

Toxicity of wastewater generated from gasification of woodchips

Technology Brief

Prepared 2002-10-16

Martin W. Fock

dk-TEKNIK ENERGY & ENVIRONMENT

The work is conducted at the Department of Water and Environmental Engineering at Lund Institute of Technology.

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 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 is expected to take care of the wastewater has been included. The following plants are included in the examinations.

- **Harboøre CHP plant**
- **Høgild CPH plant**
- **Two-stage gasifier at DTU**
- **Gasification system at Chatel-St-Denis (Switzerland)**
Scrubber water from flue-gas cleaning of incineration of woodchips
Scrubber water from flue-gas cleaning of incineration of woodchips has been examined at four different facilities.
- **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.

- **Condensate from drying of woodchips and bark**
Condensate from drying of woodchips and bark has been examined at two Swedish facilities.
- **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.
- **Condensate from power production based on natural gas**
- **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.

1. 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.

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

Table 1.1: National guidelines for Danish and European municipal wastewater treatment plants.

Table 1.1 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 NH₄-N/l but values down to 1 mg NH₄-N/l are applied for sensitive streams. In addition to the discharge limits, the discharge of wastewater is taxed.

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)

Table 1.2: Taxation of discharge from Danish wastewater treatment plants.

The actual taxes are given in table 1.2. The annual tax for a typical plant serving a small town of 10.000 people is around 160.000 DKK (21.500 EUR).

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.

2. 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.

2.1 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 2.1.

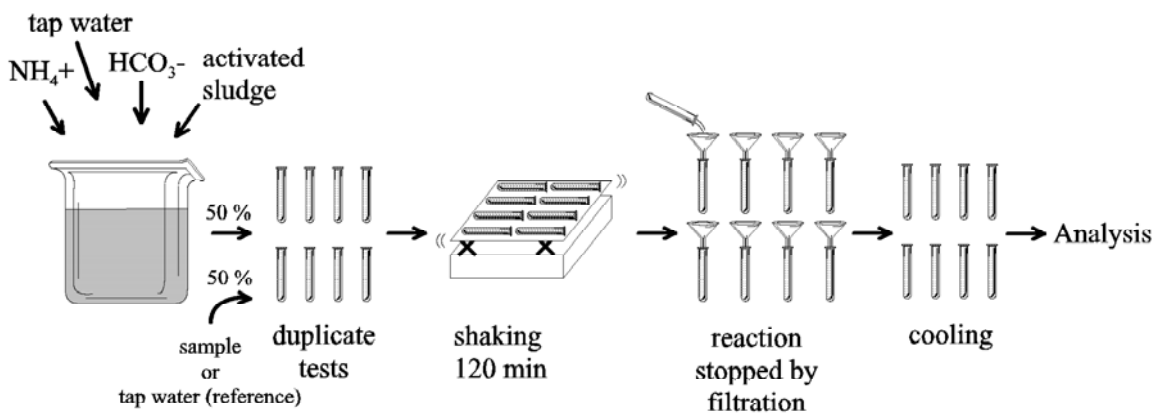


Figure 2.1. Schematic description of the screening method for determination of inhibition of nitrification.

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 2.2. The test method can be applied for pure substances as well and in such cases the concentration replace the dilution.

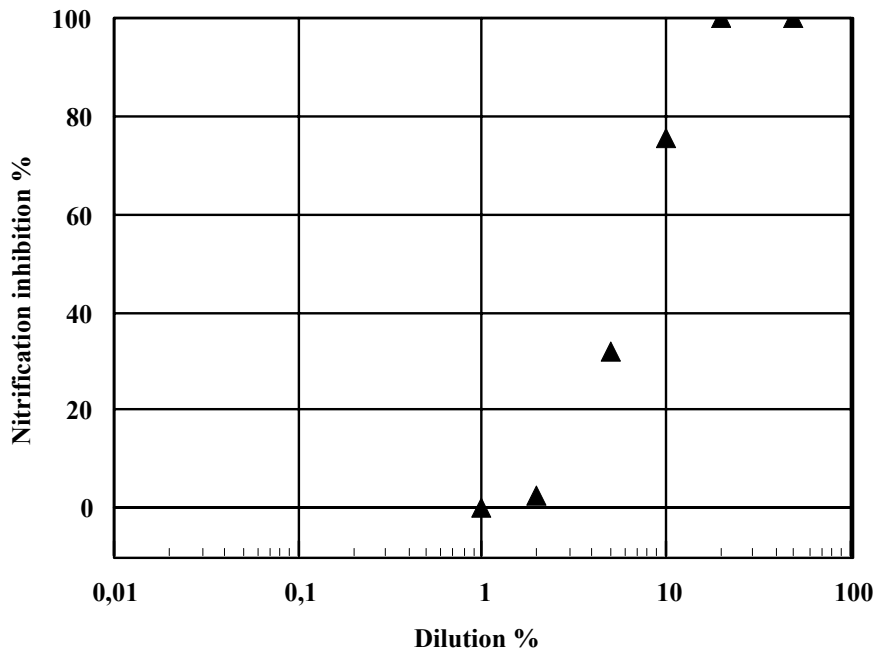


Figure 2.2. Typical dose-response relationship obtained with the screening method. The graph shows inhibition from condensate from the down-draft gasifier at Høgild.

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. The result is 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 that the two laboratories have used activated sludge from different wastewater treatment plants.

2.2 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.

3. 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 3.1 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.

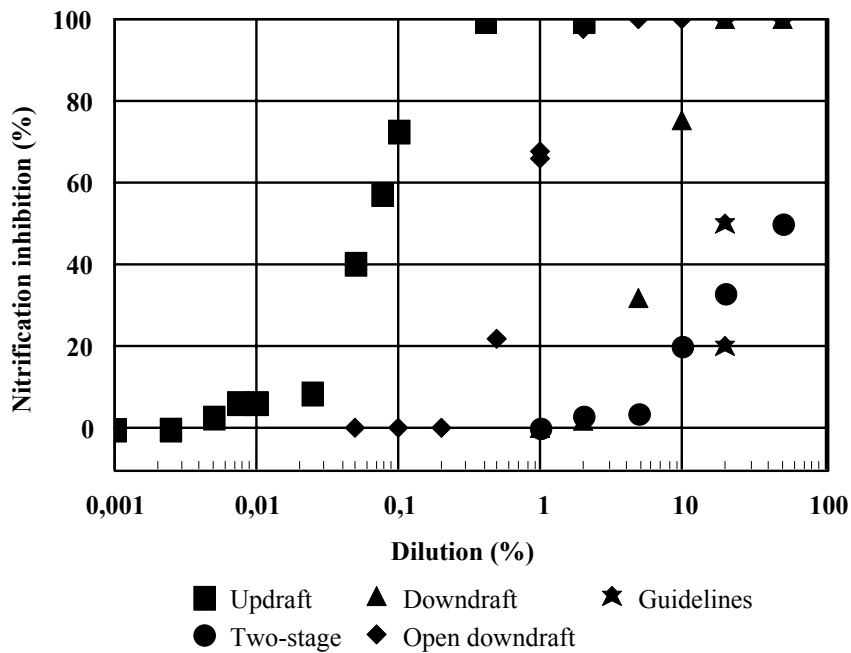


Figure 3.1. Inhibition curves from the gas cleaning system from four different gasifiers

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.