

GASASH – The improvement of the economics of biomass/waste gasification by higher carbon conversion and advanced ash management

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Abstract

Gasification technology offers an attractive way to use low-grade fuels in energy production with high efficiency and low environmental impact, particularly when the product gas is cleaned. Biomass and waste gasification and gas cleaning technologies have been developed and demonstrated but they are still at an early stage of commercialization. An issue calling for further development is the volume and quality of fly ash, since without any treatment gasification fly ash contains more un-reacted carbon compounds than fly ash originating from direct combustion of similar fuels. Fly ash disposal related costs represent a significant share of the overall operating cost of waste-based energy production. It is also expected that the cost of landfilling ash will continue to increase in EU Member States.

The primary objective of the project described in this paper was to develop sustainable and economic methods for ash management of gasification and gas cleaning process. This was done by optimising gasification and gas cleaning process in order to reduce volume of fly ash and improve ash quality. A range of different gasification ashes were characterised to enable the assessment of their suitability in potential utilisation routes. Upgrading methods for carbon rich fly ashes were also investigated and new methods were developed. The identified utilisation routes for different qualities of ashes were subjected to an extensive techno-economics evaluation.

The work reported in this paper forms part of the studies undertaken within the project "*Improvement of the economics of biomass/waste gasification by higher carbon conversion and advanced ash management (GASASH)*" which was part-funded by the European Commission under the Fifth Framework Programme (contract number ENK5-CT-2002-00635). The EC's contribution is gratefully acknowledged.

Introduction

Ash disposal cost for biomass or waste gasification process has a significant impact on the feasibility of biomass/waste gasification based energy production. Fly ash (filter dust) in particular might contain high concentrations of unburned carbon and harmful compounds restricting further utilisation, or normal disposal.

Ash related costs could be reduced by reducing ash volumes, improving the quality of ashes and developing products and technologies for the utilisation of ash as a raw material. These were the key topics of the GASASH project, which focused on improving the overall economics of biomass/waste gasification by higher carbon conversion and advanced ash management. The final objective was to develop different alternative treatment and utilisation routes for gasification fly ash and preliminary assess feasibility of these routes.

The project focused on three topics. The first task of the project concentrated on further development and improvement of fluidised-bed gasification process in order to reduce ash volumes and improve ash quality.

The second task focused on the development of new techniques for gasification and gas cleaning process. Three different methods were studied and developed: 1) thermal treatment (separate combustion) of gasification ashes, 2) fly ash oxidation process integrated to the gasifier and 3) conditioning of fly ash. All three developments were targeted reduce the carbon content of the ash, reduce ash volume or improve ash quality.

The third task focused on screening of present combustion fly ash utilisation methods and development of gasification fly ash specific utilisation routes. The most promising methods and routes were selected for more detailed evaluation and experimental studies in order to be able to assess industrial scale feasibility of them.

Finally, the technical and economic feasibility of the developed improvements was evaluated in order to define the optimal ash management procedure.

Improvement of carbon conversion and effects of bed materials

The objectives were related to improvement of carbon conversion, reduction of ash volumes and effects of bed additives in order to reduce cost related to disposal of solid residues. Work contained optimisation of bubbling fluidised bed (BFB) and circulating fluidised bed (CFB) gasification of clean waste wood, clean wood pellets, demolition wood, solid recovered fuel (SRF), orujillo and sewage sludge. Different bed materials (sand, limestone, ofita) were used in order to optimise the gasification process. Most of the gasification test trials were carried out with air but wood pellet gasification test trials with CFB gasification pilot-plant were also carried out with oxygen enriched air.

VTT carried out gasification optimisation test trials with process development unit-scale (PDU) circulating fluidised bed gasification and gas cleaning test facility and with pilot-scale bubbling fluidised bed gasification and gas cleaning test rig. Used fuels were clean waste wood and solid recovered fuel (SRF). Both fuels were gasified with both test facilities. Bed material was in all cases mixture of sand and limestone and gasification agent was air and 10-20 % steam. Gasification temperature varied from 860°C to 895°C.

High carbon conversion was achieved in all test trials. Carbon conversion in BFB gasification of clean waste wood varied from 94,4 % to 98,7 % when target was 96 %. In CFB gasification of clean waste wood carbon conversion was 98, which also was the target.

Solid recovered fuel (SRF) is typically rich in plastic and paper, which are both very reactive and produce only little char. High reactivity leads typically to high carbon conversion. In BFB gasification of SRF carbon conversion 97,5 % was achieved (target 96 %) and in CFB gasification carbon conversion varied from 96,1 to 98,0 % (target 98 %). All carbon conversions were high and technically gasification process was always stable.

The primary aim related to improved carbon conversion was to improve the quality of fly ash and reduce volume of difficult carbon containing fly ash. Table 1 summarises composition of ash fractions from bubbling fluidised bed gasification of clean waste wood. Fly ash contained 50-60 % carbon, which is still high because in most ash utilisation applications carbon content should be lower than 10...15 % or even lower.

In BFB gasification of SRF most of the fly ash was removed by the filter. Typical bulk compositions of solid mass streams are presented in Table 2. These data show that bottom ash is primarily composed of sand additive and contains no combustible material. Filter dust contained only 10.6 % of carbon, which is very low compared to waste wood derived filter dust. Low carbon content of filter dust was achieved by high reactivity of the feedstock and successful operation of the gasifier.

| Set point | BFB 0250A | BFB 0250B | BFB 0250C | BFB 0250D |
|-------------------------|-----------|-----------|-----------|-----------|
| Filter dust, wt% (d.b.) | | | | |
| C | 51.5 | 53.9 | 60.7 | 56.0 |
| H | 0.8 | 0.8 | 0.8 | 0.8 |
| N | 0.2 | 0.3 | 0.3 | 0.2 |
| O (difference) | 5.2 | 5.9 | 3.6 | 8.6 |
| Ash | 42.4 | 39.3 | 34.8 | 34.4 |
| Bottom ash, wt% (d.b.) | | | | |
| Ash | 99.7 | 99.8 | 99.6 | 99.6 |

Table 1. Composition of different ash products in BFB gasification of clean waste wood.

| Set point | CFB 0323A | CFB 0323B1 | CFB 0323B2 | CFB 0323C |
|-------------------------|------------------|------------|------------|-----------|
| Feedstock | Clean waste wood | SRF | SRF | SRF |
| Filter dust, wt% (d.b.) | | | | |
| C | 40.9 | 13.3 | 12.1 | 13.4 |
| H | 0.5 | 0.36 | 0.2 | 0.5 |
| N | 0.1 | 0.1 | 0.1 | 0.1 |
| O (difference) | 9.9 | 2.6 | 8.0 | 0.8 |
| Ash | 48.1 | 80.8 | 76.6 | 81.6 |
| Bottom ash, wt % | | | | |
| Ash | 99.5 | 99.9 | 99.8 | 99.7 |

Table 2. Composition of different ash products in CFB gasification of clean waste wood and solid recovered fuel.

ECN focused on improvement of carbon conversion based on modified bottom of fluidised bed gasifier. ECN carried out gasification test trials with clean biomass (wood), demolition wood and sewage sludge. Sewage sludge gasification test trial was related to optimised gasification but also on fractionating of fly ash by staged cooling and particulate removal. Clean biomass and demolition wood waste gasification test trials were carried out in a 500 kW CFB gasification test facility with so called High Solids Density Circulating Fluidised Bed (HSD-CFB) facility installed. Principle of this test facility is based on separation of fuel inlet and air inlet into two different zones in order to increase char reaction with air. Figure 1 illustrates the principle of HSD-CFB gasification test rig.

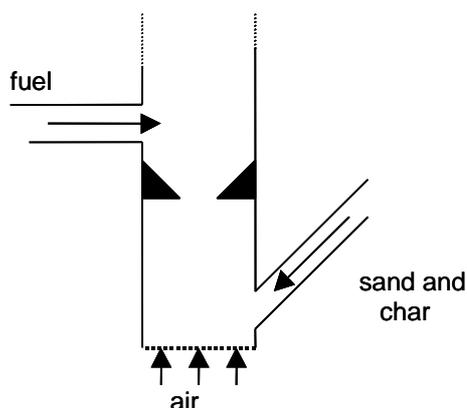


Figure 1. A schematic figure of the bottom part of the riser in a CFB designed according to HSD-CFB principle.

From gasification point of view gasification test trials with sewage sludge were successful but fractionating of fly ash did not work as planned. Carbon conversion of

sewage sludge gasification was 99 %, which was based on high air ratio and high gasification temperature.

HSD-CFB gasification reference fuel was clean biomass (wood). Gasification test trial resulted in relatively high carbon conversion, 96 %, without further changes to the gasification conditions. Test trials with demolition wood waste resulted in carbon conversion 92 %.

One way to optimise ash management in gasification of demolition wood waste could be separation of finest fraction of fuel prior gasification. The finest fraction of demolition wood contains relatively large amounts of problematic elements. If removal of finest fraction can be done successfully it would improve ash quality as well as reduce ash volume. This was studied by carrying out gasification tests with two different demolition wood fractions. The first fraction represented demolition wood as such (0-15 mm). The second fraction was prepared from demolition wood waste by separating finest fraction by sieving (3-15 mm). After sieving the second fraction contained significantly less visible impurities and dust, which had positive effect on handling, operation of feeding and bottom ash discharge systems. Most of the concentrations of metal impurities in fly ash were decreased when finest fraction was removed. However, some elements enriched, especially Cu and Zn. From ash quality and reduction of ash volume point of view effect was not significant.

The list of fuels studied in the GASASH project contained one agrobiomass, orujillo, which is available in large quantities in Southern European countries. Orujillo is a residue of the olive oil extraction industry with high heating value but it is rich in alkali metals (primarily potassium), which can cause serious deposit formation and agglomeration in FB gasification or combustion. AICIA carried out the work related to fluidised bed gasification of orujillo.

The first test trials were carried out with sand bed but tests were not successful. The bed suffered of severe defluidisation due to bed agglomeration even at low gasification temperatures. Bed material was changed from sand to ofita, which is a sub-volcanic rock (a silicate with formula $(Ca, Mg, Fe, Ti, Al)_2(SiAl)_2O_6$). Test trials with ofita bed were successful and bed agglomeration was successfully avoided. Carbon conversion (without taking into account the tars in the gas produced) varied between 73.4% and 86.1% (no reliable tar measurement system was available). Although orujillo was the most difficult fuel used in this project it was successfully gasified and carbon conversion was reasonable or even good.

Largest gasification test trials were carried out by Foster Wheeler Energia. Test trials were carried out with atmospheric pressure CFB gasification pilot plant (1.5 MW ACFBG pilot) and the main variable oxygen content of fluidisation air. The heating value of product gas can be increased by oxygen enrichment but the effects on carbon conversion are not clear: the partial pressure of oxygen is higher but on the other hand, temperature control requires lower air coefficient. Effects of different bed materials were also studied. Fuel of all test trials was pelletised wood. Test matrix contained three different oxygen levels of fluidization air, three different bed materials and two different levels of bed inventory.

Applying oxygen did not cause any significant difficulties but the effects on the process appeared quite clear: fuel feeding had to be increased to keep bed temperature constant, there was less circulation due to less primary air, temperature at the top of the

reactor was reduced and the share of combustible components of the syngas was increased.

Three different bed materials were tested: magnesium oxide, 50 % sand / 50 % coarse limestone and 50 % sand / 50 % fine P6 limestone (the same as P3 but finer fraction). The feed rate was generally 4 - 5 kg/h but with the fine limestone it was 10 kg/h.

The oxygen content of gasification air was about 23 % (m), 30 % or 40 % during most of the tests but finally it was raised to 50 %, which was the maximum level with the available equipment.

Only moderate amounts of bottom ash were removed from the gasifier during steady-state test runs. No signs of bed sintering related to fuel alkalis were observed. The bottom ash contained mostly bed make-up materials because the fuel was virtually free of solid impurities and the fine fuel ash is obviously elutriated from the reactor.

The filter ash consisted of calcium hydroxide fed after the gas cooler, elutriated bed make-up (mainly Ca or Mg), unburned carbon from the fuel and fuel ash. The unburned carbon content of filter ash seemed to increase with oxygen enrichment level of the fluidization air, as illustrated in Figure 2. Oxygen enrichment has several direct and indirect effects on gasification process but final conclusion was that oxygen enrichment of air did not decrease the unburned carbon content of filter ash to levels required for direct utilisation or landfilling.

The CO, H₂ and CH₄ contents of syngas increased with oxygen enrichment, as expected. The differences between limestone types were very small, but with MgO bed the CO and H₂ contents rose slightly higher than with limestone / sand bed as the oxygen content was increased. The tar contents of syngas were very low with MgO bed.

The carbon conversion decreased slightly with increasing oxygen content. However, it should be noted that the primary objective was to find out potential effects of the tested parameters.

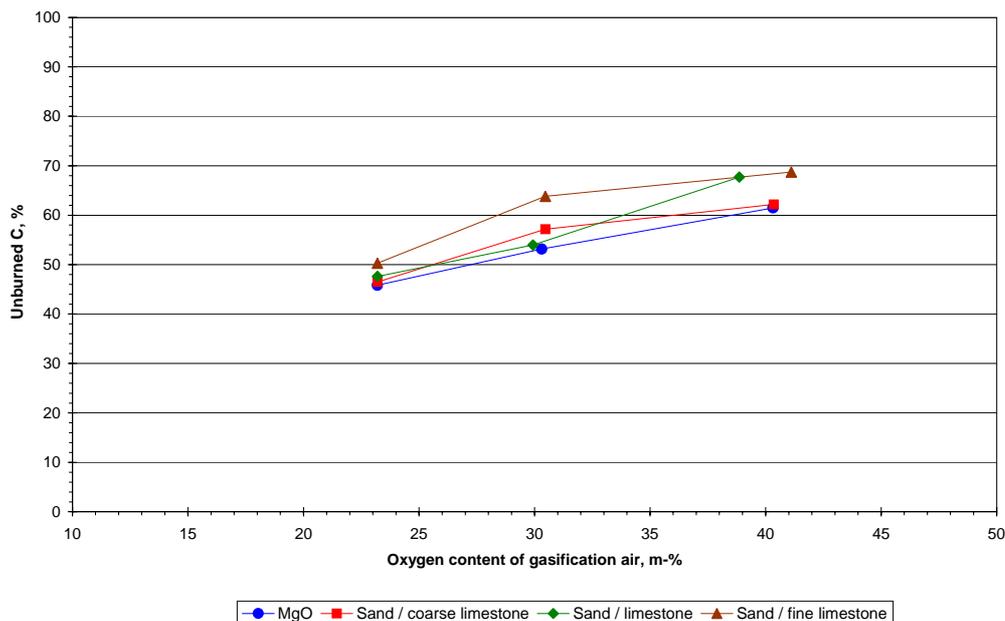


Figure 2. Unburned Carbon Content of Filter Ash.

A common conclusion related to optimisation of gasification and gas cleaning process conditions is that no universal solution can be defined but final optimisation has to be done case by case. Carbon conversion can be increased, but this does not necessarily mean that the carbon content in the fly ash is low enough for convenient utilisation options. It is expected that for many regular fuels carbon content in the fly ash cannot be lowered enough without significant drawbacks for the efficiency gasification process. Final optimisation has to be done case by case. Optimal solution depends on type of fuel and local conditions. In addition, oxygen enrichment might offer one way to have positive effect on carbon conversion but this needs further optimisation.

Process developments related to gasification and gas cleaning

The objective of process development activities was to develop technical solutions in order to reduce volume of fly ash and upgrade its quality. Efforts were focused on development of further treatment processing of fly ash and development of new components to gasification and gas cleaning process.

Development of fly ash treatment methods

FWE concentrated on development of further treatment of biomass- and waste-derived gasification fly ash. Primary aims of ash treatment were to reduce ash volume, improve ash quality and utilise the energy bound in the combustible fraction of ash.

In recent years, several types of ash treatment methods have been commercialised, e.g. fluidised bed combustion, thermal stabilisation, separation methods, chemical stabilisation and solidification. Ash treatment techniques have mainly been developed for fly ashes originating from combustion. Most of the commercial methods cannot be applied for gasification fly ashes as such due to the different ash properties, e.g. high contents of unburned carbon and PAH compounds. However, an environmentally acceptable solution can also be found for gasification ashes by combining different treatment techniques. The following ash treatment processes were considered potential for gasification fly ashes:

- CFB combustion (carbon, PAH) + solidification / encapsulation with water or chemicals (Cl, heavy metals)
- Water wash (Cl) + wet separation (carbon) + chemical stabilisation (heavy metals)
- Pelletisation + sintering (carbon & PAH destruction; Cl vaporisation; heavy metals vaporisation / stabilisation)
- Thermal stabilisation = vitrification, fusion, sintering (carbon & PAH destruction; Cl vaporisation; heavy metals vaporisation / stabilisation)

The first and third processes were selected for experimental studies. Melting methods have been found technically feasible in Japan, but due to high costs they have not been considered viable in Europe.

In the first investigation line, the objective of ash treatment was to reduce the contents of organic matter and solubility of inorganic impurities to an environmentally acceptable level. It was essential to retain inorganic elements in ash.

Gasification fly ashes were oxidised in a CFB combustor, after which combusted fly ash samples were solidified by adding some water or chemicals. In addition, after-treatment of combusted gasification fly ash through pelletisation was tested. Some encapsulation tests for solidified fly ash samples were also performed (Figure 3).

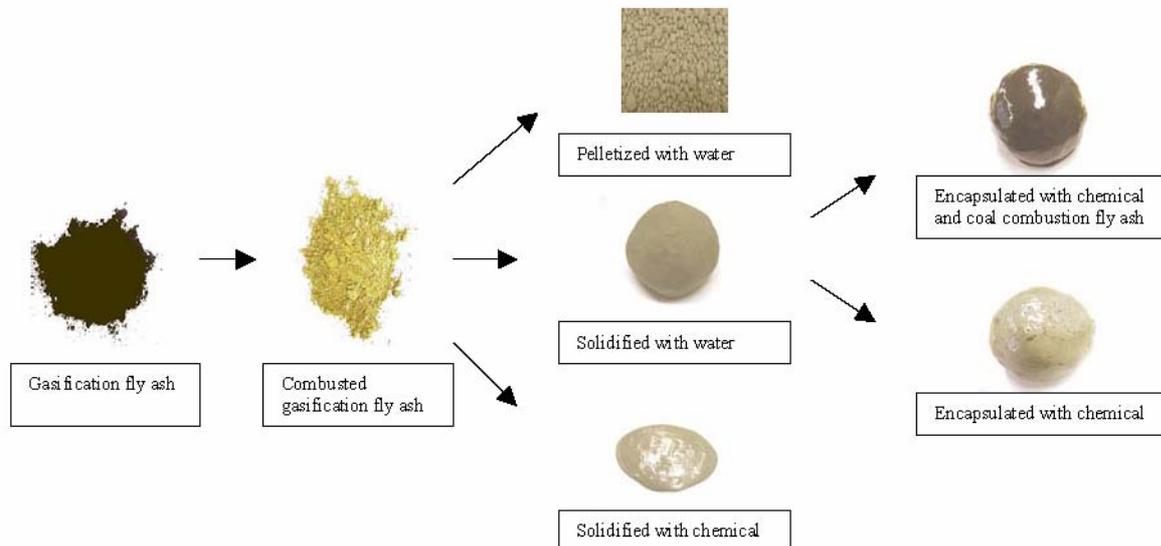


Figure 3. Ash samples from CFB combustion and solidification/encapsulation.

Combustion of gasification fly ash was studied in an atmospheric circulating fluidized bed test unit with a diameter of 100 mm and height of 3.8 m. Sand without any additives was used as the bed material. The average combustor temperature was in the range from 770 °C to 870 °C, and the flue gas was cooled near to 200 °C before filtration.

The gasification fly ashes contained enough unburned carbon to be burnt very effectively without additional energy sources. The carbon contents decreased markedly in all the ash combustion tests, from about 40 % below a limit of 2.5 %. The carbon conversions were excellent, above 98 % in all tests. Additionally, the decomposition of PAH compounds was almost complete (99.9 %). The mass of gasification fly ash could be decreased in half and very good heat recovery from the residual carbon could be achieved by fluidised bed combustion. Flue gas analyses showed very low levels of HCl and SO₂, while the small height of the test facility and the resulting short residence time at high temperatures presumably contributed to the fairly high levels of CO and NO_x. Nevertheless, the combustion efficiency was 96 % or higher in all the test runs.

The chemical analyses and flue gas contents indicated that the most part of chlorine, barium, sulphur and heavy metals left the CFB combustion process with the combustion fly ash. Especially the leaching values of chlorine and barium were relatively high in the combusted gasification fly ash. When the results of leaching tests and chemical analyses are compared with national regulations and EU criteria on the acceptance of waste at landfills, it can be concluded that oxidised gasification fly ash derived from waste fractions can be dumped into landfills for hazardous waste. Additional treatment is required before disposal at landfills for non-hazardous waste.

Due to the high leaching values of chlorine and some heavy metals in the oxidized fly ash, experimental research was continued. Because of high calcium content of the combustion fly ash, solidification of it with water was studied. Several different ash-

water mixtures were prepared and compressed into the shape of cylinders and balls, which were dried up at room temperature. However, the achieved reductions in leaching values were not significant: even if the leaching value of barium decreased below the limit value, high solubility of chlorine remained problematic.

Pelletisation of combusted fly ash was also tested. In the last solidification test, a chemical additive (TKR) was mixed with oxidised gasification fly ash in the ratio of 1:2. TKR is an environmentally safe, vegetable oil based polymer normally used as a protection material on the surfaces of concrete, metal and wood materials. TKR coating could easily solidify the combusted ash, but it had little effect on leaching of chlorine. Producing a coating from a mixture of TKR and coal combustion fly ash (filling material) turned out to be the technically and economically best solution but within a longer time period chlorine leached also from these encapsulated ash samples.

Therefore, it seems that especially preventing the leaching of chlorine is a very difficult task to be carried out by chemical or mechanical treatment methods. All results from after-treatment methods of combusted gasification fly ashes are of course specific to the tested chemicals and treatment techniques.

In the second investigation line sintering of pelletised gasification fly ash samples was studied. The objectives of the sintering studies were as follows:

- Oxidise unburned carbon and destroy other harmful organic matter.
- Evaporate chlorine and highly volatile heavy metals.
- Reduce leaching values of other inorganic impurities.

The particle size of the produced pellets ranged from 5 mm to 15 mm. Only water was used as binder in the first ash pelletising test. In the other test runs, the effects of various additives, i.e. sodium lignosulfonate, bentone and sodium silicate were studied. Tests showed that sintering of pelletised gasification fly ash requires high temperatures, 1350 °C or higher.

In the ash sintering methods, most of the problematic chlorine and highly volatile heavy metals, such as zinc, vaporize. In addition, unburned carbon oxidises very effectively. According to the available data from Japanese ash melting methods for waste-derived ashes, harmful organic matters, such as PAH compounds, dioxins and furans are completely destroyed. Presumably these compounds are not problematic in ash sintering either. In addition, the results of leaching tests indicated that sintering has a stabilising effect on some heavy metals, such as barium. According to the results of this study, sintered gasification fly ash can be disposed at landfills for non-hazardous waste. Even utilisation or inert waste category might be achievable.

The objective of work of ECN was to investigate the potential of ash separation and to explore several forms of after-treatment that are suitable for certain ash fractions. Each of these techniques should improve one or more of the characteristics of the ash to improve its quality. The basis for the work was the gasification fly ash as produced by the 80 MW(th) Circulating Fluidised Bed Gasifier located at the AMER-9 power plant of Essent Energy Productions. The gasifier is fuelled with shredded demolition wood.

Work was divided in three subtasks:

- *Exploration of separation techniques using physical characteristics of fly ash*
- *Exploration of after-treatment techniques for different fly ash fractions*
- *Pilot-scale application of selected forms of ash conditioning*

A review of screening techniques was made which may be used for separating carbon-rich fly ash into several fractions. For separation of carbon-rich fly ash, both dry and wet techniques are available. For dry systems, screening using an electric vibrating screen is the most obvious method. The particle size of carbon-rich fly ash is small making screening difficult, but not impossible. For smaller sizes relatively large screen surface areas are required, which on a larger scale may not be practical. Cohesiveness of fly ash particles is an uncertain factor. Electrostatic separation or cyclones in series are not viable alternatives.

Wet systems perform potentially better than dry systems. In particular, liquid cyclones and froth flotation are promising techniques. However, wet systems have serious disadvantages. Firstly, the need to dry the solids afterwards and secondly, the contamination of the liquid with leached compounds. Only when wetting of the solids and/or controlled leaching are part of the processing of the ash, wet techniques may be good choice.

Six forms of after-treatment were tested using explorative tests.

Dry screening was found to be capable of producing a small ash fraction with relatively high carbon content and a lower content of contaminants. The sieve fractions that were relatively clean were the larger particles: 90-180 μm mainly consisting of fractured sand particles (bed material) and $>180 \mu\text{m}$, mostly char particles. Unfortunately, these cleaner fractions are small in mass. Even if the fraction 63-90 μm is included, less than 10% of the total ash can be regarded as significantly cleaner than the rest. The two smallest (and most difficult to sieve) fractions form 70% of the total ash amounts. Thus, it is not possible to create by dry screening a cleaner bulk fraction with better perspectives for utilisation.

Pelletisation of the fly ash is possible and produces fuel pellets, which have improved characteristics for logistics and storage. It strongly increases the density (factor 4 or more) and lowers risks of handling, e.g. dust explosions and health effects. For making good pellets, AMER-CFB fly ash needed addition of water and a binder material; traditional starch is good enough. Other fly ashes can be compressed into pellets by only adding water. Pelletisation is of particular interest when the ash is used as fuel and requires transportation and storage.

Immobilisation as a filler material in a carbonaceous material like C-fix was found to produce a category 1 building material, i.e. unrestricted use, when tested in a tank test (NEN 7375). It is a technically a viable form of after-treatment, that is expected to be applicable to all utilisation options where a water repelling binder is used. Filler in asphalt is an example of this form of utilisation. Competition from other waste materials is expected.

Controlled leaching was found to be a promising after-treatment technique, suitable for removing salts. Technically it is challenging to apply it to the small particles that constitute high-carbon fly ash, but it is possible, as proven by VTT/PVO. The attractive part of the technique is that it removes Cl and alkalis, which are the components that are most often listed as showstoppers for utilisation options. When the pH is controlled, heavy metals are precipitated and the washing liquid can be disposed at low cost, in particular when discharged to the sea.

Low-temperature combustion was found to be a possible form of after-treatment converting carbon-rich fly ash into a low-carbon fly ash that is nearly identical to fly ash from combustion. Hence, all applicable utilisation options for fly ash from combustion of biomass can be used.

High-temperature combustion was found to be a technically acceptable way to convert carbon-rich biomass into building material, either by producing a clean burned-out fly ash or by producing a molten synthetic rock, also known as vitrification. Chemical analyses and leaching tests have confirmed that it is possible to produce building material that can be used in unlimited quantities according to the Dutch Building Materials Decree (DBMD).

Carbon-rich fly ash, burned and heat-treated at 1000°C was found to be strongly reduced in alkali, chlorine and heavy metal content, contaminants that are typical for limiting utilisation options. The material is still a powder and it was demonstrated in a pHstat test (PrEN 14429) that it complies to the limits of category 1 building material. Given its composition, it has a potential to be used similar to coal fly ash; potential utilisation as a raw material for cement and/or concrete. A general conclusion is, that it can be expected that material produced from AMER-CFB fly ash, which is heated above 1100°C for a sufficiently long time to evaporate problem elements, may be utilised as a building material of category 1, i.e. unlimited use. This conclusion can probably be extended to many more fly ashes from both gasification and combustion.

Fly ash was vitrified at 1400°C (and higher). It is technically possible to transform this fly ash into a synthetic rock, although the melting point is rather high. Adding fluxing agents proved that the melting point can be easily lowered to 1250-1350°C. Leaching tests showed that it is a category 1 building material, when used as gravel or as shaped building material..

Co-firing of carbon-rich gasification ash in powder coal burners is technically possible. The burned-out ashes become mixed with the coal ashes. Given the fact that the gasification ashes contain relatively large amounts of alkali and chloride, it can be calculated that they can only partly replace coal. Fly ash quality standards (EN 450), emission regulation and corrosion preventions can all act as limiting factor for co-firing.

Based on the results of the explorative tests, high-temperature combustion was selected as the after treatment technique for further research and up-scaling with the objective to transform carbon-rich fly ash into a category 1 building material.

Unmixed AMER-CFB fly ash produces two phases upon heating, one glass-like material melting at 1400°C and a stone-like material at 1550°C. To avoid formation of foam, the carbon-rich fly ash was pre-treated at 1000°C to remove carbon and chloride, both compounds that may lead to gas formation when heated further. Addition of 10-15% alumina to the burned-out fly ash was found to produce a single-phase smelt with a

sufficiently low melting point of 1250-1300°C, which solidifies into a block of glass-like material. The material looks more like obsidian than basalt. A 1 kg block of burned-out AMER-CFB fly ash with 10% added alumina, based on the mass of the end product, was made in a laboratory furnace. The block of vitrified ash was subjected to a tank leaching test (NEN 7375). The results show that all emissions are well below the limits of category 1 building material of the DBMD, i.e. unrestricted used.

In the up-scaled test, an amount of 5 kg synthetic basalt was prepared in a silicon-carbide smelter pot from pre-treated carbon-rich fly ash and 10% alumina (based on the end product). The conditions reflected the situation of full-scale smelter to such an extent, that it is expected that the end product will be representative with respect to material characteristics. The solidified smelt was recovered from the smelter pot and broken particles of 0-40 mm (granulate). The appearance of the material is the same as the lab-scale test: a black, glass-like material. In the large-scale test, part of the material has been spilled over the edge of the ceramic pot, despite the fact that it was filled less than half full and at least 20 cm below the rim. The loss due to foaming is certainly an effect that must be investigated in further research on vitrification of ashes from biomass and waste. Thus for up-scaling of vitrification, silicon-carbide pot may not be the best selection.

The material, produced in the 5 kg test was subjected to a quick availability test, a leaching test on finely ground material, done at pH = 7 and pH = 4. This resulted in compliance to criteria for category 1A building material, with exception of Sb, Ni, Co and Cu. The increased leaching of these four is the result from the very unfavourable conditions in the availability test or an artefact (Co). Antimony is the only element that may cause problems in compliance tests (DBMD), but comparing with the results of the tank test of the 1 kg sample, it can be concluded that it is highly probable that the material of the 5 kg smelt, when tested in a tank test (block) or in a percolation test (granulate 0-40 mm), will pass without difficulty and comply to the requirements of category 1A limit of the DBMD.

Developments related directly to gasification and gas cleaning process

ECN and VTT carried out development work related directly to gasification and gas cleaning process. ECN focused on optimised selective particle separation and VTT on integrated fly ash oxidation.

Staged cooling and particle separation

Selective particle separation was based on staged cooling and particle removal. The principal idea is to extract the bulk of the fly ash directly after the gasifier at a high temperature. Under those conditions notorious contaminants like Cd, Pb and Zn are in the gas phase and the extracted ashes are supposed to be relatively clean and better suited for utilisation. The unwanted gaseous elements will deposit during cooling on a small ash fraction, which may be utilised separately (or land filled). The strategy of staged cooling and particle removal is based on work by Obernberger and co-workers who have published a series of papers on this principle when applied to combustion installations. These publications prove that a bulk ash fraction can be obtained with strongly depleted concentrations of Pb, Cd and Zn, when extracting ash at high temperatures.

However, early results of the project indicated that staged cooling and particle removal is not likely to find an application in commercial gasifiers. In principle, it is a valid strategy, but there are two reasons to pursue alternative roads:

1. The strategy of “staged cooling and particle removal” results in significant extraction of ash before the end of the cooler. This is in conflict with the requirements of a “self-cleaning cooler”. This is a cooler-type where the ductwork is kept (relatively) clean by scouring the walls and pipes with entrained ash particles, which is very useful in the case of gasification of biomass. Removal of (part of) the ash prior to the end of the cooler is unwanted, because a) the larger particles are the first to be removed but these are also the most effective in keeping the deposition low and b) the scouring is most needed at the end in the colder parts of the cooler, so most particles must remain entrained by the gas until the end of the cooler. As a result, application of the latter is unlikely under the current conditions.
2. From a few runs using sewage sludge, it appears that the strategy of “staged cooling and particle removal” is only effective for a limited number of elements. In the experiments, ash was collected at 200 and 800°C. Some elements were concentrated in the “cold” ash fraction, e.g. Pb, Cd and Cl, but most elements, including Ni, Cr, Cu and Zn, showed no significant preference to concentrate in a certain fraction. One can expect that in the narrower temperature ranges in cooler, 400-600°C, the differences in ash composition will be even smaller.

To illustrate the latter, results are presented from one of the test runs in ECN's 500 kW(th) biomass gasifier using sewage sludge as fuel. Ashes were collected in a "hot" cyclone at gasification temperature (800°C), a "cold" cyclone at about 200°C and an ESP filter at ambient temperature. The temperature difference is large, so it was expected to find large differences in the distribution of many elements, in particular heavy metals. The main conclusion from these tests was that most elements show no sensitivity to the temperature of ash collection. Only for Cd, Hg, Cl and F a significantly different distribution is found, compared to the overall mass distribution. Problem elements like Ba, Ni, Cr, Cu, Pb and Zn are not significantly depleted in the bulk of the ash. The behaviour of Ba, Ni, Cr and Cu was predicted using thermodynamic equilibrium calculations, but the even distribution of Pb and Zn came as a surprise.

The overall conclusion is that the strategy of “staged cooling and particle removal” is not likely to find an application in gasification systems. It is not fully effective and conflicts with application of a self-cleaning cooler. “Staged cooling and particle removal” should not be regarded as useless. In combustion systems it is a valid approach, as well as in gasification systems where tar is not a problem and a self-cleaning cooler is not needed. For gasification, it may also be successful when only a limited number of elements, notably Cd, Zn and Pb, need to be removed. In addition, when carbon-rich fly ashes from gasification are subjected to combustion as a form of after-treatment, the combustion process can be designed with staged cooling and particle removal.

Integrated fly ash oxidiser

Fly ash or filter dust is usually rich in carbon and impurities. Oxidation (combustion) of filter dust reduces very efficiently volume by oxidising carbon and simultaneously most of metal impurities are oxidised to more stable compounds. Oxidation can be done in a separate combustion unit or using so called integrated oxidiser. The basic principle of

integrated oxidiser is oxidation of filter dust in a fluidised bed oxidiser and utilisation of released heat energy by using hot flue gas as a secondary air of fluidised bed gasifier. This integration of the oxidiser to the gasifier enables avoiding of heat exchange surfaces in oxidiser and in addition, no additional flue gas facilities are needed and simultaneously the overall carbon conversion increases very close to 100 %.

In the work of VTT integrated oxidiser was designed and constructed. Oxidiser was preliminary tested and optimised without integration to gasifier and finally the performance of the integrated oxidiser was tested by carrying out test trials with complete integration to 1 MW_{th} fluidised bed gasifier.

During development of the integrated oxidiser a specific attention was focused on the following topics:

- Successful operation of the oxidiser
- The effect of the oxidiser on the product gas.
- Verification of the gasification and gas cleaning performance of the entire process concept
- Stabilisation of gasification fly ash applying integrated oxidiser

The main component of the oxidiser is a fluidised bed oxidation reactor fluidised by air. The oxidiser was designed to be operated at 700-900°C. The lower end of this temperature window is limited by carbon conversion efficiency and upper end by risk of bed sintering. The design bed material was sand but other bed materials can also be used if needed.

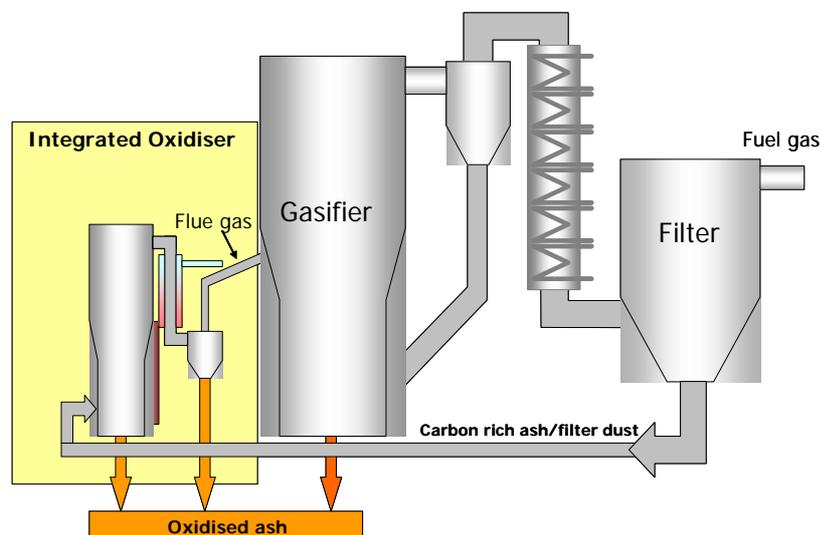


Figure 4. Integrated Oxidiser and the atmospheric pressure bubbling Fluidised-Bed (BFB) gasification pilot plant.

The bottom of the oxidiser is designed so that even some bed agglomerates can be discharged without shutting down the oxidiser. In addition to the bottom ash, ash is also removed by cyclone from flue gas of the oxidiser. Flue gas is slightly cooled prior cyclone but no efficient gas cooling can be done because of high risk of deposit formation. In large-scale application gas cooler can be operated as a gasification air

preheater. The produced heat from oxidiser was led directly to the FB gasifier as a secondary air.

The constructed oxidizer was equipped with an automatic data collection of temperatures and pressures measured at different locations. The flow rate of air was continuously measured and recorded. The feeding rate of fly ash was controlled too. In addition, on-line analysers monitored the combustion gas constituents.

The final verification test trial was carried out with complete integration to the pilot-scale BFB gasifier. The two different feedstocks used in the gasifier were (1) mixture of forest residue and wood pellets and (2) SRF (Solid Recovered Fuel) pellets. A mixture of sand and limestone P3 was used as a bed material in the gasifier at all set points.

Two feedstocks of the oxidiser were fly ash from wood gasification and from SRF gasification. Carbon content of wood gasification fly ash was reasonably high (52%) whereas fly ash from SRF gasification test contained fewer than 10% carbon.

The test programme contained a total of three set point periods during one week test trial. During two set point periods the gasifier was operated with integrated oxidiser and one set point period was a reference test without oxidiser.

Operation of the oxidiser integrated to the gasifier was very smooth and steady state. The reactor temperatures and fuel feedings of the process concept were stable. No major problems occurred during the test runs. High **carbon conversion** was achieved at all tests. **The lower heating values** of wet product gas varied from 4.0 to 4.4 MJ/m³n when oxidiser was used. and during the reference test with SRF the lower heating value was 5.2 MJ/m³n.

Chlorine content of mixed forest residue fuel was 0.02% and SRF fuel 0.5%. Limestone was added to the bed but specific chlorine removal sorbent was not used. The measured HCl-content was almost negligible (0.6-1.4 ppmv) with mixed forest residue. HCl content varied between 34-67 ppmv with SRF.

Heavy metals listed in WID (Waste Incineration Directive) were measured from the product gas after the gas cleaning. The following elements were analysed: As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, Sn, Ti, V and Zn. The sampling point was located after the filter, which was operated in the range of 425-436°C. Heavy metals except mercury are typically captured efficiently by filter in temperature below 450 °C. The results showed that very low concentration (<0.02 mg/m³_n dry) of heavy metal emission were analysed from product gas.

Filter dust from wood gasification was rich on carbon (61 wt %). In SRF gasification tests, the carbon content of filter ash was lower (19-27 wt %). Bottom ash was primarily composed of bed material and contained almost no combustible material.

The primary objective in development of oxidiser was efficient reduction of carbon content of filter dust. This objective was achieved and residual organic carbon content was very low, below 0.2 %. In test trial BFB 05/23A total carbon content of oxidised ash was higher (3.2 %) but most of this (2.9 %) was bound to inorganic carbonate.

The overall conclusion was that integrated filter dust oxidiser could be operated in stable conditions without any significant impact on performance of the gasifier. Carbon of filter dust was oxidised almost completely and final quality of oxidised filter dust was

very close to fly ash from conventional combustion, as targeted. These results showed clearly that integrated oxidiser can be used for very efficient upgrading of gasification filter dust.

Utilisation of fly ashes

Characterisation of ashes produced

Nine main fuels were selected for the investigation of the gasification fly ashes, two of them coming from full-scale gasifiers (from Lahti and Amer gasifiers). Lahti ashes are fly ashes collected in a 50-80 MWth CFB gasifier at Lahti during 100% REF (Recovered Fuel) gasification. The REF is produced from origin-classified refuses, coming from households, offices, shops and construction sites. Amer-CFB is the 80 MW(th) Circulating Fluidised Bed Gasifier located at the AMER-9 Power Plant of Essent Energy (AMER-CFB) The rest of ashes has been obtained from different partners pilot-scale plants.

| ASH | Moisture | LOI | %w/w | | | | | | | | | |
|---------------|----------|---------|--------------------------------|-------|------|------------------|--------------------------------|-------------------|------------------|-------------------------------|---------|-----|
| | | | Fe ₂ O ₃ | CaO | MgO | SiO ₂ | Al ₂ O ₃ | Na ₂ O | K ₂ O | P ₂ O ₅ | Cl | S |
| Orujillo | 1.8 | 20.3 | 5.3 | 26.1 | 8.6 | 41.0 | 8.0 | 1.3 | 8.3 | 1.5 | 0.6 | 0.1 |
| MBM | 2.1 | 16.6 | 2.9 | 44.5 | 3.6 | 12.5 | 3.5 | 4.1 | 1.5 | 18.0 | - | 0.2 |
| Waste wood | 3.7 | 63.7 | 11.0 | 45.1 | 4.0 | 21.4 | 6.2 | 0.6 | 0.7 | 1.2 | 1.2 | - |
| SRF | 1.5 | 23.8 | 3.0 | 39.0 | 3.3 | 27.9 | 21.5 | 1.5 | 0.7 | - | 2,8/4,6 | - |
| RDF Lahti | | 33,2*** | 2.1 | 44.6 | 2.9 | 19.1 | 13.4 | 1.6 | 1.4 | 0,8 (0,7**) | 4,3/2,1 | 0.3 |
| Straw | | 37,5*** | 0.3 | 14.4 | 1.2 | 32.3 | 0 | 0.2 | 6.1 | 0,4 (0,5**) | 0.8 | 0.1 |
| RDF Karhula | | 20,9*** | 7.6 | 31.8 | 2.1 | 21 | 18.2 | 0.3 | 0.7 | 2,4 (2,5**) | 8.9 | 0.3 |
| AMER-CFB | 0 | 65 | 0.97 | 6.8 | 0.94 | 17.8 | 1.4 | 0.6 | 0.9 | 0.3 | 1.07 | - |
| Sewage Sludge | - | 65 | 15.79 | 10.54 | 1.73 | 32.1 | 9.6 | 0.8 | 1.7 | 16.8 | 0.06 | 1 |

Table 3. Main elements in different ashes.

| SAMPLES | Metals in mg/kg | | | | | | | | | | | | | | | |
|----------------|-----------------|--------|------|-------|-------|------|------|-------|--------|-------|-------|------|------|------|------|-----|
| | As | Hg | Se | Mo | Zn | Pb | Cd | Co | Ni | Cr | V | Cu | Ba | Sb | Mn | Sn |
| ORUJILLO ashes | <160 | <100 | <100 | <100 | 210.5 | <160 | <16 | <10 | <100 | 761.5 | 83 | 146 | 289 | <200 | - | - |
| ORUJILLO Fuel | <160 | <100 | <100 | <100 | 182 | <160 | <16 | <10 | <100 | 646 | 60 | 182 | 270 | <200 | - | - |
| MBM | <100 | <100 | <100 | <20 | 398 | 100 | <10 | <10 | 864 | 636 | <20 | 212 | 134 | <20 | | |
| SRF | 20 | | | | 1500 | 920 | 14 | 19 | 96 | 530 | 41 | 2100 | | 180 | 860 | 150 |
| SRF | <100 | <100 | <100 | <20 | 1660 | 426 | <10 | <10 | 122 | 786 | <20 | 1474 | 1560 | <20 | | |
| Waste wood | 1430 | <100 | <100 | <20 | 8412 | 1832 | <10 | <10 | 190 | 1212 | <20 | 1436 | 2644 | <20 | | |
| RDF Lahti | 46.2 | 0.0077 | <2 | 8.27 | 5340 | 722 | 5.88 | 21.1 | 47.9 | 83 | 15 | 1900 | 1345 | 362 | 766 | - |
| AMER-CFB | 99.2 | - | 4.2 | 3.8 | 4045 | 4736 | 8.0 | 21.0 | 26.9 | 497 | 12.1 | 423 | 3744 | 41 | 841 | 39 |
| Sewage Sludge | 9.26 | 0.02 | 1.44 | 21.06 | 1965 | 246 | 0.28 | 15.51 | 113.22 | 197 | 47.48 | 921 | 861 | 11 | 1363 | 43 |

Table 4. Metal concentrations in different ashes

| SAMPLES | pH | Leachate DIN (mg/L) | | | | | | | | | | |
|----------------|-------|---------------------|--------|-------|---------|--------|--------|--------|--------|------|-------|-------|
| | | As (ppb) | Zn | Pb | Cd | Ni | Cr | V | Cu | Ba | K | P |
| ORUJILLO | 12.59 | <1 | 0.1 | 0.1 | < 0,03 | 0.1 | <0,05 | <1,9 | 0.09 | 1.83 | 27.35 | 0.02 |
| MBM | 10.25 | | 0.07 | <0.1 | <0.02 | <0,05 | <0.05 | <1,9 | <0.05 | | 100.0 | 0.01 |
| Waste wood | 9.12 | 44 | <0,02 | <0,1 | < 0,03 | <0,05 | <0,05 | <1 | <0,05 | 1.1 | | |
| SRF | 11.47 | <1 | 0.03 | 0.13 | 0.03 | 0.12 | <0,05 | <1 | <0,05 | 24.5 | | |
| RDF Lahti | 12.17 | 1 | 0.04 | 0.1 | < 0,03 | 0.08 | <0,05 | <1 | <0,05 | 49.5 | | |
| Straw | 12.93 | <1 | 0.17 | 0.14 | < 0,03 | 0.11 | <0,05 | <1 | 0.05 | 2.7 | | |
| RDF Karhula | 10.10 | <1 | 0.05 | 0.18 | 0.04 | 0.22 | <0,05 | <1 | 0.07 | 17.7 | | |
| AMER-CFB* | 11.2 | 2 | 1.18 | 76.4 | 0.00005 | 0.0003 | 0.0007 | 0.0008 | 0.0046 | 15.1 | 310 | 0.029 |
| Sewage sludge* | 11.7 | < d.l. | 0.0046 | 0.007 | 0.00003 | 0.001 | 0.004 | < d.l. | 0.064 | 0.12 | 6.9 | 0.012 |

* leaching percolation test (PrEN 14405) at L/S=10; content in leachate in mg/L

Table 5. DIN 38414 leaching test results of some ashes

The calorific value of Lahti and Amer gasification fly ashes ranges from 14 to 25 MJ/kg. These values are comparable to the heating values of peat and wood, despite of the high ash content. For the ashes analysed in GASASH-project the loss-on-ignition (LOI),

mainly carbon, ranges from 7 to 60 wt%. Leaching properties were analysed by several different methods (DIN 38414, TCLP, column tests).

Fly ash utilisation methods and utilisation of treated ashes

Some of the investigated utilisation methods can be regarded as niche applications, e.g. filler in C-Fix. This is perfectly acceptable for the small production volumes that currently exist. Moreover, in small gasification units often specific fuels are used resulting in ashes with unique characteristics, which can match with specific forms of small-scale utilisation. These "lucky matches" should also be investigated, but they do not offer solutions for all gasification ashes. Bulk utilisation options are needed, when multiple large-scale gasifiers are built in Europe. Gasification ashes *direct* bulk utilisations are not easily found. Therefore ash treatment technologies are included in the assessment of utilisation options.

Three main utilisation categories have been identified for the gasification ashes derived from biomass/waste.

1. Use as fuel: co-firing in coal/biomass-fired power plants; firing in a dedicated boiler; replacement fuel in smelters/incinerators (best option for highly polluted fly ash); firing in cement kiln
2. Use in construction: filler in asphalt or asphalt-like products (C-Fix); additives in concrete manufacturing; bulk construction / raw building material; lightweight bricks; fire-resistant material; stabilisation/solidification
3. Use in agriculture: directly as fertilizer or soil improver; as raw material

Landfill is not considered as a form of utilisation, but as an alternative to utilisation, more like a backup method. The current policy in the EU is to discourage the landfill of high calorific waste. Implementation is different in the member countries. In some countries, e.g. The Netherlands, it has become nearly impossible to landfill high-calorific waste. In the UK there are no regulations that refer specifically to high calorific value waste, but the requirements of landfill acceptance criteria set limits to the (organic) carbon content of materials for disposal.

Identification of most promising options

Application as a fuel is regarded as direct application and is not the same as disposal with energy recovery, but is in fact a higher-grade application. This is supported by the fact that the aim to use gasification ash as an alternative fuel is not the need of disposal, but the need to replace fossil fuels in the same way as the original intention of the biomass before gasification: energy production. The Commission supports this concept, see the revised version of the EU waste strategy adopted by the Commission in July 1996.

Criteria for utilisation as fertilizer/soil improver: In European Union Member States, the application of fertilisers and soil improvers is restricted with respect to the maximum allowed addition of contaminants to the soil. The 1986 Directive (EEC, 1986) included restrictions on the metals content of the sludge, each Member State setting their own limit values. These limit values for sewage sludge are often used as a reference for other materials as well.

Criteria for utilisation as building materials: With regard to direct utilisation in building materials, each Member State of the EU has its own regulations concerning the application of recycled materials in landscaping and road construction. In the Netherlands the application of waste streams (limited to stony material or soil-like material) in landscaping / road construction is regulated by maximum allowed leaching of contaminants. Within this document (and much of the GASASH project) the Dutch Building Materials Decree (DBMD) is used as a reference, but it was tried to minimise the bias and leave room for regulations from other member countries. A harmonized European Construction Products Directive (CPD) is being developed. This directive will be based on much of the same principles as the current DBMD, in which leaching of contaminants and long-term impact is guiding in the risk assessment for the application of construction products.

Criteria for utilisation as fuel: There are no specific regulations for the use of fuel, other than legislation based on the fact that ashes from gasification are being regarded as a waste product. The potential for utilisation as fuel is to be decided by the prospective buyer, who needs to take into consideration the calorific value, permits for firing waste and sufficient flue gas cleaning. Since carbon-rich fly ash has a low density, logistics will be a dominating factor. Compression (pelletisation) should be considered when utilisation does not take place in the vicinity of the location where the fly ash was produced.

Direct application/utilisation of the material without treatment

The feasibility of application of ash as a fertiliser depends on local conditions, but in a wider perspective it can be concluded that none of the ashes used in the GASASH project have a great potential to be applied directly as fertilizer. This is caused by the generally low nutritional value of available nutrients compared to the relatively high content of contaminants. Exceptions are possible for specific fuels. When the strict Dutch limit values for fertilizers are used, it is found that none of the gasification ashes comply, whereas according to Spanish limitations, the Orujillo ashes meet the criteria. The most critical components for application as a fertilizer are Cd, As, Cu, Zn and Pb.

When comparing the leaching behaviour of ashes with the criteria of the Dutch Building Materials Decree, the conclusion is that studied fly ashes cannot be *directly* used as building material, mainly due to high leaching of contaminants. Chlorine is a problem element for all ashes; Pb, Cd, Mo, Cr, Br, Se and Sb are typical problem elements for many ashes.

Some of the ashes have a high enough heating value to allow utilisation as replacement fuel (up to 25 MJ/kg). Combustion can be integrated, which has the advantage that no separate flue gas treatment is needed. This also applies to utilisation in separate installations that already have a sufficient flue gas treatment system before alternative fuels were introduced. Utilisation as an alternative fuel is one of the most promising routes for gasification ashes with a carbon content above 35 wt%. Limitations will be emissions and end-of-pipe fly ash quality if the fly ash has an established utilization that requires a certain quality (e.g. in cement production).

Direct application/utilisation of the material with pre-treatment

Quality improvement of the gasification ash will have to concentrate on the elimination or reduction of critical components. Which component is critical differs for various

combinations of fly ash and application. In fertilizer applications, the only way to improve the ash quality is to reduce the total amounts of contaminants, which is not easily done. As a result, utilisation as fertilizer after treatment is not a likely route.

In applications that are regulated by leaching limits (building materials), the possibility exists to reduce leachable amounts of contaminants by washing the ash, since this specifically eliminates soluble compounds; 75% removal of Cl is easily achieved. Other components can be made less easy to leach by manipulating the pH, e.g. by converting oxides into carbonates. Washed gasification ash could be used in direct utilisation routes towards construction products, because it eliminates the most problematic element: chloride. Still, it remains questionable whether the washed gasification ashes will be used as a building material in direct applications because of its mechanical properties. Washing may also be used to improve the potential for utilisation as a fuel, by removing chlorine, a notorious corrosive component.

Combustion in a fluidised-bed at 600-900°C converts the characteristics of the ashes completely. The composition of the fly ashes produced in the GASASH project at these conditions was found to be not suitable for direct utilisation. The ratio of nutrients compared to contaminants is still unfavourable for utilisation as fertiliser and the leaching behaviour of several samples indicates that the ashes after combustion do not comply with category 1 (unrestricted use) of the DBMD. However, some ashes comply with category 2, *i.e.* use as bulk material, shielded from contact with water.

High-temperature treatment can convert biomass ashes into synthetic basalt that complies with the limits of category 1 building material of the DBMD (unlimited use). Typically, when the temperature exceeds 1000°C, the material is sintering and problem elements (Cl, K, Pb, Zn) have been evaporated or are encapsulated into the bulk. The remaining ash is free of carbon and can be cast into moulds or broken into granulate. Technically, vitrification processes offer one of the most promising options for the utilization of gasification ashes from biomass, but the economics are unfavourable.

Use as a raw material/utilisation as component without prior treatment

Several options for utilisation as a component in the production or manufacture of products have been identified. One promising route is to use the gasification ash in asphalt or asphalt-like products (like C-fix), which is an established route for MSWI fly ash in The Netherlands. The key factor is that a non-porous, organic binder is used, which minimises contact with water. High carbon gasification fly ashes have been tested successfully as fine filler (7% w/w) in C-fix, a material with properties between asphalt and concrete. The carbon-rich ash performed better than the combustion fly ashes. In contrast to most other forms of utilisation as filler, low pozzolanic properties are not a problem.

Another form of utilisation of carbon-containing ashes from gasification of biomass or waste can be the production of (lightweight) aggregates. Biomass ashes are part of the raw material that Lytag uses to produce lightweight aggregates (fly ash from a coal-fired power plant that co-fires several kinds of biomass). The Lytag process is based on granulating and sintering at 1300 °C. The surface area is strongly reduced and potentially toxic elements are evaporated or bound into the sintered material. In the process both the inorganic fraction of the ash and the caloric value of the carbon fraction are used. Lightweight aggregates can be used to replace natural gravel in (lightweight) concrete and other applications.

A third way of using fly ash from gasification of biomass is to replace cement or cement-like products in waste stabilization¹. In particular the ashes with a high Ca-content and a low carbon content and showing pozzolanic properties are promising. E.g. Orujillo ashes have good mechanical properties and are susceptible to be used as partial replacement for cement; other ashes (SRF and wood waste) have shown good leaching properties, but display poor mechanical properties. Although potentially promising, more research is needed before this route can be identified as one of the "most promising utilisation options".

Use as a raw material/utilisation as component with prior treatment

Utilisation as a component after prior treatment opens countless opportunities. The most relevant option is the use of gasification fly ash after combustion as a filler or binder in concrete, cement or special mortars. Reduction of the carbon content and obtaining physical properties that resemble powder coal fly ash are needed. Most likely, the combusted gasification ash itself does not comply with required properties, but can be made part of a blend, whose quality depends on the application of the concrete (high grade, low grade). Good pozzolan properties are a good indicator, e.g., those ashes that have a high Ca content, either by themselves or due to the use of lime or dolomite in the gasification or combustion process. Guaranteeing a constant and predictable composition and the physical properties (loss on ignition, size fraction < 63 µm, water demand, hollow spaces, etc.) is of great concern for successful application in cement making. All ashes assessed in the GASASH project have the potential to be used as filler after thermal treatment that lowers the carbon content. Possible restrictions in this route are the high SO₄ and Cl contents and possibly alkali content of the ash after combustion.

Based on the available data, it can be concluded that the following utilisation options may be regarded as the most promising routes for the carbon-rich fly ashes that have been investigated with the GASASH project:

- Direct application as an alternative fuel
- Filler in asphalt or asphalt-like products
- Component in manufacture of lightweight aggregates
- Filler/binder in concrete mortars after low temperature treatment (combustion)
- High temperature treatment (vitrification) for the production of category 1 building material

Potentially promising utilisation options are

- Solidification/stabilisation of waste
- Component in manufacture of fire proof plates
- Component in manufacture of lightweight bricks

¹ For solidification/stabilization no separate criteria are available. Landfill criteria have been adopted.

Some form of after-treatments may be found attractive. Always the (economic) advantages and disadvantages of after-treatment must be balanced against direct utilisation. The most promising forms of after-treatment are

- Washing to remove chloride (and alkali)
- Heat-treatment to lower carbon-content

It should be noted that there is a large variation in ashes and ash qualities. The routes listed here are classified as "most promising" when the ashes as used in the GASASH project are taken as typical gasification ashes. The options are generalised suggestions based on the technical potential of the routes. The following issues should always be included the discussion:

- Different routes are the optimal alternative for different fuels, depending on specific characteristics of the ashes.
- Routes become more or less attractive, depending on local conditions. In particular gate fees and emission regulations for combustion.
- Lucky matches may always be found outside the presented selections, e.g., gasification ash from chicken litter utilised in manufacture of fertilizer.

Finally, it must be noted that consistency is the key factor for successful utilisation of gasification ashes. Ash must be generated in predictable quantities with guaranteed minimum quality. If that cannot be accomplished, landfill of ashes is nearly inevitable.

Techno-economic evaluation of different ash management chains

Several potential methods were identified and developed for the management of gasification ashes. Those methods and ash management routes which fulfilled the operational and environmental criteria in up-scaled size were evaluated economically. In this working method the sub-task results prompted in many cases new ideas for further development as the work packages were elaborated by the project partners partly separately and partly jointly together.

Identification of principal alternatives and specific methods

Several of the routes were found to be potential and were up-scaled and evaluated. The general workflow of the development testing and evaluation of methods was iterative as illustrated in the Figure 5.

Figure 6, Figure 7 and Figure 8 give an overview of the identified management routes for gasification fly ashes. Several of the routes were found to be potential and were up-scaled and evaluated further. Some identified routes were however estimated not to be potential because of environmental, technical or economical reasons.

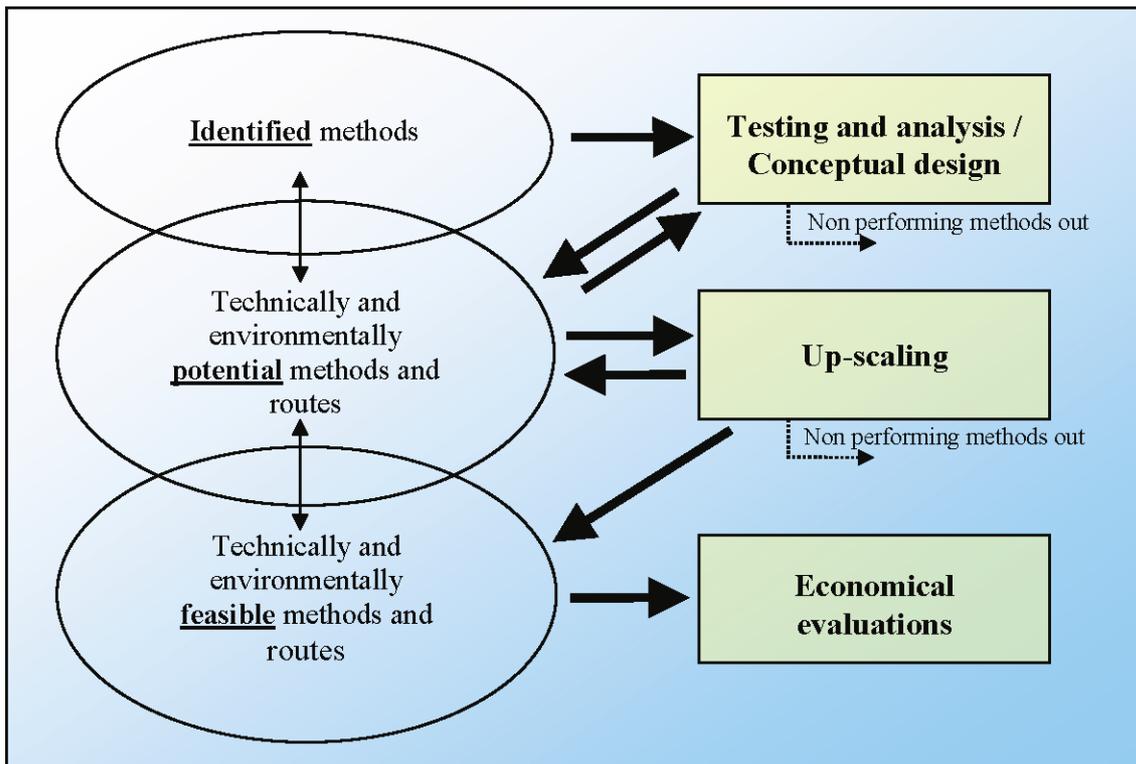


Figure 5. The iterative interactive work flow of method development, testing and evaluation.

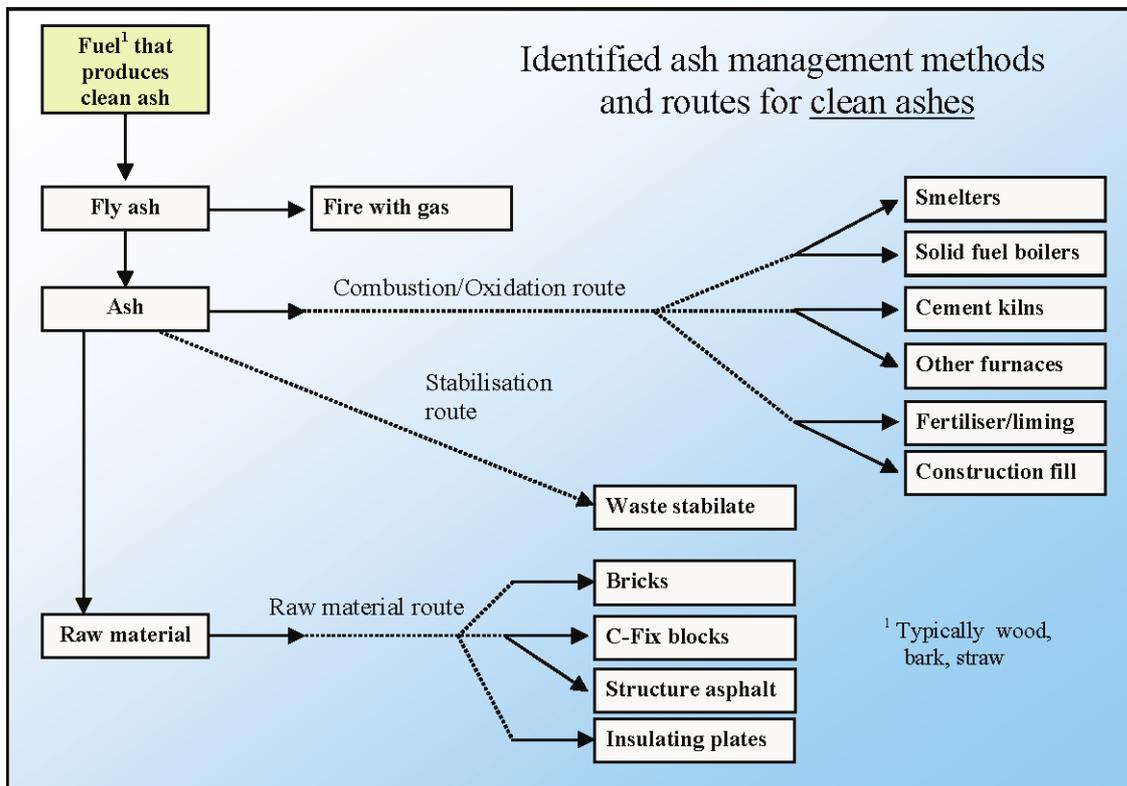


Figure 6. The identified methods and management routes for clean gasification fly ash. The figure illustrates the routes in a simplified form.

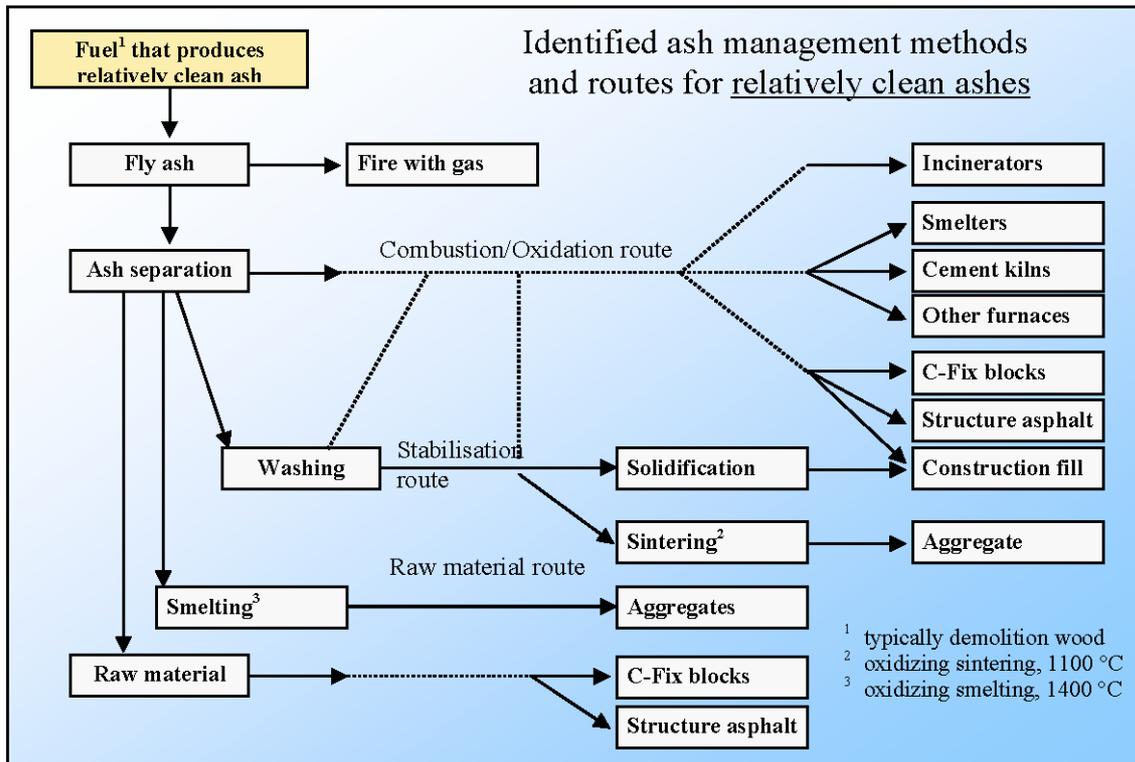


Figure 7. The identified methods and management routes for relatively clean gasification fly ash.

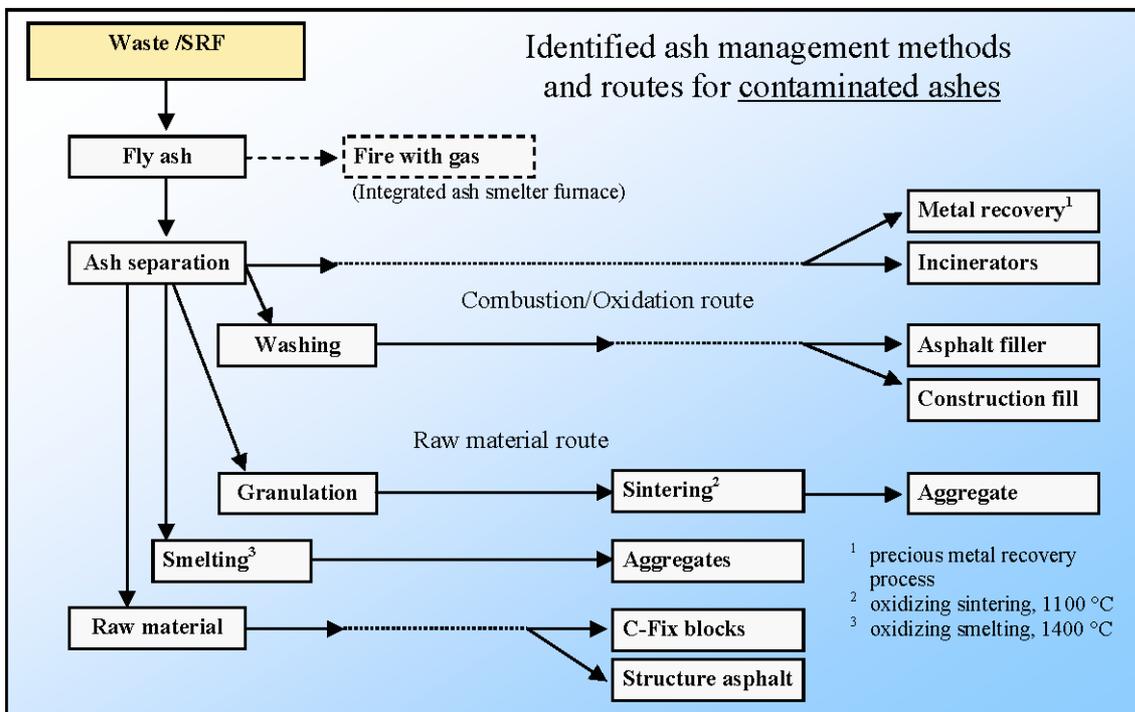


Figure 8. The identified methods and management routes for contaminated gasification fly ash.

Conceptual design and up-scaling and evaluations

The identified ash treatment methods and utilisation routes were evaluated and most of them were also tested. Those methods and routes that were estimated to be potential were taken into the next phase for conceptual design, which included the process and special equipment designs. This phase was done in many cases in co-operation with equipment manufacturers. The technical feasibility, emissions and environmental effects were evaluated during the design work. The methods which were found operationally feasible were accepted for continuation.

The operational feasibility covers in this context functionality and scalability of the method as well as environmental performance. The methods which were evaluated to convert the gasification ash into an acceptable product or raw material or to utilise the energy content of the ash were considered to meet the required functionality. The possibility to utilise a method technically in an industrial scale was used as the criteria for scalability.

Environmental performance was also one key criterion in selection of the methods for analysis. The present and known future regulations for emissions and safety were used when evaluating the environmental performance. The directives for waste incineration and landfilling were used as criteria for environmental feasibility on many cases. Also the regulations for occupational health and safety as well as present and anticipated future building material requirements were used in evaluations.

An ash production of 1 500 kg/hour for fly ash and 250 kg/hour for bottom ash (after 75 % internal circulation) were selected as the basis of up-scaling and evaluations. These capacities were estimated to be relevant for an anticipated industrial gasification plant with fuel capacity of 80 MW. Smaller scale methods can offer feasible solutions at individual cases but in general a quite large capacity is needed for economical operation.

The following methods and routes (and different combinations) were selected for economical analysis:

- **Use of fly ash as fuel** in boilers and process furnaces
- **Granulation** to improve the ash properties for further processing or utilisation as fuel
- **Washing** to improve the ash properties for further processing or utilisation as fuel
- **Fluid bed combustion** to recover the energy content of ash and to improve the ash properties
- **Integrated fluid bed oxidation** to recover the energy content of ash and to improve the ash properties
- Production of aggregate with **oxidising sintering process**
- Production of aggregate with **oxygen smelting**
- **Fertiliser and soil improvement** use of clean ash
- **Metal recovery** from bottom ash of SRF gasification

Cost and economic impacts of ash treatment and utilisation

Table 6 and Table 7 summarise the estimated ash handling costs of different methods. The cost estimates should be considered as ranges to indicate the cost level rather than exact values as there are many assumptions and uncertainties. The tables however show the relative differences for evaluation of the usefulness of different methods.

| Treatment method/route Fly ashes | Ash management cost; eur/t Low – Mean – High | Products of the method |
|---|---|--|
| Landfilling at a special site, 0-case | 150 | None |
| Use as fuel without treatment | 0 | Low grade fuel |
| Granulation and use as fuel | 17....24....31 | Low grade fuel |
| Washing and use as fuel | 14....20....29 | Low grade fuel |
| Combustion of clean ash in integrated CFB, use as construction material | 21....29....39 | Secondary construction material + energy |
| Combustion of clean ash in integrated CFB + granulation, use as forest fertiliser | 38...53...70 | Low grade fertiliser + energy |
| Combustion of clean ash in integrated BFB, use as construction material | 28....40....55 | Secondary construction material + energy |
| Washing + combustion in integrated CFB, use as construction material | 35...49...68 | Secondary construction material + energy |
| Combustion of clean ash in stand-alone CFB, use as construction material | 22....31....42 | Secondary construction material + energy |
| Combustion of contaminated ash in stand-alone CFB, use in construction | 38....54....72 | Secondary construction material + energy |
| Combustion of clean ash in stand-alone BFB, use as construction material | 29....43....58 | Secondary construction material + energy |
| Combustion of contaminated ash in stand-alone BFB, use in construction | 45....65....89 | Secondary construction material + energy |
| Oxidising sintering of clean ash, use as aggregate | 34....61....94 | Aggregate |
| Oxidising sintering of contaminated low chloride ash, use as aggregate | 79....130....179 | Aggregate |
| Washing + oxidising sintering of contaminated ash, use as aggregate | 93...150...208 | Aggregate |
| Oxidising smelting, use as aggregate | 203....274....351 | Aggregate |

Table 6. Estimates of the ash management cost levels for alternative methods and routes ash.

| Treatment method/route SRF gasification bottom ash | Ash management cost; eur/t Low – Mean – High | Products of the method |
|---|---|---------------------------------|
| Basic case, landfilling | 50 | None |
| Use as construction material without treatment | 0 | Low grade construction material |
| Metal recovery + landfilling | -175...-93...-8 (profit per ton of ash) | Metals |

Table 7. Estimates of the ash management cost levels with alternative methods and routes for bottom ash.

It should be noted that the ash handling cost is a relatively large cost item if the ash has to be landfilled in a special landfill. The ash management cost of an industrial scale gasifier is with the assumed landfilling cost of 150 eur/t for fly ash and 50 eur/t for bottom ash about 1,3 M eur/year. This is clearly a major cost item for a gasifier plant. However it is not always only a cost question, but in some cases there is no possibility to deposit large amount of ash in special landfills as there may not be such capacity available.

The estimated effect of the improvement of carbon conversion on production cost of fuel gas was also estimated. If alternative method is landfilling with 150 euro/t the economic impact of ash treatment and utilisation proved to be very attractive. The highest

reduction of production cost was estimated to be 3.0 eur/MW_h(gas) when carbon-rich and contaminant-free fly ash is used as an alternative fuel. For contaminated ashes, which can be upgraded by washing, reducing impact on production cost of fuel gas was estimated to be 2.7 eur/t. Even sintering of low chloride SRF ash and use of the product as an aggregate was estimated to have 0.4 eur/t reducing impact on production cost of energy. Cost of washing of high chloride SRF ash, sintering and use of product as an aggregate was estimated to be more or less the same than landfilling cost having no impact on production cost of fuel gas energy. In the fact, 14 of 15 studied ash treatment and utilisation routes had reducing or zero impact on energy production cost and only oxygen smelting of ash and using product as an aggregate had 2.7 eur/MW_h(gas) increasing impact on fuel gas production cost.

Finally, the economic impact of ash treatment and utilisation on production cost of electricity was estimated. Reduction of production cost of electricity was highest (8.5 euro/MWh(e)) when carbon-rich and contaminant-free fly ash is used as an alternative fuel.

Conclusions

The objective of the GASASH project was to develop further gasification and gas cleaning process, ash treatment and ash utilisation methods in order to improve the economy of gasification based energy production. Work was focused on optimisation of process conditions, development of new components and methods and development of ash treatment and utilisation methods especially suitable for high carbon containing gasification fly ash.

Optimisation of gasification and gas cleaning process could be done successfully and carbon conversion could be slightly increased. However, the results were achieved in pilot-scale environment, which does not guarantee that results could be as successfully applied directly in large-scale industrial applications. In addition, in industrial applications availability of the plant has higher priority than slightly increased carbon conversion and slightly reduced volume of ash.

Development of fly ash treatment methods produced several technically feasible methods for upgrading of fly ash. Developed methods were focused primarily on reduction of carbon and chlorine content and leachability of heavy metals. Most of technically feasible methods were based on oxidation of fly ash but fly ash washing was developed in order to remove most of chlorine of fly ash. High temperature treatment was also studied and technically it proved to be efficient method to upgrade fly ash to high quality product for construction purposes. However, cost related to high temperature treatment of fly ash was very significant.

Development of utilisation routes for any ash qualities is extremely challenging because large quantities of coal derived combustion fly ash is available in most of EU countries. Quality of combustion ashes is usually significantly better than quality of gasification fly ashes. Practically the only application, in which gasification fly ash does not compete with combustion ashes, is use of high-carbon fly ash as an alternative fuel. Most of other studied applications were based on utilisation of inorganic part of fly ash. However, potential of gasification fly ash can be improved by upgrading quality of fly ash by oxidation, washing, etc.

The most promising ash treatment and utilisation routes were finally evaluated from economic point of view. The basic case was landfilling with 150 euro/t disposal cost. Most of developed routes were estimated to be economically feasible. The most feasible was direct use of contaminate free fly ash as an alternative fuel. Combustion and especially combustion in an integrated oxidiser was assessed to be very feasible, as well as even some more complicated upgrading and utilisation routes. The only evaluated route, which did not look feasible (when alternative route is landfilling with 150 euro/t), was oxygen blown smelting and vitrification. On the other hand, final product of this route was very high quality construction material with very low leachability.

The overall conclusion was that several technically feasible alternative ash treatment and utilisation routes were developed. The economic feasibility depends on cost of an alternative disposal method. When alternative disposal method is landfilling with 150 euro/t most of the developed ash treatment and utilisation routes will be feasible also from economic point of view.

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