BIOFLEX!

ERA-NET Bioenergy

Guideline for Fuel Design
- focus on kaolin additives

Umeå University

Project ERA-NET Bioenergy "BIOFLEX!"

Prepared by: Christoffer Boman, Anders Rebbling, Robert Mack, Hans Hartmann

Place, Date: Wels, 28th February 2019

FFG Swedish Energy Agency FNR Fachagentur Nachwachsende Rohstoffe e.V. The National Centre for Research and Development

Umeå University

Contents

ERA-NET Bioenergy

- Background and Objective
- The Fuel Design concept
- Application of kaolin as fuel additive
- Guideline for kaolin additivation
- Final remarks

2

Umeå University

ERA-NET Bioenergy

Background and objectives

- There is an increasing demand for broadening of the biomass feedstock to increase fuel flexibility and innovation potential, i.e. to include more challenging assortments such as ***energy crops, bio-residues and by-products.***
- If such fuels are applied in combustion systems designed for wood fuels, they usually cause ***ash-related operational problems and increased emissions***.
- The ***huge variation of the compositions*** (ash forming matter, trace metals and nutrients) of different biomass fuels, has a vital impact on the combustion and environmental performance.
- Within the BIOFLEX! project, ***guidelines for the application and implementation of appropriate Fuel Design concepts*** were developed to promote low emissions, high efficiencies and to avoid slagging on the grate and in burners when using such challenging fuels.

3

Umeå University

ERA-NET Bioenergy

The Fuel design concept

Fuel design is a general approach of using primary fuel based measures to increase the fuel quality and combustion performance in biomass combustion and gasification applications.

The aim is to induce or promote chemical reactions between the fuels and/or additives to reduce the risk of ash related problems. Fuel design is implemented by blending the primary fuel with a secondary fuel or an additive that has to be chosen explicitly to get the best and desired effect

- **Fuel blending**  + 
- **Fuel additives**  + 

The clay **kaolin** (main component is the mineral kaolinite [$Al_2Si_2O_5(OH)_4$])

4

Umeå University

Application of kaolin additivation

Kaolin is a white plastic clay used in many industrial applications

The main mineral is kaolinite that is transformed to meta-kaolinite upon heating (at 450-600°C):

$$\mathbf{Al_2Si_2O_5(OH)_4} \rightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O$$

Meta-kaolinite has a porous structure and is very capable of incorporating (react with) alkali vapours in biomass combustion processes, thus forming high-temperature stable K/Al-silicates:

$$Al_2O_3 \cdot 2SiO_2 + \mathbf{2KOH} \rightarrow \mathbf{2KAlSiO_4} + H_2O$$

$$Al_2O_3 \cdot 2SiO_2 + \mathbf{2KOH} + 2SiO_2 \rightarrow \mathbf{2KAlSi_2O_6} + H_2O$$

$$Al_2O_3 \cdot 2SiO_2 + \mathbf{2KCl} + H_2O \rightarrow \mathbf{2KAlSiO_4} + 2HCl$$

$$Al_2O_3 \cdot 2SiO_2 + 2SiO_2 + \mathbf{2KCl} + H_2O \rightarrow \mathbf{2KAlSi_2O_6} + 2HCl$$

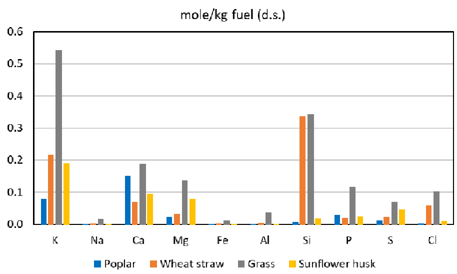
Meta-kaolinite will at higher temperatures (>1000°C) transform further to spinel and mullite structures, less capable to capture alkali vapours.

5

Umeå University

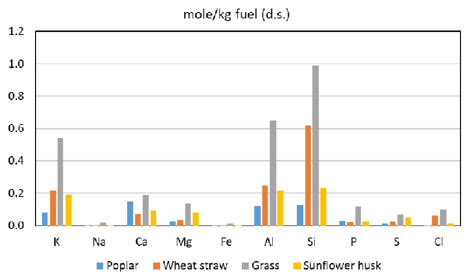
Application of kaolin additivation (cont.)

Elemental composition of the four BioFlex fuels



0.7 5.3 2.8 1.3

Elemental composition of the four BioFlex fuels with kaolin (calculated)



0.8 2.4 1.7 1.2

Index (Si+P+K)/(Ca+Mg+Al)*: Estimation of ash melting and sintering behaviour

**Obernberger I. Strategy for the application of novel characterization methods for biomass fuels: case study of straw. Energy Fuels 2014(28):1041−1052*

6

Umeå University

Application of kaolin additivation (cont.)

ERA-NET Bioenergy

The additive level should be based on basic chemical calculations, earlier experiences and some additional considerations.

As at start; a molar relation of 1:1 between alkalis in the fuel $(K+Na)_{fuel}$ and aluminium in the kaolin (Al_{kao}) is assumed. Note: kaolinite contains two Al atoms!

→ All alkalis have the theoretical possibility to be incorporated in the Al-silicate structure!

Next, calculate the additive level in weight-%, from standard fuel analysis $(mg/kg_{dry\ fuel})$ and molar weights of K, Na and kaolinite

→ For normal stemwood based wood fuels (0.3-0.4 weight-% ash), this theoretical (stoichiometric) additivation level will be around 0.15 weight-% kaolin (on dry basis).

7

Umeå University

Guideline for kaolin additivation (1)

ERA-NET Bioenergy

Type of combustion system and problem definition

Define the problem(s), e.g. slagging, deposit formation, fine particle emissions, total dust emissions, AND aim of the additivation!

- Main target (in this context) is to reduce slagging and fine PM emissions with kaolin (also reduction of alkali deposits although his is not often an issue in these applications).
- Total dust emissions most often reduced (less fine PM), but potential entrainment of coarse mineral particles (kaolin powder) needs to be considered!
- Risk for increased slag formation on the grate (for rather pure wood fuels)!

8

Umeå University

Guideline for kaolin additivation (2)

ERA-NET Bioenergy

Type of fuel(s) used/to be used

In principal three categories can be defines
i) pure wood fuels (stemwood based)
ii) ash rich woody energy crops and forest residues (if low Si), and
iii) grass/straw based fuels
P rich fuels needs special attention and are not discussed here!

- For ”clean” woody fuels (low Si), kaolin will mainly reduce fine PM emissions. But the risk for slag formation needs to be carefully assessed and maybe controlled by lowering the fuel bed temperature.
- For Si-rich straw- and grass fuels, kaolin has positive effects on both, fine PM emissions and slag formation. However, relatively high additive levels are needed to achieve significant effects!

9

Umeå University

Guideline for kaolin additivation (3)

ERA-NET Bioenergy

Additive to use

In BioFlex, a focus was on the application of the clay kaolin, due to its advantageous properties compared to most other similar aluminium-silicate based minerals.

- Different commercial qualities of kaolin exist, so both technical and economic aspects needs to be considered. Quality aspects to consider are e.g. the purity of the kaolin, the grain size, moisture content, contaminants.
- High purity kaolin is preferable, i.e. high fraction of kaolinite mineral, and with low concentrations of K, Na, Ca, Mg, and heavy metals.
- A small and homogeneous grain size distribution is preferable due to higher ”reactivity” (efficiency), BUT risk for entrainment of mineral dust particles from the bed to the flue gas system has to be considered!

10

Umeå University

Guideline for kaolin additivation (4a)

ERA-NET Bioenergy

Additivation level (kaolin dosing) within BioFlex

Examples of additivation levels applied within BioFlex are given, as well as a simple calculation approach with some considerations and recommendations.

First, calculate as theoretical (minimum) level assuming;
- 100% kaolinite mineral in the kaolin clay
- 100% of the kaolinite available for reaction with fuel alkalis
- Calculations made based on dry substance (both fuel and additive)

Then, the applied levels were increased +12-50%, due to different considerations.

Fuel	**Ash content** (wt-% ds fuel/kaolin)	**Kaolin level (theo. min)** (wt-% ds fuel/kaolin)	**Kaolin level (applied)** (wt-% ds fuel/kaolin)
Poplar	2.2	1.0	1.5
Wheat straw	4.3	2.8	3.4
Grass	8.5	7.0	8.1, 10.5
Sunflower husk	2.9	2.5	2.8

11

Umeå University

Guideline for kaolin additivation (4b)

ERA-NET Bioenergy

Calculation procedure for kaolin dosing

1. Re-calculate fuel and kaolin composition data for the major ash forming elements from mg/kg$_{fuel}$ (ds) to mole/kg$_{fuel}$ (ds).
2. Calculate the theoretical minimum amount (mole/kg$_{fuel}$ ds) additive [$Al_2Si_2O_5(OH)_4$] needed per kg fuel to capture all fuel alkali (K_{fuel}+Na_{fuel}), based on assumptions above;

$$Additive_{theo\ min} = (K_{fuel} + Na_{fuel})/2 \qquad (Eq.\ 1)$$

3. Elements (K, Na, Ca and Mg) in the additive (K_{add}, Na_{add}, …) should be adjusted for, by considering the fraction of these elements in relation to the concentration of Al in the kaolin (Al_{add});

$$Additive_{adj(I)} = Additive_{theo\ min} / ((Al_{add}-K_{add}-Na_{add}-2(Ca_{add}+Mg_{add}) / Al_{add}) \qquad (Eq.\ 2)$$

12

Umeå University

Guideline for kaolin additivation (4c)

ERA-NET Bioenergy

4. Account and adjust for other potential uncertainties and limiting effects for the additive functionality and availability, i.e. efficiency factor of e.g. 90%;

$$Additive_{adj(II)} = Additive_{adj(I)} / 0.9 \qquad (Eq.\ 3)$$

Note: The efficiency factor may, of course, be adjusted from case-to-case, e.g. if kaolin is used together with rather pure (Si-poor) woody biomass, since the Ca in the fuel may interact with the kaolinite, thus lower the capturing effect for K and Na.

5. In addition, process conditions, e.g. high bed temperatures and gas velocities through the bed, may lower the overall efficiency of the kaolin additivation.
6. Finally, the molar amount of additive needed per kg fuel can be re-calculated to mass amount per kg fuel by considering the molar mass of kaolinite (258.2 g/mole), thus also give the wt-% additivation level applied.

13

Umeå University

Guideline for kaolin additivation (5)

ERA-NET Bioenergy

Additivation approach

→ Co-pelletized (recommended!)
→ Separately (as powder mixed with the fuel)
(→ Slurry to the fuel feeding system)

Supported by BioFlex full-scale tests*, co-pelletizing the additive with the biomass fuel is recommended (if pellets are used)!

- If separate supply → suitable solution for introduction of the kaolin powder (e.g. separate screw feeder) needs to be applied!
- Long term tests are still missing to investigate aspects related to e.g. varying load operation, varying fuel quality, durability, maintenance etc.!

* Boman C, et al. Fuel additives and blending for reduction of particle emissions in biomass based medium scale heating boilers (In Swedish). Swedish Energy Agency, Final report 2019 (project nr 42008-1).

14

Guideline for kaolin additivation (6)

Implementation considerations

For full scale implementation of an additivation concept, as with kaolin, several technical, practical and economic aspects need to be considered.
Very few examples have however been performed, at least reported.

To support the application of a successful fuel additivation strategy some specific boiler operational aspects are important to enable different fuel design concepts;

1) Good process control of the boiler (→ stable load and combustion conditions)
2) Separate regulation of primary and secondary air (→ adjustable conditions on the grate)
3) Good and stable support of the additive, preferably by the additive co-pelletized with the biomass, or by a stable separately controlled additive feeding (→ adjustable and stable dosing)

Final remarks

- The use of different fuel design concepts like fuel additives or blending have great potentials to be used as efficient strategies to mitigate ash related operational problems and to reduce particle emissions!
- Within the project BioFlex, the concept of using the clay mineral kaolin as additive in small- and medium scale grate fired biomass systems has been studied, tested and further developed, resulting in the specific guidelines and recommendations!
- This project has improved the basic knowledge on fuel design strategies and promoted the next steps in full-scale testing and implementation of developed concepts!
- ***→ Broadening of the biomass feedstock and enabling a clean and efficient utilization of different challenging biomass fuels!***

BIOFLEX!

ERA-NET Bioenergy

Contact: Christoffer Boman, Umeå University
christoffer.boman@umu.se

Umeå University

17