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Department of Water and Environmental Engineering

Toxicity of wastewater generated from gasification of woodchips

The Danish Energy Agency Follow-up Programme for Combined Heat and Power production. J.nr. 51166/01-0008

June 2003

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Preface

Department of Water and Environmental Engineering, Lund Institute of Technology has participated in the Danish Energy Agency Follow-up Programme for Combined Heat and Power production (CHP) since 1998. The work has been planned end done as part of the actual research and development activities. The main focus has been on characterisation of inhibitory effects caused by wastewaters from energy production with special emphasis on gasification technologies.

The activities have been performed in a group chaired by the Danish Energy Agency and comprising other universities, research institutions and companies working with development, construction and operation of gasification plants. During the years the group has worked close together to improve understanding the basic processes and to support the practical application of new knowledge.

The present report summarises the work made at the Department of Water and Environmental Engineering and do not necessarily reflect the opinion of the Danish Energy Agency or other participant in the group.

The work has mainly been financed by the Danish Energy Agency and is a part of the Danish contribution to the work in the Gasification group of IEA. The Department has co-financed evaluation and development of the test method used in the project through a PhD-study finished in 2001.

The report contains results up to the end of 2001.

Jes la Cour Jansen
June 2003

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1. Introduction

Short historical background
Four Danish energy plans have been implemented in order to optimise the Danish energy sector to the present national and international conditions. The result has been a stabilisation of the annual gross energy consumption on 800 PJ, so there has been no increase since 1980.

This has been achieved mainly by implementation of energy savings, increasing efficiencies and establishing Combined Heat and Power (CHP) production.

The fourth and last energy plan Energy 21 was introduced in 1996. An important clue of Energy 21 is to maintain the target that Denmark must reduce the CO_2 emission by 20% by the end of 2005 compared to the 1988 level, and that the emission by the end of 2000 shall be stabilised under the 1990 level.

Energy 21 estimates that renewable energy covers 10% = 75 PJ of the country's total energy consumption in 2000. The initiatives in the field of biomass are directed towards the following subsidiary targets of Energy 21:

- Increased use of straw and woodchips at centralised power plants.
- Increased decentralised CHP generation based on straw, woodchips, biogas and landfill gas.
- Conversion of block heating units with an installed capacity above 250 kW in rural districts from fossil fuels to bio fuels.
- Right to establish bio fuel plants that were previously reserved for natural gas.
- Developing the use of energy crops such as cereal grain and rape.
- Accomplishing of a minor pilot project demonstrating the use of liquid bio fuels.

Gasification plays an important role in the plan and support is given to gasification projects from EU Joule, THERMIE, ENERGIE and FAIR. But also given from EUREKA and the Nordic Energy Research Program.

Further the Danish Energy Agency (DEA) has a number of National programs:

- The Energy Research Program (EFP) - supporting mainly strategic energy research. DEA has established an advisory committee for Environmental Friendly Power and Heat Production in order to determine the most essential research needs.
- The Development Program for Sustainable Energy (UVE) - supporting mainly the development and demonstration of renewable energy technology.
- Investment programme for heat and CHP from biomass technologies.
- The program for supporting industrial energy conservation - supporting mainly the implementation of more efficient commercially available energy technology in industries, but some support for development and demonstration activities are also granted.
- A Public Service Obligation provides the Utilities with the option to apply a part the consumer price for electricity to ensure a continuous development of Best Available Technology for electricity production.

In addition several projects related to gasification has been conducted and/or economically supported by the Danish power utilities.

The Danish Energy Agency Follow-up Programme for CPH
The Danish Energy Agency Follow-up Programme for CPH support the establishing of new CHP plants. The programme collects, evaluate and distribute production and performance data from commercial and semi-commercial/demonstration plants. The data are being controlled, registered and analysed by the general CPH monitoring program of the Danish Energy Agency.

The following institutes participate in the programme and are responsible for the validation and quality of the reported data. Danish Forrest and Landscape Research Institute (Fuel analysis), The Danish Technological Institute (Energy and environmental analysis), dk-TEKNIK ENERGY & ENVIRONMENT (Ash analysis), Danish District Heating Association (Economy analysis), Danish Utilities ENERGI E2/ELSAM (Plant operation data), Lund Institute of Technology (Wastewater analysis), RISØ National Laboratory (Tar and chemical analysis) and the Technical University of Denmark (Process analysis).

Data are presented every two months in the publication Danish Bio Energy.

The Department of Water and Environmental Engineering
The Department of Water and Environmental Engineering participate in the Danish Follow-up Programme for Small-scale Solid Biomass CHP Plants based on experience in toxicity testing of wastewater to be discharged to wastewater treatment plants and biological methods for detoxification of such wastewater. Tar-water, condensate and other wastewater streams from gasification plants, are intended to be discharged into the municipal sewer network and thereby treated in the local municipal wastewater treatment plant. However, such wastewater may contain very high concentrations of organic substances and/or substances inhibitory to nitrifying bacteria that are vital for the conversion of nitrogen in wastewater treatment plants. Discharges from industrial sources to municipal wastewater treatment plants are liable to a charge according to the content of among other things organic material and maximum permissible levels of inhibitory effects have been laid down.

In the follow-up programme the departments activities deals with three subjects related to discharge to the municipal sewer network:

- Characterisation of inhibitory effects caused by wastewaters from gasification plants, focusing on tar-water and on pure substances found in tar-water
- Biological degradation of inhibitory substances found in wastewater from gasification plants.
- Establishment of discharge permits for wastewater from gasification plants.

The report is introduced with a short presentation of gasification in Denmark. Then an overview i presented on the legislation concerning discharge of industrial wastewater such as scrubber water, condensate and other wastewater streams from gasification. Next the method for examination of toxicity to nitrifiers is presented. Two chapters describe the results from examinations of wastewater from gasifiers and from pure substances found in wastewater from gasifiers. Then results from biological detoxification of scrubber water from an up-draft gasifier are presented. Finally results of toxicity from other energy producing industries are presented.

2. Presentation of plants included in the report

The work has especially emphasised characterisation of inhibitory effects caused by wastewater from gasification plants but corresponding wastewaters from other energy producing plants based on biomass or fossil fuel has been included. Further a few internal generated similar wastewater streams from sludge treatment facilities at treatment plants that are expected to take care of the wastewater have been included. Below the gasification technologies are describes together with a short presentation of the other plants included in the examinations.

2.1 Energy production from Gasification of woodchips and straw in Denmark

Gasification has been in focus as potential technology to reach the targets in the Danish Energy plans since late 80'ties. Several research programmes have initiated research as well as commercial activities in the field.

In total 5 gasification plants have been in operation in Denmark. A small two-stage demonstration gasifier based on woodchips intended to supply a farm with heat and energy was in operation for at short period but is now closed (The Blære plant). The Haslev plant based on pyrolysis of straw has been mothballed after proving process stability.

Below is described the three Danish gasifiers, that have been in operation for longer periods and which are included in the present examination of toxicity of wastewater from gasification of wood. Two of the plants are commercially operated, while the last one has been extensively used for research. Further some pilot plants have been in operation for shorter period of time but they have not been included in the testing program up till now.

Finally inhibition results of wastewater from the gasifier at Chatel-St-Denis (Switzerland), has been included in the examination.

Harboøre CHP plant

In 2000 a complete biomass gasification process system fitted with two gas-engines of total 1,5 MW_{el} was set in operation at Harboøre district heating plant. This was the final step in a development process, which started in 1988.

Based on a traditional German up-draft moving bed gasifier Voelund in 1988-1992 experimented with a pilot unit for gasification of straw. Next step was construction of a woodchip-fired version of this gasifier, which since 1993 has been supplying gas to the boiler at Harboøre district heating plant. Thus the Harboøre gasifier operated continuously the demonstration plant served as gas producing unit for testing of a number of special features, in particular complete plant control, various gas cleaning technologies etc. In 1996 a major reconstruction was carried out resulting in full operation control of the plant with minimal operating staff and meeting the targeted number of operating hours. Since 1996 the gasification plant has produced all district heating for Harboøre. The final conversion to a CHP plant was completed late 1999.

In the year 2000 the engine and boiler CHP plant, now operated by Babcock & Wilcox Voelund, has been producing 15 000 MJ/s of heat and 900 MWh of power, with a total efficiency of 99%, due to the flue gas condensing unit installed after the boiler. The gasifier is fired with woodchips (max. 50% moisture). The electrical output was guaranteed to reach 2 times 648 kW_{el}, and a 6 MJ/s_{heat}, with an efficiency of total 85% and an electrical efficiency of 32%. One of the engines has now been pressurized for 760 kW_{el}, with a gas to electricity

efficiency of 36%. The two Jenbacher engines have been operated for 900 hours (by 2001), but the operation of the engines has been limited due to the heat consumption of Harboøre and the fact that it is necessary to get rid of the tar-contaminated wastewater by burning it together with the producer gas in the boiler. The gas cleaning is working but the wastewater from the gas cleaning is limiting the operating hours of the engines.

The gas cleaning system at Harboøre has successfully been developed in the course of the project.

Høgild CPH plant
In 2000 the Høgild plant has been converted from operation with wood blocks into conventional woodchips, with a moisture content of 35-40%. In May the new plant was put in operation and tested.

In 1994 the French Company Martezo supplied the original down-draft moving bed gasifier. However it turned out to have so many defects that a complete new gasifier and gas cleaning system were installed. The owner, Herning Municipality, contracted the reconstruction to the Danish engineering and boiler company Hollensen. In December 1998 the biomass fuelled CPH Høgild district heating was in operation, but fuelled with waste wood with limitations in size and moisture. Attempts have been made to use wood waste with higher moisture, but this has caused problems in the gasifier and gas cleaning system. In 2000 a redesign in order to obtain higher fuel flexibility was finished. This includes a drying of the fuels in the feeding system. In 2000 the engine supplied by Mercedes Denmark was in operation for 220 hours, since 1994 the engine has been operated for 7000 h. The electrical output is 130 kW_{el} and the heat output 160 MJ/s, with a guaranteed total efficiency of 80% and an electrical efficiency 24%. Higher efficiency after further redesign is expected.

Two-stage gasifier at DTU
The gasification group at Technical University of Denmark has constructed and operated a 75 kW_{th} two-stage gasification plant mainly for long term testing of the gasifier and for testing of essential components in the CHP set-up. A number of short and long term testing projects has been performed.

Gasification system at Chatel-St-Denis (Switzerland)
A plant of approximately 300 kW thermal capacity is installed and operated in Chatel-St-Denis (Switzerland). Woodchips commercially available are used without further treatment. Average moisture content is approximately 20 weight-% (dry basis).

The gasifier system has been developed at the Indian Institute of Science (IISc) in Bangalore (India). The principle bases on an open top down-draft gasifier with a secondary air inlet, through a set of nozzles, at the bottom of the gasifier. The reactor additionally has an annular of a stainless steel section at the top to recover a part of the sensible heat in the gas. The gas leaves the reactor with a temperature of approximately 450°C.

The hot producer gas leaving the gasifier is quenched in a two-stage water injection system. After the quench, the moist gas passes two granular beds with coarse and fine sand. The sand bed filters has shown a good performance for the collection of particles and tar components. The collection efficiency for particles has been found in the range of 73% to 99.8% with a mean of 86% and tar components can be removed from 50% to 97% with a mean of 73%. The clean gas leaves the sand bed filter at temperatures between 5°C and 25°C.

2.2 Energy producing plants and sludge treatment facilities included in the examination

Scrubber water and condensate has been examined at many different Danish and Swedish energy producing plants and sludge treatment facilities. As requirements for discharge of inhibiting substances is only imposed to few of the facilities the participation in the testing programme was followed by an agreement that the results could be presented without the name of the facility. However most of the facilities - but not all - have accepted that the plant name is included in the report. Only a very brief presentation is made as the facilities do not participate in the programme but just deliver samples for the testing programme.

Scrubber water from flue-gas cleaning of incineration of woodchips

Scrubber water from flue-gas cleaning of incineration of woodchips has been examined at three different facilities.

At the Harboøre gasifier the gas has for several years been used directly in the boiler for district heating. The scrubber water is discharged to the public sewer. The scrubber water has been examined twice.

Flintrännan in Malmö is a traditional woodchips fired boiler serving the district heating of Malmö city, Sweden. Scrubber water is treated with pH adjustment, polymer dosing and sand filtration before discharge directly to the Sound. Untreated as well as treated scrubber water has been examined.

Thyborøn District Heating Facility is a traditional woodchips fired boiler serving the district heating of Thyborøn in North Jutland, Denmark. The scrubber water is discharged directly to the local wastewater treatment plants without pre-treatment.

Scrubber water from flue-gas cleaning from incineration of a mixture of woodchips, peat and industrial waste

Scrubber water from flue-gas cleaning produced by incineration of a mixture of woodchips, peat and industrial waste for production of heat and steam has been examined at an industrial facility. The scrubber water is let to the biological wastewater treatment plant at the site. One examination has been made under normal operation and one at a start up of the facility.

Condensate from drying of woodchips and bark

Condensate from drying of woodchips and bark has been examined at two Swedish facilities. The plant for drying of bark and woodchips at Värnamo in Sweden has been examined twice. One examination was performed under normal operation and one at an occasion with drying of bark, where the operation was characterised as less satisfactory. The plant discharge the condensate to the local wastewater treatment plant after internal cleaning where the condensate is pH adjusted to around 9, polymer is dosed and particles is separated out in a lamella separator followed by a sand filter.

Drying condensate from production of wood pellets based on residuals from saw mills and pulp industries

Drying condensate from production of wood pellets based on residuals from saw mills and pulp industries have been examined twice at one Swedish facility.

Condensate from desulphurisation at Coal fired power plants

Condensate from desulphurisation at Coal fired power plants has been examined at two big Danish power plants -Asnæsværket and Nordjyllandsværket. Both plants discharge condensate to the public sewer after internal treatment. The internal treatment comprises

gypsum separation and precipitation of heavy metals in a system with pH adjustment, flocculation, sedimentation and sand filtration.

Condensate from power production based on natural gas
Heleneholm in Malmö, Sweden is fired with natural gas from Denmark. Flue gas condensate is discharge to the storm water system and is further let to the Sound without any further treatment. Work is in progress in order to use the condensate as water supply for the district heating. The condensate has been examined at one occasion.

Condensate from flue gas cleaning at an incineration plant for municipal solid waste
Högdalen in Stockholm, Sweden incinerates municipal solid waste and has combined power and heat production. Scrubber water from flue gas cleaning is discharge to the storm water system of the city after internal treatment comprise of pH adjustment, to-stage precipitation of heavy metals and sand filtration. The scrubber water has been examined before and after internal treatment.

Scrubber water from flue gas cleaning at waste incineration
Wastewater from the gas cleaning system at a Danish waste incineration plant has been examined.

Condensate from sludge drying
Condensate from a sludge drying facility at a big Danish wastewater treatment plant has been examined and compared to values from drying and incineration of sludge found in the literature.

3. Legislation for discharge of wastewater from industry in Denmark

In Denmark and in many other countries in Europe requirements for nitrogen removal from the municipal wastewater treatment plants have been implemented in order to reduce eutrophication of the receiving waters and especially in streams in order to reduce fish-toxicity. Table 3.I shows the Danish national guidelines for discharge of nitrogen from the largest (around 200) treatment plants together with the EU standards. The requirements in Denmark result in a reduction of about 80% of the incoming nitrogen. Around 100 of these plants, discharging into freshwater, have an additional discharge limit for ammonium. The typical requirement is 2 mg NH_4-N/l but values down to 1 mg NH_4-N/l are applied for sensitive streams.

Table 3.I: National guidelines for Danish and European municipal wastewater treatment plants.

Plant size **Connected people (PE)**	**Nitrogen** **(mg tot-N/l)**
Denmark	
< 5.000	No general guidelines
> 5.000	8
EU Wastewater directive*	
10.000 – 100.000	15
>100.000	10

* Applicable to sensitive areas

In addition to the discharge limits, the discharge of wastewater is taxed. The actual taxes (by 2003) are given in table 3.II. The annual tax for a typical plant serving a small town of 10,000 people is around 160,000 DKK (21.500 EUR).

Table 3.2. Taxation of discharge from Danish wastewater treatment plants.

Nitrogen	20 DKK/kg	(2.7 EUR/kg)
Phosphorus	110 DKK/kg	(15 EUR/kg)
Organic matter (BOD)	11 DKK/kg	(1.5 EUR/kg)

In order to keep the discharge permit and to save tax money, the municipalities tax industries that are discharging wastewater into the public sewer according to their relative load contribution to the plant.

Industrial effluents with content of substances toxic to the bacteria performing the biological conversion of ammonium into nitrate (so-called nitrifiers) have to follow national guidelines for the maximum permissible toxicity (Danish Environmental Agency, 1994). At the point of discharge, the maximum inhibition of nitrification has to be less than 20% for a 5-fold dilution of the wastewater using (ISO 9509, 1989) or similar methods for evaluation of nitrification inhibition. If the inhibition is above 20% but less than 50%, the wastewater can be discharged if the substances causing inhibition can be degraded in the wastewater treatment plant or from a general point of view can be judged as less important. If the inhibition is above 50%, permit to discharge will normally not be given. Dilution before discharge is forbidden and dilution in the sewer network cannot be taken into account.

In Sweden the Environmental Protection Agency has published a policy and recommendations for handling of nitrification-inhibiting wastewater (Swedish EPA, 1996). Based on that several Swedish municipalities have established rules for discharge of industrial effluents similar to the Danish ones described above.

4. Examination of inhibition of nitrification from wastewater

Inhibition of nitrification is in most cases evaluated by measurements of concentration changes in the substrates or products of the reaction, i.e. ammonium or NO_X. The exact mechanisms behind the inhibitory effects are known only in some rare cases. Many different microbiological mechanisms of inhibition exist and only for a few pure substances the mechanism of inhibition has been completely surveyed. For mixtures of substances the knowledge of mechanisms of inhibition is particularly limited, as very little attention has been paid to synergistic or antagonistic effects between different pure substances.

4.1 Method selection and description of the chosen method

Inhibition of nitrification is highly critical for the proper function of municipal wastewater treatment plants and different methods for evaluation of the inhibitory effects from industrial effluents have been developed. The ISO standard (ISO 9509, 1989) has been extensively used, but in order to optimise examinations of a greater number of industrial effluents a new test method for inhibition of nitrification has been introduced. The method is a screening method developed in Denmark and Sweden (Arvin *et al*., 1994) and (Swedish EPA, 1995). The basic principle of the method is that sludge from a municipal wastewater treatment plant containing nitrifying bacteria is mixed with a synthetic buffer and nutrient solution. The suspension is mixed with tap water and the wastewater under consideration in proportions, which secure the proper dilution of the wastewater. The mixture is shaken for 120 minutes, and then the nitrification is stopped by filtration and cooling of the samples. Nitrification inhibition is found by comparing the nitrate production in samples containing wastewater with reference samples without wastewater. See Figure 4.1. A detailed description of the method can be found in Appendix 1.

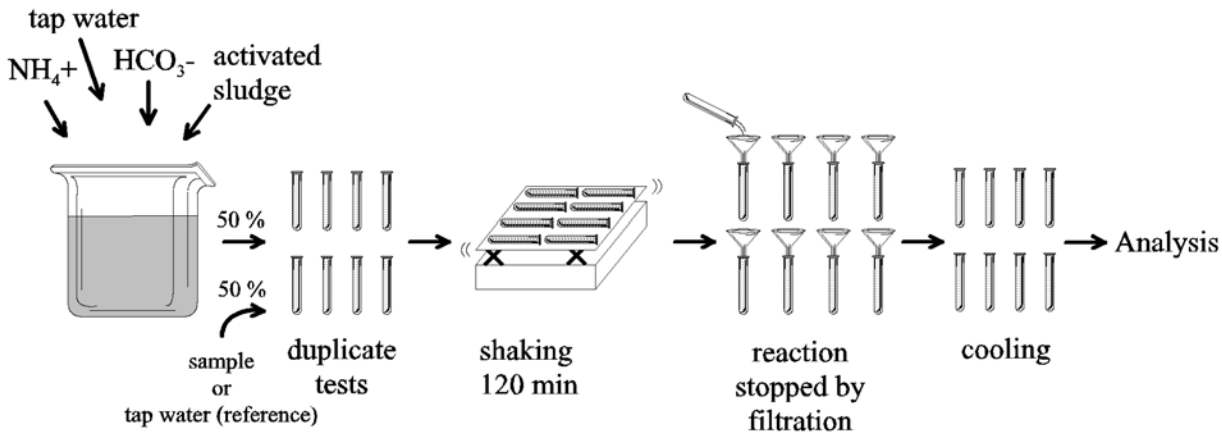

Figure 4.1. Schematic description of the screening method for determination of inhibition of nitrification.

As a standard the examination is performed with a fixed dilution of the wastewater in question and a dilution of typical 50% is used for municipal wastewater. However often the examination is performed with a series of dilutions in order to establish a dose-response relationship. The graphical presentation then typically looks like Figure 4.2. The test method can be applied for pure substances as well and in such cases the concentration replace the

dilution. As the inhibition is found from the difference between the test sample and the reference, minor negative inhibition may occur if the test sample is without inhibiting substances, due to the uncertainties related to the test. Further some substances are known to stimulate nitrifications, which also lead to negative inhibition.

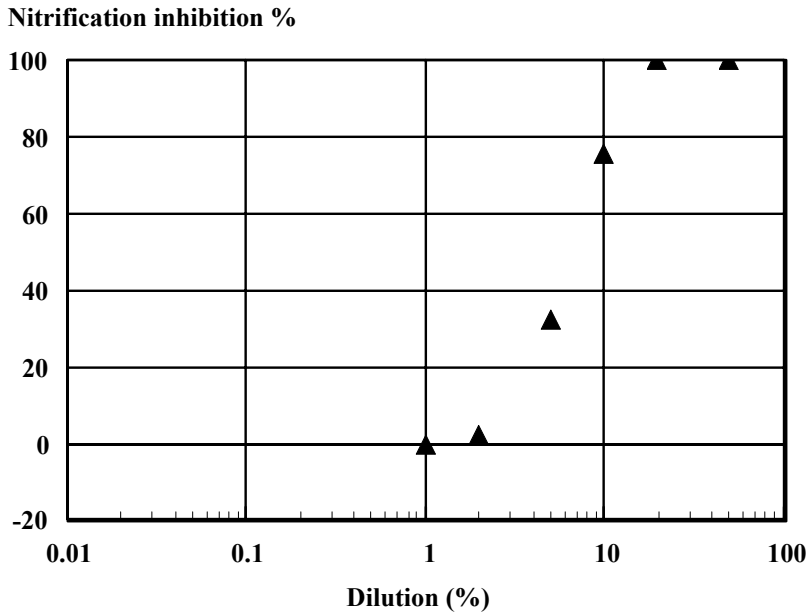

Figure 4.2. Typical dose-response relationship obtained with the screening method. The graph shows inhibition from condensate from the down-draft gasifier at Høgild.

Within the Follow-up programme the screening method has been tested against the ISO standard and an interlaboratory test has been performed between the Department of Water and Environmental Engineering and the Danish Reference Laboratory VKI (now DHI). Tar-water from the Harboøre plant was tested in parallel by the two laboratories, each with both methods. It was concluded that the two methods give similar results and the two laboratories measure similar inhibition even though slight deviations appear. These results are in line with other comparisons of the methods. The differences are probably due to different activated sludge used by the laboratories.

4.2 Method evaluation and interpretation of results

Within this project, the screening method has been further developed and evaluated. The results are briefly summarised below and described in detail in Jönsson (2001). The evaluation of the screening method has comprised the following elements:

Adaptation and choice of activated sludge type
It has been shown that activated sludge can adapt to toxicants to some degree. This means that slightly different results can be obtained with different activated sludge types. In most cases this is judged as unproblematic for the general characterisation and evaluation of the toxicity of a wastewater. However if the toxicity of a wastewater is close to the discharge requirements this effect must be considered. In addition, it was not possible to find an activated sludge type that is less or more sensitive to all the tested toxicants.

Pure cultures of nitrifying bacteria
Methods based on pure cultures of nitrifying bacteria have been evaluated against methods using activated sludge (the screening method). A larger percentage of the tested samples were judged as inhibitory by the pure-culture methods but on the other hand these methods also judged some strongly inhibitory samples as less inhibitory. The limit of detection for the pure-culture methods was in the same order of magnitude as for the screening method.

Effect of temperature
Screening tests were performed at different temperatures (15 and 20°C, respectively) in order to investigate the effect of the test temperature. No significant difference in inhibition was obtained.

Effect of nitrification rate
The nitrification rate of the activated sludge used in the screening test had no effect on the degree of inhibition found.

Effect of activated sludge concentration
It was shown that the toxicant to biomass ratio in the test tubes of the screening test might affect the results in some, but not in all, cases. If it is not known whether the toxicity of a wastewater will be affected by the activated sludge concentration or not it is recommended that the sludge concentration should not vary too much between experiments that are going to be compared.

Inhibition caused by the substrate
The inhibitory effect of some toxicants, the so-called competitive inhibitors, is affected by the concentration of ammonium in the test tubes. However, this is not a problem as long as the standard performance of the screening method is used

Sensitivity of the screening method
Special investigations were performed on two occasions in order to determine the limit of detection for the screening method. The limit of detection was about 5% inhibition for duplicate samples.

5. Inhibition found in full scale and pilot scale gasifiers

The wastewater from the gas cleaning systems at the full scale plants in Harboøre (up-draft gasifier), Høgild (down-draft gasifier) and at the experimental plants at DTU, Lyngby (two-stage gasifier) and in Chatel-St-Denis (Switzerland) (open top down-draft gasifier) has been examined. The plant in Harboøre has been extensively tested whereas the examinations at the other plants have been more limited. The examination at Høgild is from a period where the plant was operated with wood blocks before the reconstruction of the plant.

The gas cleaning systems of the plants are very different and in some cases the systems has changed dramatically. Below is presented inhibition results from untreated as well as treated wastewater.

Inhibition of nitrification from four different gasifiers.
The wastewater from the four gasifiers is very different in composition and in toxicity. At some plants samples can be taken from the final effluent of the gas cleaning system whereas other systems enable sampling inside the process. The different systems for cleaning of the gas and the wash water also differ a lot. Figure 5.1 shows typical inhibition curves from the wastewater from the gas cleaning systems from the four gasifiers. The wastewater from the up-draft gasifier at Harboøre and the two-stage gasifier at DTU comes directly from the gas cleaning systems whereas the wastewater from the down-draft gasifiers has been treated slightly before sampling.

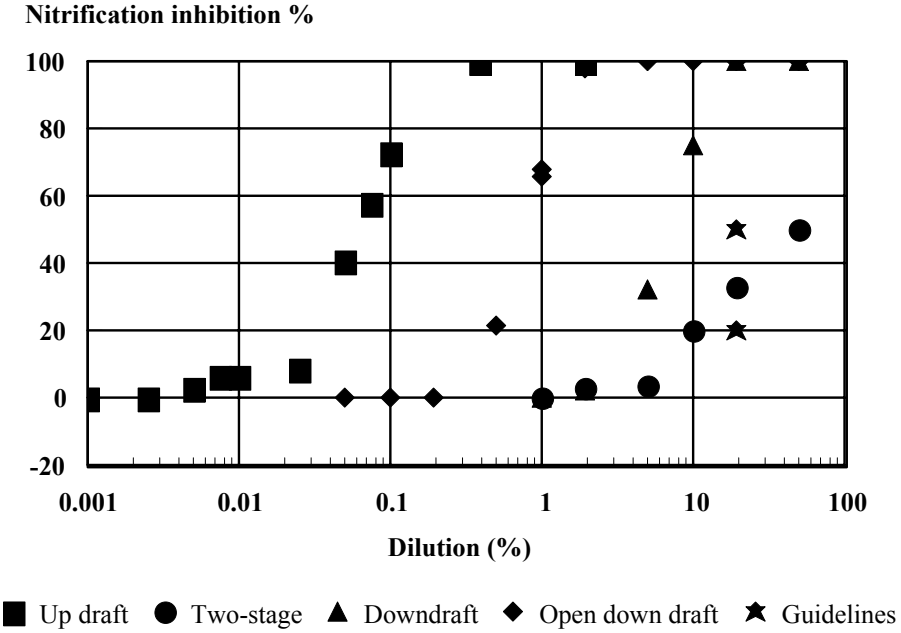

Figure 5.1. Inhibition curves for wastewater from the gas cleaning system from four different gasifiers.

It is seen that wastewater from the up-draft gasifier is about one decade more toxic to nitrifiers than the open top down-draft gasifier, two decades more toxic than the down-draft gasifier and about three decades more toxic than the wastewater from the two-stage gasifier.

Inhibition of nitrification from the gas cleaning system at Harboøre up-draft gasifier
The gas cleaning has been one of the bottlenecks for the full-scale gasifier at Harboøre. Many different systems have been tested leading to very different composition of the final wastewater to be discharged to the public sewer. The gasifier however has been in stable operation for years meaning that the untreated wastewater is rather stable in composition.

Results from raw wastewater and from three different cleaning systems are presented below in figure 5.2.

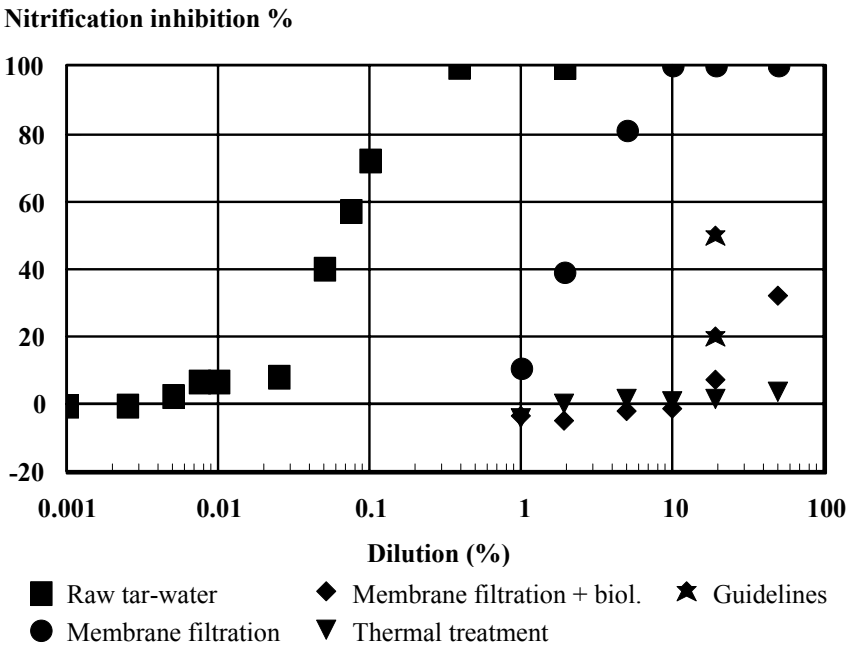

Figure 5.2. Inhibition curves from raw and treated tar-water from the up-draft gasifier at Harboøre.

It is seen that the membrane filtration reduce the toxicity by about 2 decades and that the biological treatment of the membrane-filtrated tar-water reduce the toxicity further, well below the discharge limits in Denmark. The biological treatment of the membrane-filtrated tar-water is further described in chapter 7. The thermal treatment of the raw tar-water leads to almost complete destruction of all toxic compounds.

Inhibition of nitrification from the gas cleaning system at Høgild down-draft gasifier
Wastewater from the down-draft gasifier at Høgild has been examined with respect to inhibition five times. Samples have been taken from the final effluent to the public sewer. Some samples may have been diluted before discharge. All examinations are performed before the completely rebuilding of the plant. The results are similar except for one examination where the inhibition was found to be very low. Figure 5.3 shows the results. Further a series of examinations has been performed with samples during one week but only with dilution of 20 %. They all showed inhibition of 100 %.

No testing of the inhibition from the treated condensate or from the plant after the latest rebuilding has been performed.

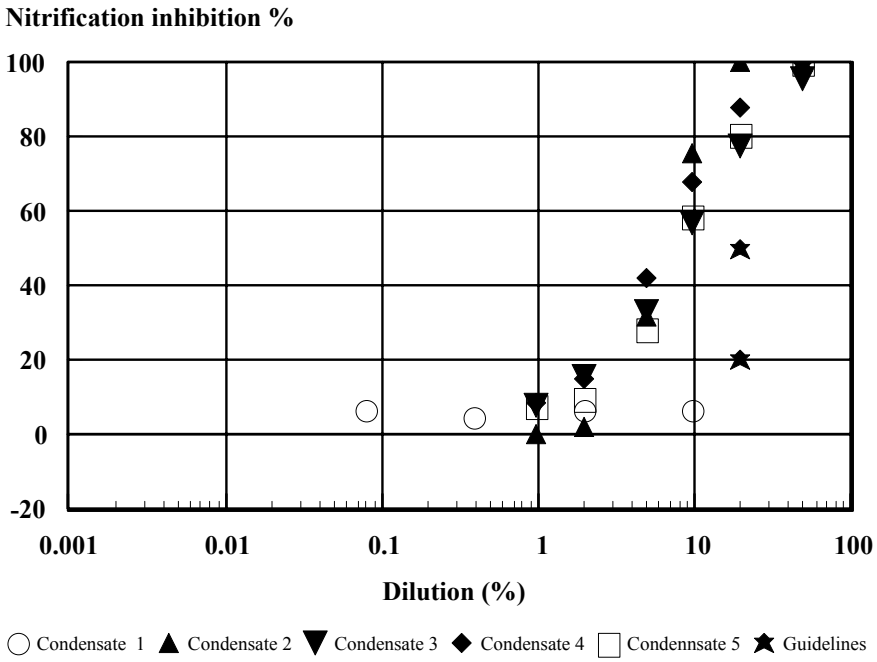

Figure 5.3 Inhibition curves for condensate from the down-draft gasifier at Høgild.

It is seen that condensates 2-5 almost give the same inhibition whereas one sample deviates and exhibits no inhibition. The reason has not been found but may be due to dilution with washing water. The System for gas cleaning has been rebuilt after the examinations.

Inhibition of nitrification from the gas cleaning system at the two-stage gasifier at DTU
Nitrification of condensate from the two-stage gasifier has been extensively studied in order to reduce the toxicity and in order to find the reason behind the toxicity, as the toxicity is limited but still not direct acceptable for discharge to the public sewer.

Figure 5.4 shows the results of inhibition of the washing water from 4 different examinations. It is seen that the inhibition is at two different levels.

In order to reduce the toxicity the wash water has been treated with activated carbon and the chemical composition of the water has been examined in order to identify the chemical substances causing the inhibition. Figure 5.5 shows the inhibition from the condensate before and after treatment with activated carbon. It is seen that activated carbon reduces the toxicity from condensate with a high initial toxicity to the low level toxicity, whereas no reduction is seen from condensate with lover initial toxicity.

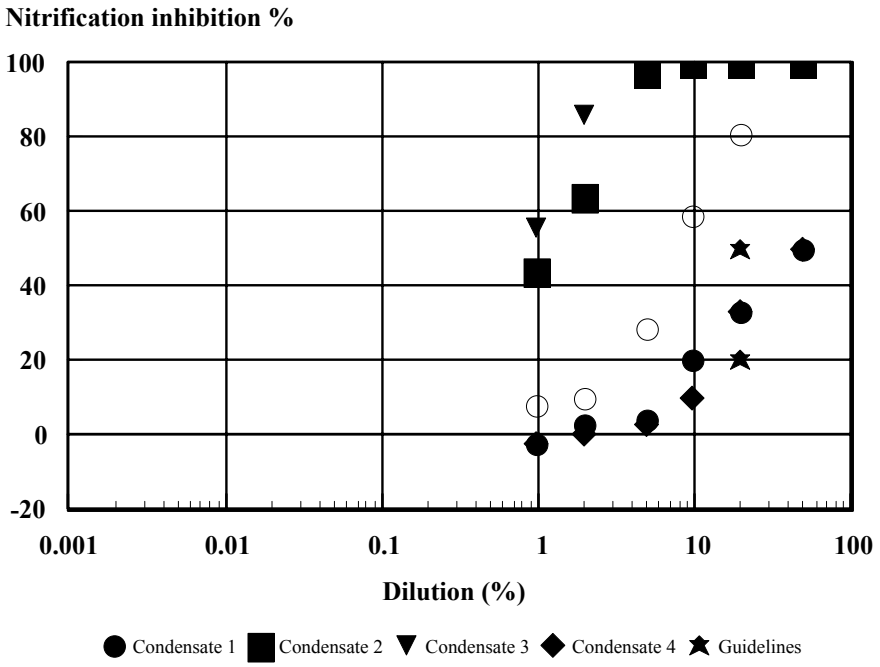

Figure 5.4. Inhibition curves for condensate from the two-stage gasifier at DTU from 4 different examinations.

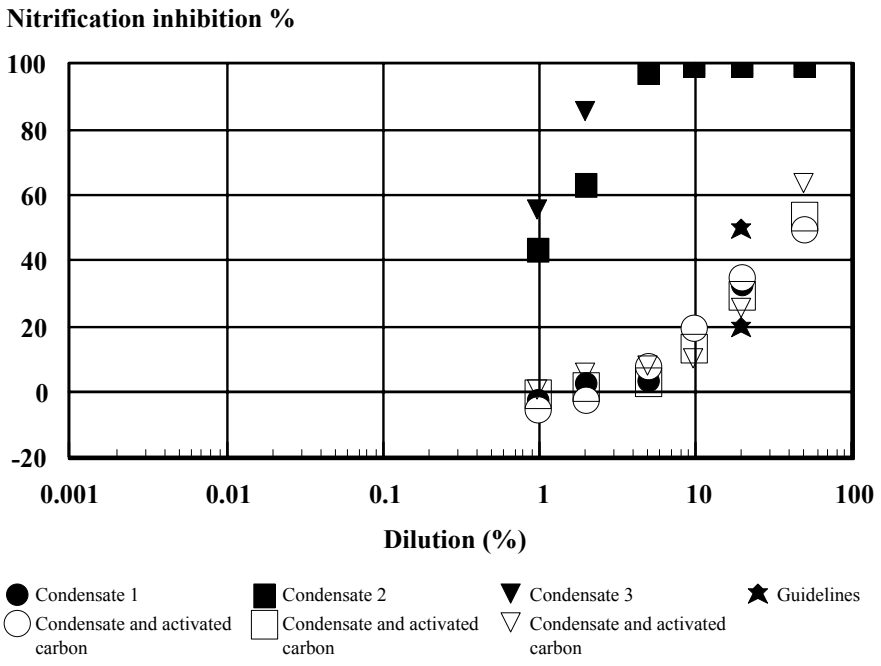

Figure 5.5. Inhibition curves for condensate from the two-stage gasifier at DTU before and after treatment with activated carbon from 3 different examinations.

In order to characterise the substances responsible for the low level inhibition condensate 4 was distilled and three fractions were obtained and tested for nitrification inhibition. Figure 5.6 shows the results. It is seen that the first fraction of the distillate is much more toxic than the condensate itself whereas the other two exhibit low toxicity. The toxic compounds at the low toxicity level are consequently easy to distil and not removed by activated carbon. Analyses of the different fractions showed at very high content of ammonium in the first distillate. As ammonium is known to be inhibitory for the nitrifiers especially at high pH the final examination of the inhibition of the condensate was concentrated on documentation of the significance of ammonium and pH for the toxicity. A series of tests were performed with varying concentration of ammonium and different levels of pH.

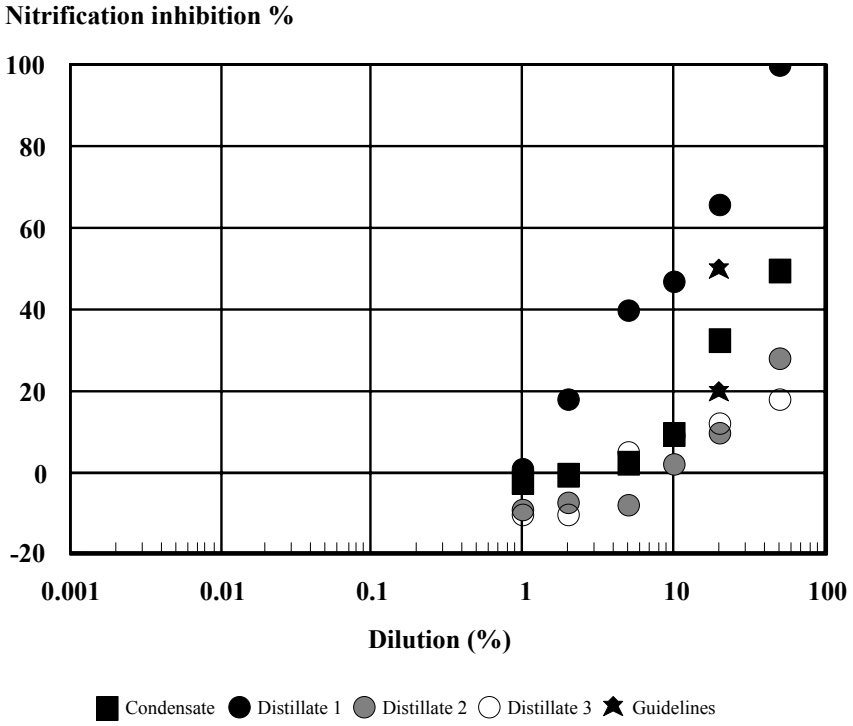

Figure 5.6. Inhibition curves for condensate and three distillates taken after each other from the two-stage gasifier at DTU.

Figure 5.7 shows the nitrification inhibition from ammonia at different pH together with the inhibition from the condensate and the distillates in figure 5.6. For each distillate the ammonium content has been measured and the inhibition is next shown as a function of that concentration. Distillate 3 did not contain ammonium and this distillate is consequently not included in the analyses. The pH in the tests of condensate and distillates is adjusted to slightly above 7 before the test. Some variation in pH appear during the test despite addition of bicarbonate as buffer due to production of acid from nitrification. However pH is in all tests kept above 7.

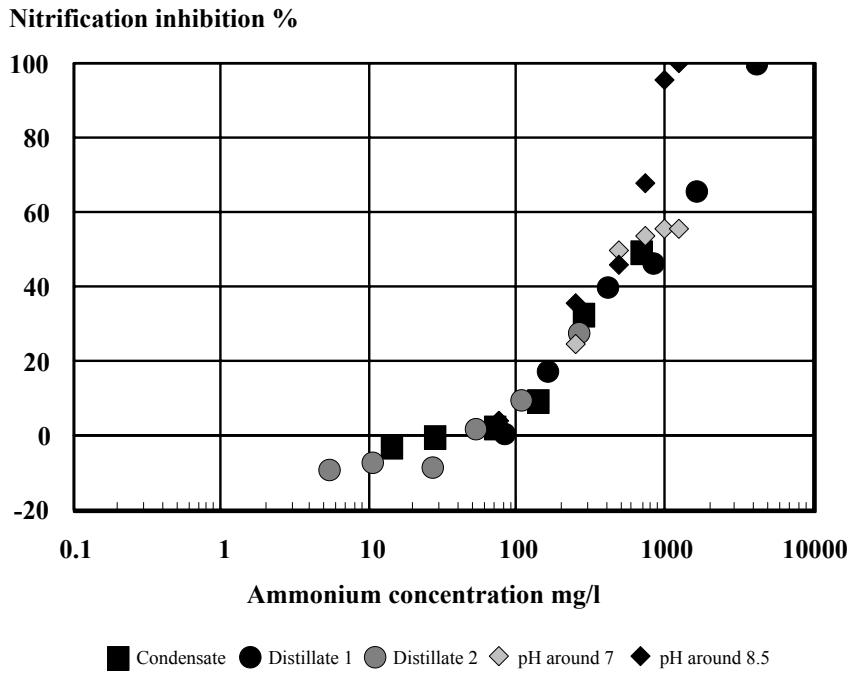

Figure 5.7. Inhibition curves for condensate and two distillates of the condensate from the two-stage gasifier at DTU as a function of the ammonium concentration in the samples together with the inhibition from ammonium at pH around 7 and around 8.5.

It is seen that the inhibition is a bit higher at high pH than at low pH especially at high ammonium concentrations. The inhibition in the condensate and distillates is very close to the inhibition from the corresponding ammonium concentrations. Consequently most of the inhibition in the condensate and the distillate can be explained by the ammonium content. In figure 5.8 this explanation of the main reason for inhibition is evaluated comparing the inhibition of the condensate together with the expected inhibition from the content of ammonium in each sample. It is seen that almost all inhibition can be explained by the content of ammonium.

The examinations have confirmed that the inhibition of condensate from the two-stage gasifier under good operation conditions or after treatment with activated carbon is attributed mainly to the content of ammonium. As ammonium is one of the substances treatment plants has been built for in Denmark, discharge of condensate can be looked upon just as other industrial discharged with high ammonium content. Dilution in the sewer network will easily bring the concentration down to a level that can be treated without problems and the only effect is increase of oxygen consumption and probably need for buffering of the wastewater.

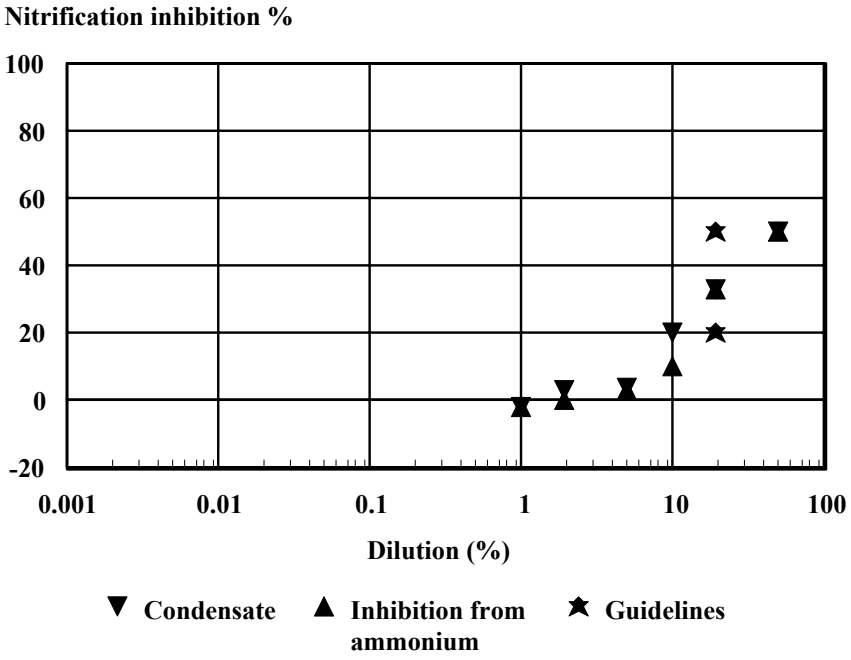

Figure 5.8. Inhibition curves for condensate and from the ammonium concentration in each sample.

Inhibition of nitrification from the gas cleaning system at the open top down-draft gasifier in Chatel-St-Denis (Switzerland)
Nitrification of wastewater from the gas cleaning system at the open top down-draft gasifier in Chatel-St-Denis has been tested before and after cleaning of the wastewater.

The "untreated sample" originates from the wash water circuit of the sand bed filters. The wash water circuit solely accomplishes the circulation and cooling of the condensate and has no additional units except a mechanical particle separation with a decanter.

The "treated sample" comes from a new wastewater treatment process. For confidentiality reasons, it can only be explained that the treatment/decontamination is based on an oxidative process.

Each of the two types of wastewater has been tested once and figure 5.9 shows the results.

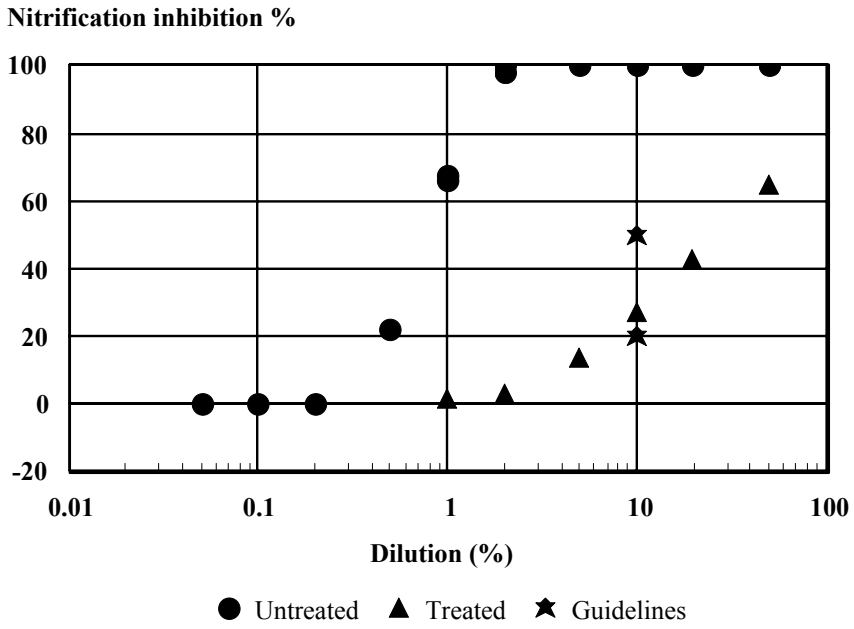

Figure 5.9. Inhibition curves from raw and treated tar-water from the open top down-draft gasifier in Chatel-St-Denis.

It is seen that the oxidative process reduces the toxicity significantly close to a level where discharge to the public sewer in Denmark can be accepted without problems.

6. Inhibition of pure substances present in wastewater from gasifiers

Some main constituents of tar-water have been identified and quantified by the laboratory at Risø, see Table 6.1. The table gives typical values for highest concentrations found during the examinations. Table 6.1 also includes substances that might be formed during thermal cracking of tar-water (e.g. hexamine), substances relevant in the context of some other energy-producing techniques than gasification of woodchips (sulphate, chloride), substances relevant to the method (ammonium, nitrite, nitrate) and a reference substance commonly used for nitrification inhibition (ATU).

As a substance was identified in tar-water, a solution of the corresponding pure substance was tested for nitrification inhibition at the laboratory at the Department of Water and Environmental Engineering at Lund Institute of Technology. The purpose of this study was to identify especially problematic substances or groups of substances present in tar-water.

Firstly, inhibition curves were determined for all substances. The screening method has been applied, and the activated sludge used in the tests originates from a treatment plant with industrial load from a variety of industrial branches. In most cases no literature data regarding nitrification inhibition was available and hence standard dilutions covering a wide spectrum of concentrations were used for the first screening test of each substance.

Thereafter attempts were made at finding out whether a substance is likely to contribute to the total inhibition of a specific tar-water by comparison of the inhibitory concentration for a substance (i.e. the inhibition curve) and the concentration of the substance found in the investigated wastewater types. In certain cases it was necessary to make supplementary analyses if, for example, data was sparse in the important region.

In some cases, synergistic and antagonistic interactions between the substances identified in tar-water were investigated. Synthetic tar-waters were prepared from pure substances so that the final concentration of each substance corresponded to the concentration in the real tar-water. The synthetic tar-waters were then analysed for nitrification inhibition.

Table 6.1. Pure substances investigated within this study.

Group	Substance	"Detected in what wastewater type"	Concentration in wastewater (g/l)
Simple alcohols	Methanol	Tar-water Down draft gasifier	3
	Ethanol		Low
Carboxylic acids	Acetate	Tar-water Down draft gasifier	30
	Formic acid	Tar-water Down draft gasifier	4.
Simple phenols	Phenol	Tar-water Down draft gasifier	0.85
Sum cresols			0.3
	o-Cresol		Similar to p-Cresol
	m-Cresol		Low
	p-Cresol		Similar to o-Cresol
Methoxy compounds	Guaiacol (2-methoxy-phenol)	Tar-water Down draft gasifier	1
	Me-Guaiacol (2-methoxy-4methyl-phenol)	Tar-water Down draft gasifier	0.5
	Anisole		-

Dihydroxybenzenes	1,2-dihydroxybenzene (pyrocatechol)	Tar-water Down draft gasifier	0.5
	1,2-dihydroxy-4-methyl-benzene (4-methyl-pyrocatechol)	Tar-water Down draft gasifier	0.2
Simple aromatic compounds*			
Aldehydes	Formaldehyde		Low
	Acetaldehyde		-
	Furfural		Low
	Cinnamic aldehyde		-
	Hexamethylentetramine		-
Reference substance	ATU		-
Inorganic substances	Ammonium		-
	Nitrite		-
	Nitrate		-
	Sulphate		-
	Chloride		-

* Inhibition results not reported, low solubility of the compounds in water, make test concentrations questionable.

6.1 Inhibition curves for pure substances

Dose-response relationships have been established for all the substances in Table 6.1 and plotted in separate figures for each group of substances below. ATU, which is a well-known and commonly used inhibitor of nitrification, has been used as a reference inhibitor within this study. ATU is also the most inhibitory substance tested, see Figure 6.1. Comparisons to a database of inhibition found in the literature (Blum and Speece, 1991) have also been performed. Blum and Speece used an activated sludge fed by a synthetic medium in their investigations while the activated sludge used within this study originated from a full-scale wastewater treatment plant. As pointed out before, different activated sludge types might exhibit different sensitivities to toxicants. Therefore it was not expected that the results of Blum and Speece would be identical to the present results, but that the results of the two investigations would rank the different substances reasonable equal.

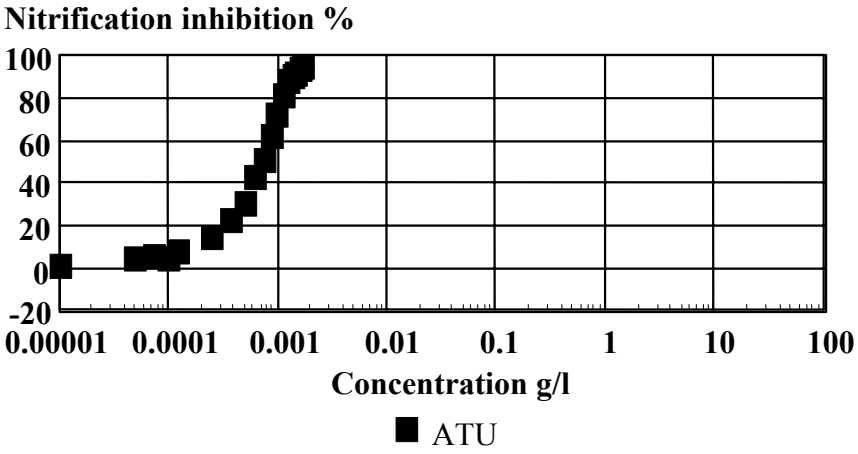

Figure 6.1. Inhibition curve for ATU.

Simple alcohols
According to the inhibition curves methanol is about ten times more inhibitory than ethanol, see Figure 6.2. Blum and Speece (1991) also found that methanol is more inhibitory to nitrifying bacteria than ethanol, but with the EC_{50} values 0.88 g/l and 3.9 g/l for methanol and ethanol, respectively. (The EC_{50} value is defined as the concentration that gives 50% reduced process rate or affected organisms.) Methanol and ethanol are easily degradable in municipal wastewater treatment plants.

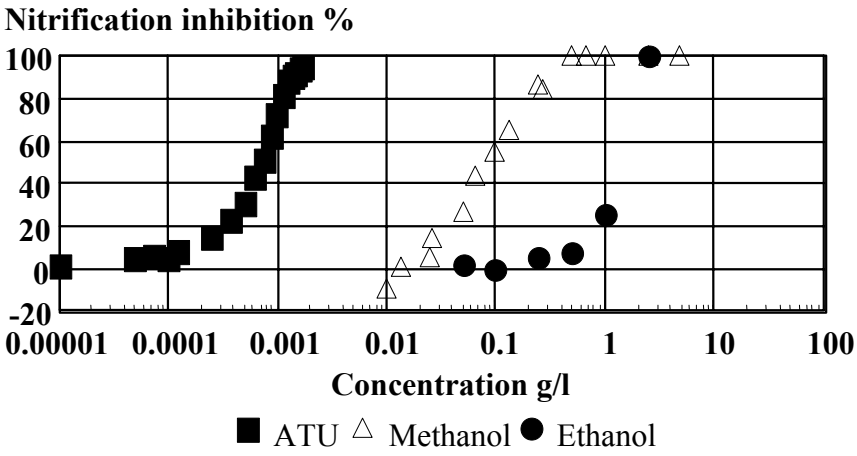

Figure 6.2. Inhibition curve for ATU, methanol and ethanol.

Carboxylic acids
The carboxylic acids was the group of organic substances found in tar-water that caused least inhibition of nitrification, see Figure 6.3, below. In addition both acetate and formic acid are known to be easily biodegradable in municipal wastewater treatment plants.

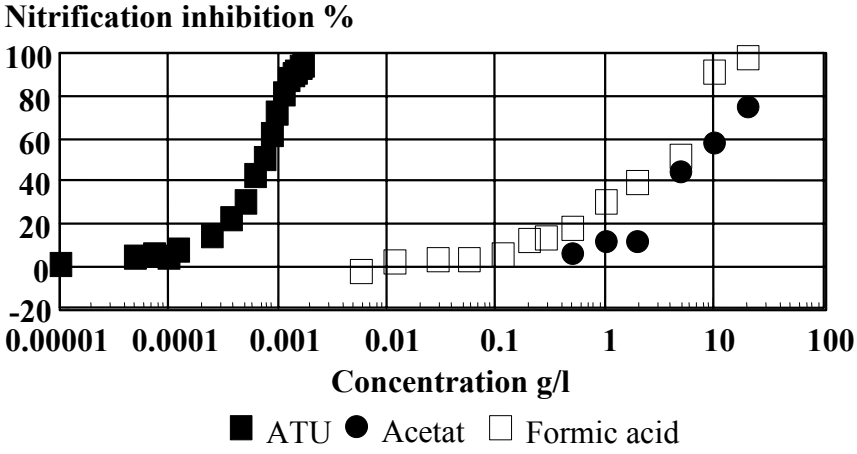

Figure 6.3. Inhibition curve for ATU, acetate and formic acid.

Simple phenols
The simple phenols detected in tar-water all turned out to be strongly inhibitory to nitrification, almost as inhibitory as the reference substance, ATU, see Figure 6.4. The four substances form a homogenous group and exhibit more or less identical inhibition curves. The simple phenols were the most inhibitory group of organic substances found in tar-water. Blum

and Speece (1991) found the EC_{50} values of phenol, m-cresol and p-cresol to be 0.021 g/l, 0.00078 g/l and 0.027 g/l, respectively, which indicates that m-cresol would be far more inhibitory to nitrification than the other two substances. No such difference was found within this study.

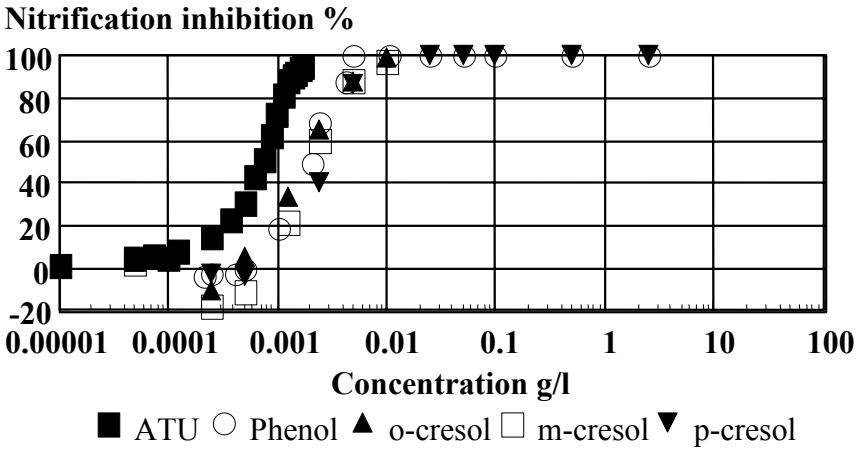

Figure 6.4. Inhibition curve for ATU, phenol, o-cresol, m-cresol and p-cresol.

Methoxy compounds
Also the group of methoxy compounds turned out to be strongly inhibitory to nitrification. Anisole and guaiacol exhibited roughly the same inhibition as the simple phenols whereas 2-methoxy-methyl-phenol (me-guaiacol) was somewhat less inhibitory.

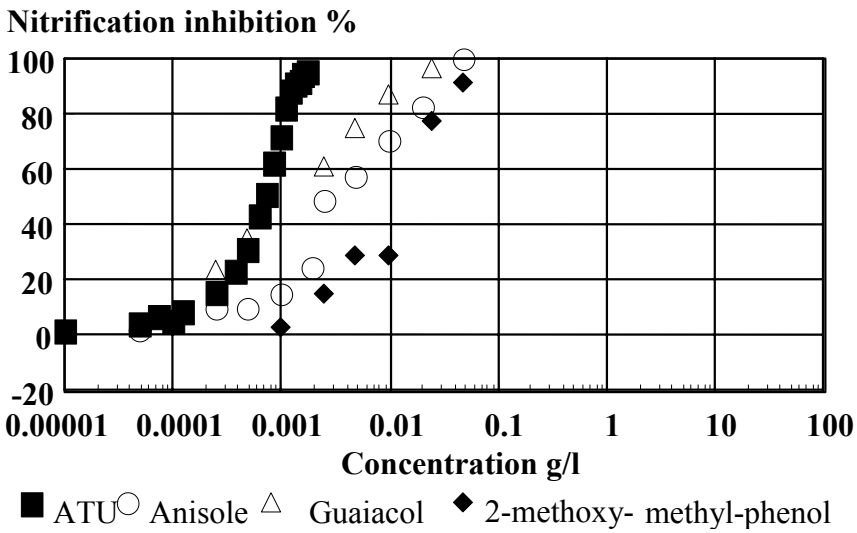

Figure 6.5. Inhibition curve for ATU, anisole, guaiacol and 2-methoxy-methyl-phenol (me-guaiacol).

Simple aromatic compounds
The inhibition curves of benzene and quinoline indicate that these substances are two decades less inhibitory than ATU (Figure 6.6). Blum and Speece (1991) found an EC_{50} value of 0.013 g/l for benzene, which is in good agreement with the inhibition curve fond within this study. Naphthalene and indéne have also been tested for nitrification inhibition, but the solubility in water of these substances is low, which resulted in uncertainties in the test performance. The

laboratory at Risø prepared two solutions using methanol as a solvent, containing indéne and naphthalene respectively. Methanol was regarded as an appropriate solvent to use as the tar-water contains methanol. The solutions were diluted until the methanol concentration did not result in any inhibitory effect. For the diluted solutions, it was shown that the resulting concentrations of indéne and naphthalene were not inhibitory.

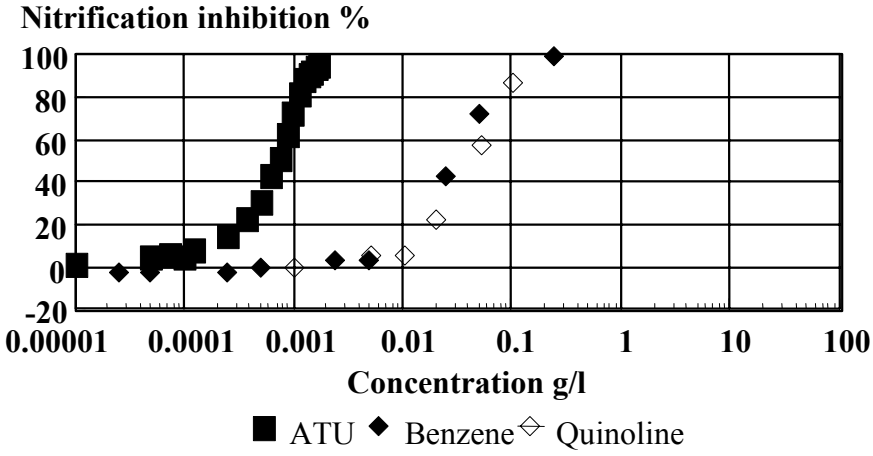

Figure 6.6. Inhibition curve for ATU, benzene and quinoline.

Dihydroxybenzenes
The tested dihydroxybenzenes are also two decades less inhibitory than ATU, see Figure 6.7, which means that the nitrification inhibition caused by these substances is in the same order of magnitude as the inhibition caused by methanol.

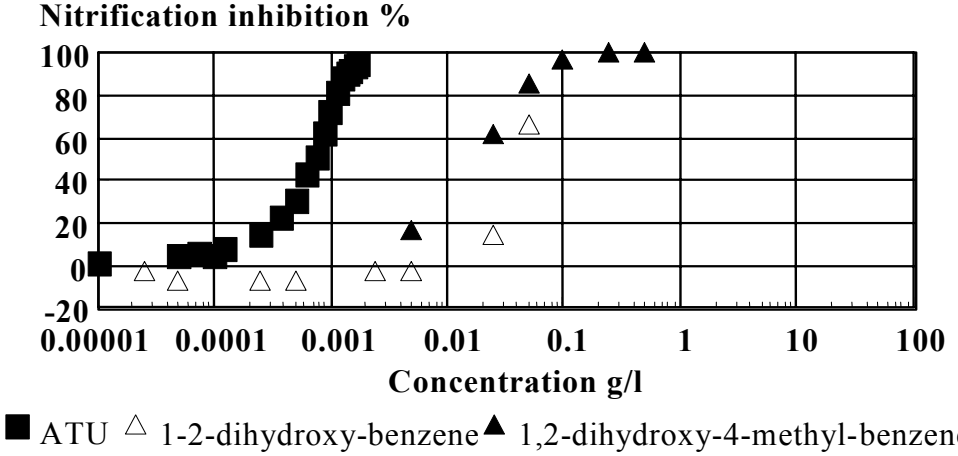

Figure 6.7. Inhibition curve for ATU, 1-2-dihydroxy-benzene and 1,2-dihydroxy-4-methyl-benzene.

Aldehydes
Furfural, cinnamic aldehyde and formaldehyde are also two decades less inhibitory than ATU, acetaldehyde is another decade less inhibitory whereas hexamine did not exhibit any significant inhibition in the test (Figure 6.8).

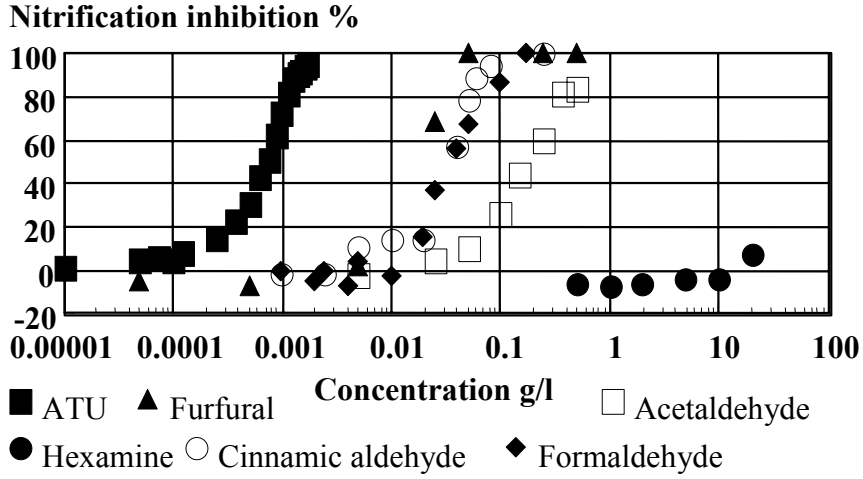

Figure 6.8. Inhibition curve for ATU, hexamine, furfural, cinnamic aldehyde, formaldehyde and acetaldehyde.

Inorganic substances
Some inorganic substances have been tested for inhibition of nitrification as some of them are relevant in the context of some other energy-producing techniques than gasification of woodchips and as some of them are relevant to the screening method itself. Figure 6.9 shows inhibition curves for ATU, ammonium, nitrite, nitrate, sulphate and chloride.

It was questioned whether the inhibition found for NaCl was caused by the sodium ion or the chloride ion. Therefore a minor study of inhibition caused by six different chlorides tested in parallel was performed. As seen in Figure 6.10 the inhibition caused by the different chlorides is roughly the same except for CaCl, which exhibits less inhibition than the others, and lithium chloride, which exhibits more inhibition.

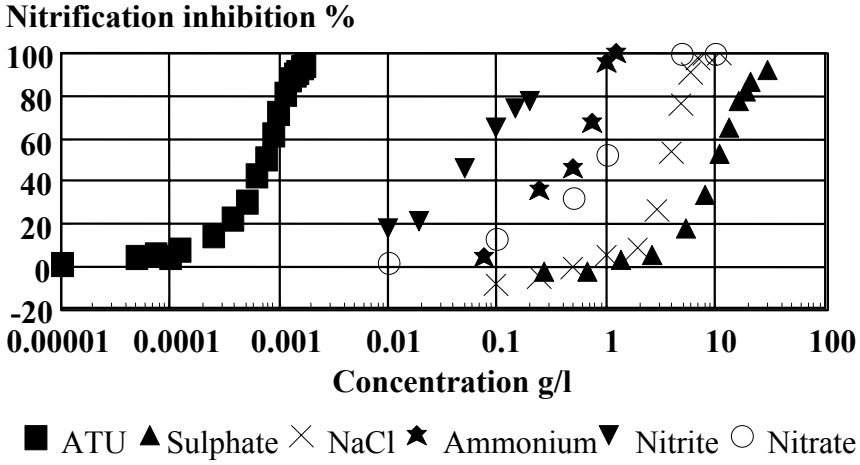

Figure 6.9. Inhibition curve for ATU, sulphate, chloride ammonium nitrite and nitrate.

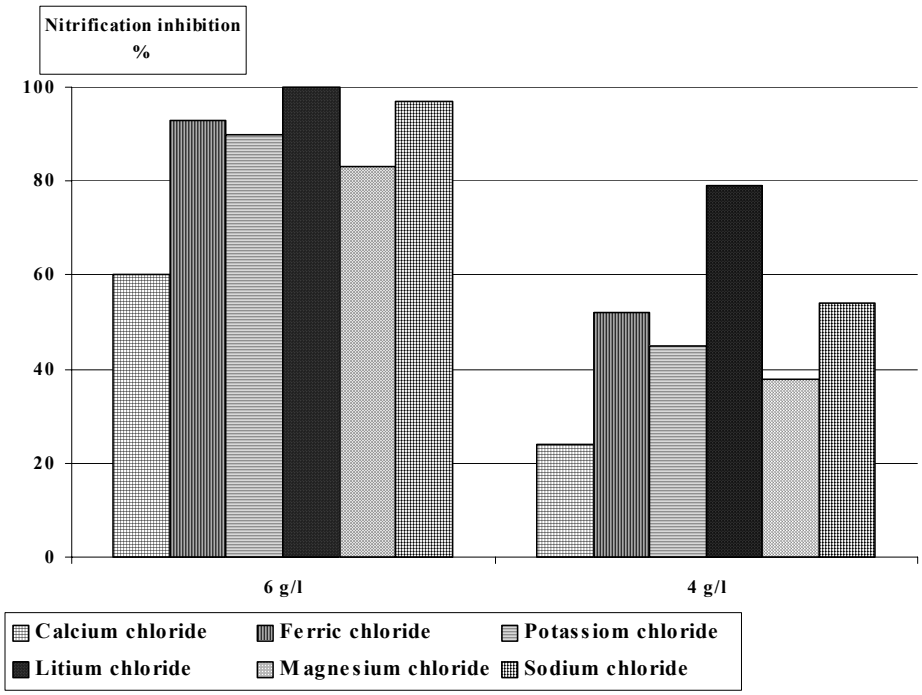

Figure 6.10. Inhibition of nitrification caused by different chlorides.

6.2 Combined effects of two or more substances

When two or more toxic substances are mixed, it is not obvious what the resulting inhibition will be. The substances may act in both a synergetic and an antagonistic way. In order to investigate the combined effect of different substances, mixtures of pure substances were prepared and tested in laboratory experiments.

This strategy might be fruitful in the search for the cause of inhibition. If it is established that a wastewater contains certain substances, it may help in explaining the toxicity if these substances are tested both alone and in mixtures.

The first two substances that were identified and quantified in tar-water were methanol and phenol. A synthetic tar-water containing the same concentrations of methanol and phenol as the tar-water was prepared, and analysed for inhibition of nitrification. The pure substances were also analysed separately in the same concentrations as in the tar-water.

In Figure 6.11, measured inhibition of methanol, phenol and a mixture of them are plotted together with the calculated sum. The chosen concentrations of methanol (1.35 g/l in the stock solutions) and phenol (0.021 g/l in the stock solutions) correspond to concentrations found in membrane-filtrated tar-water from a woodchips gasifier. The calculated sum of the measured methanol and phenol values is also given. In this case, the inhibition values can be added together as the calculated and measured sum of inhibition is practically equal.

Later, some other constituents of the membrane-filtrated tar-water from the woodchips gasifier were identified and quantified, see Table 6.1. All the constituents were analysed for nitrification inhibition, both alone and in mixtures. In Figure 6.12 it can be seen that the mixture of the identified constituents makes up a significant part of the total inhibition of the real tar-water. Thus it can be concluded that the dominating inhibitory constituents have been found, but that some unknown substances may also contribute to the inhibition to a minor extent.

Using analyses of inhibition of the pure substances, the sum of the inhibition of all known constituents in the tar-water has also been calculated. As seen in Figure 6.12, the calculated inhibition overestimates the inhibitory effect at tree of the evaluated concentrations, which means that it is uncertain whether the inhibition values of the tar-water constituents can be added together or not. Further it is seen that the synthetic and the real wastewater almost have the same toxicity indicating that the main toxicants in the wastewater have been identified.

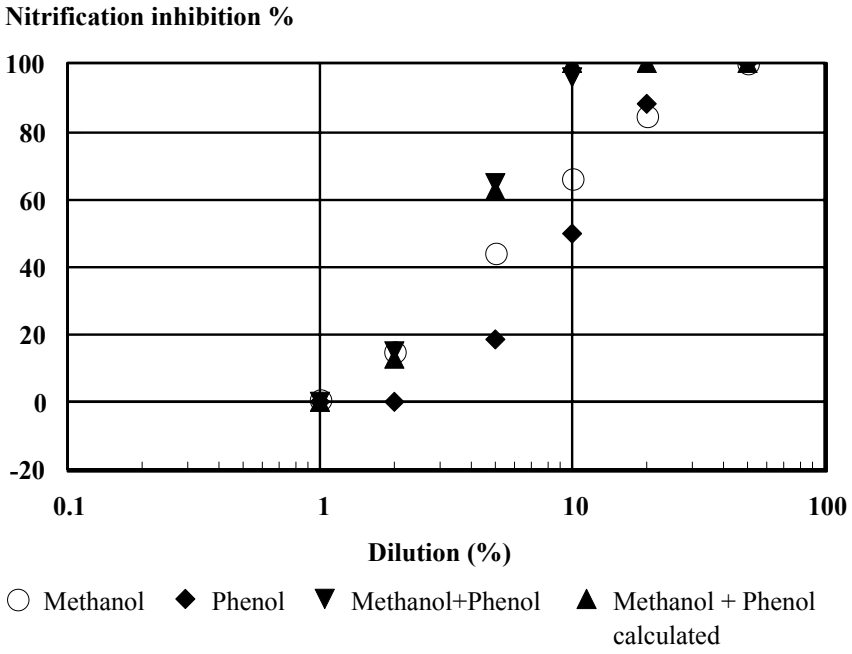

Figure 6.11. Inhibition of nitrification caused by methanol, phenol and a mixture of the two.

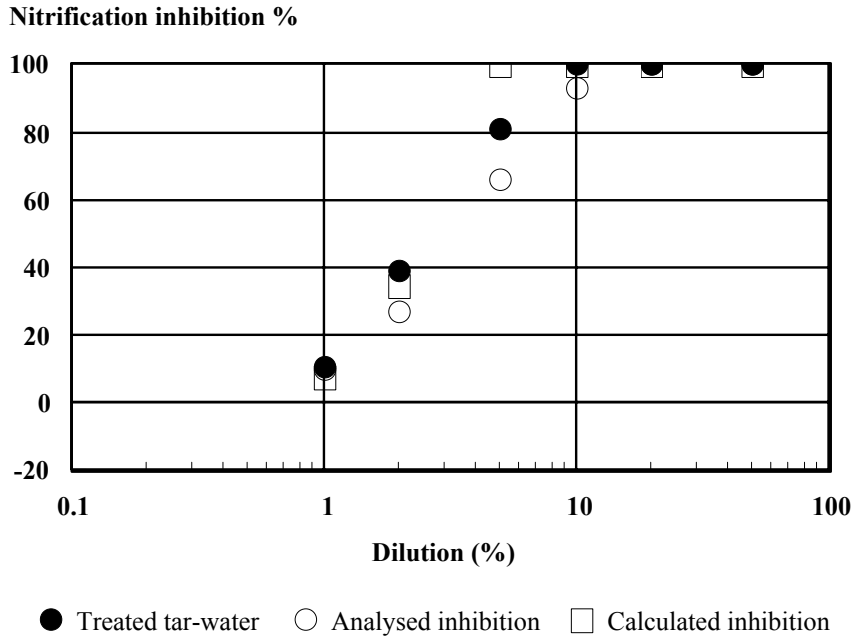

Figure 6.12. Inhibition of nitrification determined for a tar-water and for a mixture of its known constituents, together with the calculated inhibition based on analyses of each substance.

7. Biological detoxification of tar-water

The up-draft woodchips gasifier at Harboøre has been in operation for several years. In the beginning the produced gas was solely used for district heating but in 2000 two gas motors were installed in order to combine heat and power production. The gas has been cleaned in a wet process and the gas is used without great problems in the motors. However the wastewater from the gas-cleaning system (tar-water) makes up a serious problem. The tar-water together with a number of substances found in the water has been tested for nitrification inhibition as described in chapter 4 and 6. It has been demonstrated that a dramatic reduction of inhibition has to be performed before discharge to the public sewer can be accepted.

One possibility to perform such a reduction of the toxicity is to introduce membrane filtration reducing the toxicity and the content of organic substances more than one decade. The wastewater could thereafter be treated separately in order to reduce the toxicity further or the local municipality could accept the discharge if it is demonstrated that the toxicity comes from easily biodegradable organic substances. Below, an experiment for separate degradation/detoxification of membrane-filtrated tar-water is described. The description is based on (Jansen *et al*., 2001).

Laboratory-scale SBR process
The biological treatment was performed in a laboratory scale SBR process (Figure 7.1) in order to evaluate detoxification and degradability of the tar-water. The SBR was operated using a 24-hour cycle as shown in the right part of the figure with 22.5 hours of fill and aeration and 1.5 hours of sedimentation and decantation. As the tar-water does not contain enough nitrogen and phosphorus for the biological process, nitrogen and phosphorus were added to the reactor. The minimum and maximum liquid volumes in the reactor were 3 and 4 litres respectively.

During 54 days, increased amounts of membrane filtrated tar-water were added to the reactor. Then the dosage was stopped but the operational cycle was continued for 11 more days with aeration 24 hours a day. Samples were taken directly in the reactor during the latter period.

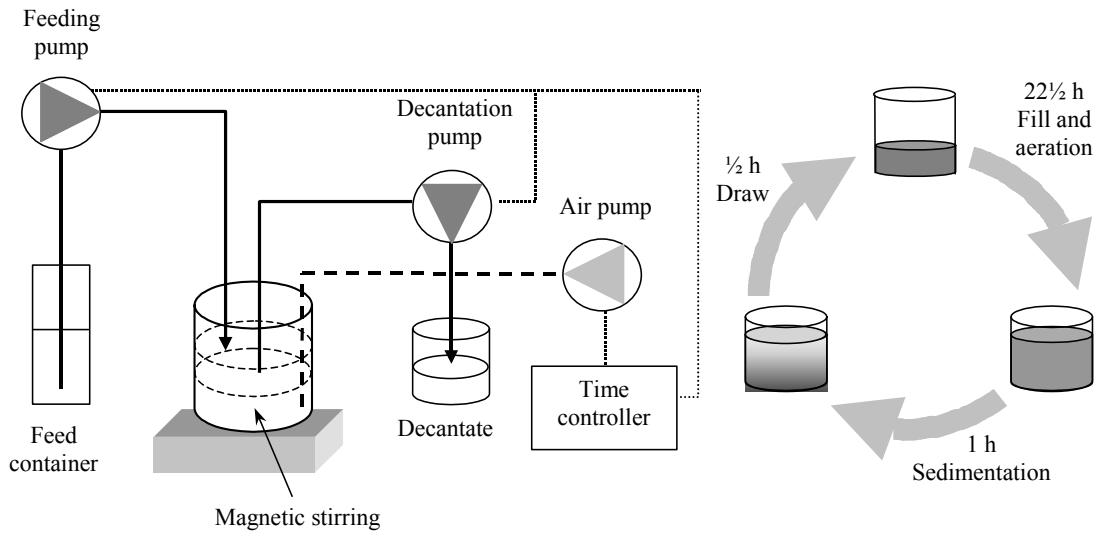

Figure 7.1. Arrangement of laboratory equipment for biological treatment of membrane-filtrated tar-water and the operational cycle applied for the SBR.

The Oxygen Uptake Rate (OUR) was measured to be able to evaluate the state of the sludge. Every day at a specified time the aeration was turned off and the decreasing oxygen concentration was followed.

Residual organic matter measured as chemical oxygen demand with dichromate (COD) was measured in the treated water and the COD removal was followed in order to evaluate the degradability of the organic matter. The toxicity to nitrifying bacteria of the treated water was measured in order to evaluate the detoxification.

Characteristics of the tar-water

It has been shown that the raw tar-water from the up-draft gasifier is highly inhibitory to nitrifying bacteria. Membrane filtration has been shown to reduce the COD concentration in the tar-water from 160 000 mg/l to 11 000 mg/l and it has also been demonstrated that this kind of treatment reduces the toxicity significantly, see figure 7.2.

It has also been shown that the tar-water contains many different inhibitory compounds. Some main constituents of the membrane-filtrated tar-water were identified and quantified, see Table 7.1. The toxicity that remains in membrane-filtrated tar-water originates to a large extent from simple organic substances (methanol, acetic and formic acid), which is expected to be accepted for discharge to the public sewer without problems. However, the membrane-filtrated tar-water also contains phenol and other phenolic substances to an extent that questions discharge into the public sewer.

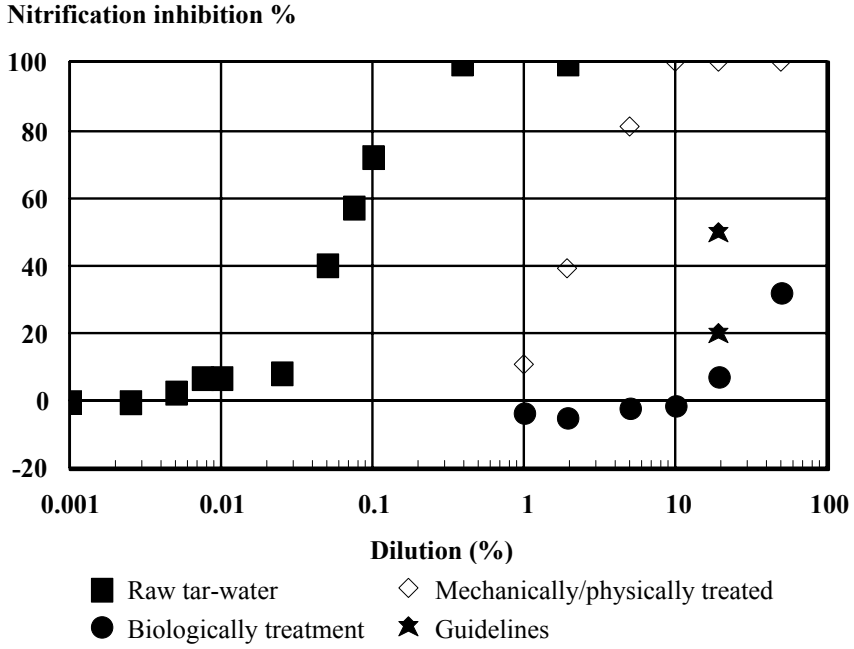

Figure 7.2. Inhibition of nitrification measured in raw, membrane-filtrated and biologically treated (day 65 in Figure 7.3) tar-water from an up-draft gasifier together with the Danish guidelines for discharge to the public sewer.

The identified constituents of membrane-filtrated tar-water are organic substances and they make up almost half the COD content of the wastewater. According to Blum and Speece (1991) the concentrations of phenol and methanol found in the tar-water correspond to 50% nitrification inhibition (EC_{50}) and much more than 50% nitrification inhibition, respectively.

Results from inhibition measurements on solutions of pure substances performed within this study are shown in Table 7.1. The stock solutions were prepared so that the concentration of the toxicant in question corresponded to the concentration in the tar-water. 50% dilution was applied in the screening test, meaning that the results given in Table 7.1 apply to half the concentration in the real tar-water. The results confirm that the total inhibitory effect of the identified organic substances is likely to be substantial. As a considerable part of the tar-water inhibition could be derived from organic substances, it was supposed that it would be possible to reduce the toxicity by biological treatment. In addition, based on measurements by Blum and Speece (1991), no dominant impact on aerobic heterotrophs by the major inhibitory substances, methanol and phenol, were expected to be found for the concentrations in question.

Table 7.1. Identified constituents of a membrane-filtrated tar-water from an up-draft woodchips gasifier. The concentrations are expressed in terms of both substance and COD. Measured inhibition found by the standard procedure of the screening method is also given.

Substance	Concentration in tar-water (mg substance/l)	Concentration in tar-water (mg COD/l)	Nitrification inhibition applying to half the concentration measured in the real tar-water (%)
Methanol	1350	2025	100
Phenol	21	50	100
Acetic acid	2220	2370	4
Formic acid	580	202	14
Guaiacol	8.6	18	61
Me-Guaiacol	2.8	6.2	4

Operational strategy of the SBR

The system was started up using sludge from the municipal wastewater treatment plant in Lund, Sweden. The treatment plant is a one stage activated sludge plant with nitrogen and phosphorus removal and a sludge age of about 20 days. Before start the Oxygen Uptake Rate (OUR) of the sludge was measured with acetate as a carbon source.

As the inhibitory substances in Table 7.I can be aerobically degraded the dosing strategy was based on a calculation of the expected degradability potential of the sludge based on the OUR measurements. All workdays OUR was measured and the potential COD reduction was calculated based on the OUR measurement, the sludge content in the reactor and an assumption of a yield coefficient of 0.5 g SS/g COD removed. In the beginning the dose was reduced compared to the calculated potential in order to admit a small adaptation time for the sludge to the tar-water but after few days of operation the dosage was increased gradually according to the calculated COD reduction potential. Figure 7.3 shows the actual COD dose each day (i. e. each operational cycle) together with the calculated COD reduction potential. The figure also includes the effluent COD.

The COD reduction potential in the reactor increased rapidly as a result of the increase in the respiration rate of the sludge due to the higher sludge load and as a result of increased sludge content in the system. It appears from the figure that the dosing strategy in general was satisfactory, leading to a rapid increase of the dosage, without overloading. However after day 36 when 100 percent tar-water was dosed the potential was too small to ensure complete removal of COD and a build-up began. A period with reduction of the COD-load stabilized

the effluent but as the load was increased again the overload appeared once more until the complete stop of tar-water supply on day 55. Within a few days after the stop of the feeding, COD was dramatically reduced. Note that after the stop of dosage the OUR measurements is of no use for calculation of the COD reduction potential as the rate is reduced as a result of reduced supply of easy degradable organic matter and not as a result of changing sludge properties.

The residual COD concentration in biologically treated tar-water was reduced to about 600-800 mg COD/l, which is less than a tenth of the COD in membrane-filtrated tar-water.

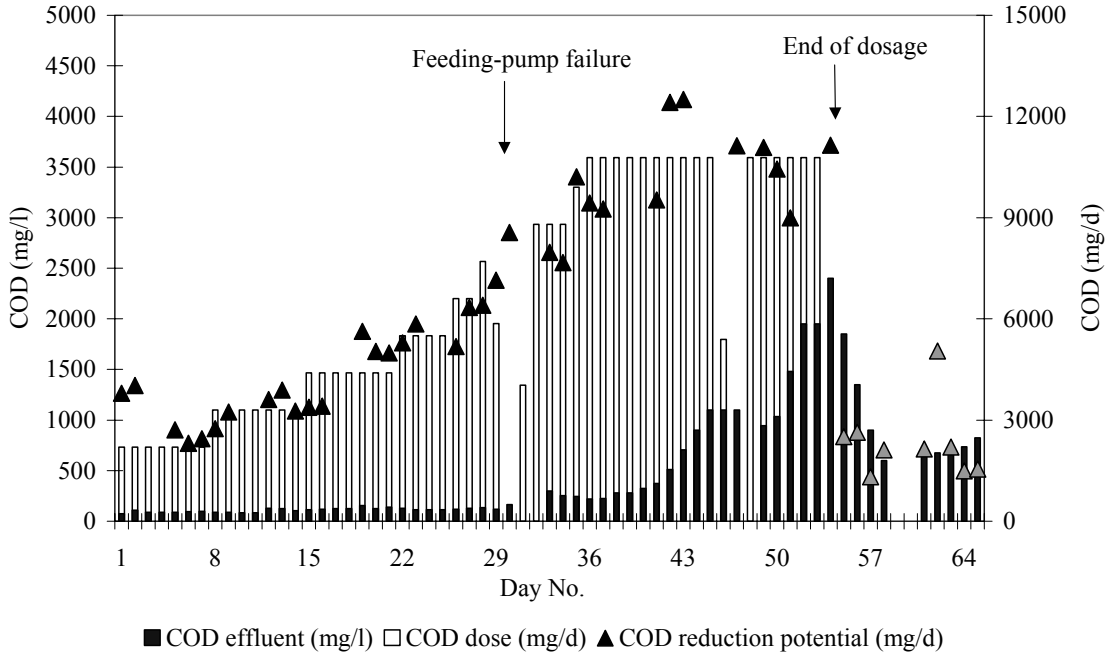

Figure 7.3. Potential COD reduction and dosing in the reactor together with the effluent COD.

Detoxification of the tar-water

The increasing percentage of tar-water in the reactor and the development of the toxicity of the treated water are shown in Figure 7.4. As seen in the figure the toxicity of the treated tar-water was kept around 20% despite an increased concentration of tar-water in the reactor up to about 80%. Compared to the results for the membrane-filtrated tar-water in Figure 7.2, it is a substantial improvement. When the concentration of tar-water in the reactor was increased to 100%, the plant was overloaded and the inhibition rose to 100%. When the feed to the reactor was stopped, the inhibition was considerably reduced within a few days, in the same rate as the organic matter was degraded. In Figure 7.2, it is seen that the resulting inhibition was reduced to less then 10% for a 20% dilution, which implies that the tar-water can be accepted for discharge into the sewer system after biological treatment.

The residual COD in the treated water was compared to the measured inhibition of the same samples. Figure 7.5 indicates that it could be possible to achieve reduced inhibition results the aeration period was extended. A possible dosing strategy could have been to add the tar-water to the reactor only during the first part of the aeration period. However, if this dosing strategy was applied, it would have been important to secure that the maximum permissible inhibition level that the system could tolerate was not exceeded.

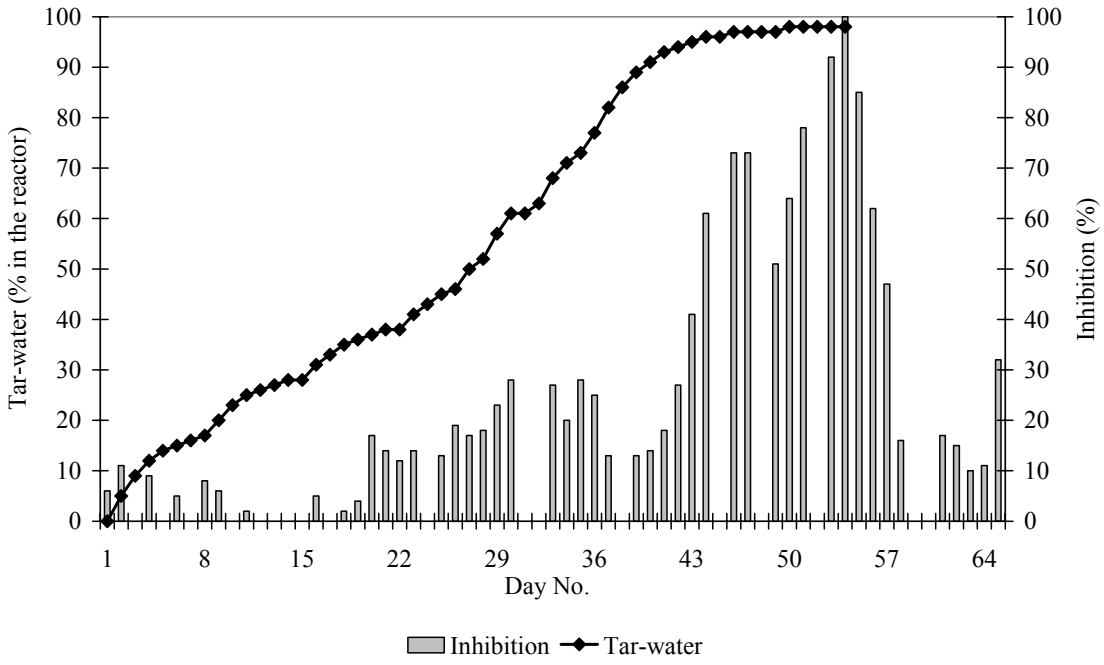

Figure 7.4. Development of inhibition in biologically treated water compared to the percentage of tar-water in the SBR. The dilution of the treated tar-water in the inhibition measurements was 50%.

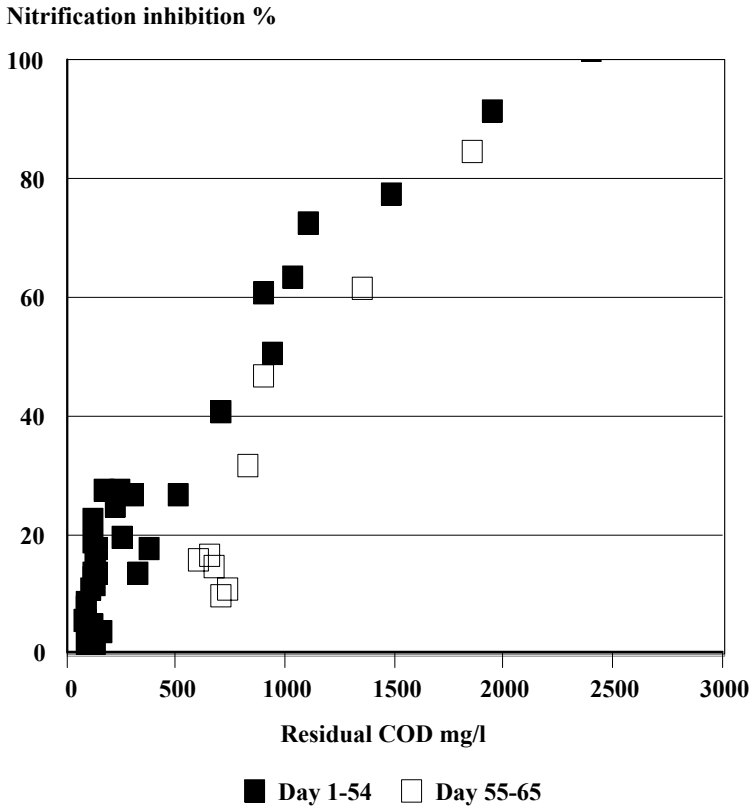

Figure 7.5. Inhibition of nitrification as a function of the COD concentration of the treated water after biological treatment for periods with and without dosage of tar-water.

To sum up, the identified compounds of a membrane-filtrated tar-water have been shown to be easily degradable organic substances such as methanol, acetate and formic acid to a large extent, but phenolic compounds such as phenol, guaiacol and Me-guaiacol are also present in significant concentrations.
Neither the raw nor the membrane-filtrated tar-water does comply with the Danish standard for wastewater discharge to the public sewer due to toxicity to nitrifying bacteria. Both groups of identified organic matter contribute to the toxicity.

The organic matter and the toxicity can be dramatically reduced in an aerobic activated sludge process after a short running-in period. The COD can be reduced with about 95% and the toxicity can be reduced to a level where it complies with the Danish standard for discharge of industrial wastewater to the public sewer.

8. Toxicity present in wastewater from other energy producing plants and from internal sources at wastewater treatment plants

Gasification, incineration and drying of organic matter often give rise to wastewater consisting of condensates or scrubber water from the gas-cleaning systems. Often, the most cost-effective way to handle these wastewater types is discharge into the public sewer. This should, however, be permitted if only it can be shown that the effluent will not harm the biological processes at the municipal wastewater treatment plant. As a comparison to wastewater generated from gasification of woodchips, other wastewater types originating from energy production and from sludge treatment processes at wastewater treatment plants have been tested and evaluated against guidelines for acceptance of discharge of wastewater to public sewers (cf. chapter 3). No attempt at identifying the inhibitory substances in these wastewaters has been made. Neither has any explanations for the measured inhibition been sought. The screening method has been applied in the tests of different wastewater types, and the activated sludge used originates from a treatment plant with industrial load from a variety of industrial branches.

Wastewater types originating from energy production
In Figure 5.1, the inhibitory effect of tar-water produced by the gas-cleaning system of different woodchips gasifiers was shown. In this chapter, inhibitory effects of wastewaters from other energy-producing systems and from internal sources at wastewater treatment plants will be shown as a comparison.

Scrubber water from cleaning of flue gas produced by incineration of woodchips for heat production has been collected from one Swedish and two Danish plants in order to test it for inhibition of nitrification. The results are shown in Figure 8.1.

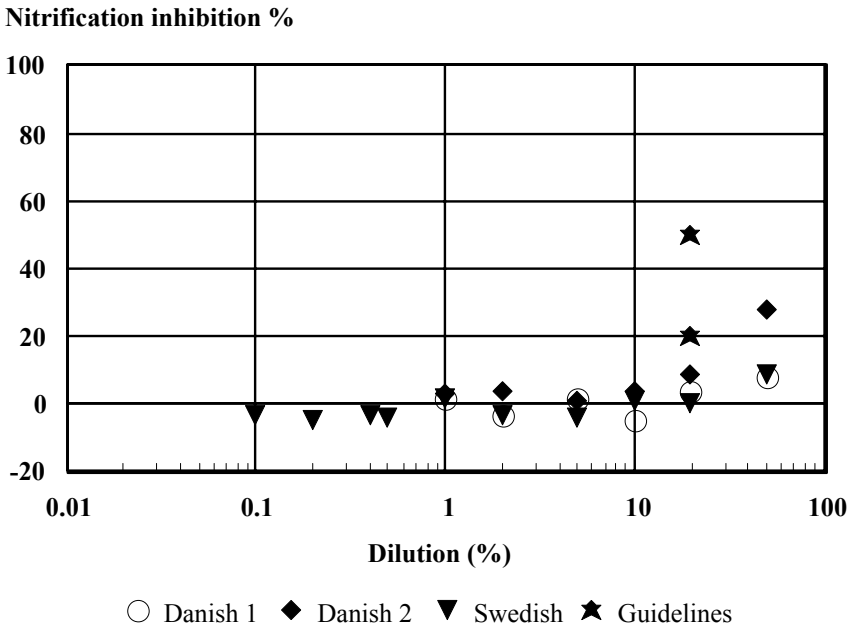

Figure 8.1. Inhibition of nitrification measured in scrubber water from flue-gas cleaning produced by incineration of woodchips, together with the Danish Guidelines for acceptance of discharge to public sewers.

Two of the wastewaters do not exhibit any significant inhibition, even at the highest concentrations tested. The third wastewater is inhibitory only at the highest concentration tested. Without further treatment, all wastewaters fulfil the Danish requirements for discharge to the public sewer system.

Scrubber water from cleaning of flue gas produced by incineration of a mixture of woodchips, peat and industrial waste has been collected in order to test it for nitrification inhibition. The results are shown in Figure 8.2. During normal operation, almost no inhibition was detected in the wastewater from the plant before or after treatment in a sand filter. However under a start-up period when the process was malfunctioning considerable inhibition was detected.

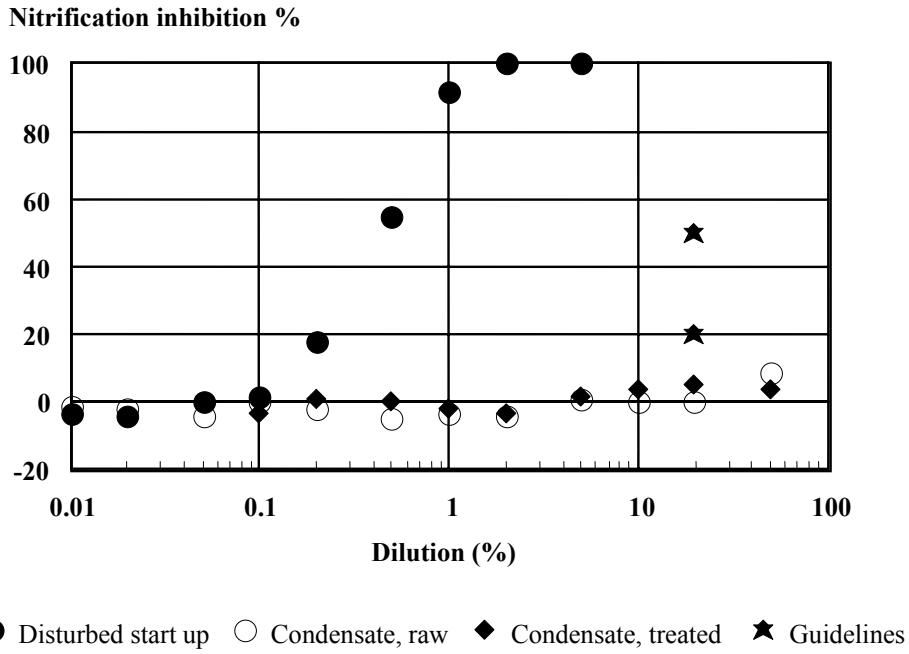

Figure 8.2. Inhibition of nitrification measured in scrubber water from flue-gas cleaning produced by incineration of a mixture of woodchips, peat and industrial waste, together with the Danish Guidelines for acceptance of discharge to public sewers.

Condensate from a drying process for woodchips and bark has also been tested for inhibition of nitrification. At normal operation, the inhibition of the wastewater is low enough to permit discharge to the public sewer system according to the Danish guidelines. Samples were also collected during a period when only bark was dried and the performance of the plant was judged as unsatisfactory. These samples did not fulfil the requirements for maximum allowable nitrification inhibition. Internal treatment consisting of pH-adjustment to pH 9 and polymer dosage followed by lamella sedimentation only marginally improves the wastewater quality regarding inhibition. (Figure 8.3.)

Condensate from a drying process in which residual products from saw mills and pulp industries are converted into wood pellets has also been tested for nitrification inhibition. In Figure 8.4 the inhibitory effect of the condensate are shown and it is seen that the wastewater samples do not fulfil the requirements for disposal into the municipal sewer system neither before nor after internal treatment. The treatment consists of chemical precipitation, lamella sedimentation and a sand filter. As seen in the figure, the internal treatment has no important effect on the inhibitory effect of the condensate.

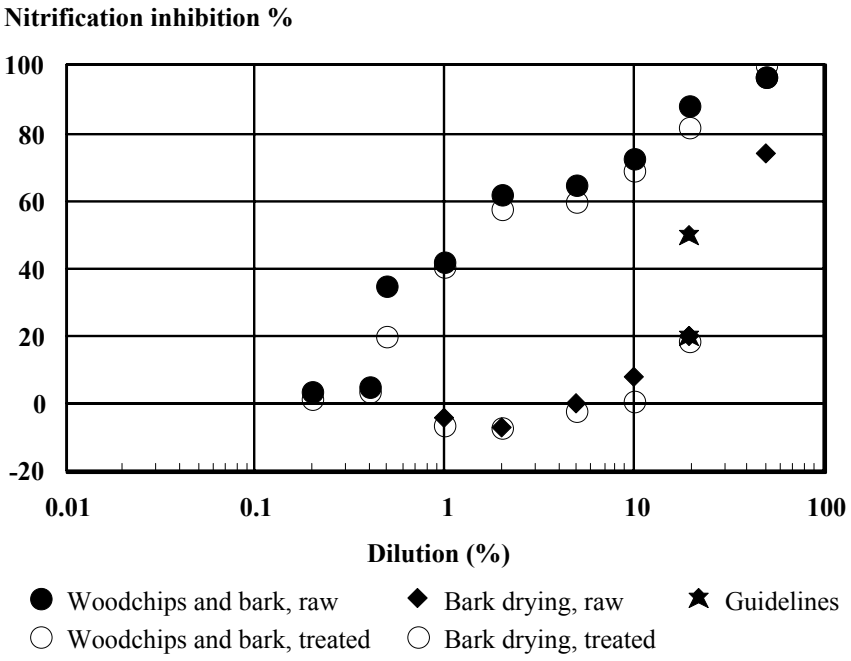

Figure 8.3. Inhibition of nitrification caused by condensate arising from drying of woodchips and bark, before and after internal wastewater treatment, together with the Danish Guidelines for acceptance of discharge to public sewers.

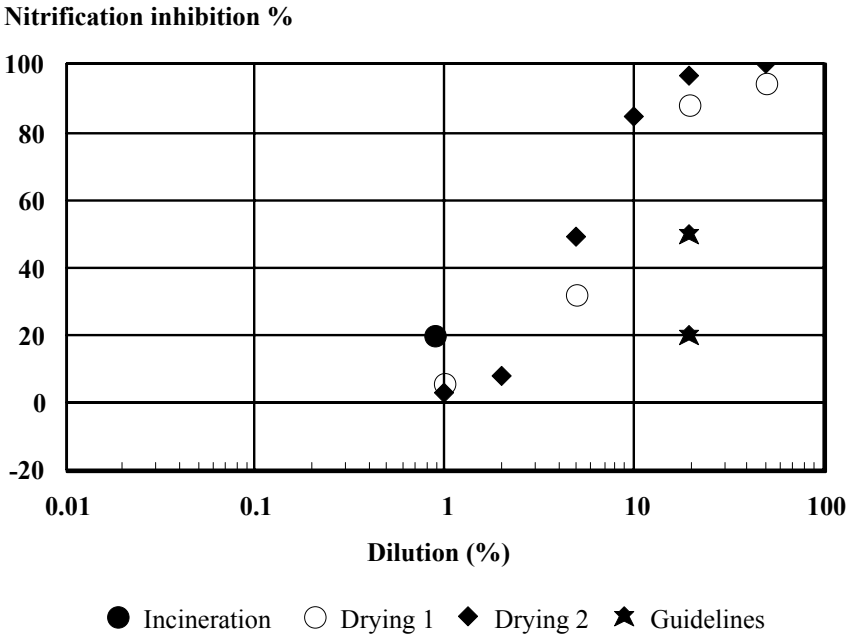

Figure 8.4. Inhibition of nitrification caused by condensate arising from drying of residual products from saw mills and pulp industries, before and after internal wastewater treatment, together with the Danish Guidelines for acceptance of discharge to public sewers.

Condensates from desulphurisation of flue gas have been collected at two Danish coal-fired power plants. Samples have also been taken of condensate from the gas-cleaning system of an energy-producing plant fired with natural gas. As is seen in Figure 8.5, no significant

inhibition was detected in the wastewater from the plant fired by natural gas. Only moderate inhibition was found for the two coal-fired power plants.

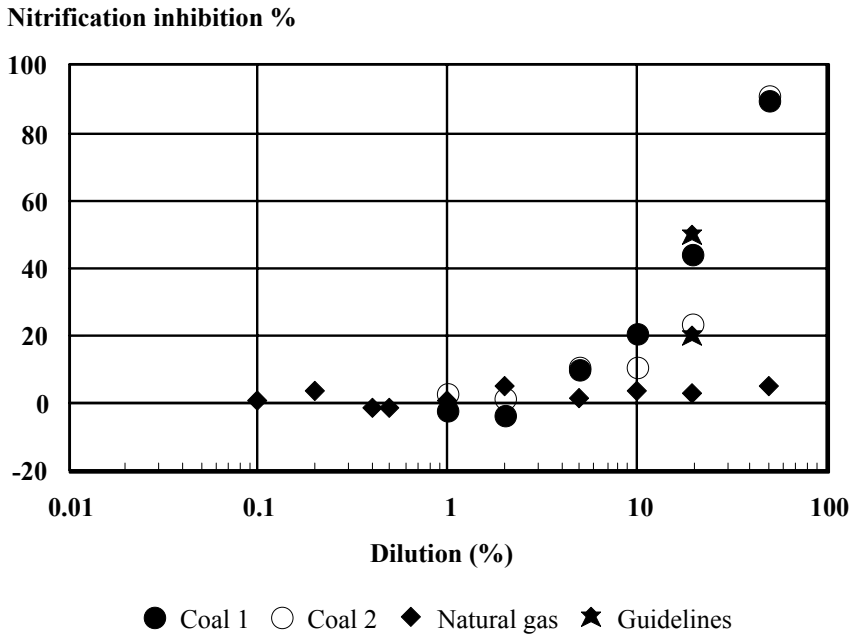

Figure 8.5. Inhibition of nitrification caused by condensates from energy-producing plants fired with natural gas and coal, respectively. The Danish Guidelines for acceptance of discharge to public sewers are also included.

Wastewater from the gas-cleaning system of a plant where municipal waste is incinerated was also subjected to nitrification-inhibition measurements. Samples were taken before internal treatment at the plant. The wastewater was found to be moderately inhibitory. (Figure 8.6.)

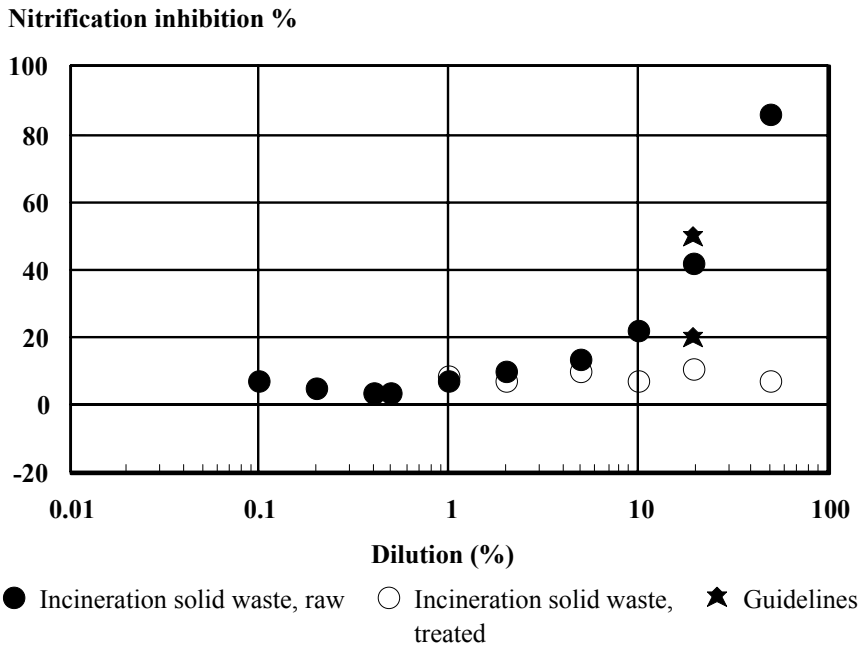

Figure 8.6. Inhibition of nitrification caused by wastewater from the gas-cleaning system of a plant where municipal waste is incinerated. The Danish Guidelines for acceptance of discharge to public sewers are shown too as a comparison.

To sum up, the examined wastewater types from energy-producing plants can be classified according to their toxicity. Raw tar-water from the up-draft gasifier is the outstandingly most inhibitory wastewater tested, cf. chapter 5. Membrane-filtrated tar-water from the same up-draft gasifier is still inhibitory to an extent that does not fulfil the Danish guidelines for acceptance of discharge to public sewers. The same applies to the condensate from a drying process in which residual products from saw mills and pulp industries are converted into wood pellets. It can also be concluded that processes that normally produce non-inhibitory wastewaters might produce much more toxic wastewaters if the process performance is unsatisfactory.

Condensates from coal-fired power plants and untreated condensate arising from incineration of municipal waste are moderately inhibitory to nitrification. Energy production based on incineration of woodchips, incineration of natural gas, incineration of a mixture of either woodchips, peat and industrial waste or sawdust, bark and peat give rise to condensates with little or no inhibition. The same applies for drying of a mixture of bark and woodchips.

Internal sources of inhibition at a wastewater treatment plant

Internal wastewater flows from sludge treatment processes might also give rise to inhibitory wastewater streams. In recent years, sludge incineration and sludge-drying processes have been implemented at some Danish wastewater treatment plants.

Condensate produced by the cleaning of gas from a sludge-drying unit has been subjected to nitrification-inhibition measurements (see Figure 8.7). Sinkjær *et al*. (1996) reported 20% inhibition at a percentage of condensate from a sludge-drying process of 0.9%. Within the same investigation they also found inhibition according to Figure 8.7 for scrubber water produced when flue gas from a sludge incineration plant was cleaned. The inhibitory effect of the scrubber water from the sludge incineration plant can however be reduced by a factor of 2-4 if the whole flue-gas flow is incinerated at temperatures above 850°C.

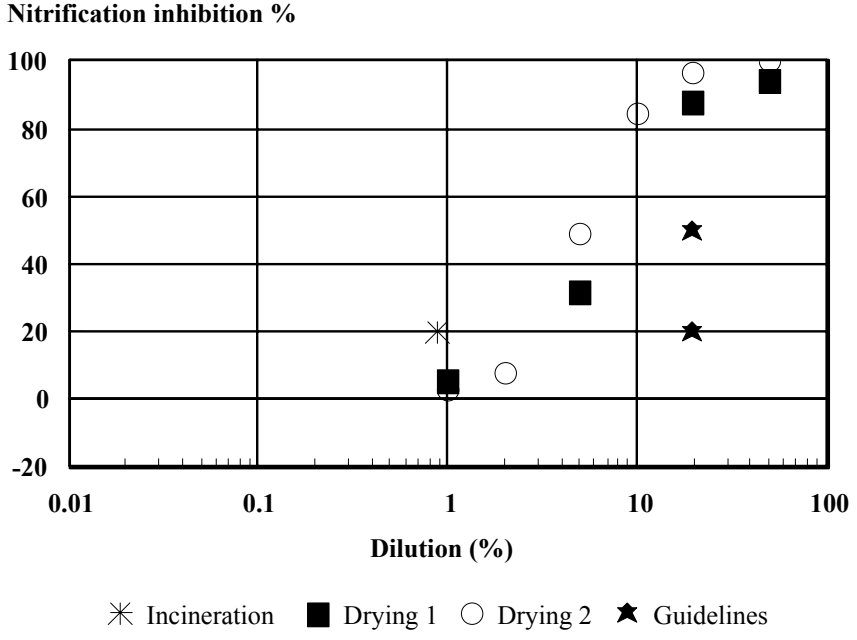

Figure 8.7. Inhibition of nitrification caused by scrubber water from a sludge incineration plant and by condensates from two sludge-drying units. Data for " ■" and " ✳" are obtained from Sinkjær *et al*. (1996) while " ○" represents data found within this study.

Wastewater originating from incineration or drying units at the wastewater treatment plants themselves might contribute substantially to the total load of inhibitory substances affecting the biological processes. These internal sources of inhibition can be as inhibitory as the wastewaters from wood-drying processes and almost as inhibitory as membrane-filtrated tar-water.

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Appendix 1

Screening Method for Determination of Inhibition of Nitrification of Activated Sludge

1. Introduction

This instruction specifies a rapid screening method for determination of short-term inhibitory effects of test substances (e.g. wastewater) on nitrifying bacteria in activated sludge. The inhibitory effects are estimated over an exposure period of two hours (the exposure time may be shortened or prolonged, see 10.1).

This method is suitable for tests with nitrifying activated sludge derived from domestic sewage, but it is possible to use any nitrifying activated sludge, for example activated sludge derived from industrial wastewater or synthetic sewage, provided that the nitrification rate of the sludge is suitable (see 9 and 10.1).

The method is applicable to wastewaters and chemical substances that are soluble in water, but insoluble substances may also be tested, if care is taken to ensure as much homogeneity as possible. Even volatile substances may be tested in this method, as the reaction takes place in capped test tubes. Initial controls to ascertain that the oxygen and ammonium contents in the test tubes are sufficient shall be performed (see 9).

The inhibitory effect of a test substance may be different for different activated sludges. For example, an industrial wastewater may cause less inhibition to an activated sludge adapted to this particular industrial wastewater than to a domestic activated sludge.

2. Definitions

2.1 Activated sludge: Accumulated biological mass (floc) produced in the treatment of wastewater by the growth of bacteria and other microorganisms in the presence of dissolved oxygen (ISO 6107-1, 1996). Activated sludge contains both active microorganisms and inert organic and inorganic material.

2.2 Total Suspended Solids (SS): The concentration of particles, suspended solids, expressed as grams of dry matter per litre, which is retained at a filter of specified pore size when a known volume of suspension is filtered (SS 02 81 12, 1983).

2.3 Volatile Suspended Solids (VSS): The concentration of volatile suspended solids is the organic fraction of SS analysed according to (SS 02 81 12, 1983).

2.4 Substrates: Ammonia, carbonate and phosphate.

2.5 Activated sludge suspension: A mixture of activated sludge, substrates and tap water (see 5.6)

2.6 Test substances: wastewaters, pure chemicals, mixtures and chemical products.

2.7 Oxidised nitrogen: $NO_2 + NO_3 = NO_X$

2.8 Nitrification: The oxidation of ammonium salts by bacteria. Usually, the end product of such an oxidation is nitrate (ISO 6107-1, 1996).

2.9 Nitrification rate: Biological oxidation of ammonium per unit of time expressed as mg N/(g VSS·h), mg N/(g SS·h) or mg N/(l·h) where N is NH_4-N or NO_X-N.

2.10 Inhibition of nitrification: The decrease in nitrification rate in a test tube containing activated sludge, substrates and test substance compared to the nitrification rate in a reference test tube where tap water is added instead of test substance. The decrease or degree of inhibition is expressed as a percentage of the nitrification rate in the reference test tubes.

3. Principle

The test is performed at a constant temperature, usually between 20°C and 25°C, in an atmosphere free from dust and toxic vapours. The nitrification reaction takes place in capped test tubes in which nitrifying sludge suspension (including substrates) and either tap water or test substances are added. In order to ensure that the concentration of ammonium will not be rate limiting, the concentration of activated sludge is, based on an estimated nitrification rate, adjusted so that the ammonium concentration in the test tubes will be more than 3 mg NH_4-N/l at the end of the test. Aeration and mixing take place by shaking of the tubes, the oxygen being supplied by the air head space in the tubes. Of the total volume of the tubes, 1/3 is liquid and 2/3 is air (or pure oxygen, see 10.2). Parallel aeration of a nitrifying sludge in the presence and absence of test substances is made during two hours. (The exposure time may be shortened or prolonged, see 10.1.) The nitrification rate is calculated either as the increase of oxidised nitrogen related to sludge concentration and time (g NO_X-N/(g VSS·h)) or as the decrease of ammonia related to sludge concentration and time (g NH_4-N/(g VSS·h)). The inhibition caused by the test substance is then calculated by comparison of the nitrification rates obtained in the test tubes containing test substance and tap water respectively. Note that the nitrification rates based on the decrease in ammonia and on the increase in oxidised nitrogen are not directly comparable, as ammonia for example may be used for cell synthesis instead of being converted to nitrite or nitrate.

4. Interferences

The interferences of the method are the same that apply for the determination of oxidised nitrogen and are dependent on the method used for this determination.

High organic matter concentrations in the test tubes of the screening test may result in lower nitrification activity because of heterotrophic consumption of oxygen. If the COD concentration in the test tubes exceeds 400 mg COD/l and the heterotrophic oxygen consumption rate ($R_{HETR.} \cdot VSS_{TT}$) exceeds 90 mg O_2/(l·h), the method can be modified according to 10.2. ($R_{HETR.}$ = heterotrophic respiration rate expressed in mg O_2/(g VSS·h), VSS_{TT} = the concentration of suspended solids in the test tubes (g VSS/l).)

High amounts of ammonia/ammonium may result in inhibition of nitrification. If the samples to be tested contain high ammonium concentrations, the method can be modified according to 10.3.

5. Materials and Reagents

5.1 Nitrifying activated sludge

It is possible to use any type of activated sludge in this method, provided that it is nitrifying. If the nitrification rate of the sludge is unknown, a preliminary test to find the nitrification rate is performed (see 10.1).

Analyses of SS and VSS concentrations of the nitrifying activated sludge should be performed if the concentrations are unknown. If needed, the sludge may be concentrated by for example sedimentation or centrifugation. Activated sludge should be used within 24 hours of collection and it should be maintained under aerobic conditions during storage.

5.2 Substrates

Ammonium sulphate [$(NH_4)_2SO_4$] of analytical quality, e. g. Merck 1217.

Sodium bicarbonate [$NaHCO_3$] of analytical quality, e. g. Merck 6329.

KH_2PO_4 of analytical quality, e. g. Merck 5108.

5.3 Acid / Base

HCl or NaOH is used for pH adjustments.

5.4 Tap water

The sludge suspension is prepared using tap water and tap water is also added to the reference tubes instead of test substances. If the tap water is chlorinated, it must be dechlorinated by aeration at room temperature overnight before using it in the test.

Note that if the tap water contains oxidised nitrogen, the calculation of the nitrification rate has to be adjusted according to 10.4.

5.5 Reagent-grade water

Distilled or deionised water is used to prepare dilutions of the test substances.

5.6 Activated sludge suspension

The nitrifying activated sludge is concentrated to a suitable volatile suspended solids concentration, see below. The concentration may be carried out by sedimentation or centrifugation.

Initial control according to section 9 shall be performed in order to ensure that the ammonium content in the test tubes is sufficient for a successful test.

Preparation of activated sludge suspension

The prepared activated sludge suspension shall have a volatile suspended solids concentration of 1.5-6 g VSS/l, an ammonia concentration of 50 mg N/l, bicarbonate concentration of 8 mM and a phosphate concentration of 10 mg PO_4-P/l. pH is adjusted to 7.5±0.5.

- Dissolve 0.236 g ammonium sulphate [$(NH_4)_2SO_4$], 0.672 g sodium bicarbonate [$NaHCO_3$] and 0,044 g KH_2PO_4 in some tap water in a one-litre beaker. (If the samples to be tested contain high amounts of ammonia, the ammonium sulphate should be excluded from the activated sludge suspension, see 10.3.)
- Ensure that the oxygen concentration of the nitrifying activated sludge is less than 0.5 mg O_2/l before it is mixed with the substrates.
- Add activated sludge so that the final VSS concentration of the sludge suspension will be between 1.5-6 g VSS/l. It shall be ascertained that the chosen VSS concentration does not lead to total ammonium depletion in the test period (see 9).
- pH is adjusted to 7.5±0.5 with HCl or NaOH. Fill up with tap water to 1000 ml.
- The VSS concentration of the activated sludge suspension is determined by triple analysis.

5.7 Test substances

Stock solution or suspension of the test substances may be prepared.

6 Equipment (Apparatus)

a. Test tubes with caps and a capacity of 30 ml
b. Rack for the test tubes
c. Shaker for the test tubes
d. Wide-bore pipettes
e. pH-meter (The probe must be suitable for fast determinations of pH in the test tubes after the incubation.)
f. Thermometer, range 0-50°C
h. Timer
i. Magnetic stirrer with stirring bar
j. Beaker, 1000 ml
k. Filters and funnels (filters of glass fibre or paper which does not release nitrogen)
l. Apparatus necessary for analytical determination of ammonia and oxidised nitrogen in solution
m. Glass fibre filter disks of 0.45µm pore size

n. Filtration apparatus, i.e. a membrane filter funnel
o. Suction flask, of sufficient capacity for sample size selected
p. Drying oven, for operation at 105±3°C
q. Muffle furnace for operation at 550°C
r. Analytical balance, capable of weighing to 0.1 mg

7 Procedure

7.1: Prepare the activated sludge suspension according to 5.6. Place the suspension in a beaker on a magnetic stirrer and provide gently mixing.

7.2: Ensure that the sludge suspension and test substances are of the same temperature, equal to the ambient temperature.

7.3: Check the pH and temperature of the test substances just before the start of the test. If pH of the test substances deviates more than 0.5 pH units from 7.5, pH shall be adjusted with HCl or NaOH.

7.4: Prepare a set of test tubes for the test. Use two test tubes for each concentration of test substance and nine test tubes for references with tap water.

7.5: Add 5 ml of tap water (5.4) to each test tube used as reference. Add 5 ml of test substance (or diluted test substance) to the test tubes used as samples.

7.6: Add to each test tube 5 ml of activated sludge suspension (5.6) with a wide-bore pipette. Close the test tube, place it on the shaker and start shaking. The incubation time begins when the sludge suspension is added. It is important to add the sludge suspension to the test tubes with fixed time intervals in such a way that the incubation time is the same (2 hours) for all test tubes.
Start one set of reference test tubes (with 0, 1 and 2 hours incubation time respectively) in the beginning of the test, one set in the middle and one in the end.

Test tubes used as references with incubation time 0 hours do not need to be placed on the shaker. Mix the content and filter it to stop the reaction. Analyse the oxidised nitrogen concentration and the ammonium concentration. The test tubes used as references with incubation time 1 hour are used to check the linearity in oxidised nitrogen production during the test.

7.7: Incubate all test tubes for 2 hours at a constant temperature and aerate by shaking.

7.8: After 2 hours, measure pH and temperature in at least one of the duplicate test tubes and in all reference test tubes, and then stop the nitrification reaction by filtering the samples. Analyse the oxidised nitrogen concentration of the filtrates. For references, the ammonium concentration should be analysed too. To assure the same incubation time for all test tubes, stop the reactions using the same time intervals as when the test was started.

8 Calculations of results

The initial concentrations of oxidised nitrogen and ammonium in the test tubes are calculated from measured N concentrations in the test substance and in the controls with incubation time 0 hours. Note that if the tap water contains oxidised nitrogen, the initial concentration of oxidised nitrogen in the test tubes ($N_{TT,0}$) has to be calculated according to the modified equation found in 10.4.

$$N_{TT,0} = N_{C,0} + N_{TS} \cdot \frac{V_{TS}}{V_{TT}}$$

where
$N_{TT,0}$ = the initial concentration of oxidised nitrogen in the test tubes (mg N/l),
$N_{C,0}$ = average concentration of oxidised nitrogen in the three controls with incubation time 0 hour (mg N/l),
N_{TS} = concentration of oxidised nitrogen in the test substance (mg N/l),
V_{TS} = the volume of test substance added to the test tube (ml),
V_{TT} = the total volume of liquids added to the test tube (= 10 ml).

The concentration of volatile suspended solids in the test tubes (VSS_{TT}) is calculated from the analysis of volatile suspended solids in the sludge suspension (VSS_{SS}).

$$VSS_{TT} = VSS_{SS} \cdot \frac{V_{SS}}{V_{TT}}$$

where

VSS_{TT} = the concentration of suspended solids in the test tube (g VSS/l),
VSS_{SS} = the concentration of suspended solids in the sludge suspension (g VSS/l),
V_{SS} = the volume of sludge suspension added to the test tube (ml).
V_{TT} = the total volume of liquids added to the test tube (= 10 ml).

The nitrification rate ($R_{NITR.}$) is calculated as follows:

$$R_{NITR.} = \frac{N_{TT,end} - N_{TT,0}}{t \cdot VSS_{TT}}$$

where

$R_{NITR.}$ = nitrification rate (mg N/(g VSS·h))
$N_{TT,end}$ = the final concentration of oxidised nitrogen in the test tubes (mg N/l),
$N_{TT,0}$ = the initial concentration of oxidised nitrogen in the test tubes (mg N/l),
t = the incubation time (h),
VSS_{TT} = the concentration of suspended solids in the test tube (g VSS/l).

The percentage inhibition of production of oxidised nitrogen is calculated as follows:

$$I = \frac{R_{NITR,C} - R_{NITR,S}}{R_{NITR,C}} \cdot 100$$

where

I = inhibition of nitrification (%)
$R_{NITR,C}$ = average nitrification rate of the test tubes containing tap water (mg N/(g VSS·h)),
$R_{NITR,S}$ = average nitrification rate of the test tubes containing sample (mg N/(g VSS·h)).

9 Initial control to perform before starting a screening test

The decrease in ammonium concentration in the test tubes during a test (Δ_{NH4}) should be between 8 and 22 mg NH_4-N/l. In practise, it is convenient to aim at ca. 15 mg NH_4-N/l in order to ensure a successful test. Suitable combinations of nitrification rate and VSS concentrations can be estimated by the following equation:

$$\Delta_{NH4} = R_{NITR.} \cdot VSS_{TT} \cdot t$$

where

Δ_{NH4} = The decrease in the ammonium concentration during the test (mg N/l)
$R_{NITR.}$ = Nitrification rate of the activated sludge (mg NH_4-N/g·VSS·h)
VSS_{TT} = Volatile suspended solids concentration in the test tubes (g VSS/l)
t = Incubation time (2 hours)

10 Modifications

10.1 Nitrification rate

If the nitrification rate of the nitrifying activated sludge is unknown, a preliminary test with tap water is performed. For example 10 test tubes can be prepared so that five duplicate samples are incubated 0, 30, 60, 120 and 180 minutes, respectively.

If the nitrification rate is outside the suitable range, the incubation time of the test should be adjusted (i. e. shortened if the nitrification rate is too high and prolonged if the nitrification rate is too low). Compare section 9.

10.2 Organic matter

If the oxygen concentration in the test tubes decreases too much, the nitrification activity will be limited. High amounts of easily biodegradable organic matter in the samples to be tested may result in low dissolved oxygen concentrations due to oxygen consumption of heterotrophic microorganisms in the activated sludge. The dissolved oxygen concentration of the test tubes should not be allowed to drop below 4 mg O_2/l.

If the COD concentration in the test tubes exceeds 400 mg COD/l and the heterotrophic oxygen consumption rate ($R_{HETR.} \cdot VSS_{TT}$) exceeds 90 mg O_2/(l·h), it may be necessary to introduce pure oxygen in the head space of the test tubes. Follow the normal procedure (see section 7) and before closing the tubes, add pure oxygen to the gas phase, for example with a Pasteur pipette, for 30 seconds. This modification of the method will allow investigations of samples without any limit of the concentration of organic material.

Note: All organic material has been regarded as easily biodegradable when the limit of organic material content in the test tubes has been set to 400 mg COD_{Cr}/l. In practice, it may be possible to test solutions with a far higher content of organic material using air in the head space of the test tubes, provided that the biodegradability of the organic material and the heterotrophic respiration rate of the activated sludge used are low.

10.3 Ammonium

High concentrations of ammonium may result in inhibition of nitrification. If the samples to be tested contain high ammonium concentrations, the ammonia should be excluded from the sludge suspension. Instead, an ammonium solution is prepared from which suitable amounts are put in the different test tubes immediately before the sludge suspension is added. The volume of ammonia solution put into each test tube is adjusted so that the initial ammonium concentration in each test tube does not exceed 100 mg NH_4-N/l.

10.4 Tap water contains oxidised nitrogen

If the tap water contains oxidised nitrogen, the initial concentration of oxidised nitrogen in the test tubes ($N_{TT,0}$) is calculated as follows:

$$N_{TT,0} = N_{SS} \cdot \frac{V_{SS}}{V_{TT}} + N_{TS} \cdot \frac{V_{TS}}{V_{TT}} + N_W \cdot \frac{V_W}{V_{TT}}$$

where
$N_{TT,0}$ = the initial concentration of oxidised nitrogen in the test tubes (mg N/l),
N_{SS} = average concentration of oxidised nitrogen in three samples from the sludge suspension (mg N/l),
V_{SS} = the volume of sludge suspension added to the test tube (ml),
V_{TT} = the total volume of liquids added to the test tube (= 10 ml),
N_{TS} = concentration of oxidised nitrogen in the test substance (mg N/l),
V_{TS} = the volume of test substance added to the test tube (ml),
N_W = concentration of oxidised nitrogen in the tap water (mg N/l),
V_W = the volume of tap water added to the test tube (ml).

11 Report of analysis

The test report shall include in particular:

a) all the data needed for the identification of the samples tested;

b) the specific nitrification rate of the activated sludge;

c) the method of preparation of the samples:

- for wastewaters, the manner and duration of storage of the samples and, if necessary, the conditions in which sampling, decantation, filtration and thawing of the samples were carried out;

- for pure chemicals, the method of preparation of the stock solutions and the test solutions;

d) the source, concentration and pretreatment method of the activated sludge;

e) the results of the test in the form of percentage inhibition of each concentration of test substance;

f) in the case of chemical analyses of the substances, the method used;

g) the test temperature with limits;

h) the pH of the test with limits;

i) any operating detail not specified in this description of the method and incidents, which may have affected the results.

12 References

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