HIGHBIO - INTERREG NORD
2008 - 2011

Highly Refined Bio Energy Products through Gasification

Potential utilisation applications for gasification bioashes

Sari Kilpimaa
University of Oulu
HighBio project seminar
24.5.2011

Gränslösa möjligheter
EUROPEISKA UNIONEN
Europeiska regionala utvecklingsfonden
INTERREG IV A NORD

UNIVERSITY of OULU
OULUN YLIOPISTO

Content of presentation

- Introduction
- Utilisation applications tested to gasification ash samples
- Other utilisation applications for gasification bioashes (in literature)
- Conclusions

Introduction

- Bioash is formed in the thermal treatment (burning, gasification) of biomass
- Properties of ash from the burning and gasification processes may differ
- Properties of ashes differ depending for example on gasification technique and used fuel

Introduction

Highly Refined Bio Energy Products through Gasification

- Many potential utilisation applications to bioash from the burning process have been presented
- Few utilisation applications for the gasification ashes
- Utilisation applications developed for ash from the combustion process cannot be directly applied to gasification ashes
- Utilisation of ashes should always be considered as case-specific

Utilisation applications tested to gasification ashes during the project

- Utilisation as a fertiliser
- Utilisation as a soil conditioning agent
- Use as a fuel
- Use as an adsorbent

Gasification ash samples

- Produced in Finland
- The raw material was Finnish wood
- The ash 1 was produced by a gasifier, which is a combination of an updraft and downdraft gasifier
- The ash 2 was obtained from a pilot-plant which uses a downdraft gasifier

Use as a fertiliser

- Gasification ashes are typically less attractive as a fertiliser than combustion ashes
- Utilisation of the carbon-rich ashes are difficult:
  - Inert carbon matrix lowers nutrient value
  - Carbon is hydrophobic
- Carbon content < 10 % that the utilisation as a fertiliser would be reasonable
- Legislation defines the maximum concentration values of heavy metals allowed in fertilisers

Nutrient concentrations in gasification ashes

Nutrient	Unit	Ash 1	Ash 2	Soil
P	mg kg^{-1} (d.w.)	131	374	10
K	mg kg^{-1} (d.w.)	3133	2324	100
Mg	mg kg^{-1} (d.w.)	1617	3224	200
Ca	mg kg^{-1} (d.w.)	8489	42 344	1600

Highly Refined Bio Energy Products through Gasification

Total heavy metal concentrations in gasification ashes

Element	Unit	Limit value (forest fertiliser)	Limit value (agricultural use)	Ash 1	Ash 2
Cd	mg kg^{-1} (d.w.)	15	1.5	< 0.3	6.3
Cu	mg kg^{-1} (d.w.)	700	600	15	130
Pb	mg kg^{-1} (d.w.)	150	100	< 3	25
Cr	mg kg^{-1} (d.w.)	300	300	7	210
Zn	mg kg^{-1} (d.w.)	4500	1500	85	7950
As	mg kg^{-1} (d.w.)	30	25	< 3	< 3
Ni	mg kg^{-1} (d.w.)	150	100	3	110
Hg	mg kg^{-1} (d.w.)	1.0	1.0	< 0.040	0.040

Utilisation as a conditioning agent

- Useful conditioning agents
  - Strongly alkaline
  - Good liming capacity
- The liming effect value of commercial limestone produced by SMA Saxo Mineral Ltd. is 38 % (Ca equivalents; d.w.)

Parameter	Unit	Ash 1	Ash 2
pH		10.7	9.0
Neutralising value	% Ca	3.8	8.0
Liming capacity	$t\ t^{-1}$	10	4.8

Highly Refined Bio Energy Products through Gasification

Use as a fuel

- Potential utilisation application for gasification ash with significant amount of unburned carbon
- Possible when
  - Carbon content is > 35 %
  - Combustion heat is higher than 15 MJ/kg
- Utilisation ashes as a fuel does not completely solve the problem because the combustion of the high-carbon content ashes creates the low-carbon content ashes

Parameter	Unit	Ash 1	Ash 2
TC	%	89.4	60.9
Heat of combustion	MJ kg^{-1}	31.8	23.0

Use as an adsorbent

- Carbon content of gasification ash is high
- Activated carbon can be prepared for example from wood → chemical or physical activation
- Adsorption capacity is depending for example
  - Specific surface area
  - Particle size
  - Pore size
- Properties of ash from gasification process are better after chemical activation

Chemical activation

- Tested chemical activating agents:
  - 0.1 M HCl
  - 5 M $ZnCl_2$
  - 0.1 M H_2SO_4
  - 5 M KOH
  - HCl (37 %)
  - HNO_3 (65 %)

→ Best result by using 5 M $ZnCl_2$: BET 410 **m^2/g**
(before chemical activation BET 12.4 m^2/g)

Commercial activated carbon BET 920 m^2/g

Other potential utilisation applications

- Use in construction industry
- After-treatment of ashes

Use in construction industry

- Filler in asphalt, raw building material, lightweight bricks, stabilization agent, etc.
- Utilisation in the cement and concrete industry without pretreatment is not possible
- Case-specific; technical and environmental specifications for building materials

After-treatment of ash

- After-treatment is choice if direct utilisation is not possible
- Potential treatment method for example to the ashes which have too many contaminants
- Methods: controlled leaching, sieving, etc.
- After-treatment in all cases outweigh costs

Conclusions

- Utilisation of ashes has to always do a case-specific because properties differ a lot
- The results obtained during project indicates:
  - Gasification ashes would be good adsorbents after chemical activation
  - Use as a fuel is possible
  - Gasification ashes are not effective fertilisers or soil conditioning agents

HIGHBIO - INTERREG NORD
2008 - 2011

Highly Refined Bio Energy Products through Gasification

Thank You for Your Attention!

Researcher Sari Kilpimaa, M.Sc. (Chem.)
University of Oulu
Department of Chemistry
sari.kilpimaa@oulu.fi

UNIVERSITY of OULU
OULUN YLIOPISTO