process has only very little influence upon the content of alkali metals in the oil as seen in Table 12.2. This is because K and Na are very soluble in ethanol, but unfortunately are left behind in the oil when the ethanol is distilled off. These components can normally be removed through a simple washing process with water, as the alkalis salts are very soluble in water. This process has been tried out on oil from DDGS, and the results are presented in Table 12.3.

The effect of the washing process is very evident on the ash content, whereby both the potassium and phosphorous content is reduced significantly. The washing process itself is a simple process widely used in the oil industry, and it is expected that the process also will be effective on extracted oil from manure.

12.5 Chemical components in the CatLiq bio oils

To determine the chemical constituents of the bio oils, GC-MS analysis of the oils have been performed. In both cases, C16 and C18 fatty acids are the dominant constituents. The chemical components are listed in order of importance in Table 4. The main difference between the two types of oil is the aromatic compounds present in the oils, both assumed responsible for viscosity and density differences between the two bio oils.

Table 12.4: Over-all results of GC-MS analysis of CatLiq oil from DDGS and Manure

DDGS CatLiq oil	Mass %	Manure CatLiq oil	Mass %
Fatty acids	64	Fatty acids	51
Pyrroles	9	Pyrroles	27
Indoles	6	Indoles	10
Phenols	2	Phenols	6
Cyclonpentenones	2	Cyclonpentenones	5
Amides	10	Amides	1
Others	7	Others	1

13 Uses of mineral product

The ash fraction leaving the CatLiq process mainly contains inorganic elements from the biomass feed such as phosphorus, nitrogen, sulfur, calcium and heavy metals.

The ash is removed in several places in the CatLiq process, which are:

- The salt trap or hydro cyclones
- The centrifuge used to separate a light oil from the water phase
- Directly from the bio oil itself via extraction

The ash fraction obtained inside the CatLiq loop (salt trap or hydro cyclone) and the ash removed in the centrifuge or from the oil directly will typically vary slightly in composition, but the ash fractions will eventually all be mixed together to form one fraction only.

The composition of the ash leaving the CatLiq system is directly related to the composition of the feed, but is also influenced by effects such as dissolution of alkali ions from the homogeneous catalyst. Furthermore small amounts of metals such as chromium and nickel in the ash do not originate from the biomass itself but are a result of wear and tear of pre-treatment equipments.

Some elements of the feed such as phosphorus are mainly recovered in the ash fraction. Nitrogen and sulfur from the biomass is also mainly found in ash fraction (S) and in the water fraction (N).

As can be seen in Table 13.1 the levels of phosphate and calcium are quite high whereas the levels of magnesium, potassium and iron are relatively low. Yet all of them are valuable plant nutrients. Thus the ash is a potentially interesting fertilizer “as is” or interesting as raw material for production of conventional fertilizers. The phosphate content in of the ash is too high to allow for use as filler in cement production like conventional fly ash.

The ash fraction from the CatLiq process is not considered as a bio ash and requires a separate approval by the authorities if to be spread out on farm land in Denmark. There is some uncertainty to how it should be classified and which regulations it should follow. Currently the ash product must comply with the rules in the “slambekendtgørelsen” and use on farm land must be approved on a case by case basis by local authorities. The specific limits in slambekendtgørelsen can be seen in Table 13.2.

Several detailed analysis of the ash fraction from test runs with manure have been performed. Whilst the ash contains PAH elements, the total value is in all case below 1 mg/kg on dry basis.

The phosphate solubility is another important aspect to consider when screening a product for its fertilizer potential as is. In order for plants to be able to utilize phosphate for growth the phosphorus must be in a water-soluble form. Most phosphate minerals used today, are almost insoluble in water and thus must be converted into a more soluble form before they can be used as fertilizers. This is done by dissolution using strong acids followed by neutralization using bases such ammonia. One of the large producers is Yara, who annually converts 700,000 tons of apatite ore into fertilizers. In comparison the Demonstration plant is expected to produce about 800 tons of phosphate rich ash annually

Table 13.1: Average composition of Some CatLiq ash phases (on dry basis)

Elements	Content	Units
Total-P	13.2	%
K	3.0	%
Na	1.1	%
Ca	18.4	%
Mg	3.8	%
Al	0.37	%
Fe	2.3	%
Zn	1164	ppm
Ba	154	ppm
Mn	1384	ppm
Cu	333	ppm
Pb	7.60	ppm
Cd	0,45	ppm
Cr	553	ppm
Ni	695	ppm
Hg	0,20	ppm
As	1.92	ppm

Table 13.2: The limits specified in “slambekendtgørelsen”

	mg / kg dry matter	mg / kg total P
Cadmium (Cd)	0,8	100
Mercury (Hg)	0,8	200
Lead (Pb)	120	10000
Nickel (Ni)	30	2500
Chromium (Cr)	100	
Zink (Zn)	4000	
Cupper (Cu)	1000	
LAS (linear alkylbenzenesulphonates)	1300	
ΣPAH (polyaromatic hydrocarbons)	3	
NPE (nonylphenolethoxylates)	10	
DEHP (di(2-ethylhexyl)phthalate)	50	

When assessing the accessibility of phosphorus the solubility in both water and citric acid is analyzed. Ash products from several CatLiq trials have been analyzed to elucidate the solubility of its phosphorus components. As expected the water solubility was rather low, 2-10%. The citrate solubility was much higher, 37-50%. This means that the ash probably cannot directly substitute a conventional type of boost phosphate fertilizer, but it might be used as an organic fertilizer that slowly releases its phosphor over time. The content of nitrogen in the ash is low and therefore separate addition of ammonium or nitrate would be required.

The content of the heavy metals in the ash samples analyzed is well below the limits in slambekendtgørelsen, except for nickel and chromium, see Table 13.2 . The rather high levels of nickel and chromium must originate from the plant equipments, especially from the pretreatment part. The content of chromium and nickel in absolute numbers is however very low and there should be no risk of mechanical weakening of tubes, heat exchangers and reactors. Nevertheless the problem must be addressed if the ash should be used as fertilizer.

According to Kommunekemi, who are developing a method for converting bio-ash to phosphate fertilizer, it is difficult to selectively remove Nickel and Chromium. As the metals are released uniformly from the surface of process components in contact with the process liquid, the total corrosion rate is determined by the internal surface are. .

14 Basic design of demonstration plant

The design of the EUDP plant is different from the pilot plant, see Figure 14.1.

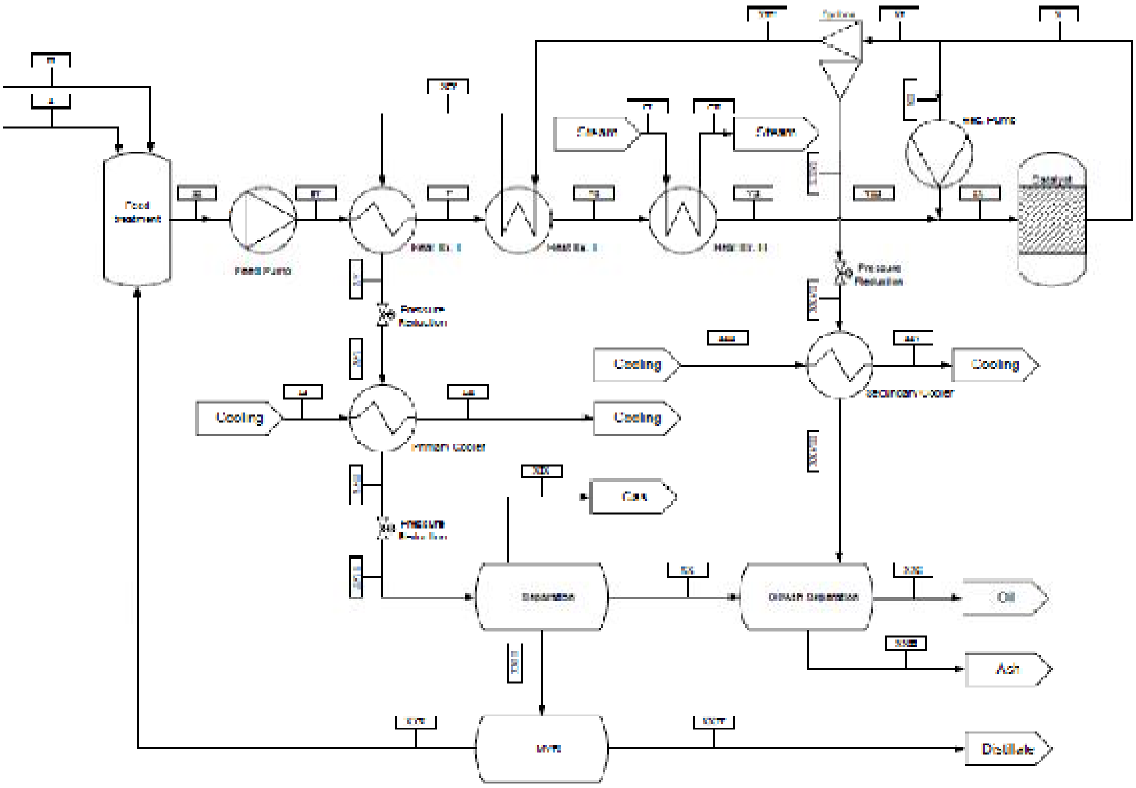

Figure 14.1. Schematic drawing of the EUDP plant

The EUDP plant is designed to have a flow through the feed pump of 6,000 kg/h and a key difference compared to the pilot plant of SCF is the use of regenerative heat exchange to reduce overall energy consumption of the process.

14.1 Pretreatment

The main purpose of the pretreatment is to change the incoming biomass into a pumpable homogeneous feed solution with the correct dry matter content, particle size and to add the chemicals required by the CatLiq process.

The water and chemicals added in the pretreatment are KOH, NaOH or NH_3 and MVR concentrate.

The main steps in the pretreatment are:

- Mixing of manure/biomass with water.

- Cutting down fibers and removal of heavy objects.
- Dewatering of feed to the correct dry matter content.
- Addition of chemicals, homogeneous catalyst and pH adjustment

In order to make the cutting down of the fibers possible and to remove larger particles, the manure is mixed with water as the first step of the pretreatment. This mixing is done in batch mixing tanks or in a continuous mixing tank, depending of the choice of supplier.

It is foreseen that the level of dry matter will be between 7% and 10% after the mixing. At this level of dry matter, the screening of particles and cutting of fibers are very easy to handle by many different kind of shredding technologies.

Finally the biomass solution is dewatered to the desired dry matter content by use of adjustable standard dewatering equipment. It is foreseen that the dry matter content in the dewatered feed will be between 18-25%. The reject water from the dewatering process together with waste water from the oil separation (MVR concentrate, see chapter 14.9), are used as mixing water in the first step of the pretreatment and the chemicals and pH adjustment will be done in this water loop.

14.2 **Feed pressurization**

The feed pump increases the pressure of the feed to the specified process pressure, 250 bars, prior to heating to ensure, that no gas phase is formed during heating.

14.3 **Feed heating**

The optimal reaction temperature for the catalytic reactions to proceed is in the range 350-370^{o}C. Fast heating is essential for the plant performance, bio oil yield and quality. Hence, heating of the feed to reaction temperature is divided into three consecutive steps in order to provide a rapid heating and re-use as much process heat as possible.

The first heater pre-heats the feed to a temperature of approximately ~150°C. The second heater will ensure that the residence time in the above mentioned region can be minimized by having a high heating rate and preheat the feed to ~315°C. The last heater will heat up the feed to the process temperature.

The heating media for the heat exchangers one and two is the hot product flow leaving the recirculation loop. The third heater is using superheated steam from NJV3 as the hot media, see also Figure 8.1.

14.4 **Reactor**

The reactor system consists of two identical fixed bed reactors, comprising a heterogeneous catalyst in a monolithic structure. Such monolithic catalyst design are known to be robust to high particles concentrations and widely used for e.g. SCR DeNOx and cleaning of exhaust.

14.5 **Recirculation loop**

The process is equipped with a recirculation loop around the reactor. The recirculation ensures a sufficiently high concentration of reaction intermediates at the entrance of the catalytic reactor. On mass flow basis the recirculation ratio is four times that of the inlet flow.

14.6 **Hydro cyclone and outlet system**

The biomass material fed to the process naturally contains inorganic material. During the degradation and conversion of the biomass feed, the inorganics are converted into different inorganic salts. Due to the near critical water conditions in the process, the solubility for most salts is very low and salts may form particles. The separation is further helped by the fact, that the density of water is very low around the critical temperature of water. The removal of solid particles takes place in a battery of hydro cyclones. The cyclones are located in the high temperature and pressure region to ensure maximum particle removal.

The cyclone has a continuous outtake from the plant. The outtake is cooled and pressure reduced in a separate stream. The separate stream is led to a downstream process separation.

14.7 **Cooling**

HeatEx2 and HeatEx1 reduce the temperature of the product significantly. Before the cooler, most of the pressure is reduced in order to reduce the design pressure and cost of the cooler. The cooler uses water from NJV3. The particles which are taken out from the cyclones are cooled in a separate cooler.

14.8 **Pressure reduction**

The pressure reduction happens in capillary pipes. The pressure is reduced by changing the length of the pipes. The length is changed automatically. This principle is used for both outtakes, both from cyclone and the main process. The pressure reduction on the main process line is split in two. Most pressure is reduced before the main cooler. The remaining pressure is reduced after the cooler.

14.9 Separation

The product coming from the high pressure zone will at ambient conditions consist of four phases: oil, water with dissolved organics, gas and ash. The product taken directly from the system (via the hydro cyclones) will be a reflection of the fluid in the pressurized system and hence contain all 4 phases. To obtain an efficient process it is crucial that the product components can be separated from each other and that the water and salt fractions can be utilized or recycled.

14.9.1 Separation of oil/water/particles

The oil itself is often heavier than the water phase. The first separation stage takes place in a horizontal separation tank based on gravimetrical separation. The heavy oil and ash will sediment and is taken out through the bottom outlet. If top-oil is present it is withdrawn through the top outlet together with the water. The heavy phase contains ash, which is removed in a centrifuge eventually combined with an extraction system. Likewise the top-oil is separated from the water-phase by centrifugation. The two oil phases are mixed together and stored before combustion in the power plant.

14.9.2 Separation of water/oil/organics

The water will be withdrawn from the top of the separator tank and subsequently centrifuged to remove remains of oil or particles. The centrifuged water phase contains dissolved organics and salts, which are feed to the MVR system. Both fractions are mainly recovered in the concentrate from the MVR, which is recycled to the process.

The distillate is water of technical quality. The distillate is only cleaned sufficiently to be suitable as water to the flue gas desulphurization (FGD) unit. If necessary the water can be cleaned further.

15 Feasibility study

The economy of a demonstration plant is critical due to high capital cost and high operational cost. The step is however mandatory to prove that the CatLiq technology is scalable and the process reliable from a performance point of view. Following this SCF investigated the capital investment costs, operational costs, and overall economic feasibility for respectively a five (5) ton per hour demonstration plant and a twenty (20) tons per hour industrial scale plant.

15.1 Capital investment (CapEx) for Demonstration plant

The CapEx estimate for the demonstration plant is covering all cost for engineering, erection and commissioning of the plant. Furthermore, civil engineering, construction of buildings, infrastructure between the demonstration plant and NJV and electrical installations and controls (using normal NJV standards for electrical installations and control for power plants) are included to provide the full picture of the cost involved when building a CatLiq demonstration plant. Quotations from equipment suppliers have been used wherever possible without considering any specific equipment requirement or sales and delivery terms which eventually will be required by Vattenfall. Based on experience from similar development and building projects, a contingency of 20% has been applied to all figures.

Using these assumptions, the investment costs are estimated to DKK 128 million. This is a net number without considering any funding from EUDP and including both development cost of training software for plant operation and expected extra engineering hours supplied by SCF due to the plant being the first of its kind. The capacity of the plant is 5 tons feed solution per hour, equivalent to about 3.8 tons manure fiber (dewatered) per hour.

15.2 Economic viability of the demonstration plant

The Plant will be a demonstration plant that is expected to run for 3,000 hours first year increasing to 6,500 hours in subsequent years. The calculations are based on the following assumptions:

- Part of CapEx to be financed by Vattenfall is DKK 65 million
- OpEx is DKK 6.2 million for heat, power, logistic, catalyst, manpower, spare parts and maintenance
- Feed cost: 0 DKK per ton, DKK 50 in transportation cost per ton (included in OpEx)
- Heat produced will be exempt from tariffs and power produced will carry a subsidy of DKK 0.15 per kWh
- CatLiq® oil production will be around 2,000 tons of oil per year (TPY) with a calorific value of 35.5 GJ/ton, based on the assumption of 6,500 hours of processing per year

- CatLiq® gas production will be 4,000 GJ per year and is burned in the boiler where it substitutes coal

- CatLiq® oil is used to substitute fossil fuel oil in heat and power production at NJV (NJV used approx. 7,000 tons of oil in 2008) where it per ton will carry a value of DKK 4,170 including value of CO_2 reduction, tariff reductions and subsidy for power production

The projected cash flow from the operation of the plant will in year two and onwards be:

Cash flow operations			
Income		**kr. 8.602.224**	
Income oil	kr. 8.339.806		
Income - gas+heat	kr. 262.418		
Production cost		**-kr. 6.232.179**	
Cash flow operations		**kr. 2.370.045**	
Ratio (CapEx/"cash flow")		27,43	years

Table 15.1: Payback time for Demonstration plant

Hence it will be possible to run the plant with a small positive cash flow per year from year four and onwards – however at an interest rate of 0% it will take approx. 27 years to return the initial investment of DKK 65 million.

15.3 Economic viability of an industrial scale plant

In contrast to the economy of a demonstration plant, which under normal conditions will have a critical economy due to relatively high investment and operating cost compared to potential production, it is absolute essential that the economy of a full scale industrial plant is attractive. The capital investment for a CatLiq plant with a capacity for 20 tons dewatered manure fibers per hour is considerable, and a potential investor needs reassurance that there will be a payback on the investment made.

To perform the calculation, a number of assumptions and estimates have to made, all having a basis in the current Demonstration plant and expectations. Following assumptions have been made prior to the calculations:

- The capacity of the industrial scale plant is set to 20 tons feed per hour, with a annual availability of 8,000 hours

- The feed is a “typical” biomass with a heating value on water free basis but ash containing basis of around 16 GJ/ton

- Energy recovery in the oil phase is 85% and dry matter used in the feed is 25%

- CapEx is estimated to DKK 220 million. The relatively low increase in CapEx compared to a 5 t/h plant is due to economies of scale having a considerable and positive influence here. Furthermore, total engineering costs and other project related costs are only expected to be minor influenced by the up scaling of the plant

- OpEx is estimated to DKK 16.5 million covering cost for heat, power, logistic, catalyst, manpower, spare parts and maintenance

- Feed cost are set to 0 DKK per ton, but a cost of DKK 50 in transportation cost per ton is applied (included in OpEx)

- Heat produced will be exempt from tariffs and power produced will carry a subsidy of DKK 0.15 per kWh (green electricity)

- CatLiq® oil production will be 14,000 tons of oil per year (TPY) with a calorific value of 35.5 GJ/ton, based on the assumption of 8,000 hours of processing per year

- CatLiq® gas production will be 30,000 GJ per year and is burned in the boiler where it substitutes coal

- CatLiq® oil is used to substitute fossil fuel oil in heat and power production where it per ton will carry a value of DKK 4,170 including value of CO2 reduction, tariff reductions and subsidy for power production (2008 figures)

Cash flow operations		
Income		**kr. 60.274.453**
Income oil	kr. 58.378.640	
Income - gas+heat	kr. 1.895.813	
Production cost		**-kr. 24.515.947**
Cash flow operations		**kr. 35.758.506**
Ratio (CapEx/"cash flow")		**6,15 years**

Table 15.2: Payback time for industrial scale plant (20 tons/hour)

Besides the lower investment cost per ton of oil produced, the main difference in the full scale scenario compared to the Demonstration plant are:

- Higher energy recovery levels (85% instead of 70%)

- Higher dry matter in feed (25% instead of 20%)

- Higher availability of plant on annul basis (8,000 hours instead of 6,500)

A more detailed analysis of the figures is illustrated in table 15.3

Cash flow operations	**Key figures - Base scenario**
Oil production (tpy)	**14.000**
Production cost	**(24.515.947)**
Feed cost incl. Transportation	(8.000.000)
Heat	(2.356.347)
Power	(3.609.600)
Catalyst	(6.000.000)
Operators	(750.000)
Service and maintenance	(3.800.000)
Income Gas and Excess heat	**1.895.813**
Increased power production due to pre-heating of boiler water	300.800
Savings on coal due to gas combustion	662.353
Value CO2 reduction	337.660
Subsidy per kwh	595.000
Income from oil (per ton of oil)	**4.170**
Value of Catliq oil substituting fossil oil (adjusted for heating value difference)	2.246
Value CO2 reduction	328
Reduced energy tariff (heat)	1.034
Subsidy per kwh	562

Table 15.3: Detailed analysis of industrial plant

As expected, the figures for the industrial plant are attractive and present a very different picture compared to the Demonstration plant. Some of the assumptions have not been validated yet, but considering on-going and future research activities within CatLiq the ambitions are considered as realistic.

A variation of parameters will have a direct effect on the economic feasibility calculations. To illustrate this, different scenarios have been considered this way indicating both up-sides and down-sides to the presented plant economy. The variations made are:

- Variations in oil production per year. Possible through changes in dry matter of feed, feed energy , ash content, maximum dry matter, and energy recovery, see figure 15.1
- Variations in CapEx cost for 20 t/h plant, see figure 15.2
- Variations in feed cost (DKK/ton), see figure 15.3
- Variations in value of CatLiq oil. Possible through changes in fossil oil prices, see figure 15.4. Changes can also occur through changes in “green” subsidies (CO2 value, green electricity, etc), but this is not considered here

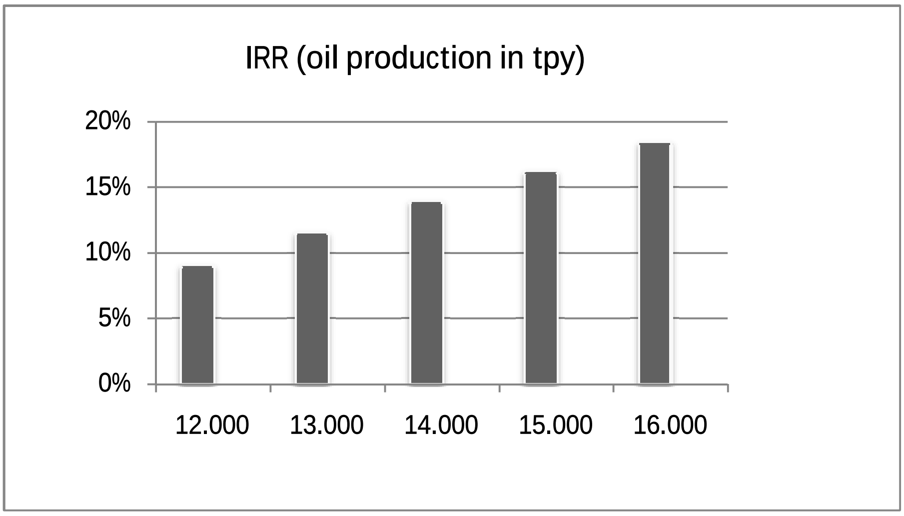

Figure 15.1: Effect of oil production

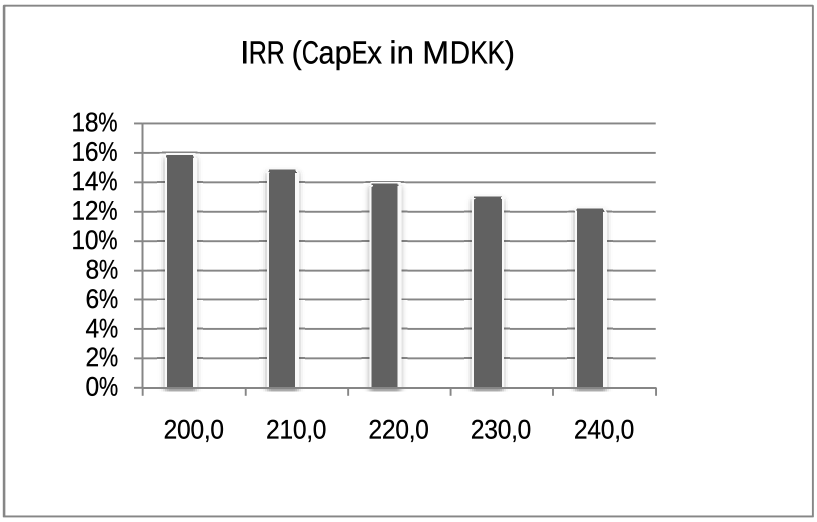

Figure 15.2: Effect of CapEx

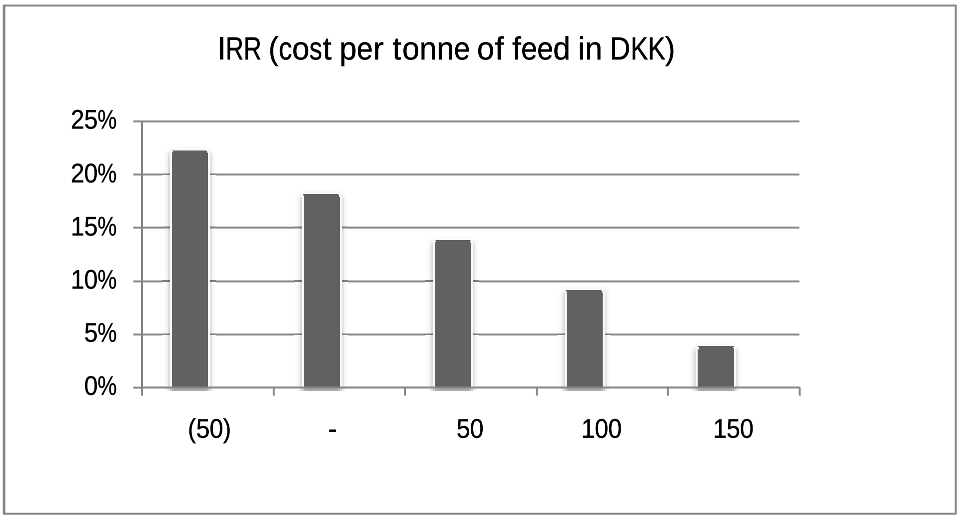

Figure 15.3: Effect of feed cost

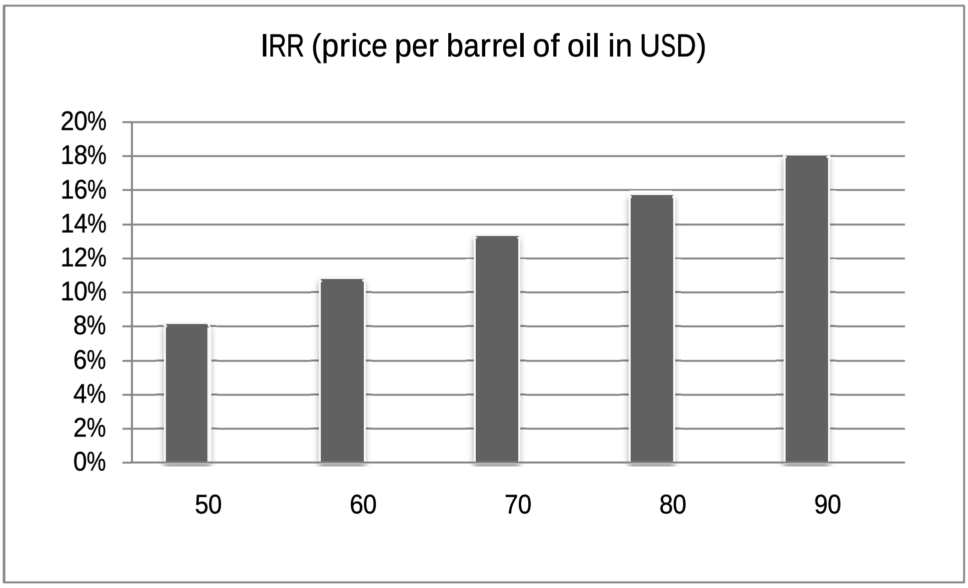

Figure 15.4: Effect of oil price, subsidy system unchanged

The general conclusion from the analysis is that the economy of a 20 ton per hour CatLiq plant looks attractive. The attractiveness is dependent upon many external factors where feed cost and green value of the bio oil play a major role. Especially the latter is a key factor to establish a market for a green bio fuel like CatLiq bio oil and to create confidence at the investor. The subsidy for green heat and power produced should hence be comparable to subsidies applied for competing technologies such as e.g. biogas.

16 Conclusion

An intensive test- and development program has been executed over the period August 2009 to July 2010 with the purpose of preparing a basic design for a CatLiq demonstration plant and providing technical and economic documentation for the process to the extent possible. The project has resulted in the necessary data to support the basic design and feasibility study of a demonstration plant.

The achievements of the project have on several occasions exceeded the original targets set by the project group, and SCF has increased its knowledge about lignocellulosic feed and conversion hereof considerably during the cause of the project.

17 Change log

Date:	Init.:	Vers.:	Page or paragraph	Short description of change or revision
				Document created