FINAL REPORT

Part 1

CONTRACT N° : ENK5 – CT2002 – 00675

PROJECT N° :

ACRONYM : DETAR

TITLE : Degradation of Tar-water from Biomass Gasification

PROJECT CO-ORDINATOR : Babcock & Wilcox Volund (VRD) – DK

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Executive publishable summary

Biomass gasification product gas is often wet scrubbed or cooled to remove tar and particles before use in gas engines and even for dry gas cleaning it is necessary to perform a final cooling process. Because of the considerable amounts of water vapour in the product gas, contaminated water will be produced (even the best schedules do not completely remove all traces of tars and particles) and these effluents will result in environmental problems if not cleaned before discharged to the urban sewerage network.
The overall objective of the present project is to evaluate the full-scale application of supercritical wet oxidation and gasification (SCWO/G). The process under study refers to the aqueous oxidation/reduction of organic contaminants at pressures and temperatures above critical data for water. The use of the developed technology can improve the electric efficiency of biomass gasification based Combined Heat and Power (CHP) and therefore reduce energy production related CO_2 emission. When biomass utilisation is increased in this way it will be possible to create local employment for the handling of the biomass fuel and also for the actual operation of the plant.
In the project, waste water, from an updraft gasification based CHP plant, is used. The experiments are carried out at both laboratory scale (2 kg/h unit) and pilot scale (50 – 60 kg/h Process Development Unit - PDU).
From January 2003 to December 2005 more than 300 samples were analysed by IWC. Feedstock, liquid products and gaseous products were characterised and quantified. Different methods have been available for the analysis of tar-water. The methods are approved for Bio Crude Oil (BCO) at IWC. The aqueous matrix of the tar-water was a challenge, and therefore the analysis methods needed further developments and adaptations. This was solved in the early stages of the work performed by IWC.
First of all, the storage stability of the feedstock was tested under different storage conditions for six weeks. Only small changes in the composition were observed, thus the transport and storage of the samples were no problem.
The first series of experiments were conducted on the lab scale unit, and covered both Super Critical Water Gasification (SCWG) and Super Critical Water Oxidation (SCWO).
The knowledge and the results from these experiments were used for the construction of the process development unit, and the establishment of the global kinetics of TOC (Total Organic Carbon) gasification and oxidation in SCW has been estimated. An analysis of the species concentration for the feedstock and the products of SCWG of waste water, measured in WP1, have lead to identify the main reaction paths. Also kinetic constants have been evaluated for the decomposition/gasification in SCW of the dominating tar compounds. Moreover, a transport model has been developed and validated for the PDU (pilot scale reactor) using the measurements carried out in WP2. Process simulations have been made for different operating conditions and with and without the presence of catalysts. Extensive parametric and sensitivity analyses have been performed to assess the role of process parameters.
A software tool has been developed in order to assist the engineers in the design of an up-scaled reactor as a part of the work in WP3, and the basic economic figures of a full scale plant covering the needs of a plant of the size of the Harboore gasification plant, are described in WP 4.
The economic figures, for the treatment of 1 ton of waste water from the updraft gasification plant, have been estimated in WP4. The price is lower than the one for treatment of liquid hazardous waste, but still too high for the biomass gasification plants, as the treatment will consume almost 2/3 of the income generated by the sale of electricity produced on the biomass gasification plant (based on the Danish prices for electricity produced on biomass).

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Acronyms and abbreviations

Some acronyms and abbreviations used are defined locally in the report, but for convenience a list is given below:

CHP	Combined Heat and Power
DETAR	Project Title acronym: Degradation of Tar-water from biomass Gasification
EXCO	Executive Committee
GC	Gas Chromatograph
HGO	Partner Henrik G. Olrik Engineering (DK)
IWC	Partner Institute of Wood Chemistry (D)
KK	Partner Kommunekemi (DK)
LSU	Laboratory Scale Unit
MS	Mass Spectrometer
PC	Personal Computer
PDU	Process Development Unit
PTA	Project Technical Advisor
RES	Renewable Energy Source
SCW	Super Critical Wet …
SCWG	Super Critical Wet Gasification
SCWO	Super Critical Wet Oxidation
TOC	Total Organic carbon
UNINA	Partner University of Napoli (I)
VRD	Partner Babcock & Wilcox Volund R&D Centre (DK)
WP	Work Package

Objectives and strategic aspects

Contribution to EU policy needs

Biomass is in the long term perspective scheduled to become a significantly used fuel for efficient environmentally friendly Combined Heat and Power (CHP) production in Europe. Important examples of initiatives are: The White Paper (1997), the Kyoto Protocol (1997), the Green Paper (2000) and the proposal for a Directive "On the Promotion of Electricity from renewable Energy Sources in the Internal Electricity Market" (28/12 2000).

Many of the CHP technologies presently being developed for biomass energetic utilisation are based on gasification and the basic problem of efficient and environmentally friendly cleaning of producer gas for use in gas engines and gas turbines still causes considerable troubles.

The most feasible way for cleaning the producer gas seems to be through wet gas cleaning, where applicability with gas engines has already been verified.

Biomass gasification product gas may be wet scrubbed or cooled to remove tar and particles before use in gas engines but even for dry gas cleaning based processes it is necessary to perform a final cooling process. Because of the considerable amounts of water vapour in the product gas, contaminated water will be produced and these effluents will result in environmental problems if not cleaned before discharged.

In this project a novel approach for cleaning of tar contaminated water derived from wet gas cleaning systems will be analysed and verified for industrial application based on previous introductory experiments with a Laboratory Scale Unit (LSU). The new process – DETAR – appears to offer energetic and capital/operational cost advantages to processes already available and DETAR can therefore be considered an important contribution to the European energy policies, specifically the doubling of the RES share of energy production by 2010.

Socio-economic perspectives

On another level the DETAR technology will make increased use of agricultural and forestry residues in the power production industry environmentally more feasible if fully developed. This will lead to a possible increase in the employment of local people in this industry, because the rational utilisation of biomass waste will require the development of an infrastructure.

Specifically, this may lead to:

- An increase in the profits of agricultural/forest areas, where residues can be sold
- A reduction in the unemployment in rural areas through jobs in a new sector of power production from biomass
- A development in decentralised activities, thus avoiding depopulation of areas already neglected
- New job possibilities by a change in the agricultural production through biomass cultivation instead of surplus food production

Improving the quality of life and the social standard in these communities and environments will consequently over time lead to improvements in health and living conditions in general.

While these futures are true for most schemes aimed at improved energetic utilisation of biomass, the present project indicates a means of really making them happen. The technology to be developed in the DETAR project for industrial application is not exclusively aimed at supporting the gasification technology primarily marketed by one of the partners (namely, biomass updraft gasification including wet gas cleaning) but is considered equally applicable for other gasification technologies as well and further for general cleaning of contaminated industrial discharge water. Especially effluents from industries, that wish to secure that their waste water is treated in isolated facilities and at high temperatures, are considered as an interesting market application. Therefore, the size of the market for

application of the technology is considered very large and may eventually create extra job opportunities in the manufacturing industry.

Scientific/technological objectives

The overall objective is to evaluate the full scale application of supercritical wet oxidation/gasification (SCWO/G). Indeed liquid effluents from biomass gasification plants are too dilute to incinerate and yet too toxic for bio-treatment. The process study refers to the aqueous oxidation/gasification of organic (and inorganic) materials at pressures and temperatures above the critical data for water. More specific objectives are:

1) to characterise the chemical composition of waste water from updraft gasification of wood (in particular, light tar components which are soluble in water and therefore difficult to remove),
2) to apply and optimise SCWO/G of such waste water at laboratory (2 kg/h) and pilot (50 kg/h) scale,
3) to formulate kinetic and transport models for the SCWO/G process including validation and process simulation,
4) to provide a chemical characterisation of the effluent water from the SCWO/G process,
5) to extend the results of the analysis carried out for the effluents (of a wet gas cleaning process) from a 5 MW_{TH} updraft wood-chips gasification based CHP plant to other gasifier configurations and other gas cleaning technologies, based on literature information,
6) to provide a full scale evaluation of the process for both the technical (energetic and environmental) and the economic aspects.

Scientific and Technical performance

DETAR project overview
The project is structured into several Work-Packages:

Work Package 0: Process development unit (PDU)
(this WP is not included in ENK5-CT2002-00675, but the status is important for that project)
In WP0 a Pilot Scale Plant (or PDU) will be designed, built, installed and preliminary tested at partner KK. The capacity of the PDU is anticipated to be 50 – 60 kg/h of tar contaminated wastewater and the design is based on the experiments of WP2 (SCWO/G at Laboratory and Pilot scale) using the already existing Laboratory Scale Unit (LSU) to be operated and optimised in that WP. The PDU will be used for further experiments in WP2 and – together with the simulation results of WP3 (Kinetic and mathematical modelling) – to evaluate the operation and economy for a full scale application in WP4 (Full Scale implementation).

Work Package 1: Chemical characterisation
In WP1 a detailed chemical characterisation in terms of composition and amounts of the contaminants present in both raw tar-water from biomass gasification product gas cleaning and in wastewater cleaned using SCWO/G technology will be provided. Also the global kinetic mechanisms of tar-water degradation will be formulated. The work will be based on raw tar-water from an updraft biomass gasifier operated by partner VRD and cleaned wastewater from the Laboratory Scale Unit (LSU) and Process Development Unit (PDU) operated in the DETAR project.

Work Package 2: SCWO/G at Laboratory and Pilot scale
In WP2 the Laboratory Scale Unit (LSU) and the Process Development Unit (PDU) will be operated to determine the influence of temperature, pressure and residence time on the super-critical gasification and combustion of organic pollutants in tar-water. The 2 experimental units will be used to establish the optimal operation variables (reactor throughput and acidity of feed, catalytic effects, etc.). Also the extension to other gasifier configurations (than biomass updraft gasification) and gas cleaning systems will be studied. The work is closely supported by WP1 (Chemical Characterisation) and important for WP3 (Kinetic and Mathematical Modelling). Also, the initial experiments using the LSU are important for the design developed in WP0 (Process Development Unit).

Work Package 3: Kinetic and Mathematical modelling
In WP3 kinetic constants for the global mechanisms of wet oxidation/gasification of tar-water at supercritical conditions will be estimated based on information from literature and the results from WP1 (Chemical Characterisation). Also, a model for the three-zone (pre-heater, supercritical reactor and reaction chamber) system of waste water treatment will develop on two levels: A comprehensive Mathematical Model and a simplified Mathematical PC-tool. The mathematical model will be validated based on data from WP2 (SCWO/G at Laboratory and Pilot Scale) and the SCWO/G process will be simulated for parameter sensitivity and scale-up purposes, to be used in WP4 (Full scale implementation).

Work Package 4: Full scale implementation
In WP4 the process characteristics determined at pilot scale and the simulations of the process carried out through the computer model will be used for the preparation of a full-scale layout for 1000 kg/h. It is anticipated that the industrial application will be based on five units of 200kg/h. This work will include capital/operational cost and heat/mass balances. Furthermore, the results of the chemical and biological compatibility on waste water) will be used for an evaluation of environmental impact caused by a power system based on updraft wood/biomass gasification, wet gas cleaning and supercritical gasification/combustion of tar water. Finally, a comparison will be provided for alternative solutions based on different gasification units/gas cleaning systems.

Work Package 5: Co-ordination and Reporting
The objective of WP5 is to provide an effective and efficient project management in order to meet deadlines and targets established for each Work Package
The DETAR project will be co-ordinated by partner VRD, who will be responsible for Handling of all communication with EU, Ensuring that relevant communication is distributed, Ensuring that project deliverables are available on time and Organising and chairing of the Executive Committee Meetings (EXCO meetings).

In the following paragraphs the Scientific and Technical performance in the DETAR Work Packages is reviewed.

Work Package 0: Process development unit (PDU)

The work package 0 is not a part of the EU-funded project, but it is mentioned here to give basic understanding of the work performed in the DETAR project. In the early stages of the DETAR project, the experimental work was performed on a laboratory model that could handle 1 l/h of wastewater. As planned from the start of the project, the planning and building of the Process Development Unit was started along with WP 1 at the start of the DETAR project. Results and know how from these early experiments, were used in the design and built Process of the Development Unit. The building of the Process Development Unit was partly financed by the Danish Energy Agency and partly by the 3 Industrial partners in the current project.

The baseline design for the PDU is specified by:
- Wastewater (at 40°C) at a flow 60 (kg/h) of which 55 (kg/h) is discharged as distillate and 5 (kg/h) as remanence (water contaminated with soluble salts and organic compounds)
- Operation pressure 250 (bar) and a reactor temperature of 550°C
- A reasonable level of heat recovery in the upper heat exchanger (i.e. an assumed effectiveness of 70%)

The PDU – which is now installed at partner KK – is shown below:

In the PDU Frame the reactor is mounted vertically with the gas/liquid separators (right) and control and data acquisition system (left) in the front. The pump/motor assembly is placed in front of the PDU Frame.

Picture 0.1: SCWG/O Product Development Unit installed at Kommunekemi DK.

In view of a preliminary optimisation of the energetic performance, it was decided to carry on with SCWG experiments until September 2004. At the end of this period the modifications for the

subsequent SCWO experiments was implemented. After a commissioning and fault finding period, a test session covering SCWO was performed at the beginning of December 2004.

After this test the reactor was dismantled in order to gain knowledge about the reliability of the materials used for the construction of the reactor.

In general things looked fine but there was a problem with some off the heating elements, so new ones had to be installed. A rebuild of the PDU was performed, and the line of SCWO-experiments were continued and conducted as planned.

Work Package 1: Chemical characterisation

Storage Stability

The first tar-water sample (the actual feedstock for the SCWG/O processes) was delivered by Babcock & Wilcox Volund in order to test the storage stability under different storage conditions. Aliquot parts of the sample were taken and stored for six weeks under two different conditions: (1) cool and dark (refrigerator); (2) room temperature and daylight.

Changes were monitored by comparison of the GC/MS results with the initial feedstock sample. The most obvious differences were observed at room temperature and daylight (Figure 1.1).

Most prominent variations

1 Hydroxypropanone
2 Propanoic acid
3 2-Hydroxy-2-
   cyclopenten-1-one
4 1,2-Benzenediol
   (=Catechol)
5 4-Methyl-catechol
6 Guaiacyl acetone
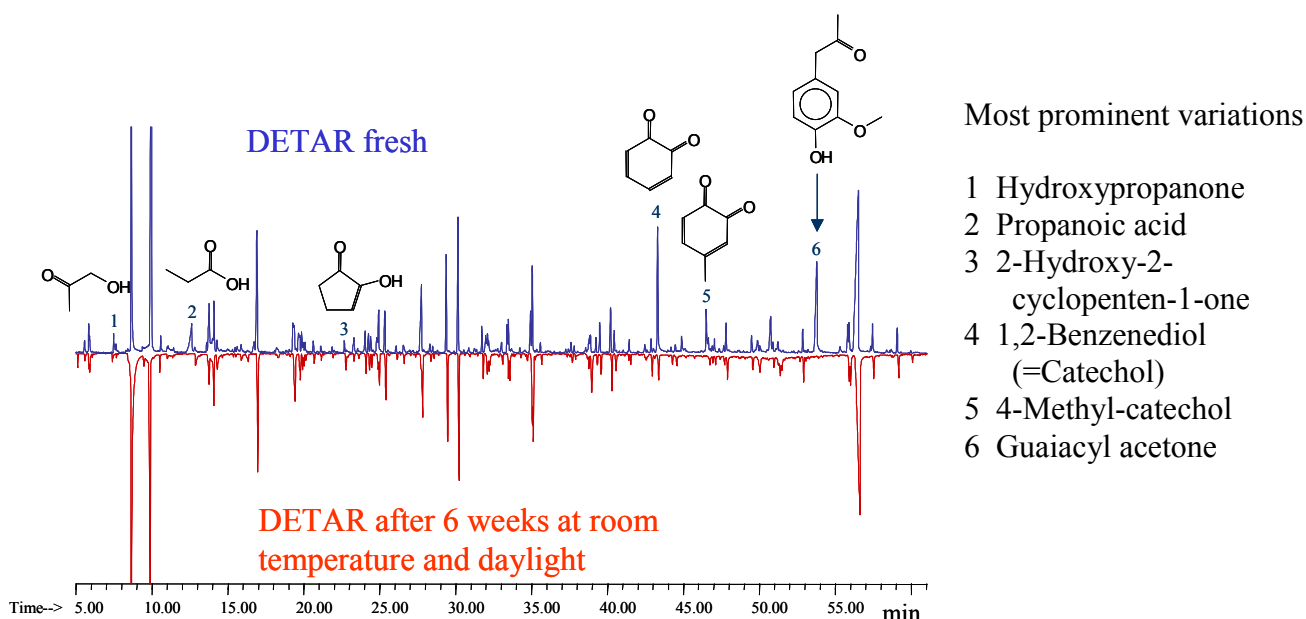
Figure 1.1: Storage stability of first tar-water sample

In conclusion, the composition of this first sample is not changing very much, only some components of the whole composition have altered their concentrations. Therefore, no analytical problems are expected due to transportation from the Danish to the German partner or in relation to using the same basic feedstock for the completion of the experiments.

SPE-Tests

The first delivered sample of the tar-water (feedstock) was subjected to SPE (Solid Phase Extraction) experiments, in order to establish a list of compounds in the feedstock. SPE cartridges with different retaining mechanisms were tested to fractionate the feedstock. Apart from C18 material, also a SAX (strong anionic exchange) and a MAX (medium anionic exchange) were tested. Unfortunately, not all substances that were applied on the anionic exchange SPE cartridges could be recovered. They did not elute even by using hydrochloric acid.

The C18 material seems to be best suited to divide the tar-water into fractions. For the non-retained

components other separation mechanisms were tested. However, due to the aqueous matrix of the DETAR samples, only reversed phase materials can be applied.

The fractionation of the samples helped to identify the constituents for the first time in the feedstock.

Identification of components

The first delivered samples, which were not only produced in gasification but also in oxidation mode, were analysed to find the constituents (experiment 3.01 – 3.12). The components in the feedstock as well as products from the gasification and the oxidation mode were analysed (Table 1.1 show the identified substances in the feedstock).

Table 1.1	Identified substances of feedstock (after SPE) (31 substances)
1,2-Benzenediol (++)	Acetic acid (+++)
1,3-Benzenediol (++)	Cyclopentanone (+)
1,4-Benzenediol (++)	Dihydro-2(3H)-furanone (++)
1,2-Ethanediol (+++)	Dihydro-5-methyl-2(3)H-furanone * (+)
1-Hydroxy-2-propanone * (+++)	Dihydroconiferylalcohol (+)
2,5-Hexandione * (+)	x,y-Dimethyl phenol (+)
2-Acetylfurane * (+)	Dimethyl-2-cyclopenten-1-one * (+)
2-Butanone (+)	Furaldehyde-2 * (+++)
2-Cyclopenten-1-one (+)	Guaiacyl acetone (+)
2-Hydroxy-3-methyl-2-cyclopenten-1-one * (+)	m-Cresol (++)
2-Methyl-2-cyclopenten-1-one * (+++)	o-Cresol (++)
3-Hydroxy-2-butanone (+)	p-Cresol (++)
4-Ethyl guaiacol (+)	Phenol (+++)
4-Methyl guaiacol * (++)	Propanoic acid (+)
5-Methyl-2-furaldehyde * (+)	Tetrahydro-(2H)-pyran-2-one (+)
Acetaldehyde (+)	

amount: (+) low, (++) medium, (+++) high

Gaseous samples

In the beginning of the DETAR project the storage of the gaseous samples was a problem. The first gas samples were delivered in two connected plastic syringes for storage and transport. The main problems were differences in CO and CO_2, compared to the analyses made by Kommunekemi . It was noticed by pressure differences that gas diffusion took place through the plastic material. These plastic syringes are not hermetically sealed for gas samples Therefore; the results from IWC were not comparable with those from KK. Hence the gases were filled and transported in appropriate bags, produced by "LINDE", which made it possible to store and transport the gaseous samples without noticeable losses.

In gasification mode, different gases were identified and quantified (CO, CO_2, methane, higher hydrocarbons), in oxidation mode almost all organic substance is converted into CO_2.

Hydrogen could only be analysed by KK, not by IWC, because helium was the only allowable carrier gas for the gas chromatograph. The thermal conductivity of helium is similar to hydrogen and during the analysis process it is not possible to distinguish clearly among the two gases.

WP1 conclusions

- The storage stability of the feedstock was analysed. After 6 weeks storage at room temperature and daylight the composition of the feedstock showed only minor changes.
- The components of the feedstock as well as products from gasification and oxidation were identified.
- Several major constituents are detected (e.g. levoglucosan), which are only present in the feedstock. They are completely destroyed by heating to super critical state.
- Other substances (e.g. furaldehyde-2) are destroyed by increasing temperature in the reactor chamber.
- In gasification mode there are many components in the liquid samples detectable. Their amounts are mostly decreasing with higher temperatures.
- In oxidation mode it can be seen that acetic acid is the most stable constituent or a product of the reactions. Its amount is increasing under sub-critical conditions (bleed off samples) and is almost completely destroyed under supercritical conditions.
- In oxidation mode almost all organic substance is converted into CO_2, corresponding to the level of TOC.
- The components of the feedstock, product liquids and bleed offs from several experiments were quantified. Therefore a 3-point-calibration for 60 different components was done.
- Latest experiments showed excellent cleaning effectiveness. All substances except acetic acid are destroyed. Its amount is increasing under sub-critical conditions and decreasing under supercritical conditions. At higher temperatures also acetic acid is destroyed.

Work Package 2: SCWO/G at Laboratory and Pilot scale

Prior to this project, a series of test was performed on the laboratory scale unit (LSU). The tests were performed in order to get some indications about the possible potential of the super critical wet gasification (SCWG) and oxidation (SCWO) process in relation to cleaning of waste water from upstream gasification of biomass.

The experiments were performed on equipment designed for relatively low concentrations of organic pollutants, and the flow pattern inside the reactor was unknown, so the results where only to be regarded as indications about the efficiency of the method when used on the waste water.

Results from the tests showed that there was a reduction of approx. 50 % measured on TOC (total organic carbon) when the reactor was performing in SCWG-mode and in SCWO-mode the reduction was approx. 95 % measured on TOC.

The results of the early work were considered promising, and it was decided to expand the work of super critical water processes, both in terms of gasification and in terms of oxidation, which lead to this project. It was decided to use the LSU for the chemical and kinetic experiments needed in order to establish a mathematical model for the process.

For the use in this project the characteristics of the reactor needed to be known, so the first part of the work on the LSU was performed in order to do so.

Characterisation of the LSU reactor

To gain knowledge about the characteristics of the reactor, a series of experiments where planned. The following topics where considered as the most important:

> Average retention time in the reaction zone

> The degree of mixing in the reactor zone

The test runs where planned as follows: The LSU was started and brought to the desired temperature and stabilised. The start up where performed using clean water. When stabile conditions where attained, the feedstock was changed from clean water to a mixture containing dyestuff and phosphoric acid.

Samples where taken consecutively from both liquid streams at pre-determined intervals, in most cases sample-time was chosen to be one minute.

As an example the Figure 2.1 below gives a picture of test run 3, which is performed at 500°C. The curves show the degree of absorption created by non-degraded dyestuff in relation to the accumulated amount of product flow.

The concentration of unreacted red dyestuff is obtained from absorption measurements using a spectrophotometer (Thermo Spectronic, Helios ε) with a 1 cm cuvette. Distilled water is used as a blank. The dyestuff exhibits maximum absorption at 510 nm (figure 3), however, due to contamination of some of the samples, the average from 450 to 490 nm is used in stead.
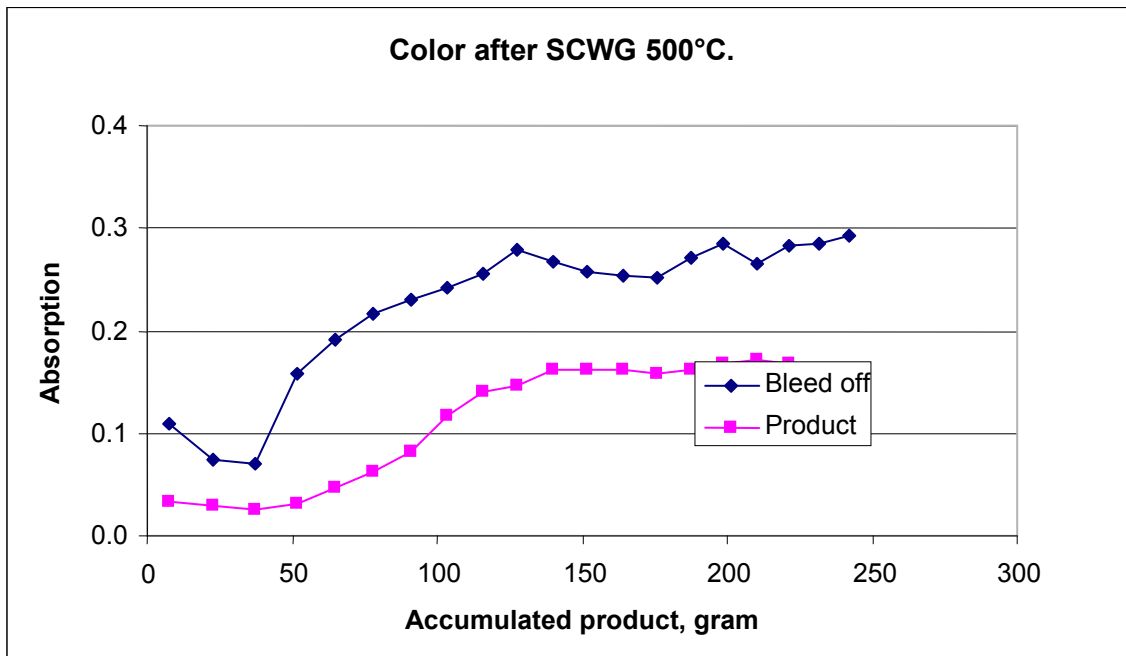
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Figure 2.1: Absorption after SCWG at 500°C, feedstock mixture measured to approx. 1.2.

The Figure 2.2 below gives a picture of the distribution of phosphor in relation to the accumulated amount of product flow.
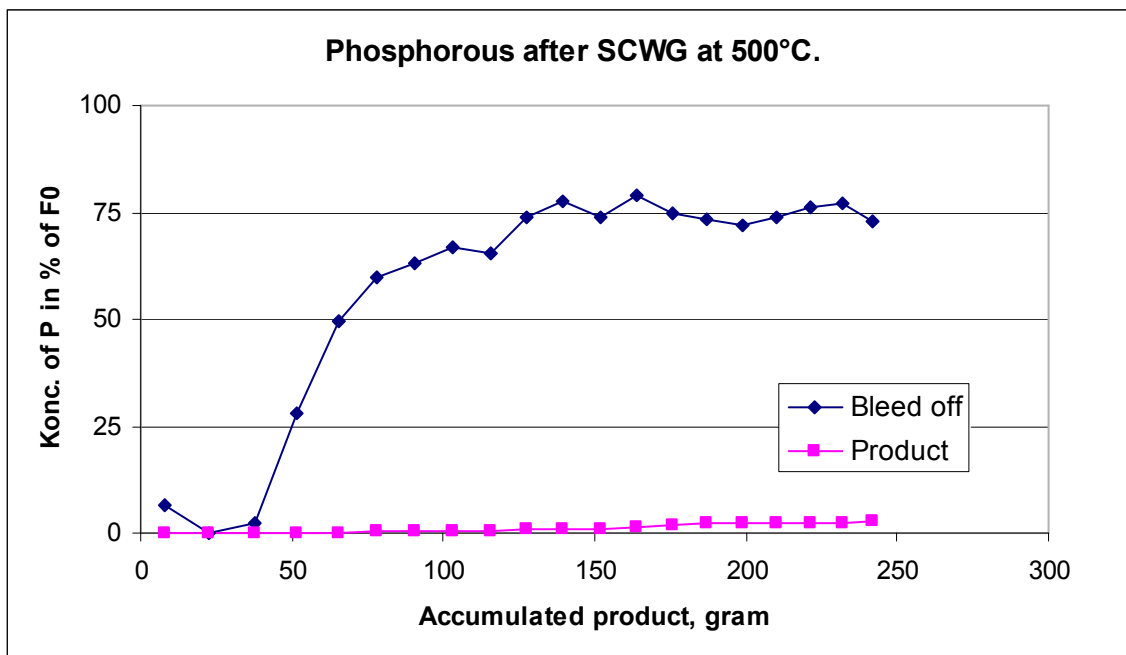

Figure 2.2: Concentration of P after SCWG at 500°C

A total of 6 test runs were performed to determine if the reactor behaved as a back-mix or a plug flow reactor.

The figure 2.3 below shows a comparison of the actual colour with the calculated values for plug flow and back mix reactor.
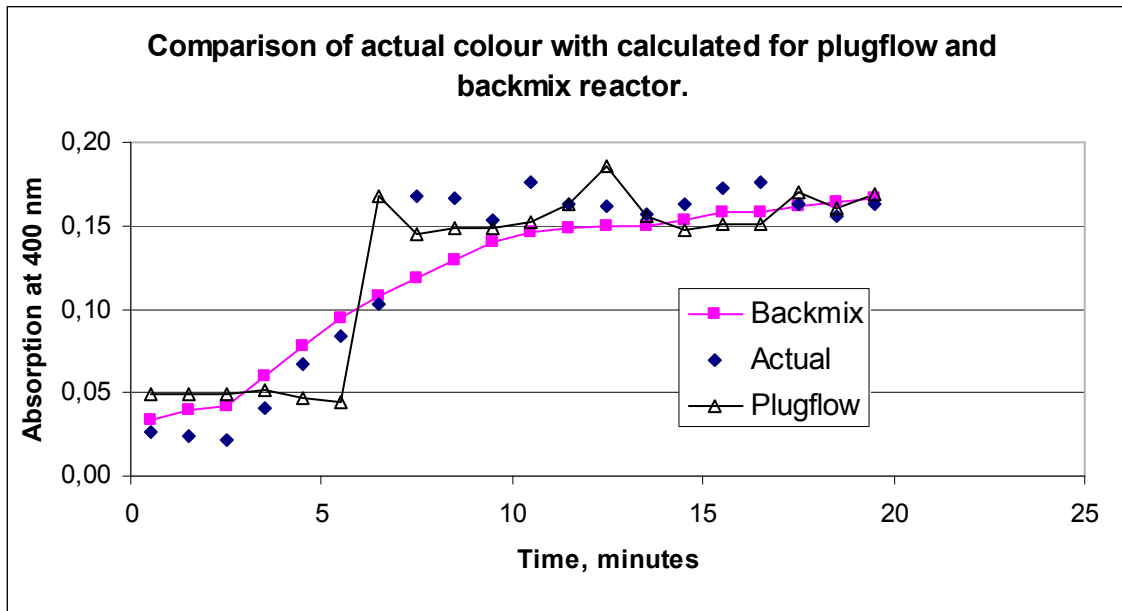
Figure 2.3: Comparison of actual flow and calculated values for backmix and plugflow reactor.

In order to cure the problem with plug-flow versus back-mix reactor, the reactor chamber was filled with baffle plates. The baffle plates secured plug flow conditions, and the temperature variation was stabilized. The long reaction times were not shortened as expected, however new experiments proved that a major part of the problems was absorption/desorbing of dye from the different surfaces of the equipment, rather than the feed mixing with stagnant water inside the reactor.

Gasification experiments on the LSU

A total of 28 experiments were performed in gasification mode on the Lab Scale Unit. Different conditions, regarding concentration of feedstock and temperature in the reaction chamber, along with the addition of catalyst, were applied in the line of experiments.

The figure below show results from the gasification tests. The experiments where all performed without the addition of a catalyst. Results from experiments series 3 and 4, is incorporated in the figure.
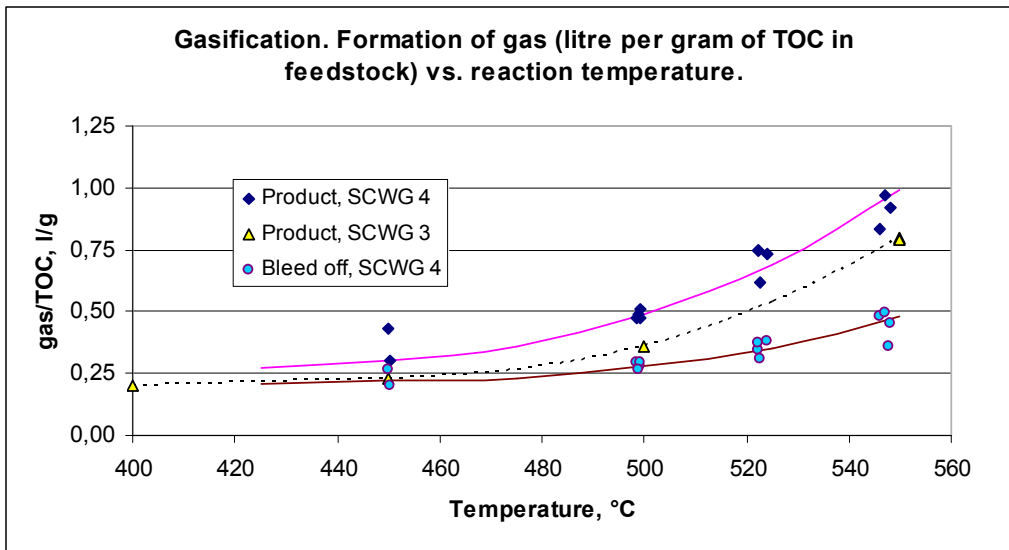
Figure 2.4: Formation of gas vs. reaction temperature, trend-lines added. [Litres of gas/gram TOC]

The experiments shows as expected an increase in the conversion rate with an increase in the temperature inside the reactor, and at the same time it is observed that part of the reaction already happens inside the heat exchange part of the equipment. % TOC (on a W/W basis) left in the product and in the bleed off, is shown in the figure below.
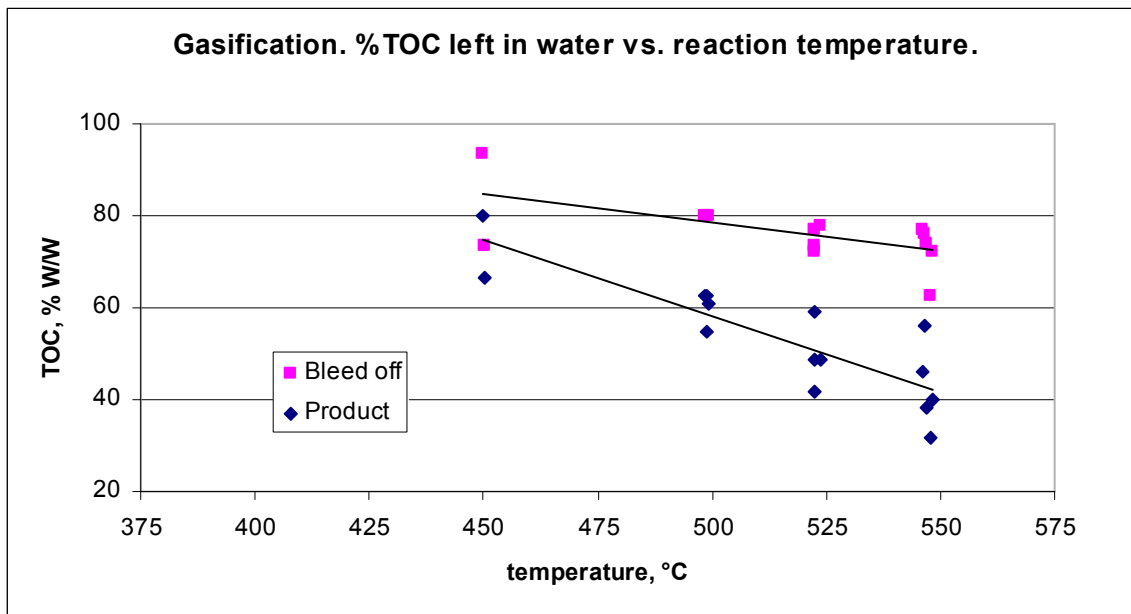
Figure 2.5: TOC left in water vs. reaction temperature, trend-lines added.

From this series of test it can be seen that approx. half of the TOC in the waste water is changed to gas at a reactor temperature of 550°C.

At the same time it is observed, as in the earlier experiment, that a tar like phase is produced in the process. The amount of this tar decreases with increasing temperature.

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Gasification on the PDU

The Process Development Unit is designed and constructed as a semiautomatic unit, which can operate without constant attention. The critical factors are controlled by a process computer (PLC), and all the relevant temperatures, flows and pressures are logged by the aid of a PC containing the relevant software.

In the gas/liquid separation cylinders there is clear evidence that a large amount of the carbon is converted to tar, the picture to the left show the deposits on the walls of the cylinder, further more it is later proven that some of the carbon is accumulated inside the free space in the bottom heat exchanger zone.

A further improvement over the LSU is the fact that the gas composition is now measured online, during the experiments on the PDU. The measuring system covers 4 gases: O_2, CO_2, CO and H_2. This gives some indications about the heating value of the gas, and as the figure below shows: The heating value (lower) of the gas increases with the gasification temperature.

Figure 2.6: SCWG of waste water from Harboore in the PDU, MJ/Nm^3 vs. temperature.

The PDU gave the possibility to raise the temperature inside the reactor to 600°C, which showed an improvement in the reduction of TOC, but even at 600°C, about 20% of the carbon is left in the product stream.
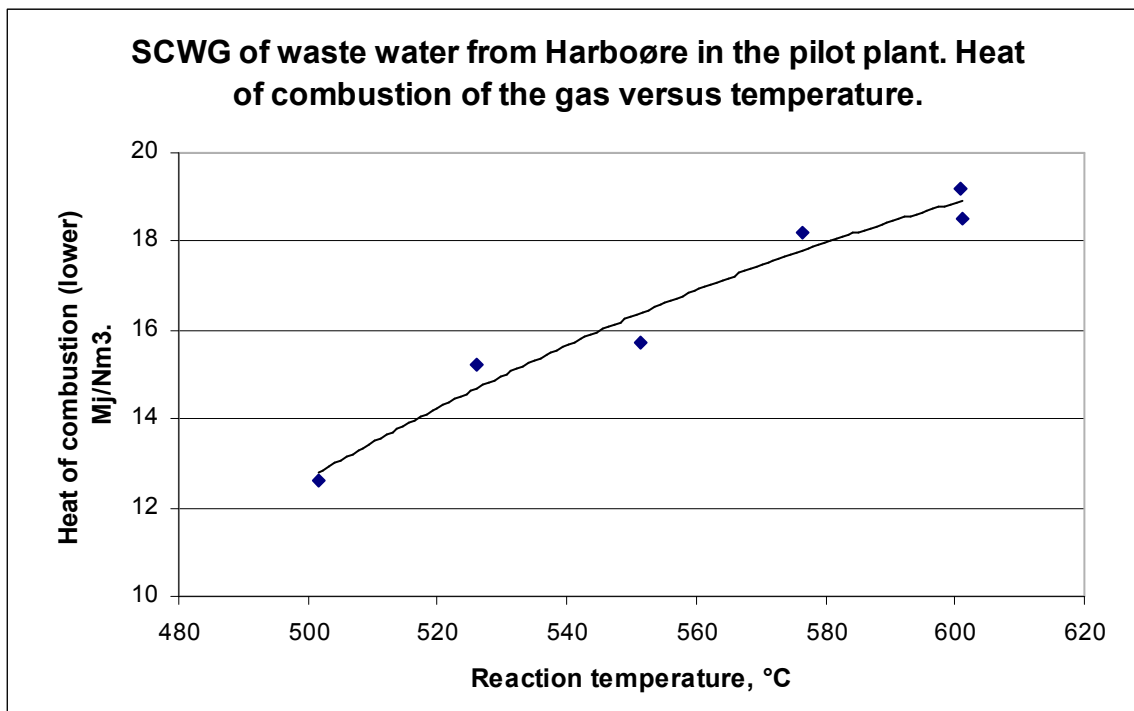
The experiments performed with catalyst in the supercritical zone, showed a clear improvement over the earlier experiments. At 600°C the TOC left is 2,3%, The value without carbon catalyst was 20%, At lower temperatures the amount of TOC left in the product rises to 17,5% at 500°C. Values from a series of experiments are shown in the figure below.
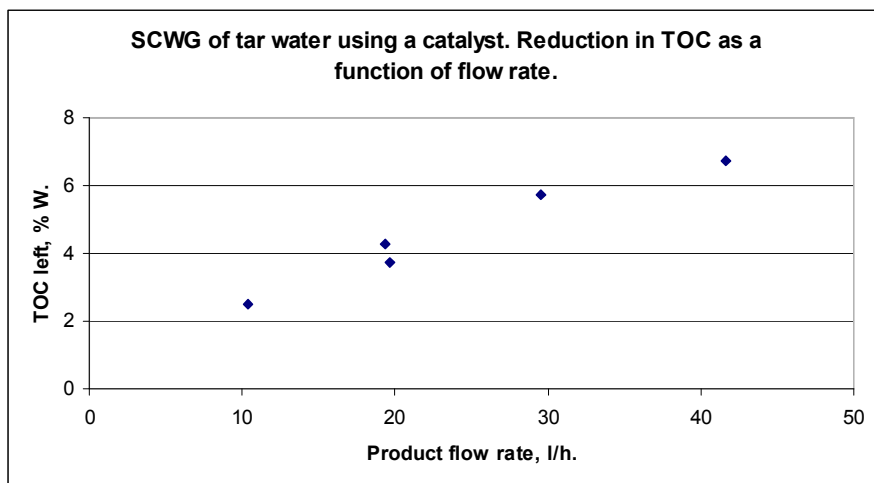
Figure 2.7: SCWG of tar water using a catalyst.

An examination, of the carbon balance, reveals that the result from earlier experiments, where 20 % of the carbon was missing, still is the case in the experiments involving the catalyst.

Conclusion on the gasification experiments

The general conclusion on the gasification experiments is that a catalyst incorporated in the supercritical zone is necessary to achieve results that will make it possible to use the process in industrial scale.
The waste water should be cleaned at least to a degree where no visible tars or other impurities are visible in the product, as the impurities gives problems in the pump, both during depressurizing after gasification and during pressurizing when oxidising, and this level was only achieved with the aid of a catalyst placed in the reaction chamber in combination with a temperature in the reaction zone of 550 to 600°C.
Unfortunately the long term experiment showed that the expected lifetime of the catalyst is far to short both in relation to the operation of the plant and in terms of economical issues.
When running the plant in gasification mode without the catalyst, the amount of tar generated in the process came to such extend that it was impossible to run the pump for more than a few hours between cleaning intervals.
Besides the problems with the lifetime of the catalyst, the problem with the accumulation of carbon inside the unit is unsolved and partly un-described – it is not known at present if the amount accumulated inside reaches equilibrium or if the reactor simply is blocked when operated for a prolonged period.

Oxidation

In the experiment conducted on the LSU, the oxidising agent had to be mixed together with the waste water, before the water was pumped into the unit.

On the PDU an extra cylinder is added to the pump, and this cylinder is designed for the pumping of a mixture of liquid and gas. This way it is possible to use pure oxygen, atmospheric air or other gasses as oxidizing agents in the process.

Results from the first series of SCWO experiments differed from the LSU experiments on the fact that the temperature needed in order to obtain cleaning efficiencies above 99% had dropped from 500 to 450°C. The exact reason is not clear at this point as several things could have influenced the results:

- The feed was contaminated with catalyst.
- The oxidizing agent was pure O_2 instead of H_2O_2, as used during the LSU experiments.
- The temperature in the reaction chamber is more stable in the PDU than in the LSU.
- The influence originating from the physical changes in the equipment.

Contrary to the LSU experiments, the gas from the PDU contained no CO, only CO_2 and excess O_2. The loss of carbon was lower in this series of experiments compared to the gasification experiments, only around 9%, one of the reasons could also be that the degree of dilution was different here, as the feed for the PDU only had a TOC level of 2 g/l (LSU level was around 12 to 25 g/l).

This series of experiments came to an abrupt halt, as one off the heating elements developed a leak. The heating elements in zone 3 had failed during the experiments, but it was possible to continue, until the element leaked. The picture below shows the failed heating elements.
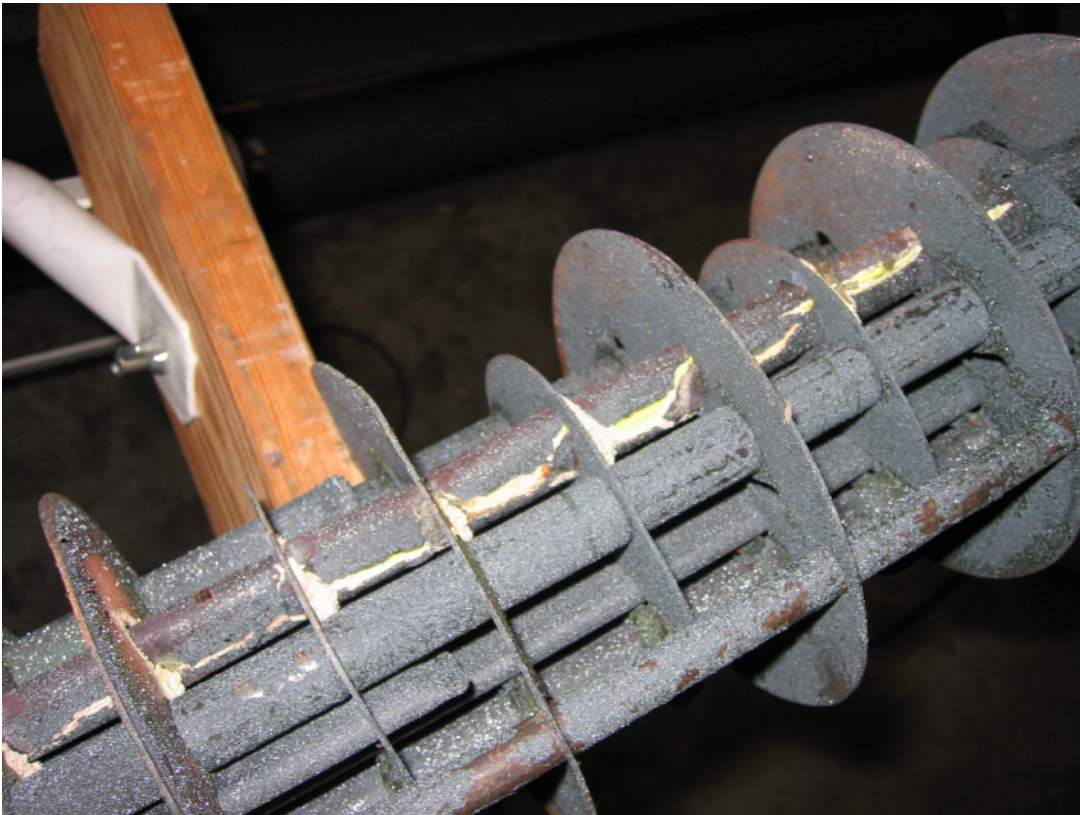
Picture 2.1: Failed heating elements from the PDU.

During the next months, the reactor was dismantled, inspected and a decision was made to rebuild the internals of the reactor with new heating elements, baffle plates and liner.

After the rebuild the series of experiments continued. These experiments continued the line of SCWO experiments, with the difference that atmospheric air was used as the oxidizing agent. During the rebuild, a few changes were made on the reactor, mainly the heating elements.

Sample	Oxidizing agent	Reaction temperature	Product flow rate	TOC in feed	TOC in product	TOC left	Cleaning efficiency
		°C	l/h	mg/l	mg/l	% W	% W
13,01	air	601	22,2	1950	1,6	0,08%	99,92%
13,02	air	553	23,7	1950	2,6	0,13%	99,87%
13,03	air	501	16,8	2190	4,3	0,20%	99,80%
13,04	air	452	18,2	2190	302	13,8%	86,2%
13,05	air	401	18,7	2080	411	19,8%	80,2%
13,06	air	386	19,3	2080	424	20,4%	79,6%
13,07	air	370		2080	270	13,0%	87,0%
13,08	air	373	23,2	2080	303	14,6%	85,4%
13,09	oxygen	371	20,5	2400	370	15,4%	84,6%
13,10	oxygen	385	20,4	2400	420	17,5%	82,5%
13,11	oxygen	401	20,6	2300	500	21,7%	78,3%

Table 2.1: Cleaning efficiency with air or O_2 as oxidizing agent

The table 2.1 above shows the comparison of atmospheric air and pure O_2 as oxidizing agents, and as can be seen there are no significant differences. The fact that the degree of cleaning is higher when running under sub-critical conditions could be explained by the fact that the retention time in the reactor is higher (a factor of 2) when running sub-critical because of a shift in the water density. Comparing the cleaning effect at the higher temperatures shows that more than 500°C are needed to reach cleaning efficiencies above 99,5%. This deviates from the earlier experiment on the PDU using O_2, but possible explanations are the fact that potash were added as catalyst, and that O_2 were used as oxidizer, as it is possible that the oxidizing effect of O_2 is better than atmospheric air at 450°C.

Above 500°C there are no visible differences when oxidizing tar water diluted to a TOC of 2 g/l.

Variation of the concentration of TOC in the feedstock gave some important results. It became clear that the residual TOC rises more than proportionally with the concentration of TOC in the feed, given that all the other parameters are comparable. In figure 2.8 14.2 a comparison is made between the results from SCWO of feedstock containing 2 g/l and 7 g/l TOC. As can be seen, at a TOC-level of 7 g/l, 550°C is needed to achieve more than 99% conversion in comparison with the results from a TOC-level of 2 g/l where only 475°C is needed to achieve more than 99% conversion.
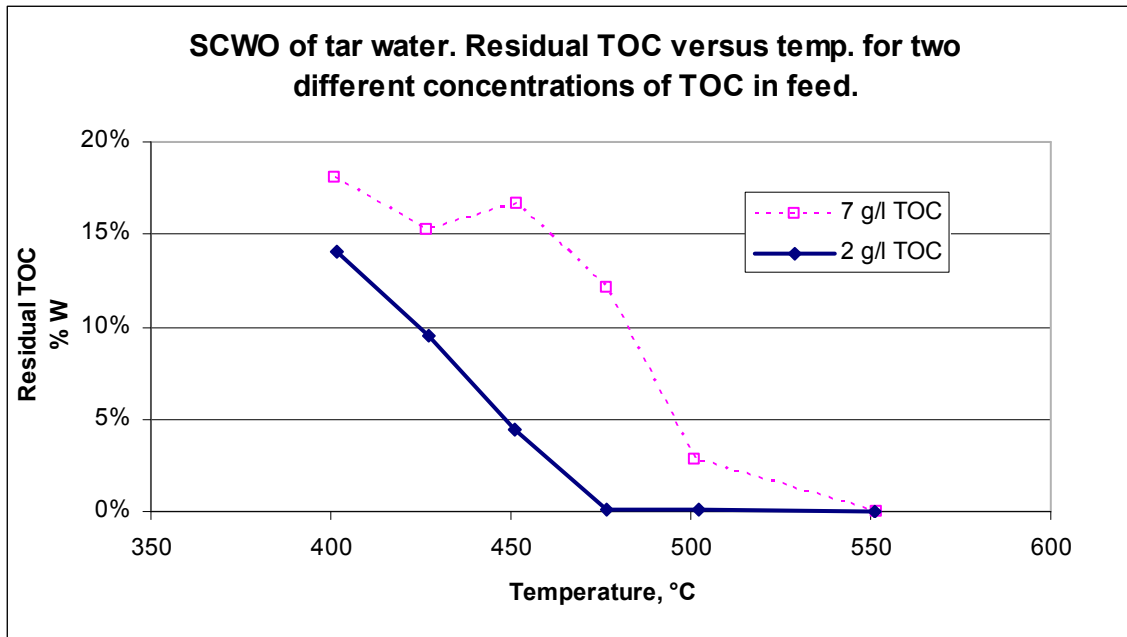
Figure 2.8: TOC/°C for two different concentrations of TOC. Experiments performed on the PDU.

The carbon balance shows that under the oxidizing conditions an amount equal to approx 6% of the original carbon is lost/left inside the reactor. This is an improvement over the 20% mentioned in the gasification experiments but still enough to be a potential problem when running the plant for a prolonged period.

Conclusion on the oxidation experiments

In general the oxidation experiments ran with fewer problems than the gasification experiments when looking at the process inside the reactor. The pump presented some problems during the process of pumping both liquid and gas, but in general these where solved by only minor modifications to the system. Real long term stability problems still need to be solved before the pump enters a stage where it can be used industrially.

The amount of TOC left in the product stream is depending on TOC in the feedstock and/or the temperature in the reaction zone. This gives important information to the design of a full scale plant. If the gasification process could produce stable values with more than 98% degradation of TOC, a reactor temperature of 500°C when performing oxidation, should be able to produce cleaned water of such quality, that it could be discharged of to the local biological treatment plant.

Accumulation of carbon inside the unit is still unsolved, but the level is lower, around 6%, during the oxidation experiments. It is not known at present if the amount accumulated inside reaches equilibrium or if the reactor simply is blocked when operated for a prolonged period.

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WP2 conclusions

All in all a large number of experiments have been performed on both the LSU and the PDU, covering both gasification and oxidation. These series of experiments have delivered important material for the DETAR project, and for the project partners, and contributed to the general knowledge of SCW-processes.

A large number of process variables have been tested in order to gain knowledge about the optimum conditions for both Super Critical Wet Oxidation and for Super Critical Wet Gasification.

Several catalysts have been tested both catalysts mounted inside the reactor, and dissolved catalysts. Coupled with WP1 and WP3 this work marks the foundation of the project, and the early experiments on the LSU gave important information for the work in WP0, the construction of the Process Development Unit.

Work Package 3: Kinetic and Mathematical modelling

The technology of SCWG is particularly suited for the treatment of wet biomass and, in the case of SCWO, also for waste water generated form biomass gasification plants. The objectives of the WP3 consist in the determination of the relevant process kinetics and the development and validation of a transport model for the supercritical reactor. The achievement of these objectives is of great importance for the implementation of the technology on a practical scale.

A critical review of the state of the art on the kinetic modeling of supercritical water gasification/oxidation (SCWO/G) of tar and tar components has been carried out. The kinetics of SCWO/G has been determined for the TOC (total organic carbon) of the tar fraction soluble in water. Gasification and oxidation of TOC are described as an irreversible, first-order, Arrhenius rate reaction with activation energy of about 76kJ/mol and a pre-exponential factor of $897s^{-1}$ (gasification) and 7740 s^{-1} (oxidation). Kinetic data on the SCWO/G of tar are not available from the literature. However, it has been found that, for gasification, good agreement is obtained with the parameters determined for glucose decomposition, indicating that the time evolution of the TOC is controlled by the rate of disappearance of the hydrolysis products which are qualitatively the same in each cases. Furthermore, it has been observed that the order of magnitude of the tar oxidation kinetics is the same as for two model compounds, i.e., phenol and acetic acid. The effects of catalysts have been described by assuming that the activation energy of the catalytic reactions is the same as evaluated for non-catalytic conversion and by adequate re-evaluation of the pre-exponential factor. Values have been obtained for the separate effects of active carbon, potash and ammonia as catalyst on SCWG and of active carbon on SCWO (tar water mixtures).

In the case of SCWG, a first order kinetic law has been applied to describe the behavior of six tar compounds ((5H)furan-2-one, 2-hydroxy-3-methyl-2-cyclopentene-1-one 2-furaldehyde, guaicol,1-hydroxy-2-butanone, acetol), resulting in activation energies between 32 and 193 kJ/mol. As the gasification of activated carbon catalyst also plays a role in determining the catalyst lifetime, the related gasification kinetics have also been determined. It has been assumed that the reaction rate is proportional to the water mass fraction and the specific surface of char and includes the usual Arrhenius dependence on temperature. The kinetic parameters (activation energy 144kJ/mol and the pre-exponential factor $3.4902ms^{-1}$ are in good agreement with literature values.

A mathematical model has been developed for the pilot scale reactor, which is comprehensive with respect to reaction kinetics and transport phenomena. In accordance with the experimental plant, the reactants and products have been assumed to flow in countercurrent streams and different sections for the heat exchanger and the reaction zones have been described.

In the mathematical formulation the following assumptions have been made:

1. The system is one-dimensional along the flow direction.
2. Processes are in a steady state.
3. Given the small percentage of tar, the properties of the fluid coincide with those of supercritical water and are temperature dependent.
4. The pressure is constant.
5. The behavior of tar is described by the TOC content of the tar-water.
6. The external high-pressure wall exchanges heat with the environment.
7. The external heat flux generated by the thermal resistance is entirely used for the reactants.
8. Heat and mass transfer occurs by convection (transport by conduction and diffusion is negligible for the conditions of interest).
9. Countercurrent heat transfer between reactants and products is modelled in terms of global heat transfer coefficients and heat transfer surfaces, both variable with the different zones of the reactor.
10. One-step reactions are included, according to the kinetics previously determined. More precisely, it is considered that tar may be gasified according to three chemical processes:

> 1) Homogeneous gasification in the absence of catalysts.
> 2) Homogenous gasification with catalysts dissolved in water.
> 3) Heterogeneous gasification in the presence of activated carbon, which, depending on the specific experimental conditions, may or may not occur simultaneously. Oxidation of tar is assumed to occur according to the following chemical processes:
>> a) Homogeneous oxidation in the absence of catalysts.
>> b) Heterogeneous oxidation in the presence of activated carbon.

Model validation has been carried out by using the TOC conversion and the temperatures as measured and simulated for all the SCWO/G tests carried out with the PDU, obtaining good or acceptable agreement. Extensive parametric and sensitivity analyses have been made to investigate the effects of operating variables (for instance, the inlet temperature in the HE section, the total electric power supplied, the inlet mass flow rate, the TOC mass fraction in the feed and the effects of catalyst) and the applicability of simplifications in the mathematical description of the problem.

Some of the subjects covered during WP3 were presented at the 14th Biomass conference in Paris (2005)

- C. Di Blasi, A. Galgano, C. Branca, B. Teislev, T. R. Nissen, O. Malmros, Modeling a supercritical reactor for the degradation of tar-water from biomass gasification, 14th European Biomass Conference and Exhibition, 17-21 October 2005, Paris, in press.

- C. Di Blasi, C. Branca, A. Galgano, D. Meier, I. Brodzinski, O. Malmros, Gasification and oxidation kinetics of wood-tar in supercritical water, 14th European Biomass Conference and Exhibition, 17-21 October 2005, Paris, in press.

Work Package 3: Mathematical pc-tool, software for the design of the DETAR reactor

A mathematical tool DETAR was developed in order to establish the dimensions of the 50 (kg/h) Process Development Unit and also to be used in connection with upscaling.

The programme "DETAR" is based on some practical engineering assumptions and a successive solution of the energy balance in small steps throughout the system (including heat transfer models based on the flow geometry). Furthermore, the programme utilises a previously developed mathematical model for the thermodynamic and thermophysical properties of Water Substance – including special considerations for the formulation and iterations close to the Super critical point for water.

The software is programmed in the language Visual Basic® and in its executable form consists of:

- DETAR.exe, which is the actual programme
- MakeH2O.exe, which is programme for the generation of fast access Steam tables – which for IP considerations isolates the actual source code for the Steam model from the DETAR. This program is not directly executable, and must be called by a "SHELL" command from another programme with the "Commandline" parameter containing the pressure (in Pa) (in Visual Basic: H2Otable = "makeH2O.exe " + Str (pSCW): Shell (H2Otable)). The table generated may be viewed by clicking the menu-bar
- DETARHELP.hlp, which is the DETAR Help facility (programmed in WinHelp®) including detailed information on the operation of the software
- Msflxgrid.ocx, which is an ActiveX component (property of Microsoft Windows®), for the scroll-able data tables used in DETAR

During the application, DETAR will – from time to time – generate an updated (Windows Notepad®) steam table (in H2O.txt) with the thermodynamic and thermophysical properties currently required.

The programme may generate a printed design report (containing relevant data and other information) and the temperature and residence time profiles (from the scroll-able data tables) may be exported for further study and manipulation in an Excel® spread-sheet.

The menu-structure is presented below, and the DETAR opening screen is shown overleaf.

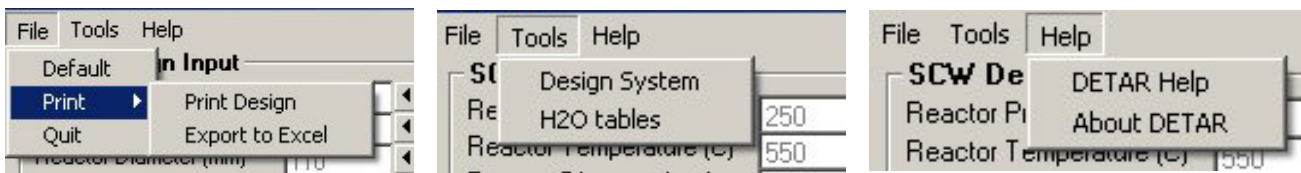Figure 3.1: Scroll menus for the DETAR design software.

Submenu "File":   "Default" will recover the initial data as used in the DETAR project
                  "Print" will make a hardcopy report or export data to Excel
                  "Quit" will terminate the program

Submenu "Tools": "Design System" will enable modifications to the system
                  "H2O tables" will display the Steam Tables

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Submenu "Help":   "DETAR Help" will invoke the User Manual
                           "About DETAR" will provide Misc'l information about DETAR
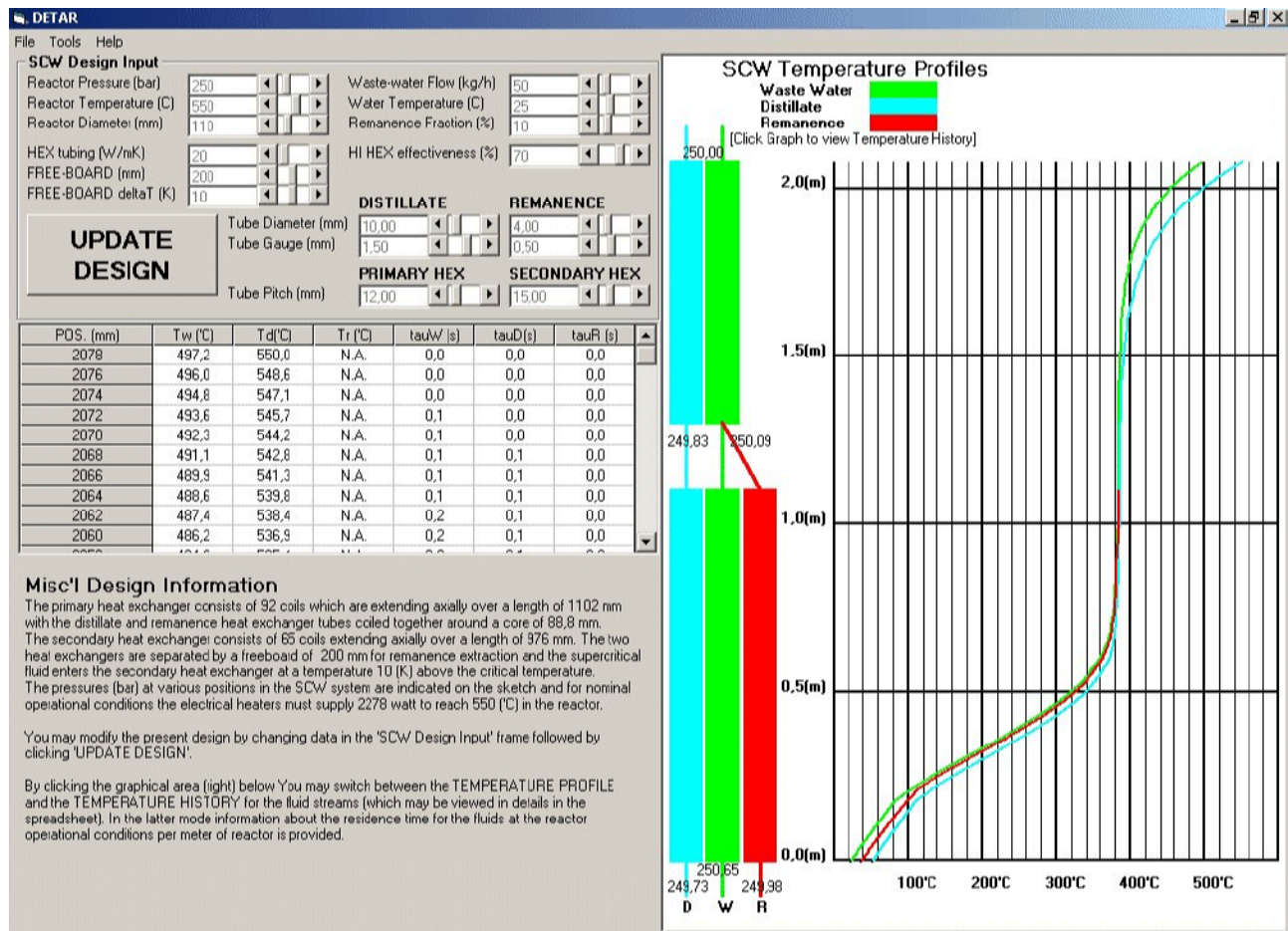
Figure 3.2: Screen dump of the result page from the DETAR software.

The opening screen is using a set of default data, which are representative for the PDU (Process Development Unit) built and tested during the DETAR project.

In the upper left part, the system load and geometry is adjusted followed by clicking "UPDATE DESIGN". The temperature and residence time profiles are then calculated and can be reviewed in the scroll-able table and the graphs (by clicking in the graphical area, the presentation is switched between "Temperature Profiles" and "Temperature History").

In the lower left part of the screen, some relevant information is summarised.

WP3 Conclusions

The research activities carried out have allowed the determination of the global kinetics for SCWO/G of tars generated from updraft gasification of wood and the development and validation of a transport model for the supercritical reactor. Both achievements are important in the view of practical applications of the SCWO/G technology for the treatment of waste water from industrial gasification plants.

The software developed incorporates the knowledge gathered trough the experiments and will make an upscaling of the reactor possible.

Work Package 4: Full scale implementation

Overall design considerations

The purpose of the work-package 4 is to establish a foundation for a full scale plant, suitable to handle the wastewater produced by the Harbooere gasification plant.
At the start of the project it were decided that ideally the plant should use wet gasification under super-critical conditions. This of course meant that the quality of the waste water after the gasification process needed to be so clean, that discharge trough the municipal system was possible.

From the early experiments it was clear that it was not possible to reach the desired level of cleaning by operating in the gasification mode alone, therefore it was expected from the start that a minor amount of the organic polluting elements, should be removed by super critical wet oxidation.

Materials

During inspections throughout the project, it was found that the general condition of the reactor proved to be good, in almost any cases, as there was no visible pitting corrosion. In the localized area around the shift from water to super critical water, some surface rust is evident. There was no reduction in the wall thickness of the liner at any point. Picture 4.1 show an example of the corrosion of the liner used in the reactor.

Picture 4.1: Close view of corrosion on the liner.

Basic data and assumptions

The biomass gasification plant in Harboore DK, supplies heat to the local community. The plant is the sole provider of the heat to approx. 630 households. Plant load, and thereby the production of electricity, is dictated by the amount of heat used in the community.

The amount of wastewater produced varies along with the load of the plant, the figure below shows the yearly variations in the waste water generation.
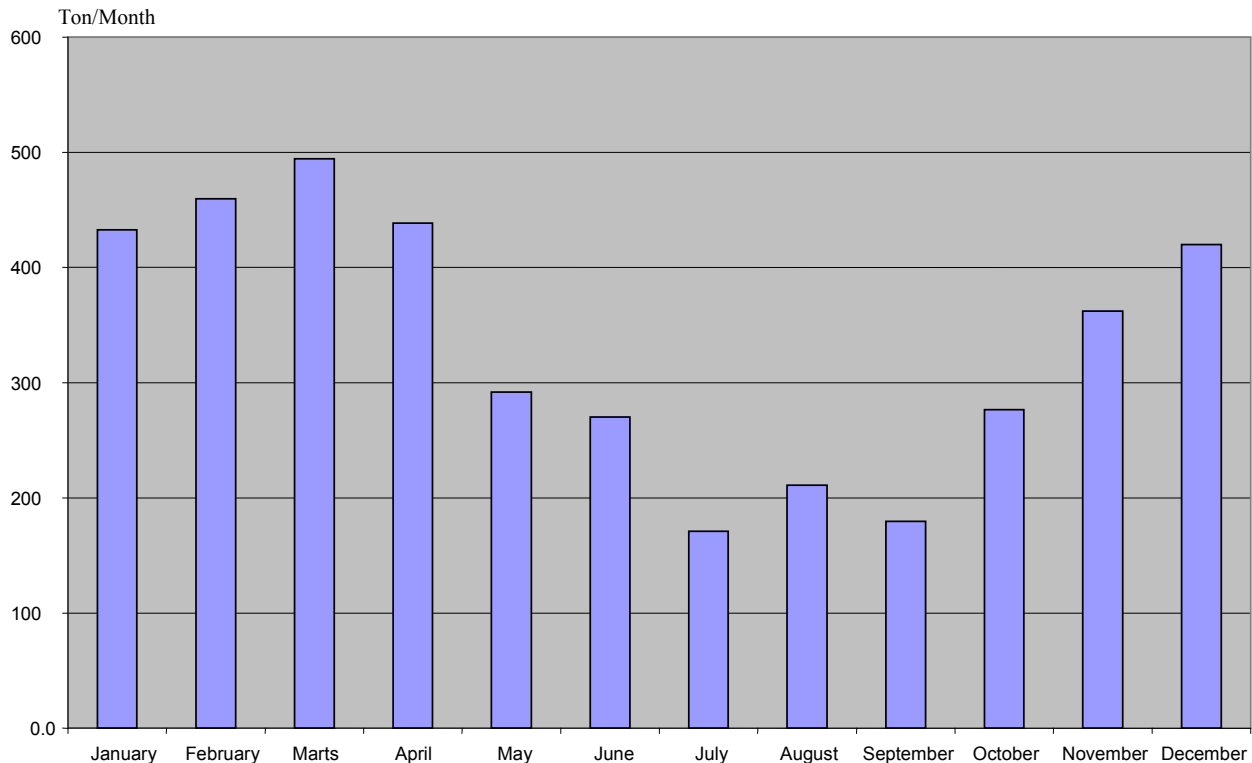
Ton/Month

Figure 4.1: The generated amount of wastewater pr. month.

The total yearly amount of wastewater is set to 4000 ton.

The daily average in the max load period is approx 16 ton/day – equals 667 kg/hour.

Average pollution, measured as TOC (Total Organic Carbon) is 70g/kg, giving a yearly amount of 280 ton carbon in the wastewater.

Mass Balance of plant

The mass balance calculation is based on 4000 ton waste water/year.

The following tables show the mass balance (table 4.1) and the energy balance (table 4.2) of the plant, when combining the Super Critical Wet Gasification with the Super Critical Wet Oxidation for the cleaning of the polluted wastewater.

Gasification - dissolved catalyst		year	day (average)	hour (average)	hour (peak)
Waste water stream ton/		4000	11,0	0,46	0,67
carbon [g/l] amount ton/	70	280	0,8	0,03	0,05
Product/Bleed off	95% / 5%				
Product [ton/]	95%	3800	10,4	0,43	0,64
TOC left product [kg/]	5%	13300	36	1,5	2,2
Bleed off [ton/]	5%	200	0,548	0,023	0,034
TOC left bleed off [kg/]	90%	630	1,73	0,07	0,11
Figures for dissolved catalyst					
Gas production [Nl/g(TOC)]	2,4				
Heating value of gas [MJ/Nm^3]	11,6				
Gas [Nm^3/]		638568	1750	73	107
Energy production [MJ/]		7407388,8	20294	846	1244
Energy production [KJ/s]				235	346
Power production (η_{el}=37%) [kWh]		761315	2086	87	128

Table 4.1: Mass flows of the full scale SCWG/O plant, based on a dissolved catalyst.

Energy balance		year	day (average)	hour (average)	hour (peak)
dT Heat exchanger °C	50				
Heat loss trough dt in heat exchanger [kW]	27				
Heat loss trough dt in heat exchanger [kWh/]		232222	636	27	39
Heat loss from unit, convection [kW]	5				
Heat loss from unit, convection [kWh/]		43800	120,0	5,0	5,0
Energy from gasification* of "TOC" [KJ/mol]	33				
Content in wastewater [g/l]	70				
Contribution from TOC [kW]	22,0				
Contribution to reactor heat balance		193035	529	22	36
Net. Heat input to maintain reactor temperature [kWh/]		82988	227	9	8
Power consumption pump unit [kW]	7				
Power consumption pump unit [kWh/]		61320	168	7	10
Net. power production (ηel=37%) [kWh]		617007	1690	70	110

Table 4.2: Energy balance of the SCWG process using a dissolved catalyst.

As can be seen from table 4.2, there is a net contribution of energy from the gasification stage. The main energy loss from the reactor is trough the ΔT in the heat exchanger at the bottom of the reactor.

After the step where gasification of the initial amount of TOC is performed, an oxidation step is needed in order to reach a sufficient level of cleaning.

Table 4.3 gives the main figures of the process.

Oxidation - dissolved catalyst		year	day (average)	hour (average)	hour (peak)
Waste water stream ton/		3800	10,4	0,43	0,67
carbon [g/l] amount ton/	3,5	13,3	0,0364	0,0015	0,0024
	95% /				
Product/Bleed off	5%				
Product [ton/]	95%	3610	9,9	0,41	0,64
TOC left product [kg/]	0%	0	0,00	0,00	0,00
Bleed off [ton/]	5%	190	0,521	0,022	0,034
TOC left bleed off [kg/]	50%	16,625	0,05	0,00	0,00
Figures for dissolved catalyst					
Gas production [Nl/g(TOC)]	20				
Heating value of gas [MJ/Nm3]	0				
Gas [Nm3/]		265668	728	30	47
Energy production [MJ/]		0	0	0	0
Energy production [KJ/s]				0	0
Power production (ηel=37%) [kWh]		0	0	0	0

Table 4.3: Mass flows of the full scale SCWO plant, based on a first step gasification with a dissolved catalyst followed by the oxidation step.

Energy balance		year	day (average)	hour (average)	hour (peak)
dT Heat exchanger °C	50				
Heat loss trough dt in heat exchanger [kW]	25				
Heat loss trough dt in heat exchanger [kWh/]		220611	604	25	39
Heat loss from unit, convection [kW]	5				
Heat loss from unit, convection [kWh/]		43800	120,0	5,0	5,0
Energy from oxidation* of "TOC" [KJ/mol]	28				
Content in wastewater [g/l]	3,5				
Contribution from TOC [kW]	1,0				
Contribution to reactor heat balance		8620	24	1	2
Net. Heat input to maintain reactor temperature [kWh/]		255791	701	29	42
Powerconsumption pump unit [kW]	12				
Powerconsumption pump unit [kWh/]		105120	288	7	19
Net. power production [kWh]		-360911	-989	-36	-61

Table 4.4: Energy balance of the SCWO process.

To sum up the general influence on the total energy situation for the biomass gasification plant, the amounts are summarized in table 4.4 below.

Gasification - dissolved catalyst followed by oxidation	year	day (average)	hour (average)	hour (peak)
Power production (ηel=37%) gasification [kWh]	617007	1690	70	110
Power production oxidation [kWh]	-360911	-1019	-37	-60
Total power [kWh/] from SCWG/O process	256097	671	33	49
Total power from wood chip gasification plant	5150670	14111	588	
Gain on total electric efficiency [%]	1,39			

Table 4.4: A general view of the energy balance, of the biomass plant, incorporating the SCWG/O process.

As can be seen, there is a noticeable gain in total electric efficiency, so all in all the process adds to the general efficiency off the biomass gasification plant. The total electric efficiency on the plant is raised from 28% to 29.4 because of the contribution of gas from the SCWG process to the gas system, thereby raising (or replacing) the amount of gas available for the gas engines.

The figure below shows the calculation of the heat exchanger system. The calculation is done on the software developed to simulate the SCWG/O system, and the software is build on knowledge gained trough the experimental work performed during the DETAR-test sessions.
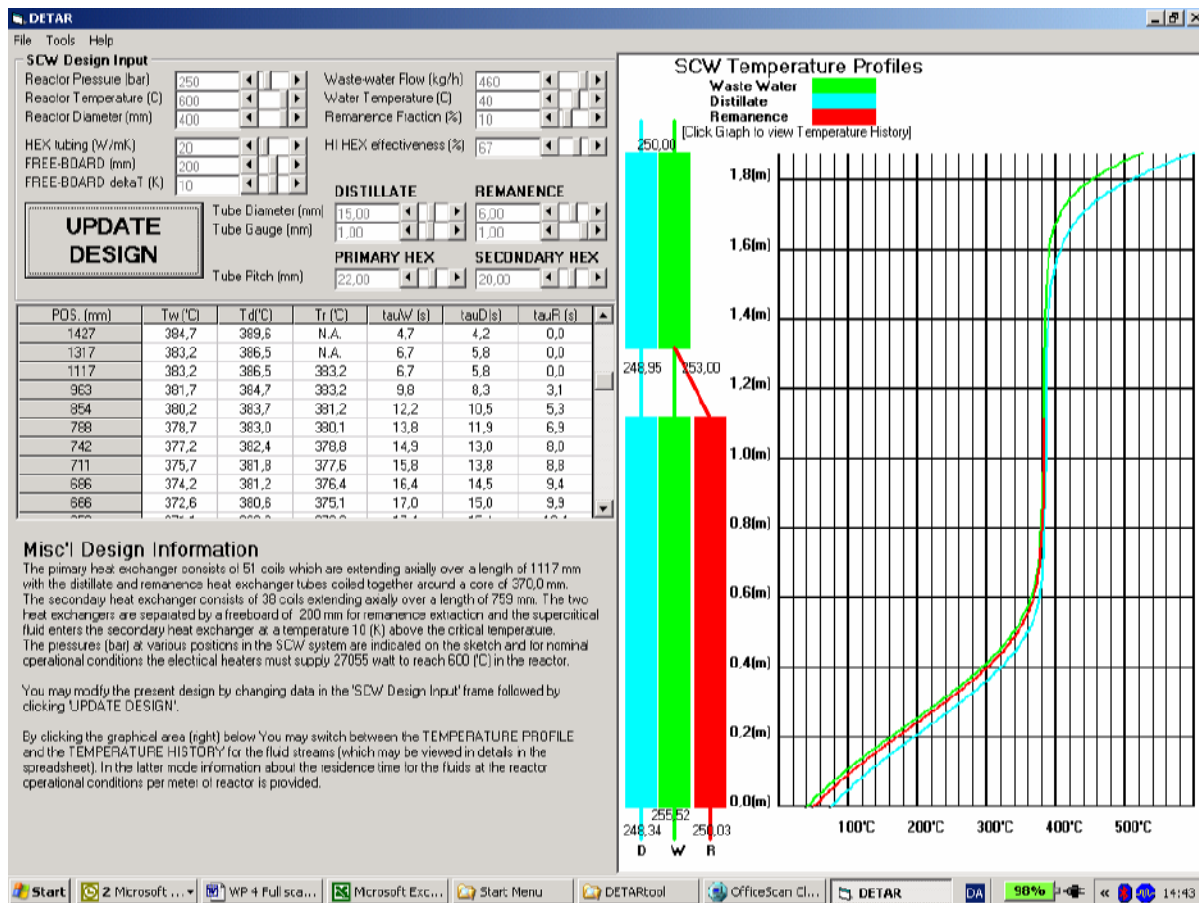
Picture 4.2: Results from the DETAR software tool.

The software allows you to change various important parameters related to the design of the reactor, and returns figures for actual pressure at different levels and the requested amount of additional heat input above the second heat exchanger.

SCWG/O plant economics

Based on the technical data supplied, the cost of the plant can bee decided. The total cost for the plant includes the different containers and storage vessels needed for the plant to function at a sufficient state. There are no buildings or basic installations included in the price.

On the figure 4.3 below, a single unit installation is shown. The frame in which the unit is mounted has the dimensions of a 20 ft standard container.
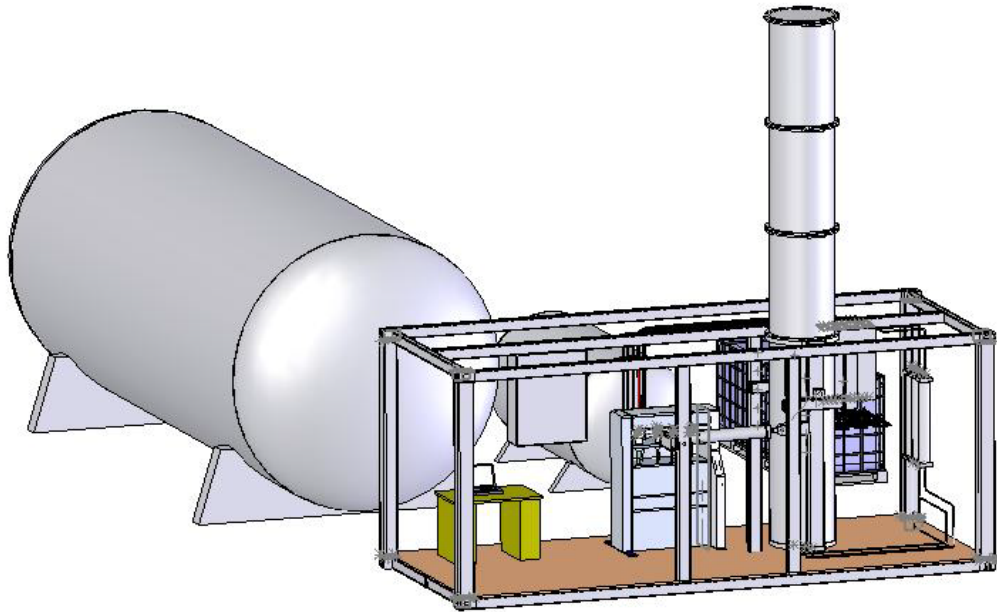

Figure 4.3: 3-D drawing of a single unit SCWG/O plant

The containers and the equipment needed are basically the same for both the gasification and the oxidation facility.

To cover the need for the treatment of the water from the Harboore gasifier, 2 units are needed, one for gasification and one for oxidation.

Although the price pr. ton waste water treated as hazardous waste normally is in the region of 200 Euro/ton (DK price level), the figures for treating the waste water with this type of plant are still too high. The cost will eat up almost 2/3 of the income generated by the sale of electricity produced on the biomass gasification plant (based on the Danish prices for electricity produced on biomass).

Environmental impact

To give an indication of the quality of the cleaned water, it was decided to have the water tested by Professor Jes la Cour at Lunds University, Sweden. It was decided to test only the water from the oxidation run, as the amount of TOC and the chemical analyses of the water from the gasification experiments made it clear that the inhibition would supersede the limits given by the Danish legislation.

The university have the knowledge and experience in checking the quality of the water discharged by different types of biomass gasifier types. As the chemical analyses already performed shows that the level of contaminants is low, only a few chemical analyses are performed by Lunds University. These analyses are performed in order to characterize the water before the nitrification inhibition is examined. In table 4.1 the amount of acetic acid is given along with a remark about the experimental conditions.

Sample identification	Content of acetic acid mg/ml	Remarks on Experimental conditions
14.12	0.0	Surplus of oxygen, varying flow
14.13	0.0	Surplus of oxygen, varying flow
14.14	0.3	Surplus of oxygen, varying flow
14.15	0.9	Surplus of oxygen, varying flow
14.16	1.0	Surplus of oxygen, varying flow
12.18	0.0	Different levels of surplus oxygen
12.19	0.0	Different levels of surplus oxygen
12.20	0.0	Demineralised water together with oxygen

Table 4.6: Chemical description of samples

As the content of organic material was low, all samples were tested in 50% dilution and the sample with the highest COD content in 6 dilutions from 1-50%. Since the two other samples with elevated COD also showed inhibition in 50% dilution they were diluted further and tested as well.

Table 4.2 shows the results and Figure 1 the inhibition curves. Together with the inhibition results the Danish guidelines for discharge into public sewers are given. If the inhibition is below 20% in a dilution of 20% it is expected that the water can be discharged to the public sewer. Between 20% and 50% inhibition further examination is required in order to verify that the inhibition is expected not to be persistent in a biological treatment system. Above 50% the water is only accepted in very special cases.

Sample identification	14.12	14.13	14.14	14.15	14.16	12.18	12.19	12.20	Guidelines
Dilution				Nitrification inhibition %					
50	4	4	9	43	63	2	2	1	
20			3	21	35				20-50*
10			-1	5	24				
5			-3	5	14				
2					10				
1					8				

Table 4.7: Result from examination of the nitrification inhibition from the samples.
> * Danish guidelines. In 20% dilution water is accepted for discharge into the public sewer. Between 20% and 50% inhibition further examinations are needed and above 50% inhibition no discharge is normally accepted.
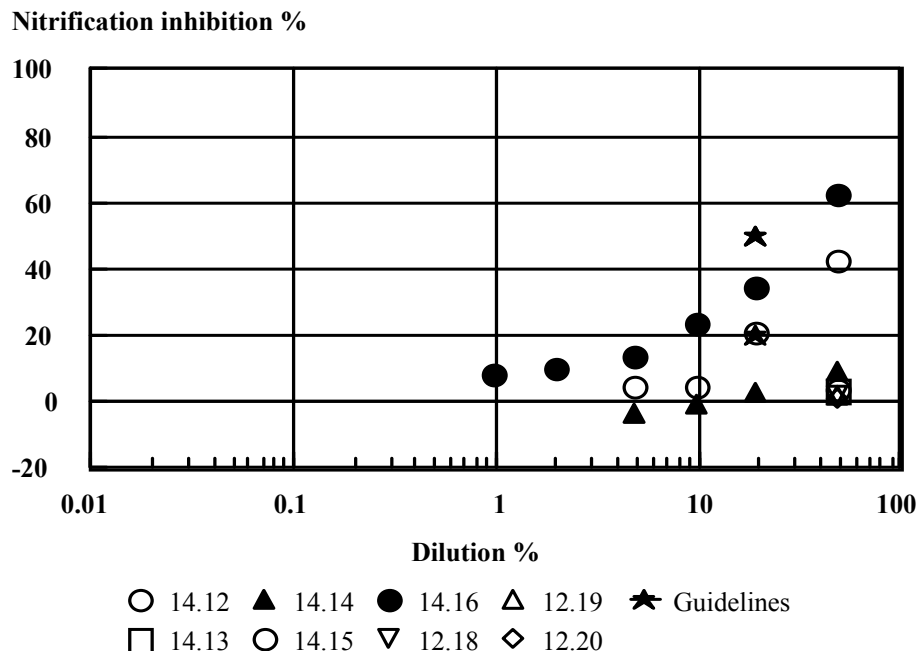
Nitrification inhibition %

Figure 4.4: Inhibition from 8 samples from SWCO/G-treatment of tar-water from the up-draft gasifier in Harboøre.

The Table and Figure show that the samples with low COD content give no inhibition. The method has a detection limit around 3-5% and all results within −5-+5% can be characterised as without detected inhibition. The three samples with content of acetic acid show inhibition almost proportional to the COD content. From previous experiments the level of inhibition from acetic acid is known and the actual level is about a factor of 10 lower than the level giving the actual inhibition. Acetic acid is consequently not the full explanation for the inhibition but merely an indicator of the presence of other pollutants. The two samples with the highest inhibition do not comply with the Danish regulation as both is in the range where discharge only can be accepted after further examination and documentation that the inhibition level and the substances responsible for inhibition can be discharged without problems.

Waste water from other gasifier plants.

Waste water from other gasifier types can be treated by this technique as well. The gasifier in the case of the Harboore gasifier is of the updraft type, which generates large amount of waste water, due to the fact that it operates with woodchips with a water content of 35% to 50%.

Other types of gasifier types like downdraft or 2-stage gasifiers, preferably use dry woodchips, the amount of waste water is smaller and due to higher gas temperatures through the gasification process, the water does not contain the same amount of pollutants as the water from the updraft type.

The water from these other types of gasifiers could be compared to the water quality generated from the SCWG-process. This means, that in order to clean this waste water stream, only the SCWO stage is needed. This lowers of course the investments, but it has no influence on the electric efficiency of the total gasification plant.

On the other hand, this part of the plant is considered the most stable and easiest to perform in practise, and throughout the experiments covering SCWO, it proved the least problems in terms of stability both for the reactor and for the pump.

WP4 Conclusion

Based on the economics of the process, the process does not seem ideal. In order to come inside an economical interesting frame, the Super Critical Gasification Process needs to be developed further. Of special interest will be the discovering of a catalyst, which will make it possible to clean the water by SCWG alone, to such extent that no further treatment is needed before the discharge to the municipal system.

This was close to being achieved during the experiments conducted in the DETAR project, but only for short periods of time, as the catalyst that performed very well only did so for a short period of time.

The oxidation step proved to be relatively easy to control, and this part can be incorporated in other areas than biomass gasification.

Materials suitable for the building of SCWG/O plants have been thoroughly investigated, but one of the important conclusion on the work performed in the DETAR project is, that by applying the right techniques in terms of securing a low concentration of salts in the zone where the water goes from the liquid phase to the supercritical phase, makes it possible to use more common types of materials for the building of the reactor.

With respect to the pump, it was proven that it was possible to reuse some of the pumping energy. This of course lowers the amount of energy used for raising the pressure of the feedstock. This is of some importance, although the amount of energy that is lost by means of dT in the heat exchanger sections is by far the largest amount.

Further work on the SCWO process step might make it possible to lower the process temperature, which again will lower the price of a plant considerably. If temperatures below 500 °C are proven to be satisfactory, due to the aid of an oxidation catalyst or the like, considerable savings can be done on the process reactor.

Conclusion

The activities planned at the start of the project have all been performed. The large amount of experimental work performed have given important information both in terms of solutions for mechanical design issues for super critical water gasification and super critical water oxidation systems and for the development and validation of a transport model for the supercritical reactor. Both achievements are important in view of practical applications of the SCWO/G technology for the treatment of waste water from industrial gasification plants.

The knowledge about the components in the tar-water has been greatly improved, along with understandings about the degradation of the tar components during storage. The most prominent changes occurred in tar water stored and subjected to room temperature and sunlight over a 6 week period. The changes proved to be small, which was important in the planning of the experiments. The

fact that only minor changes were seen, gave the possibility to use water from the same batch during the entire project.

All in all a large number of experiments have been performed on both the LSU and the PDU, covering both gasification and oxidation. These series of experiments have delivered important material for the DETAR project, and for the project partners, and contributed to the general knowledge of SCW-processes.

A large number of process variables have been tested in order to gain knowledge about the optimum conditions for both Super Critical Wet Oxidation and for Super Critical Wet Gasification.

Several catalysts have been tested both catalysts mounted inside the reactor, and dissolved catalysts. Coupled with WP1 and WP3 this work marks the foundation of the project, and the early experiments on the LSU gave important information for the work in WP0, the construction of the Process Development Unit.

A mathematical model has been developed for the pilot scale reactor, which is comprehensive with respect to reaction kinetics and transport phenomena. Model validation has been carried out by using the TOC conversion and the temperatures as measured and simulated for all the SCWO/G tests carried out with the PDU, obtaining good or acceptable agreement. Extensive parametric and sensitivity analyses have been made to investigate the effects of operating variables (for instance, the inlet temperature in the HE section, the total electric power supplied, the inlet mass flow rate, the TOC mass fraction in the feed and the effects of catalyst) and the applicability of simplifications in the mathematical description of the problem.

A software tool has been produced in order to assist engineers in the process of up-scaling the current reactor to full scale units. The software assists in the design of the heat exchangers and gives important figures like tube diameters, pitch and the like. Several parameters can be changed in order to evaluate the chosen dimensions.

A full scale plant has been outlined in the DETAR project, as a part of the work package 4. The construction of the plant, based on the knowledge gained from the experiments on the PDU, is by far possible, but the economics of the plant are still not satisfactory. Further work in the field of efficient catalysts for the gasification process under super critical water conditions, might change that as an efficient catalyst opens up for the possibility of conducting the treatment of the waste water by gasification alone. This will influence strongly on the economics, and might move the process into economically attractive territory.

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