ECN-RX--05-182

Utilization of ashes from biomass combustion and gasification

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Published at 14th European Biomass Conference & Exhibition,

Paris, France, 17-21 October 2005

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	cked/Approved/Issued by: MMM Veringa	ECN Biomass

November 2005

UTILIZATION OF ASHES FROM BIOMASS COMBUSTION AND GASIFICATION

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ABSTRACT: Utilization of ashes in useful applications will contribute to the sustainable use of biomass for power generation. Returning of the ashes to the locations where the biomass was harvested is presented as the most sustainable option to pursue, because it returns nutrients to the original soils. For ashes that cannot be recycled, alternative options are discussed: utilization as fertilizer or as raw material for the production of fertilizer, utilization as building material or as component in building products, and utilization as fuel. A separation between bottom ashes, fly ashes from combustion and carbon-rich fly ash from fluidized bed gasification was made. Primary conclusion was that the various ash streams from different fuels and installation types require different forms of utilization. Bulk utilization of ashes is most likely to be found in building materials or fuels (only high-carbon ashes). Niche applications and lucky matches between ash and special applications may be found, but are not contributing to the solutions for the bulk of the ashes. For certain ash streams after-treatment is needed. The key factors for success in all forms of utilization are consistency of ash quality and availability of large quantities.

Keywords: ash, bio-energy strategy, recovery of residues

1 INTRODUCTION

Utilization of ashes is part of sustainable power generation from biomass and contributes to the green image, while landfill of biomass ashes may be interpreted as wasting of valuable nutrients. The search for utilization options must deal with largely different kinds of biomass ash. Fuel composition and installation type are the primary factors that influence ash quality. Variations in the inorganic fraction of fuels are directly reflected in the ash compositions. The different kinds of installations result in multiple kinds of ash flows, each with differences in morphology, composition and leaching behavior. The main classifications of ashes are between fly ash and bottom ash, and between ashes from fluidized bed combustion. fluidized bed gasification, grate stokers and entrained flow gasification.

In the waste management hierarchy, see Figure 1, landfill is the least attractive alternative. However for many practical situations it happens to be the most economic alternative. Landfill serves as the bottom-line for comparisons of utilization options. Any proposed kind of utilization must have economic advantages compared to land fill. Carbon-rich fly ashes from fluidized bed gasification are particularly difficult kinds of ashes. The unique position of this kind of fly ashes is mainly due to the high caloric value as a result of the relatively high amounts of unburned carbon. Other characteristics are that the gasification fly ash has a low density and are difficult to handle. Contact with air should be avoided to avoid spontaneous ignition and possibly dust explosions. Disposal of high caloric ashes in landfills is discouraged or made nearly impossible (by means of very high gate fees) in many European countries. For high-carbon fly ashes, after-burning plus landfill should serve as the bottom-line option. The potential problems associated with gasification fly ash should not be a deterrent for implementation of gasification as a technique for biomass conversion, but its fly ashes require special attention.

At ECN, two projects were completed recently: BIOAS aimed at utilization of ashes

from combustion of clean biomass and GASASH aimed at utilization of gasification ashes. GASASH is a EU 5th Framework project together with VTT, Foster Wheeler, AICIA, PVO and Essent Energy Production.



Figure 1 Proximity principle

2 RECYCLING OF NUTRIENTS

The most sustainable way to deal with biomass ashes is to minimize ash content in the fuel, i.e. to harvest biomass in such a way that nutrients and other ash-forming components remain on site and are not removed together with the biomass. Sustainable forestry techniques that minimize the amount of nutrients during harvesting of trees are under development and should be pursued from the point of view of ash management.

Returning of biomass ashes to the locations where the biomass was harvested can be regarded as the next best sustainable option. It brings back the nutrients to the original soils and hence closes mineral recycles. In the long run, recycling avoids problems with depletion and exhaustion of the soils, unless the soils are fertilized in other ways. For recycling, combustion ashes seem more appropriate, but in principle, gasification ashes can also be used. The requirements of trees or crops and sustainable conditioning of the soil should be leading principles. E.g., ash recycling should not result in an uncontrolled pH shock in the soils.

Biomass ashes should be recycled whenever possible, but the ash quality must be high enough to prevent pollution as a result of the spreading of ashes. Most European countries with a history in the use of biomass for energy (Finland, Sweden, Denmark, Austria and Germany among others) have established legislation that enables and controls the recycling of biomass ashes to forests and agricultural areas. Ash recycling is happening in a number of these countries, but the total amounts that are recycled are very small compared to the total production of biomass ash. Often ashes contain too high contents of heavy metals (Cd, but also Pb and Zn) even when the ashes originate from clean, untreated biomass. The problem exists mainly for fly ashes and less for bottom ashes, but the amounts of nutrients in bottom ashes are also often lower.

It can be argued that under special circumstances it might be acceptable to return more ash than the legal limits allow. This might be done, only if the biomass ashes are recycled without any other material being added to the soils, because in that case all contaminants originate from that particular area and there will be no net increase in contaminants. Such a system is possible, but probably difficult to monitor and enforce.

3 BULK UTILIZATION OPTIONS

Despite recycling of ashes being the most sustainable form of ash utilization, there will be large amounts of biomass ash produced that cannot be recycled for a number of reasons. Some landowners do not want to recycle ashes, e.g. recreational areas or natural reserves. Also there are large streams of biomass of which it is not possible to trace back the original place of harvest. Finally, there may be no legal possibilities or ashes are simply not clean. For all these streams of biomass ashes, an alternative form of utilization must be found. Three global utilization options have been investigated and will be discussed in the next sections:

- Utilization as (raw material for) fertilizer,
- Application as building material or as component in the manufacture of building material,
- Re-use as fuel

Niche applications will always exist, as well as special cases where the characteristics and quality of a certain kind of ash from a perfect match with a certain form of utilization. These "lucky matches" are not discussed because they do not represent bulk utilization options.

4 UTILISATION AS FERTILIZER

Biomass ashes may be used directly as a fertilizer or soil improver or may be used as a raw material in the production of mineral fertilizer. The ashes are returned to the soil, but the location is not necessarily the same as where the biomass originated. Utilization as (raw material for) fertilizer saves primary resources and can be seen as an example of sustainable use of biomass.

Utilization of biomass ashes in allpurpose fertilizers is limited. The three elements in complete fertilizers are N, P and K. Biomass ashes can only be a significant source of potassium, because a) ashes from thermal processes are nearly free of nitrogen, and b) phosphorus is present in a form that has a very poor solubility at soil conditions. For use as fertilizer in forests, the slow release of P may not be a problem, in particular on more acidic soils.

There are alternatives in fertilizer production (other than direct utilization as general-purpose fertilizer). Biomass ashes may be blended with complementary materials, or biomass can be used in the same way as mineral resources: dissolution of K and P at very low pH and then processed in regular fertilizer production.

Biomass ashes may also be used for other elements than N, P and K. Many ashes contain significant amounts of Ca, Mg, Na and S, which represent an agricultural value, In particular when dolomite or limestone is added during gasification or combustion, the ashes can be a valuable source of Ca and Mg and used as soil improver (pH control).

When used in fertilizer or soil improver, existing legislation must be applied. Wood ash from combustion of untreated wood is permitted as fertilizer according to the EU regulations for biological farming. However, national legislation must also allow fertilizers to be used. In the Netherlands (and many other countries) legislation is aimed at environmental protection. The Dutch Fertilizer Act allows the use of a listed number of materials, but biomass ashes are not on the list. In addition, an allowance can be obtained by following an acceptance procedure. In this procedure, first the minimum dosage of fertilizer needed for agricultural usefulness is determined based on the content of nutrients. Secondly. а permissible maximum dosage is determined based on the content of contaminants. A material can only be admitted as fertilizer when the minimum useful dosage is less than the maximum allowed dosage. In the BIOAS Project, the potential for acceptance as fertilizer was calculated for two kinds of fly ash produced in combustion installations in the Netherlands that use only clean biomass as fuel. The result was that for both ashes in all possible agricultural applications, there were too many contaminants compared to nutrients. Cadmium turned out to be the biggest problem, but also Zn and As can prohibit direct utilization as fertilizer. Bottom ashes of both installations were not taken into account, because these already found a useful application as construction material. The conclusion is that - at least in the Netherlands use of clean biomass result in production of clean fly ashes. The result can be different for bottom ashes other biomass ashes, e.g. grown outside industrialized areas or from specific kinds of plants or specific parts of plant that do not take up contaminants from the soil. So far, no-one has ever applied for allowance and started the above-mentioned procedure for recognition. Apparently, there is no need for this kind of fertilizer.

Utilization as component in fertilizer or as raw material in the manufacture of fertilizer is in principle possible. In the Netherlands, the end product is tested for acceptance as fertilizer. The origin of the elements composing the fertilizer is not relevant. However, in practice, biomass ashes are not attractive as raw material because they have a low ratio of nutrients compared to contaminants. Mineral sources are preferred because they are cleaner. Exceptions may exist, e.g. ash from chicken litter may be a desired raw material for K and P. Another example may be Ca-rich fly ash from fluidized bed combustion of clean wood (no bark, etc.) where dolomite was added to the bed.

Gasification ashes appear to be less attractive as fertilizer than combustion ashes. The ashes contain an inert carbon matrix that lowers nutrient value. Other effects of the carbon are that the ashes are to a certain extend hydrophobic (poor contact with water) and that certain trace elements are bound, which can be an advantage or disadvantage. The mere fact that the ashes contain carbon is not enough to prohibit utilization, but the possibility that PAHs are adsorbed on the ashes can be a problem.

In all forms of utilization as (raw material for) fertilizer, production volumes and consistency are key factors. The profit margins are small in the fertilizer industry, so it is important that ashes become available at low prices, in large quantities and with a predictable composition. Currently, most ashes do not fulfill these criteria. Typically, installation owners buy fuels for the lowest price and pay less attention to the effects of fuel quality on ash quality.

The conclusion is that utilization of biomass ash as (raw material for) fertilizer should be pursued as a sustainable option of ash utilization, because nutrients are returned to the biosphere and non-renewable sources are saved. In practice, it will be very difficult.

5 UTILISATION AS BUILDING MATERIAL

Utilization of biomass ashes as building material or as raw material in the manufacture of building products can be regarded as a sustainable form of utilization when the use of ashes saves the use of non-renewable resources. When applied, biomass ashes must be subjected to the same technical criteria and environmental regulations as any other material.

Bottom ashes are the easiest ashes for utilization as building material. Bottom ashes from fluidized bed combustion or gasification consists for a large part of sand and may replace other kinds of sand in road construction or landscaping. Bottom ashes from grate stokers and entrained-flow gasification can be made into granulate and find its way to road constructions and concrete. Fly ashes from biomass combustion are among the more difficult materials for utilization. Direct utilization as a bulk building material replacing sand or gravel is almost not possible, because it is such a fine powder. Utilization as component in cement or concrete is a more likely option. Typical biomass fly ash is different from coal fly ash and does not comply with the criteria of EN-450. Alkali and chlorine are often the problematic components. In addition, there are components present in certain biomass fly ashes (e.g. phosphates) not listed in EN-450, that have a negative effect on the quality of the concrete when biomass ash is used as substitute for coal fly ash.

One way of utilizing biomass fly ash is as filler in cement blends or in mortars for special applications. There are other possibilities. An often-mentioned option is the manufacture of lightweight aggregates, such as Lytag. Currently, Lytag aggregates are made from coal fly ash that includes a certain fraction of biomass ashes resulting from direct co-firing at the power plant. In The Netherlands, initiatives to produce LWA using high temperature processes (Lytag) or low temperature process have not been very successful until now. It is impossible to discuss all options, because there is a large variation in ash composition and building materials. For each kind of biomass fly ash the possibilities must be investigated separately.

The possibilities for utilization of carbonrich fly ash from fluidized bed gasification in building products is almost zero. However, at least one niche product has been found: as filler in C-FIX, a concrete-like material made with heavy petroleum residue as binder. Made with gasification fly ashes as filler, acceptable C-FIX blocks with a good flexural strength were produced.

Besides technical requirements, there are also environmental specifications for building materials. In the Netherlands all stone-like building materials must comply with the regulations of the Dutch Building Materials Decree. Compliance is based on leaching of the end product. The origins and characteristics of the individual components is not important, only its behavior as an end product. A percolation test exists for bulk granular material and a tank test is used for shaped building materials. Similar testing procedures are expected to become part of the EU Construction Products Directive. The liquids produced in the leaching tests are analyzed for about 20 contaminating components. For each component, leached amounts (expressed as in mg component per kg original material or per square meter exposed surface) are compared to an upper and a lower limit. When all components stay below the lower limit, the building material is classified as 'category 1' and can be used in unlimited quantities. When one or more components exceeds the lower limit, but all components stay below the upper limit, the material is classified as 'category 2', which means that it can be used when shielded from direct contact with water (rain water or ground water). If one or more component exceeds the upper limit, the material cannot be used as building material.

At ECN a large number of different biomass ashes have been subjected to leaching tests in the past years. Generally, it was found that bottom ashes from different kinds of installations are cat. 1 of cat. 2 building material. Fly ashes from biomass combustion or gasification are more difficult. None of the untreated biomass fly ash samples tested at ECN has been classified as cat. 1. Only a few complied with the limits for cat. 2 applications. The problem elements for combustion fly ashes are typically Mo, Se, Cr and For gasification ashes Cl. from demolition wood the problem elements were Pb and Ba.

For all applications where biomass fly ash is used as a component in the manufacture of building materials, the leaching behavior of the fly ash itself is not important. As mentioned before, compliance tests for the DBMD are done only on the end product, not on raw material. It is important to avoid mixing with the objective to dilute the ashes. Blending and mixing is allowed, when it has a technical function, i.e. when the components contribute to the useful characteristics of the end product, e.g. improved strength or larger pH buffer capacity.

Utilization as building material or as component in the production of building products currently offers the best options for ashes from combustion of biomass. The biggest challenge is consistency. Together with the availability of large volumes, consistency is the key factor for success. Biomass ashes are only attractive when it is available in larger quantities at a predictable quality even when this is a lower quality.

6 UTILISATION AS FUEL

Utilization as fuel is a viable option for ashes with a significant amount of unburned carbon. In practice, this option is limited to carbon-rich fly ashes from fluidized bed gasification. Utilization as fuel is a logical and preferred option, because it is use ashes with the same objective as the original material: generating heat and power. Utilization as fuel is not the same as waste incineration with recovery of energy. First estimates indicate that utilization as a fuel is possible when the carbon content is larger than 35 wt% or the caloric value is higher than 15 MJ/kg.

The fact that gasification fly ashes are fine powder can be an advantage when co-fired in a PF burner: no milling required. On the other hand transport and handling of combustible powder has increased health and safety risk, e.g., dust explosion. When produced volumes are small, gasification ashes of several installations can be collected, possibly blended and then sold as replacement fuel for installations like cement kilns, steel mills or even coal-fired power plants.

Logistics are the crucial factor in utilization of gasification fly ash as fuel. The fly ash is a very light material with a density of about 200 kg/m³. Transport and storage of such a light material is relatively expensive, in particular when the distance between production and utilization is large. One way to improve this situation is to compact the fly ashes into pellets, granulates or even briquettes. At ECN, explorative pelletisation tests were performed. Some gasification ashes can be pelletised by adding only water, e.g. when they are rich in Ca-compounds or have other components that act as binders. Other ashes may need addition of a binder. The traditional binders for charcoal briquettes, e.g., starch, work very well. Pelletisation increases the material density by about a factor 6. Depending on the shapes of the pellets or granulates bulk density can increase up to a factor 4. This means a significant reduction in the number of trucks needed for transportation. There are additional advantages. Pellets have better flowing characteristics. There is more compaction during no transportation. Dust is drastically lower, so that exposure to ambient conditions becomes possible. Health and safety risks are much lower. The fly ash can be transported in containers or big bags rather than tanks. Storage is easier and takes less space.

One of the most obvious ways to improve the situation with respect to logistics of high-carbon fly ash is to use the fuel in the vicinity of the gasifier. Even better would it be to combine gasification and combustion, e.g. indirect gasification (Battelle concept, ECN's Milena concept or VTT's integrated oxidizer).

Utilization as fuel in combustion processes does not completely solve the problem of finding a sustainable way of utilizing biomass ashes. Combustion creates low-carbon combustion ashes, which are virtually identical to ashes from combustion of biomass. Answers to the question what to do with lowcarbon ashes produced in biomass-fired installations can be found elsewhere in this paper.

Co-firing of high-carbon ashes will result in biomass ashes being incorporated in end products or byproducts. Proper utilization of the lowcarbon ashes becomes the responsibility of the buyer of the ashes. Also, the buyer of the ashes must take care of appropriate flue gas cleaning. Probably, the combustion facility needs to be licensed according to the local implementation of the EU Waste Incinerator Directive.

A market for fuels from gasification fly ash is non-existent, but preliminary estimates indicate that it is the most economical way of utilizing high-carbon fly ashes. Similar to utilization as fertilizer or building material, consistency and availability in large quantities are key factors for success. Water content and the caloric value are most important, but the behavior of the (large) inorganic fraction in the combustion chamber is also of importance when considering using biomass ashes as fuel.

7 AFTERTREATMENT

Direct utilization of fly ashes from gasification as fuel is an attractive possibility, but not likely the solution for all ash streams. Certain ashes will require some kind of aftertreatment. This is particularly true for highcarbon gasification ashes that have a low caloric value or too many contaminants. For all forms of after-treatment, the benefits should outweigh the additional costs. The economics will determine whether certain after-treatment techniques will become successful. Gate fees for land fill play a dominant role.

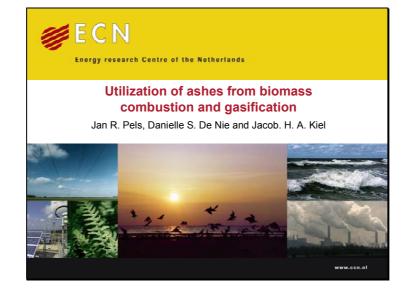
In the framework of the GASASH project, ECN and the other partners have explored several forms of after-treatment. These include controlled leaching, high-temperature and lowtemperature combustion, screen sieving, immobilization (e.g. C-Fix) and pelletisation. All of the explored techniques were found to be technically possible - to a certain extent and can be used to improve ash quality. The latter two techniques have been briefly introduced in the preceding sections. The other techniques will be the subject of future publications that will be done in co-operation with the GASASH partners.

8 CONCLUSIONS

Return of ash from thermal conversion of biomass to the original soils, where the biomass was harvested, is the most ecological and sustainable way to utilize the ashes and should be pursued, since it returns nutrients and closes the mineral cycle. Utilization as (raw material for) production of fertilizer may be a viable option for clean ashes with a high amount of nutrients compared to contaminants. For ashes from combustion of biomass. utilization as building material or as component in the manufacture of building products is the most likely option. For carbonrich fly ashes from fluidized-bed gasification, utilization as fuel is an obvious route. Some ashes may require after-treatment before utilization, but there will likely remains certain ash fractions that have to be land filled. Consistency and availability of large quantities are the key factors for all forms of utilization.

9 ACKNOWLEDGEMENT

The authors wish to thank SenterNovem and the EU 5th Framework for financial support, and NMI, C-FIX, AMFERT, Van Werven Recycling, the partners of the GASASH project and many others for useful discussions.



ECN

Biomass ash is "the third problem"

First problem: Where do I get a large enough supply of cheap fuel?

Second problem: How do I get the installation running and stable?

Third problem: What do I do with all those ashes?

PANIC!!!

Quick scan for solutions:

"Can't we use the appropriate disposal routes?"

"In concrete, of course, just like coal ashes!"

"The recycling company is taking care of that."

"Well, I think we need to landfill it, but that is so expensive"

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Objective

To investigate which options exist for utilization of ashes from biomass combustion and gasification

Approach

3

- Results from project BIOAS: fly ash and bottom ash from combustion of *clean* biomass
 - "When viable forms of utilization exist, they will certainly be found for clean biomass ashes"
- Selected results from project GASASH: carbon-rich fly ash from gasification (with VTT, PVO, Foster Wheeler, AICIA, EMC and Essent Energy Production)
 - Standard ash: gasification fly ash from AMER-CFB gasifier (85 MWth) fuelled with demolition wood

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Different kinds of ash, fuel and installations

Grate stokers:

- 95% bottom ash: slags, sand and unburned wood
- fly ash: white powder, 80% soluble salts, accumulated heavy metals
- Fluidized-bed combustion: equal amounts of
 - Bottom ash: mainly sand, bed material and inerts/ash from the fuel
 Fly ash: grey powder, bulk of fuel-bound ash + fragmented sand
- Fly asn: grey powder, bu
 Fluidized-bed gasification:
 - Bottom ash: mainly sand, bed material and inerts/ash from the fuel
 - Fly ash: black powder, bulk of fuel-bound ash + char + fragmented sand poeder, carbon content 10 70 wt%

And many more

- Entrained-flow gasification: bottom slag and flyslag
- Fly ash = filter ash, cyclone ash and cooler ash

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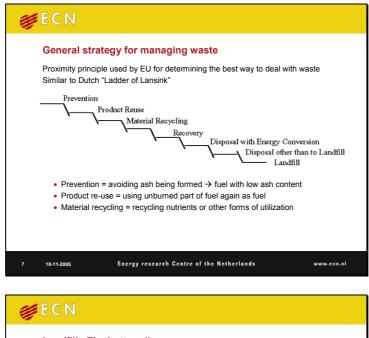
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	CHP Lelystad Bottom ash	CHP Lelystad Fly ash	NARGUS Fly ash	AMER-CFB Fly ash
Ash (wt%)	99.7	98.3	95	35
K (wt%)	7.5	37.5	2.8	0.7
P (wt%)	0.6	1.4	2.7	0.14
Ca (wt%)	16.6	2.5	13.7	4.9
Mg (wt%)	1.7	0.4	1.2	0.6
S (wt%)	0.7	11.6	0.9	0.6
Si (wt%)	(22.1)	0.23	19.3	7.6
Pb (mg/kg)	440	1300	120	4500
Zn (mg/kg)	450	10800	470	4000
Cd (mg/kg)	6	40	4	8
CI (mg/kg)	7000	125000	0.3	10000
Numbers are	are on dry basis indications, real as ECN's BFB combus		how large varia	ations

ECN-RX--05-182



Landfill - The bottom-line

Combustion ashes can be landfilled without much difficulties · Costs vary between countries

- Classification varies from inert to hazardous waste
- Bottom ash or sintered ash: from almost nothing to \in 100 per ton
- Fly ashes: from € 50 € 300 per ton

High-carbon fly ashes are high-calorific waste Discouraged by EU and made expensive or impossible by national legislation

Extremely simplified calculation

• Ash content of average biomass: 4% (dry basis)

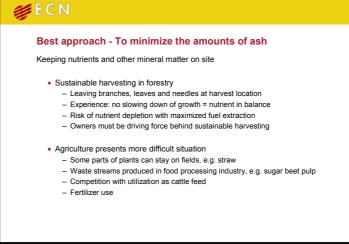
- Gate fee for average biomass ash: € 100/ton
- Cost of ash disposal: € 4 per ton dry fuel
- Compare: prices for biomass fuel € 0 40 per ton

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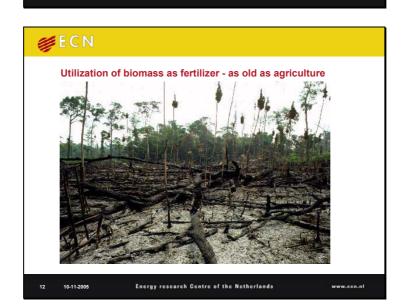
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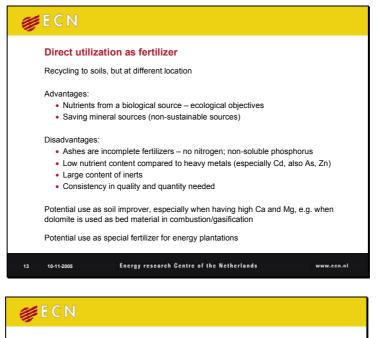
the need for bulk applications.

Niche applications exist, but do not diminish

Fuel

11





Utilization as raw material in fertilizer production

Utilization as raw material for fertilizer possible – only end product must comply with legislation, origin of minerals not relevant.

The same issues apply:

• Ashes are incomplete fertilizers - no nitrogen; non-soluble phosphorus

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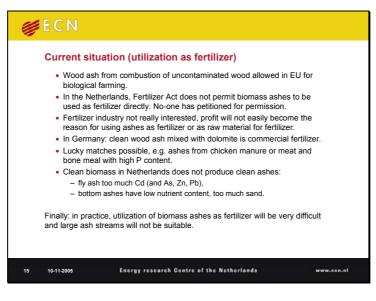
- · Low nutrient content compared to contaminants
- · Larger amounts of inerts
- Mineral sources are cleaner and more reliable
- Consistency in quality and quantity

Gasification ashes (high-carbon ashes)

- theoretically possible practical obstacles
 - even more inert material
 - poor contact with water
 - possibility of PAHs adsorbed on char

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