ThermalNet

CombNet/GasNet/PyNe

CombNet

GasNet

PyNe

Gas cleaning in flue gas from combustion of biomass

Kurt Carlsson, Firma EcoExpoert

Deliverable 2E-3

Intelligent Energy Europe

PyNe is also sponsored by IEA Bioenergy

ThermalNet
CombNet/GasNet/PyNe

CombNet
www.combnet.com

CombNet:

S van Loo
Procede Group BV
PO Box 328
Enschede
NL-7500 AH
Netherlands

Tel: +31 53 489 4355 / 4636
Fax: +31 53 489 5399
Email: sjaak.vanloo@procede.nl

GasNet
www.gasnet.uk.net

GasNet:

Prof Hermann Hofbauer
Technical University of Vienna
Institut für Verfahrenstechnik
Brennstofftechnik und Umweltechnik
Getreidemarkt 9/166
Wien
A-1060, Austria

Tel: +43 1 58801 15970
Fax: +43 1 587 6394
Email: hhofba@mail.zserv.tuwien.ac.at

PyNe
www.pyne.co.uk

PyNe:

Prof Tony Bridgwater
Aston University
Bio-Energy Research Group
Chemical Engineering and Applied Chemistry
Aston Triangle
Birmingham, West Midlands
B4 7ET, UK

Tel: +44 121 204 3381
Fax: +44 121 204 3680
Email: a.v.bridgwater@aston.ac.uk

Preface

ThermalNet, supported by the EC through Intelligent Energy – Europe programme, has established a closely integrated cluster of three networks on thermal processing of biomass for fuels and electricity. This includes combustion, gasification and pyrolysis, with a common focus of providing support for more rapid and more effective implementation of all the technologies in the market place by addressing technical, non-technical and commercial issues. The whole chain is considered from biomass production to end-use applications. Information about ThermalNet and the outputs from the project can be found on the website www.thermalnet.co.uk.

Work package 2E within ThermalNet deals with Gas treatment and is lead by TPS Termiska Processer AB. One of the deliverables of this work package is to produce reports of particular items of interest to gas treatment. The present report by Kurt Carlsson, Firma EcoExpert, is one of two reports that are produced as Deliverable 2E-3.

I would like to thank the author for his work and also for the initiative to make this report.

Eva K. Larsson
TPS Termiska Processer AB

Gas cleaning in flue gas from combustion of biomass

Paper prepared for the EU project ThermalNet in January 2008

Kurt Carlsson Firma **EcoExpert**
kurti.carlsson@tele2.se

Summary

Biomass referred to in this paper comprises fuels classified as clean biomass and contaminated biomass classified as waste.

There are two EU Directives on emissions related to these two fuel types, one regarding large boilers burning solid, liquid and gaseous fuels, thus including clean biomass, and one directive dealing with combustion of waste.

Besides the above mentioned directives, an Integrated Prevention and Pollution Control (IPPC) Directive requires **Best Available Technique (BAT)**.

Particles from biomass combustion consists of two fractions; one fraction from evaporation and condensation, the submicron fraction - particles smaller than one micron (µm) and one fraction with larger particles - the supermicron fraction.

The small particles can penetrate down to the narrow alveoli in the lungs and are therefore very harmful. It is therefore particularly important to remove the sub-micron particles.

There are three proven, reliable, common and effective types of equipment for the removal of all particles: Dry and wet electrostatic precipitators and fabric filter. A wet electrostatic precipitator placed downstream of a condenser for low temperature heat recovery is a good wet solution. In other cases, wet systems are seldom a good solution for particulate removal only.

Water soluble gases are removed effectively in wet and dry absorption but dry scrubbers require an excess of chemicals for a high removal efficiency. Wet scrubbers normally require special treatment of the waste water.

Selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR) methods are available for the removal of **nitrogen oxides** (NO_x).

Mercury and **dioxin** can be removed in several ways.

Gas cleaning of complex flue gases can be realized in many ways in either a few steps or in several. Each plant is more or less unique and must be evaluated separately for an optimal solution. Some examples are given in this report.

Gas cleaning in flue gas from combustion of biomass

Content

Page

Biomass 2
Biomass combustion 2
EU Directives 3
Gas cleaning 4
Removal of particles 4
Mass force separators 5
Cyclones 5
Sand bed filters 6
Wet scrubbers (WS) 6
Adhesion separators 7
Fabric Filter (FF) 7
Electrostatic precipitator (ESP) 7
Flue gases and dust from biomass combustion 9
Removal of particles - practical solutions 10
Dry methods 10
Cyclones 10
Dry electrostatic precipitator (DESP) 10
Fabric filters 11
Electrified gravel (sand) bed filter 11
Wet methods for the removal of particles 11
Scrubbers 12
Electrified wet scrubber (EWS) 12
Wet scrubbers with condensation (CWS) 12
Wet electrostatic precipitators (WESP) 12
Removal of water soluble gases 13
Wet absorption 13
Dry absorption (Dry scrubbing) 15
Wet or Dry Absorption of water soluble gases 16
Removal of Nitrogen Oxides - NOx 17
Removal of Dioxin and Mercury 18
Examples of gas cleaning combinations with Best Available Technique - BAT 21
1. "Clean" biomass such as wood and forest residues 21
2. Contaminated biomass, classified as waste 24
References 28

BIOMASS

Biomass is material from vegetation, it can be used as a fuel in various boilers and combustors. Biomass fuels emit carbon dioxide (CO_2) when carbon reacts with oxygen (O_2) during combustion but because the biomass has absorbed the carbon from the CO_2 in the atmosphere during its growth, the combustion of biomass is considered to be CO_2-neutral.

Biomass can be clean, such as wood chip, which contains cellulose, hemicelluloses, lignin and ash. The main components of biomass are carbon, oxygen and hydrogen but it also contains nitrogen, sulphur and, normally, small amounts of chlorides. The main part of the ash comprises Ca, K, Si, Mg, Mn, Al, Fe, P, Na and Zn.

Biomass can be contaminated, which is the case with, for instance, demolition material which, also even after sorting, often contains sulphur from gypsum board, chlorine from PVC and ash, mortar, sand, etc. The amount and composition of the impurities varies considerably of course.

BIOMASS COMBUSTION

During combustion, various kinds of impurities are generated and some of them we find in the flue gas. Most of these are related to the composition of the biomass: particles from ash, NOx from nitrogen, SO_2 from sulphur, etc. We can also find impurities related to incomplete or bad combustion e.g. particles such as soot and unburned matter, carbon monoxide and other gaseous organic compounds (TOC) such as dioxin. Dioxin are aromatic molecules in which chlorine replaces hydrogen. Dioxin is very toxic. The amount of chlorine necessary for the formation of dioxin is very low. Dioxin have for instance been measured in flue gas after boilers fuelled with wood chips from the American west coast or wood chips contaminated with calcium chloride which had been used in very small amounts during transport to prevent freezing.

Some metals in the ash, such as lead (Pb), evaporate during combustion and react, condense and/or sublime during cooling in the boiler. Upstream of the gas cleaning installation, normally at a temperature < 200°C, we find all metals as solid particles, except mercury. Mercury evaporates during combustion and reacts in the boiler but remains mainly in its gaseous form.

The impurities in the flue gas are harmful if they are emitted to the atmosphere. Flue gas cleaning must be installed to eliminate or at least reduce this problem. The degree of cleaning depends on federal, regional and local regulations but regional and local authorities, organisations and individuals have often an opinion on an actual plant due to its size, location, etc.

EU DIRECTIVES

EU directives on emissions from various boilers, dependent on type of fuel and size of plants, exist. Combustion of "clean" biomass has the same requirements as for fossil fuels - Requirements for large (> 50 MW) boilers (2001/80/EG).
Contaminated biomass is often classified as waste and must fulfil the requirements stated in the directive on combustion of waste (2000/76/EG).

The following **table 1** is a short summary of the requirements on emission to atmosphere for biomass and waste burning plants from the two EU directives 2001/80/EG and 2000/76/EG.
All figures are given in mg/m³(ntp), dry flue gas at mentioned O_2-concentration.
ntp=normal temperature 273 K and pressure 101.3 kPa.
Dioxin (I-TEQ) in ng/m³ (ntp). I-TEQ = International toxic equivalents. HM= heavy metals

	Biomass Power input in MWth			Waste 24 h average
	50-100	100-300	>300	All plants
Dust				
Solid fuel 6%O_2	50	30	30	
Liquid fuel 3%O_2	50	30	30	
All fuels 11%O_2				10
SO_2				
Solid fuel 6%O_2	200	200	200	
Liquid fuel 3%O_2	850	400 to 200	200	
All fuels 11%O_2				50
NOx as NO_2				
Solid fuel 6%O_2	400	300	200	
Liquid fuel 3%O_2	400	200	200	
All fuels 11%O_2				200
HCL 11%O_2		No EU regulation		10
HF -"-		-"-		1
Cd+Tl -"-		"		0.05
Hg -"-		"		0.05
Σ 9 HM -"-		-"-		0.5
Dioxin -"- (ng/m³)		-"-		0,1
CO -"-		?		10
TOC -"-		?		10

Besides these two EU directives, there is one general EU directive, IPPC 96/61/EC, which is important. This **IPPC (Integrated Pollution Prevention and Control**) deals with the whole plant. **Emission limit values are based on Best Available Techniques (BAT)** and the IPPC provides flexibility for the licensing authorities with respect to the local conditions for the actual plant.

BAT means that the required emission limits will be lower, and become lower as new design of equipment and system become available and proven.

Gas cleaning

The gas cleaning systems can be divided as follows:

1. Removal of particles or dust collection.
2. Removal of water soluble gases: SO_2, HCl, HF and NH_3.
3. Removal of NOx, mainly NO.
4. Removal of the very toxic substances Dioxin and Mercury (Hg)

One equipment or system can be specific for a certain pollutant or can, sometimes with some additions, take care of the whole gas cleaning. There are often several possible solutions for an actual plant with respect to emission limits, performance, reliability, costs, etc. Only after an, often thorough, evaluation can an optimal combination be agreed for an actual plant.

Removal of particles

Particles are released and emitted from a lot of natural and anthropogenic sources in the world. Particles in the atmosphere have a great influence on climate, weather, human health, corrosion, vegetation, etc. Particles smaller than some microns (µm) are particularly harmful for man as these small particles penetrate down to the smallest lung alveoli. Several studies have found a relationship between the concentration of small particles in the air, mainly from diesel engines and boilers, and diseases and deaths. In addition, these small particles, which have a very large surface, adsorb various unpleasant gaseous matter. It is therefore very important to remove these very small particles.

The properties of the particles in the flue gas and flue gas itself influence of course the behaviour of the particles during the particulate removal process. The most important parameters in the removal are:

Particles

Physical properties
- Phase of particles – solid or liquid
- Particle size, particle size distribution and concentration
- Particle density and particle shape

Chemical properties
- Chemical composition
- Hygroscopicity, agglomeration and incrustation properties.

Electrical properties
- Resistivity
- Electrical strength

Flue gas
- Composition and temperature

There are in principle three available forces for the separation of particles from a gas:

Mass or inertia force
Surface or adhesion force
Electrical force

Cyclones and conventional wet scrubbers are typical mass force separators.

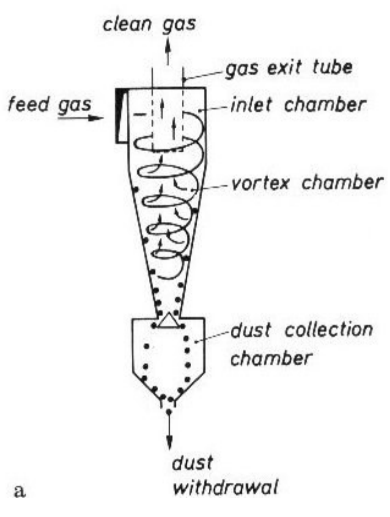
Fabric filter is a typical adhesion force separator.

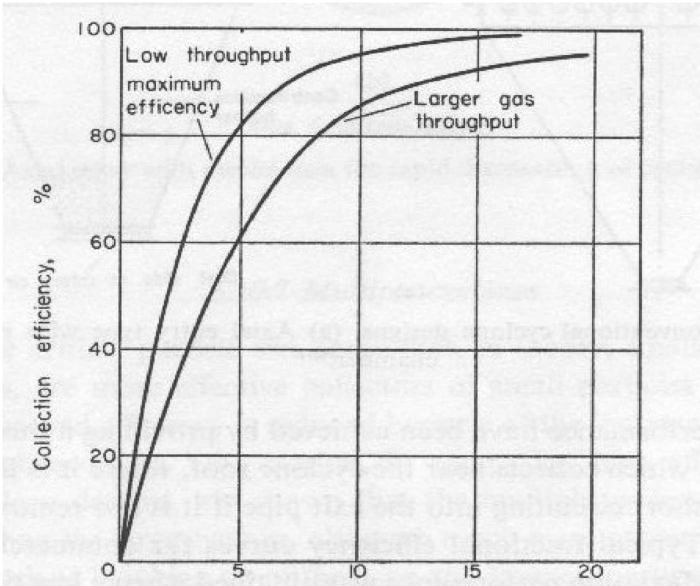
Electrical is the dominant force in an electrostatic precipitator.

Mass force separators

Cyclones

Cyclones are totally dependent on mass for the removal. Flue gas and particles are introduced tangentially into a cylinder so that a rotational movement is obtained. Centrifugal forces carry the particles toward the wall of the cylinder, to the vortex chamber and then to the dust collection chamber. Cyclones, and other mass force separators can be characterized by the **particle cut diameter**. A mass force separator has a removal efficiency of 50% for the stated cut particle diameter. Particles with diameters larger than the particle cut diameter are removed with higher rates and smaller particles, with less mass, are removed with lower efficiency. The curve which describes the removal efficiency for various particle sizes is called **the fractional efficiency curve**, which is normally more or less steep.





Particle size µm

Sketch of a typical cyclone and fractional efficiency curves for two types of cyclones, one with high efficiency and a particle cut diameter of about 2 µm and another with a particle cut diameter of almost 4 µm and larger gas throughput.

Cyclones can be designed for a cut diameter from some to some ten µm, thus they do not remove many harmful particles – particles smaller than some µm. They can be designed for tangential or axial inlet and can operate horizontally or vertically. Several small cyclones are often located in parallel – often named multicyclones. The design and operation of the dust discharge is important for the efficiency, no leakage of air is permitted – a secondary circuit is sometimes necessary.

A cyclone battery (i.e. a number of cyclones in series) can be designed for extreme conditions – cyclones in circulating fluidised bed (CFBC) and pressurized fluid beds (PFBC) are examples of such applications.

Cyclones are also used for droplet removal after wet scrubbers.

Sand bed filters

Sand bed filters also use mass forces for removal of particles. When the particles are deflected during passage through the sand bed they stick on the surface and are collected. The particle cut diameter for a well designed sand bed filter is around one µm and it can then remove the main part of the coarse particles. The fractional efficiency curve is normally steep so the removal of particles smaller than one µm is limited. By introducing electrostatic fields in the sand bed the removal of small harmful particles can be improved.

A sand bed filter is robust and can stand extreme conditions.

Wet scrubbers

Wet scrubbers also rely on mass forces for the removal of particles. The working principle is the same as for sand bed filters – instead of sand water droplets are used.

Wet scrubbers can be designed in many ways from

- Column, open spray and packed bed scrubbers with a rather low power consumption, similar to cyclones to
- High velocity venturis with high power consumption

The particle cut diameter is very dependent on the velocity difference between droplets and particles. Higher velocity difference requires more power.

For column and similar scrubbers, the cut diameter is around one µm at an energy consumption of about 0,5 kWh/1000 m^3 flue gas.
For the high efficiency venturi scrubber, the typical cut diameter 0,1 µm is obtained at an energy consumption of 3 – 4 kWh/1000m^3.

It is very important to *saturate* the flue gas with water vapour so that particles can absorb water and then increase in size and weight. *Condensation* after saturation gives another improvement when the water vapour condenses on the small particles. By optimised design and high flue gas humidity the removal of small particles can be much improved at the same time as low temperature heat is recovered.

The removal of small particles can also be done using electrical forces, normally by charging particles and droplets with opposite charge.

Liquid droplets downstream of a wet scrubber, with and without the removed particles, are much bigger than the dust particles and can easily be removed in cyclones and baffle separators.

Adhesion separators

Fabric Filter (FF), other names are Bag(house)filter, Fibrous filter, Textile filter

The most common adhesion separator, fabric filter, normally has a large area of woven or needled fabric which the flue gas has to flow through. During passage, the particles are removed by deflection (mass forces), interception, diffusion (adhesion forces) and electrical forces. It is the combination of these forces which gives this type of filter its unique performance of almost 100 % removal efficiency for most kinds of dust, independent of particle size (correctly designed, operated and maintained). Fabric filters can operate up to 200 - 250 °C with common fabrics, higher temperatures require special material.

The dust cake which is formed on the fabric is regularly removed by shaking, pulsing, gas reversing, etc.

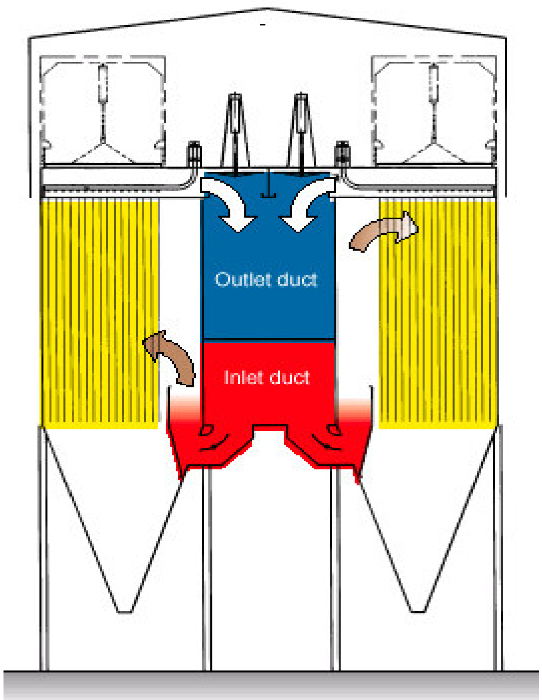
Pulse cleaned fabric filter (FF).

Filtration takes place on and in the yellow bags which are supported by cages. Filtration direction is from outside to inside.

The bags are, normally with the gas online, cleaned with short distinctive air pulses from the top of the bags. The bags are expanded and part of the dust cake is removed.

Big FF are built with compartments which each can be isolated from the flue gas with dampers in the ducts.

All service, e.g. inspection and exchange of bags are made from the clean gas side, above the yellow bags.



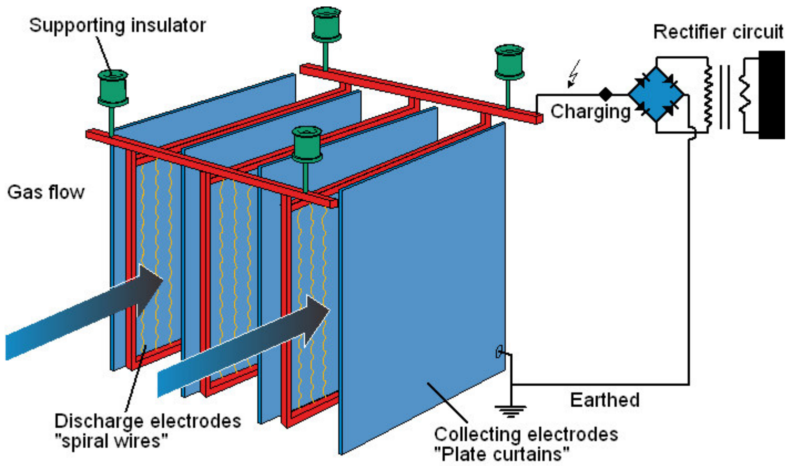
Electrostatic precipitator (ESP)

The principle of an electrostatic precipitator is very simple: charge the particles, separate them from the gas in an electrostatic field to a collector and remove the dust layer by dry or wet methods.

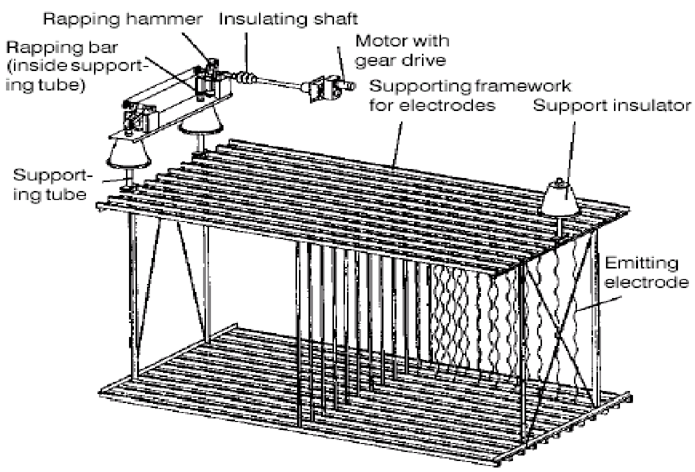
Charging of particles is good for particles bigger than about one µm – field charging – and for particles smaller than about 0,2 µm – diffusion charging. This phenomenon is one of the reasons why electrostatic precipitators often have a lower removal efficiency for about 0,5 µm particles.
Dry ESP:s are sensitive to dust with high resistivity as flashes can occur in the dust layer on the collector, but high voltage pulsing decreases this risk.

In principle, an ESP can be designed for very high removal efficiency for all particle sizes, simply by increasing the size. Construction material is mild steel and therefore DESP:s can operate up to about 350 °C.

The principle of an electrostatic precipitator with the electrodes and the high tension system



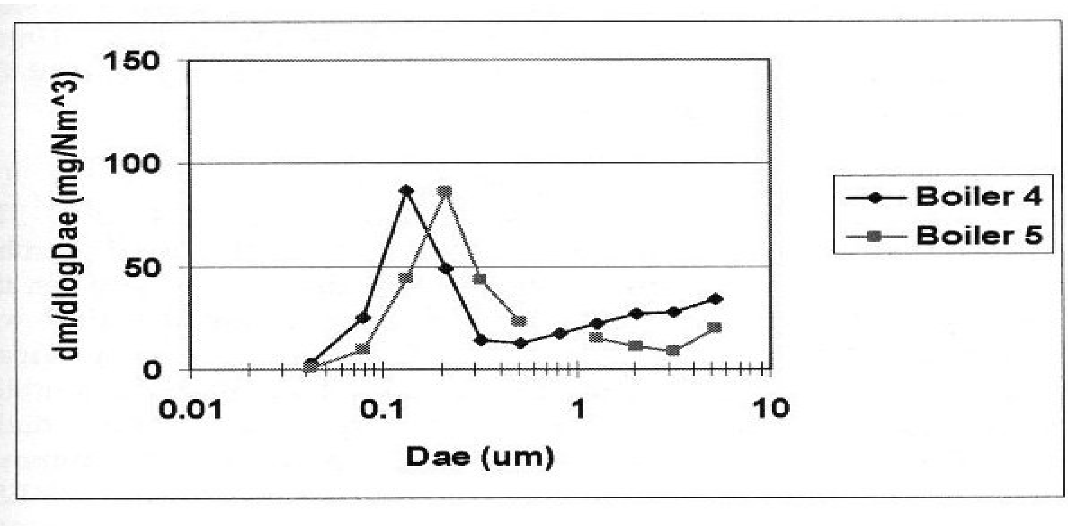
The mechanical system of a dry electrostatic precipitator (DESP) with three insulators and the rapping system from the top



FLUE GASES AND DUST FROM BIOMASS COMBUSTION

The fuel – biomass – can be variable and is often more or less contaminated. It can be dry or wet, thus giving wet or dry flue gas. The combustion method and quality varies of course also providing more or less unburnt matter. Nevertheless, for the removal of particles the following general statement can perhaps be made:

- The dust often comprises two fractions: one fraction with particles smaller than 1 (one) µm and one fraction with bigger particles.
- ***The small particles, the submicron fraction,*** are comprised of compounds which evaporate during combustion and then react, condense, etc. when the flue gas is cooled, normally in a boiler. The evaporation rate depends on the ash composition and the combustion temperature. Chlorides in the fuel increase the evaporation rate. Small particles often have a high concentration of potassium (K), sulphur (S) and chlorine (Cl).
- When the combustion is bad a lot of small soot particles can be generated which are then added to the small particulate fraction
- The amount of ***big particles (≥ 1 µm), the supermicron fraction***, can vary a lot. In a well designed and operated grate fired boiler the ash is removed as bottom ash and very little coarse ash is found in the flue gas after the boiler. On the other hand in a pulverized fuel fired boiler and some fluidised bed boilers we find almost all the ash as dust after the boiler. Besides this inorganic part also unburnt matter can of course appear.



Submicron particle size distribution measured downstream of multicyclones (MC) in two grate fired boilers operating on wood fuels with low ash content. Particle size, measured with impactor, in aerodynamic diameter Dae. The mass concentration of this submicron fraction is calculated to be 50 - 70 mg/m³(ntp) or somewhat lower than measured concentration.

REMOVAL OF PARTICLES - PRACTICAL SOLUTIONS

Dry methods

For the dry removal of particles there is well known equipment available: cyclones, dry electrostatic precipitators (DESP) and barrier separators – among others fabric filters (FF) and gravel bed filters. The operating temperature for dry gas cleaning installations after biomass boilers are well above any dew point and normally below 200 °C.

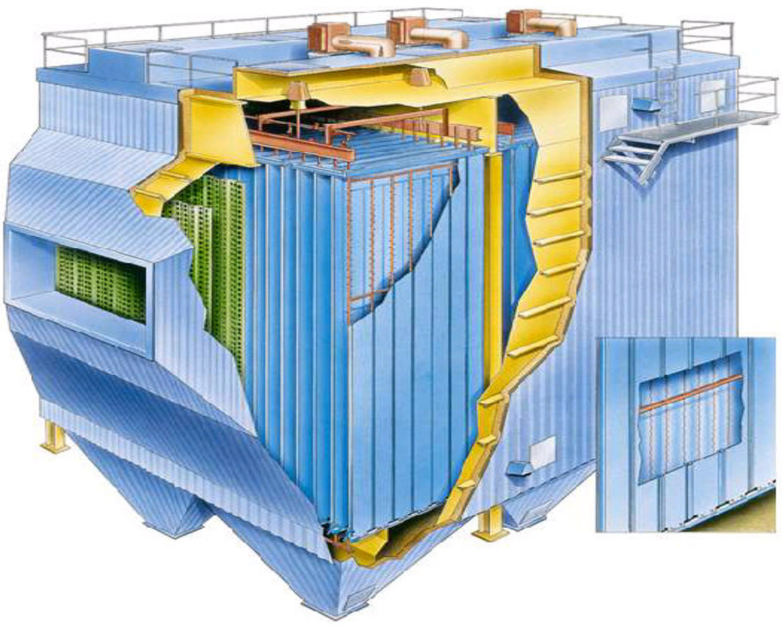
Cyclones

Cyclones are rather efficient for the coarse fraction but have minor effect on the submicron particles. The main application for cyclones in modern biomass plants is as precollectors. A special application is the cyclones at about 900 °C in circulating fluidized bed boilers (CFBC:s). There are of course many plants in operation and the experience is extensive. An alternative to cyclones as a precollector would be a Louvre type separator which operate with a sharp controlled deflection. The particle cut diameter is 10 – 20 µm and the fractional efficiency curve is not very steep.

Dry electrostatic precipitator (DESP)

Dry electrostatic precipitators *(DESP)* are very common after biomass combustion. There are several hundreds of DESP:s in operation from small ones in grate fired boilers to very big for combined heat and power (CHP)-plants. One very special and demanding application is the removal of chemicals from flue gas after soda recovery boilers. DESP is very common in all boilers and combustors in the pulp and paper industry.

Sketch of a rather big DESP with three separate electrical systems/rectifiers.



Operating conditions are normally good for DESP after biomass boilers as the electrical properties of the dust and flue gas are favourable. Low or moderate resistivity results in stable operation and good DESP performance.

It is normally possible to design a DESP for a total dust emissions lower than 10 mg/m³(ntp). A precollector is sometimes necessary especially if there are unburned big particles present.

But there is at least one exception. Combustion of biomass with a high concentration of chlorides generates a fine dust with a high resistivity and the DESP does not operate very well. Combustion of unwashed straw is one example. Fortunately, the fabric filter is a good alternative in this application.

Fabric filters

Fabric filters (FF) have not been so common for the removal of particles from biomass combustion but with further tightening emission limits it will increase its market share. The biggest advantage with FF is the very high removal efficiency almost independently of the particle size and distribution. Thus, it is normally possible to design a fabric filter for a dust emission of less than 10 mg/m³. A fabric filter must operate with rather dry dust otherwise it cannot be removed from the fabric. On the other hand, it can tolerate a certain amount of droplets but the ratio of droplets to dry dust must be controlled. A fabric filter shall normally be designed so that a dust cake can be formed on the fabric. This dust cake will then work as a filter media and in this dust cake droplets can be removed. Droplets and sticky dust must be prevented from penetrating into the fabric.

A fabric filter is an excellent bed absorber and this property is used in many plants where not only particles but also gaseous impurities (SO_2, HCl, etc.) have to be removed. By injecting a dry fine powder e.g. hydrated lime, absorption/reaction takes place in the filtercake simultaneously with the removal of particles. This, often very cost effective, method is used in many waste burning plants and in plants burning contaminated biomass from various sources.

Electrified gravel (sand) bed filter

The electrified gravel (sand) bed filter (EGB-filter) has removal properties similar to a conventional DESP. The standard design gives emission of about 10 mg/m³ from a wood waste fired boiler. It is not sensitive to high resistivity dust, nor sticky dust and there is no risk of fire. One maker has delivered 100 EGB-filters, of them about 10 to biomass combustion plants.

Wet methods for the removal of particles

Adiabatic wet scubbers operate around the water dew point of the flue gas, normally 55 - 65 °C for biomass boilers. With condensation the temperature depends on the cooling power but there are plats operating as low as 30 - 35 °C.

The main wet systems for particulate removal are:

- low pressure drop scrubber - spray, tray, column, etc
- high pressure drop scrubber - among others venturi
- electrified wet scrubbers,
- scrubbers with condensation and
- wet electrostatic precipitators (WESP).

Scrubbers
Low pressure drop scrubbers have a cut diameter of 0,5 - 1 µm and can then remove about 50 % of the submicron particles.
High pressure drop scrubbers have a cut diameter of 0,1 – 0,5 µm and a removal efficiency of about 90 % of the fine dust.
Both types remove the coarse particles, the supermicron fraction, very well. There are very few installations just for dust collection.

Electrified wet scrubber (EWS)
There is at least one maker of an *electrified wet scrubber (EWS), the* French company LAB SA in Lyon .They use it as final separator of particles in an air pollution control chain (often DESP + wet scrubbers + EWS) for Waste-to-Energy plants. The emission of particles from such a plant is normally very low.

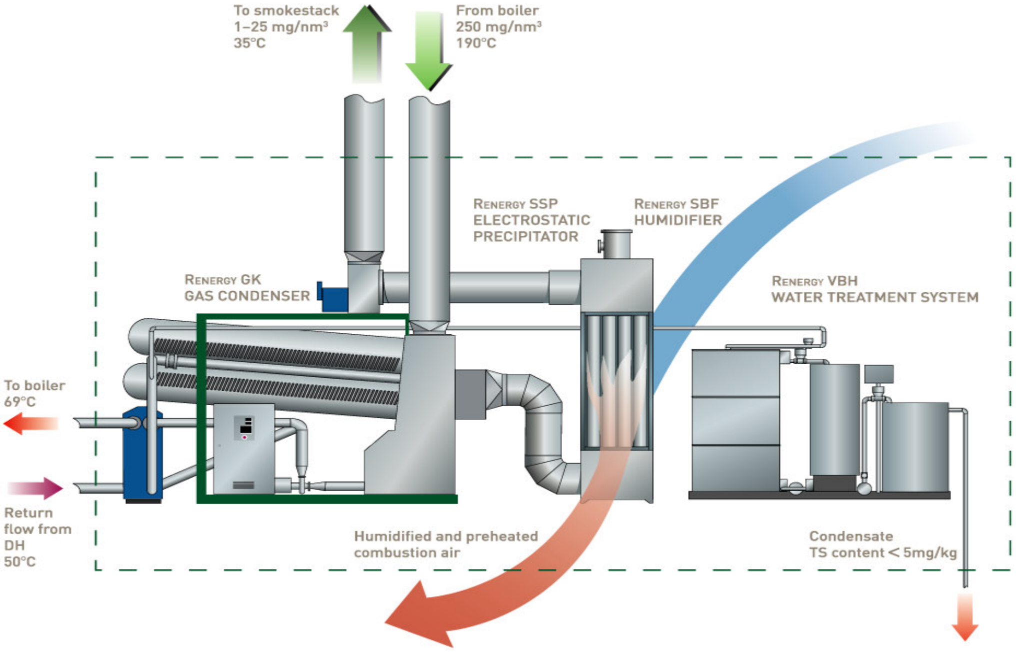
Wet scrubbers with condensation (CWS)
Wet scrubbers with condensation (CWS) are installed mainly for energy recovery and are then often just called the condensation unit.The cold surfaces for the condensation are either cold droplets in a scrubber, cold surfaces in a heat exchanger or a combination. There are several units in operation in the Scandinavian countries. Condensation, like electrical forces, improves the removal of submicron particles. A well, also for removal of particles, designed condensation unit has a dust removal efficiency between low- and high pressure drop scrubbers.

Wet electrostatic precipitators (WESP)
Wet electrostatic precipitators (WESP) are very effective particle separators. They are not dependent on the dust resistivity, as are DESP, as the dust is flushed off, more or less continuously, from the collecting plates. For the same reason, there is no reentrainment of collected dust. The WESP can be designed for a very high dust removal.

When low temperature heat is to be recovered by condensation the combination of a condenser and a wet electrostatic precipitator is often a good solution at least for small and medium size boilers. The WESP is very effective in removing submicron particles independently of the dust composition. Precollection of the coarse dust in e.g. cyclones is normally necessary. In some countries around the Baltic this combination is common in boilers up to 20-25 MW. One maker has delivered more than 70 units of this combination. WESP is also useful in combination with wet scrubbers for gaseous impurities.

Wet scrubbers can be a solution when a water treatment plant is available. In other cases, wet gas cleaning for pure particulate removal, without recovery of low temperature heat by condensation, is seldom the best solution.

A wet electrostatic precipitator downstream a multicyclone and a condensor for a biomass fuelled boiler



REMOVAL OF WATER SOLUBLE GASES

Typical water soluble gases from biomass boilers are:

- Sulphur dioxide (SO_2)
- Hydrochloric acid (HCl)
- Hydrofluoric acid (HF) and
- Ammonia (NH_3)

Some other water soluble gases can sometimes also be detected but then in very low concentrations. These soluble gases can be removed with wet or dry methods.

Wet absorption

Absorption of water soluble gases in wet phase is an old technology. Suitable equipment is wet scrubbers with a large gas/liquid contact area such as spray, tray, column or plate scrubbers, that is more or less the same as for the removal of supermicron particles. Absorption can be physical or chemical but even if the absorption can be pure physical, such as for HCl, chemical reactions are always involved during neutralization.

Sulphur dioxide (SO_2) is normally absorbed, neutralized and, at least partly, oxidized by a calcium carbonate (limestone) slurry or a sodium hydroxide (caustic soda) solution and oxygen.

$SO_2 + 2NaOH + ½O_2 \rightarrow Na_2SO_4 + H_2O$
$SO_2 + CaCO_3 + ½O_2 \rightarrow CaSO_4 + CO_2$

Gypsum ($CaSO_4$) can be used in cement or gypsum board if it is clean enough. Sodium sulphate (Na_2SO_4) has no use but has to be discharged to a recipient.

Hydrogen chloride and fluoride are also neutralized by sodium or calcium

$HCl\ (HF) + NaOH \rightarrow NaCl\ (NaF) + H_2O$
$2HCl\ (2HF) + CaCO_3 \rightarrow CaCl_2\ (CaF_2) + CO_2 + H_20$

Residues are difficult to reuse and must normally be discharged to a recipient.

Ammonia (NH_3) is soluble in water and can be neutralized with HCl or SO_2 or other acids.

$NH_3 + HCl \leftrightarrow NH_4Cl$

The concentration of ammonia in the flue gas after combustion is normally low but when ammonia or urea is added in excess into the end of the combustion zone to remove NOx the concentration of ammonia - often called ammonia slip - can reach unacceptable levels. A wet scrubber absorbs the ammonia slip effectively and we have converted an air pollution problem to a water problem. It is normally not permitted to discharge ammonia or ammonia salts to recipients.

One solution is to use the ammonia-(salt) solution as ammonia source in the SNCR process and inject it into the upper part of the boiler at a temperature of about 900°C. SNCR means Selective Non-Catalytic Reduction of nitrogen oxides (NOx) - NOx reacts with ammonia resulting in nitrogen (N_2). This reaction takes place directly in the flue gas at high temperature and, in the presence of a catalyst, also at lower temperatures - 170-450 °C. It is then called Selective Catalytic Reduction -SCR. A SCR catalyst can also be designed to remove NH_3-slip by reaction with the remaining NOx in the flue gas - a slip catalyst. More about SCR and SNCR in the section on deNOx.
Ammonia can also be driven off from the liquid by stripping.

The equipment for absorption - the absorber or scrubber or wet scrubber - can be designed in many ways but the principle is always the same: to attain good contact between liquid and gas at low power consumption.

The most common constructions of absorbers are

- spray absorbers in which the gas meets falling droplets. Power consumption comes mainly from the pumping of liquid. These absorbers are commonly used for SO_2-absorption with limestone and for gypsum production.

- packed columns where the flue gas flows through a bed of wetted packing.
- plate or tray columns in which the gas passes plates or trays with flowing liquid. The plates have openings like bubbles caps, sieves, valves, etc. The gas bubbles through and very little pumping power is consumed. Instead, the power consumption comes from the gas side with higher pressure drop over the absorber.

Wet scrubbing is very effective as the gas/liquid contact is good, the mobility of the molecules in the liquid is high and the reactions are fast. The reactions are also almost complete and therefore no excess of chemicals is needed.

Dry absorption (Dry scrubbing)

With dry absorption we mean here a sorption and chemical reaction between impurities in flue gas and an absorbent which is injected into the gas. The reaction products are removed in a dust collector and **the residues from the process are always dry.**

Compared to wet scrubbing, dry **absorption** is a rather new development. **Adsorption** on e.g. charcoal has been known for a long time but absorption in dry and/or semi-dry phase where the reaction products penetrate into the inner part of the absorbent was not practiced, at least as far as the author of this paper knows, until 30-40 years ago when it was tested on Energy from Waste (EfW) plants for $HCl/HF/SO_2$ removal.

The dry absorption solution proved to be a cost-effective way to solve, not only EfW:s demand but also, heat and power stations, metal smelters, glass- and ceramic processes and others. To the Dry Absorption principle also variants belong such as semi-dry, spray-drying, wet-dry, dry-dry, etc.

The principle is simple: precoat a filter with an absorbent with a large specific surface, let the flue gas pass through the precoated filter, unwanted impurities react with the absorbent, particles are removed simultaneously, remove the filter cake, precoat again and so on.

For $HCl/HF/SO_2$- removal after combustion of biomass there are mainly two absorbents which are possible namely, calcium hydroxide, $Ca(OH)_2$ - slaked lime - and sodium bicarbonate, $NaHCO_3$ - baking soda.

$Ca(OH)_2$ obtains a rather large specific surface already during the slaking process. Bicarbonate has a low specific surface but when it is heated to 150-160°C or higher CO_2 and H_2O is driven off leaving Na_2CO_3 with many pores and a large specific surface.

$$2NaHCO_3 + \text{heat} \rightarrow Na_2CO_3 + CO_2 + H_20$$

For good absorption calcium hydroxide is dependent on a certain temperature in relation to the humidity in the flue gas because the $Ca(OH)_2$ must be able to absorb water either added as a slurry, wetted powder or absorbed from the humidity in the flue gas. If for instance $SO_2 >> HCl$ the flue gas temperature must be decreased to about 60°C for a good reaction between $Ca(OH)_2$, water and SO_2.

HCl reacts with $Ca(OH)_2$ and $Ca(Cl)_2$ is formed. It is very hygroscopic and even deliquescent and thus the water and SO_2/HCl/HF absorption takes place at a higher temperature. If HCl-concentration > SO_2 which is common in EfW-plants a suitable operation temperature is around 140°C.

Sodium carbonate, which is generated from the added sodium bicarbonate, is very reactive and not dependent on water nor humidity. It can therefore be used to absorb SO_2, HCl or HF as well as a mixture of these gases in a wide temperature range of 150 to 300°C with and without water in the flue gas.
Sodium bicarbonate is more expensive than calcium hydroxide but less excess is necessary and the amount of residues is smaller.

The main process steps in dry absorption are

1. correction of temperature and, for $Ca(OH)_2$, humidity of the flue gas
2. injection of sorbents - calcium hydroxide or sodium bicarbonate
3. absorption and reaction
4. removal of the particles - the reaction products
5. handling and disposal of the residues

The two first steps can be made in many ways but 3. and 4. are almost always performed today in a fabric filter which is the key equipment in the dry absorption process.

Dry absorption is a cost-effective solution for the gas cleaning for many plants burning contaminated biomass. The main drawback of the process is that an excess of absorbent always is necessary which then also results in bigger amounts of residues compared to wet scrubbers, at least if the comparison is made on a dry matter basis.

Wet or Dry Absorption of water soluble gases

Wet gas cleaning systems as wet absorption always generate a waste water but dry absorption gives a dry residue. Water treatment systems can be rather complex.

Here are some examples when wet absorption has some advantages:

- Cheap chemicals such as limestone can be used
- No excess of chemicals
- Reusable residues such as gypsum

- If low temperature energy recovery by condensation is installed, waste water is generated there and a wet absorption system can use the same water treatment
- A condensation stage can itself remove water soluble gases if it is designed and/or adapted also for that purpose.

REMOVAL OF NITROGEN OXIDES - NOX

Nitrogen oxides in flue gas from combustion of biomass mainly arise from the oxidation of nitrogen in the fuel during combustion. NOx- production from nitrogen (N_2) in the air can also take place if there are very high (local) temperatures (>1200 - 1300°C) in the furnace.
The NOx comprises normally > 95% NO.

NO is a stable gas with low solubility in water but a particular reaction with ammonia can be and is used to reduce the NOx-emission:

$$4NO + 4NH_3 + O2 \leftrightarrow 4N_2 + 6H_20$$

This special reaction takes place

1. directly in the flue gas at a temperature between 850 and 1000°C and is named Selective Non Catalytic Reduction (SNCR) or
2. with assistance of a catalyst in a temperature range of 170 - 450°C- Selective Catalytic Reduction - SCR

The SNCR-process is effective if the conditions are good with stable flows and concentrations and a reasonable residence time for the reaction. But even at good conditions an excess of ammonia is needed for high NOx-removal. The non-reacted ammonia results in an increased concentration in the flue gas (ammonia slip). Wet scrubbers (see above under wet absorbtion) or an SCR-unit (see below) can reduce this slip. SNCR is often a cost-effective way for NOx-reduction in biomass combustion.

A Selective Catalytic Reduction (SCR) - unit can, in principle, be designed for any NOx-removal. The process is well-known with many installations on various processes running for a long time.

Three main locations of the catalyst are possible:

- high dust location - upstream of any dust cleaning at a temperature of 250 to 400°C
- low dust location - downstream of the dust cleaning in the same temperature area as above
- tail end location. The catalyst is located here at the end of the gas cleaning train with - except for NOx - "clean" flue gas. If the gas is very clean the operating temperature can be as low as 170 - 180°C.

The SCR-process was developed for coal fired boilers and there are many installations from the 1980's with generally very good experiences. Today, all new coal fired boilers are equipped with high dust catalysts located upstream of the air preheater.

EfW-plants have also been equipped with SCR for a long time, the first almost 20 years ago. Until today almost all EfW SCR installations are tail end, downstream either dry absorption, wet absorption or TC (Total Cleaning) but at least one promising test in a high dust location is ongoing in a plant burning mainly Municipal Solid Waste (MSW).

Sweden has a balanced fee system for NOx emission to the atmosphere for heat and power plants. If the emission for an actual plant is above the equilibrium level it has to pay SEK 40 per kg emitted NOx, calculated as NO_2, to a pool. If on the other hand, the emission is below this equilibrium level the pool pays the plant. It is not a taxation system since the pool shall balance. Therefore, many biomass plants in Sweden burning various kinds of wood and forest residues have installed high dust SCR.

Deactivation takes place more or less in all SCR- high dust- installations due to mainly penetration of potassium salts. The rate of deactivation depends not only on the ash composition but also on the combustion, boiler and the type of catalyst. In some plants, the deactivation rate has been unacceptable and the catalysts have been reactivated by washing, SO_2-treatment or a combination. The process has been successful but the deactivation has of course returned.

Some catalyst makers now have so much experience that they are willing to design and guarantee a high dust catalyst, at least for boilers burning "clean" biomass.

Low dust SCR-catalysts, downstream a DESP at about 300 °C, should also be possible. A problem with DESP:s at this temperature level is that Dioxin can be formed even at very low Cl- concentrations.

REMOVAL OF DIOXIN AND MERCURY

Dioxin is a short name for chlorinated dibenzo(p)-dioxin and furan compounds. To simplify the evaluation, the 17 most toxic isomers (of 210 in total) are summarized with individual factors to a dioxin equivalent - Dioxin I-TEQ - and it is this equivalent which is maximized to 0,1 ng/m³ in the EU directive.

Dioxin is, as mentioned before, the common name of organic compounds with basically two aromatic rings connected to each other over one (Furans) or two (Dioxins) oxygen atoms. The hydrogen atoms in the bensen rings are replaced by chlorine atoms in various degrees and they are very toxic.

Dioxin is normally not found directly after the combustion but is formed by complex reactions in the boiler/gas cleaning part at about 200- 450°C. The Cl-concentration necessary is very low. Organic precursors are necessary and therefore there is no dioxin formation after perfect combustion.

A catalyst for SCR is an oxidizing catalyst and can break down dioxin. The catalyst must often be bigger than required for SCR-deNOx.
FF-fabrics with catalyst in the fabric material are marketed by the Gore company Recommended temperature is 190°C.

Dioxin are heavy aromatic molecules which have a great affinity to, particularly organic, surfaces and this phenomenon is used for cleaning - adsorption. Material with a large surface, such as activated carbon, is of course effective but also char, plastic and rubber is used. A common solution is to inject powdered activated carbon in the flue gas upstream of a fabric filter (FF), often together with e.g. hydrated lime (for SO_2/HCl- removal). FF is a very efficient reactor and the dioxin concentration can be reduced to < 0.01 ng/m³.

Another solution is to install a packed bed tower filled with small pieces of plastic or rubber often impregnated with activated carbon. Scrubbers operating with oil have also been, at least, tested.

When the activated carbon, plastic, rubber and oil have been saturated with dioxin and other organic compounds it is normally destroyed by combustion in the same boiler.

The emission of dioxin to the atmosphere can be kept very low with modern air pollution control (APC). It is also important to design the boiler and APC- system for a low dioxin concentration in the ashes.

The EU-directive for ***mercury* (*Hg*) *and its compounds*** demands a maximum emission of 50 µg/m³ for plants burning waste. This is a very generous level as Hg is very toxic and as it accumulates in nature.

Mercury has successively been phased out from our society during the latest 20 years and the concentration in waste is now normally low. However, metallic mercury, which has been emitted from natural and anthropogenic sources during centuries has precipitated and accumulated all over our world, particularly in the cold areas. Therefore, we find mercury also in wood and forest residues.

All the mercury in the fuel is evaporated during combustion and after some transformations in the cooling sections we have roughly **three forms of mercury** in the flue gas upstream of the gas cleaning**: particulate mercury**, **gaseous oxidized mercury and gaseous metallic mercury.** When chlorides are present in the flue gas, such as in MSW-plants, the oxidized part is mainly mercury chloride - $HgCl_2$.

Particulate mercury is removed in good dust separators such as DESP, WESP and FF. Oxidized mercury, which often is the dominating part of the mercury in the flue gas, at least in MSW-plants, can be removed in wet and dry scrubbers. The

wet scrubber must be designed so that removed oxidized mercury is not reduced to the metallic form and then evaporates from the liquid. If there is HCl in the flue gas a prescrubber with low pH is often a good solution. Dry scrubbers with additives- activated carbon is the most common - can remove both oxidized and metallic mercury.
The document Waste in Sweden reports a total mercury emission from combustion of 3,1 Mton mixed waste of less than 40 kg for the year 2004. If these Swedish MSW-plants had emitted the permitted level of mercury, 50 μ/m^3, the total emission would have been about 20 times higher or about 800 kg

Another comparison: USA (EPA) reports that about 50 000 kg of mercury is emitted from forest fires in USA in a year, more than from all power stations in USA. I mention this just to get a perspective on the situation.

EXAMPLES OF GAS CLEANING COMBINATIONS WITH BEST AVAILABLE TECHNIQUE - BAT

1. "Clean" biomass such as wood and forest residues

1.1 Removal of particles and NOx without condensation

DeNOx: SNCR and/or HighDustSCR

1.1.1 No removal of submicron particles - Small licensed boilers, skilled personal and clean fuels - MultiCyclones (MC).

1.1.2 Removal of sub-micron particles

1.1.2.1 Removal of sub-micron particles with, often, low operating cost: Dry Electrostatic Precipitator DESP

A modern DESP at a biomass fired boiler. The ESP is its own house thus reducing the investment cost.

1.1.2.2 Removal of sub-micron particles with very low particulate emissions - Fabric filter (FF)

**Combustion of straw generates many small particles with a high resistivity. Fabric filters do a good job in this application.
Below the Dong/Masnedö plant in Denmark with the two FF compartments to the left which can be seen before the housing has been erected. To the right, the whole plant after completion. Unit generates 9 MW electric and 23 MW heat for district heating**

1.2 Removal of particles and NOx with condensation

DeNOx: SNCR and/or HighDustSCR.

1.2.1 Limited removal of sub-micron particles - Small licensed boilers, skilled personal and clean fuels : MC + WetScrubber (WS) / /Condenser (C) + Waste Water Cleaning (WWC)

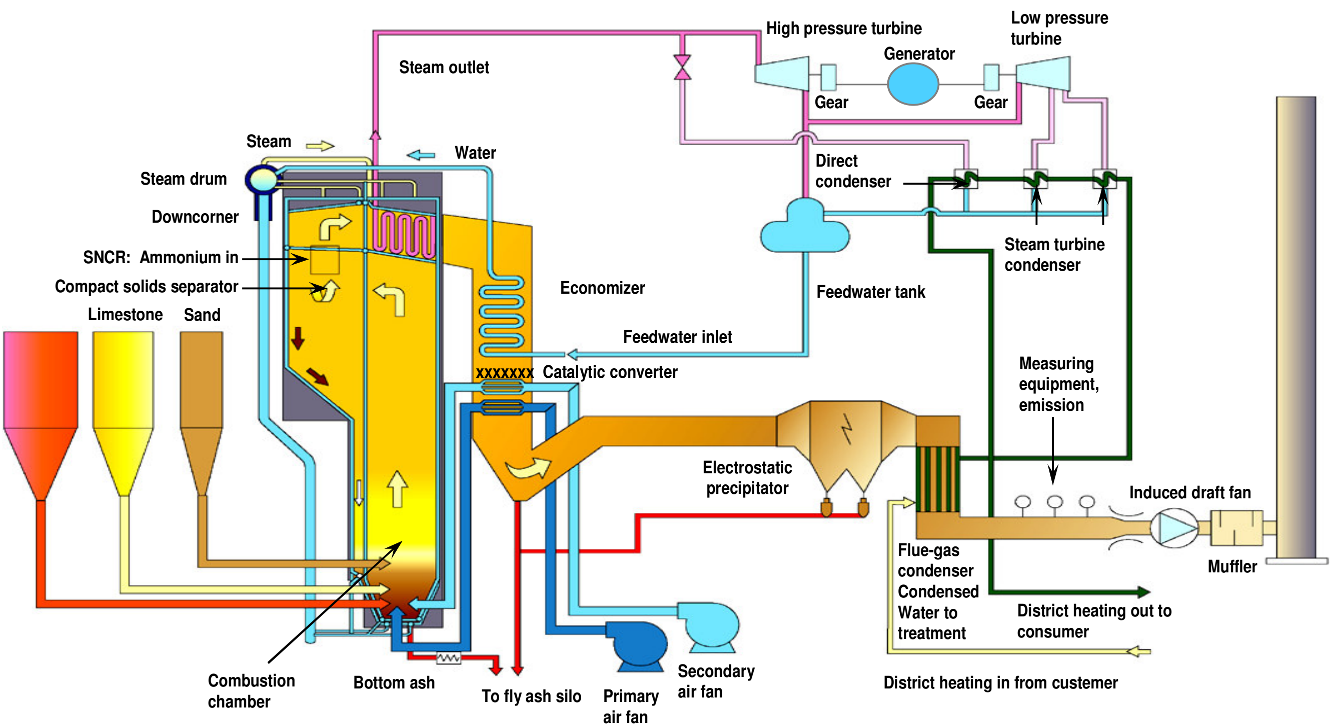
1.2.2 Removal of sub-micron particles

1.2.2.1 Wet method with WESP: MC + C + WESP + WWC

Wet Electrostatic Precipitator downstream of a multicyclone and a condenser for a steam boiler fuelled with forest and similar residues.

1.2.2.2 Wet method with DESP or FF + C + WWC

Sandviksverket, own and operated by VEAB, burns mainly forest residues, in a CFBC generating 38 MW electric and 66-76 MW heat for district heating. Steam: flow=147 ton/h, p=140 bar, t=540°C. The typical gas cleaning comprises: SNCR + NH_3-slip catalyst + DESP + C



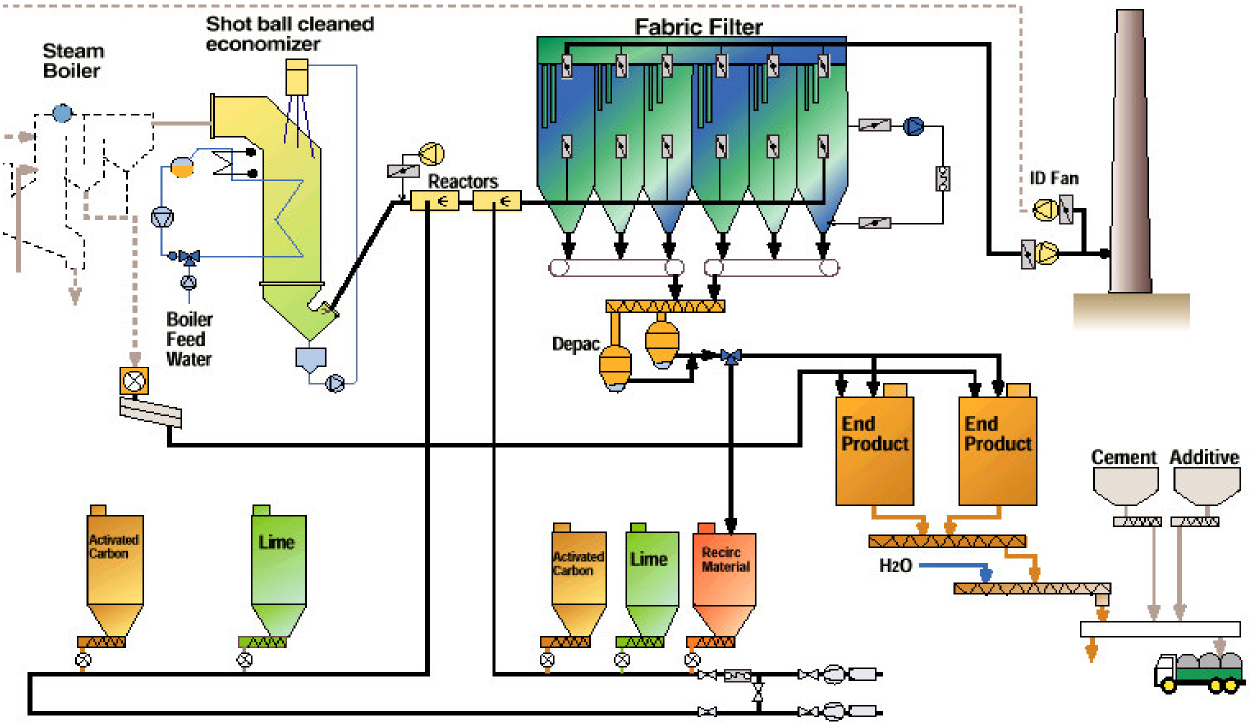
2. Contaminated biomass, classified as waste

DeNOx: SNCR, TailEndSCR.

2.1 Dry method: Dry or SemiDry Absorption (DA)

OPERATIONS DATA 2005

Treated waste (of which biomass 290.000 tons)	757,000	tons
Electricity production (net)	510	Gwh_{el}
District heating	491	Gwh_{th}
Fossil fuels saving (Tons of Oil Equivalent)	> 150,000	TOE
CO_2 avoided emissions	> 400,000	tons



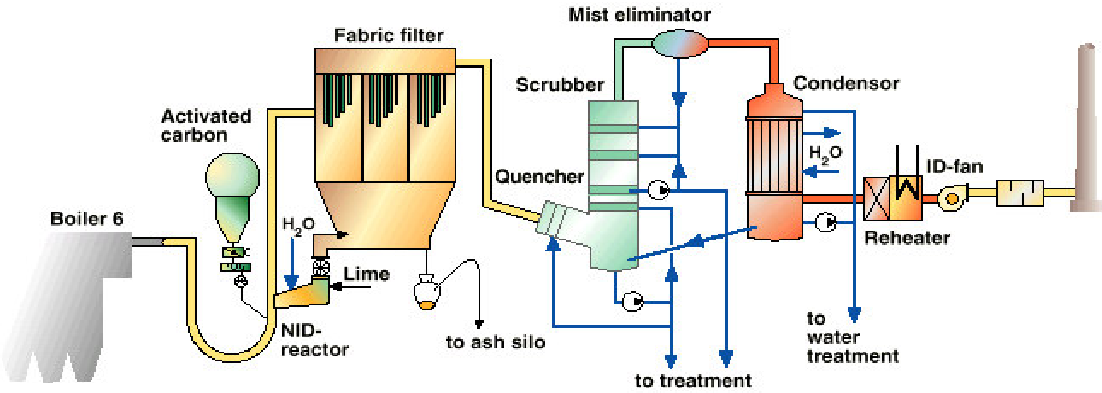
The Termoutilizzatore in Brecsia, burning MSW and residues from paper industries, comprises three units each equipped with a dry absorption system for gas cleaning. In the first step the gas temperature is decreased and controlled in an economizer. Sorbents are injected downstream and the real cleaning takes place in the fabric filter by filtration, absorption and adsorption, or in short: Filsorption.

STACK EMISSIONS

All values in mg/Nm3 (except for Dioxin - ng/Nm3) Values referred to dry gas, normal conditions, 11 % O2	PLANT AUTHORIZATION LIMITS 1993	PLANT DESIGN DATA 1994	EUROPEAN UNION LIMITS 2000	ACTUAL OPERATION DATA 2005
Particulate matter	10	3	10	0,4
Suplhure doxide	150	40	50	6,5
Nitrogen oxides (NOx)	200	100	200	<80
Chlorine acid (HCl)	30	20	10	3,5
Fluorine acid (HF)	1	1	1	0,1
Carbon monoxide	100	40	50	15
Heavy metals	2	0,5	0,5	0,01
Cadmium (Cd)	0,1	0,02	0,05	0,002
Mercury (Hg)	0,1	0,02	0,05	0,002
PAH (Policyclic aromatic hydrocarbon)	0,05	0,01	-	0,00001
Dioxin (TCDD Teq) ng/Nm3	0,1	0,1	0,1	0,002

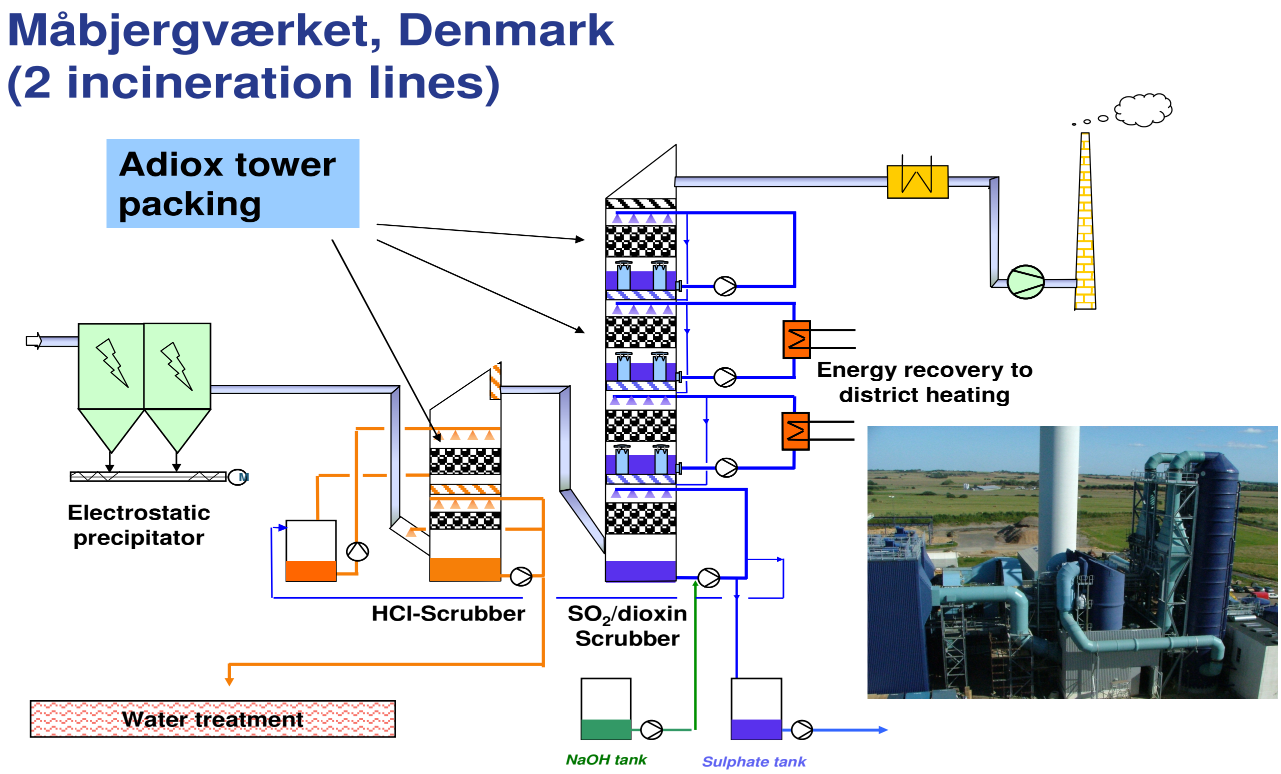
2.2 Wet methods with and without condensation

2.2.1 Wet method 1: DA + WS/C + WWC



The no. 6 boiler in Stockholm/Högdalen burns recycled material, classified as waste, in a circulating 90 MW(th) fluidized bed. Gas cleaning comprises a dry absorption system type "moist dust" with lime and activated carbon followed by a two stages wet scrubber and a condensing unit. SNCR is reducing NOx and NH_3-slip is absorbed in the wet scrubber. The ammonia solution from the wet scrubber is used in the SNCR-system.

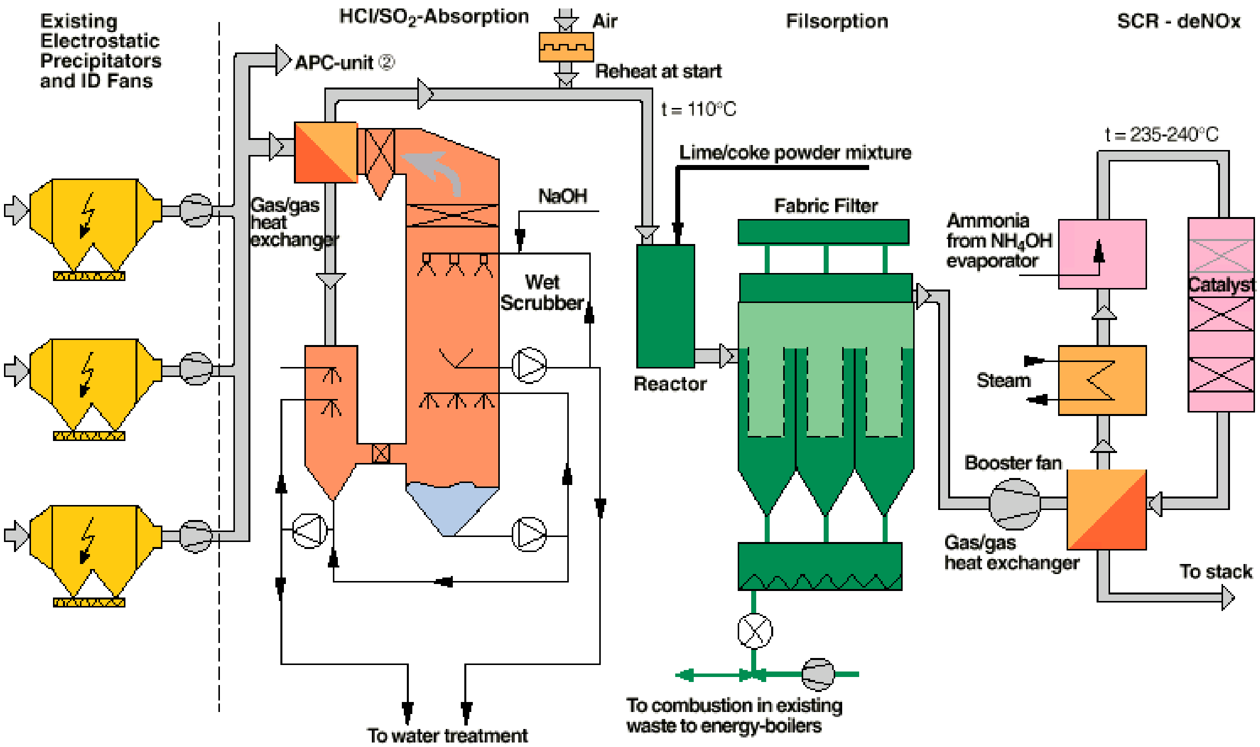
2.2.2 Wet method 2: DESP or FF + WS/C + WWC



Måbjergverket, owned and operated by Dong, has two incineration units, each burning 9 ton waste/h, and gas cleaning comprising SNCR, DESP and a multistage WS/C: 1st stage quenches the gas and removes HCl and mercury compounds, 2nd mainly SO_2-removal, 3rd and 4th: low temperature heat recovery by condensation. Some stages are equipped with a special packing, called Adiox, for adsorption of dioxin, they also remove some particles. As wet scrubbers transfer a pollutant from air to water the waste water treatment is an important part of the total pollution control.

2.2.3 Wet method 3: DESP or MC for small plants + WS/C + WESP + WWC

2.2.4 Wet method 4: DESP + WS/C + WWC + DA + SCR



Flue gas cleaning for three MSW-boilers at KVA Luzern (CH) comprising dry electrostatic precipitators, three stages wet scrubber, fabric filter with additives (Filsorption) and Tail-End SCR. The SCR-system operates with clean gas at a low temperature. The plants own steam is therefore used for the final reheat. The ash from the Filsorption unit containing dioxin and other organic matter is destroyed by combustion in its own MSW-furnaces.

REFERENCES

Strauss: Industrial Gas Cleaning, second edition. Pergamon Press 1975.

Brauer, Varma: Air Pollution Control Equipment. Springer Verlag 1981.

Lillieblad: Combustion Aerosols from Pulverised Coal Combustion and Biomass Grate Combustion - Filtration aspects. Lic. thesis Växjö Univ. 2003.

Lind, Hokkinen, Jokiniemi: Fine particle and trace element emissions from waste combustion - Comparison of fluidized bed and grate firing.
Fuel Processing Technology, July 2007.

Bonomo; Industrial Installation and Testing of an Innovative Catalyst System for NOx-removal in WtE units. WTERT 2006, Annual Meeting at Columbia University N.Y, Oct 19-20 2006

Larsson: Study of Catalyst Deactivation in three Different Industrial Processes.
Dr. Thesis. Växjö University 2007

Schnieper, Carlsson: Lucerne 2000 - A New Cost-Effective Solution to Air Pollution Control. Filtration and Separation March 1998.

Personal contacts with following companies: Alstom, Filcon, Götaverken Miljö, Svensk Rökgasenergi, VEAB