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The effect of papermaking sludge as an additive to biomass pellets on the final quality of the fuel

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ABSTRACT

The ever increasing demand on top quality solid biofuel in form of biopellets is limited by the sources and properties of raw materials. The best quality biopellets are suitable for burning in small scale boilers up to 100 kW$_t$. The most limiting factor of this fuel is the ash melting temperature. Therefore the use of cheaper and readily available phytomass as a raw material is considerably restrictive. The research in this paper is based on the theory of the chemical process of ash creation and on the effect of additives on this process. The objective of the study is to find and apply an effective and available additive to produce the best quality phytomass-based fuel pellets, suitable for small scale boilers. A by-product of the paper recycling process, papermaking sludge was used as the most effective additive to wheat straw. This is due to the high content of calcite and kaolin in the sludge. It was also confirmed by experiments that the composition of sludge including cellulose fibres very positively affects the physical and mechanical properties of the composite pellets. Our research deals with an experiment concerning an appropriate production process of composite fuel based on wheat straw. Different weight proportions of papermaking sludge were added and the effect of the sludge on the fuel parameters, especially on the ash melting behaviour, was observed. The final quality of the composite fuel was thoroughly tested by physical, mechanical and thermal methods, and its properties were compared to European and International Standards for Biofuels. The results of the experiments demonstrate that the composite pellets produced by the above-mentioned process have a high level of fuel quality and, due to high ash melting temperature, they are suitable for small scale boilers. The results have shown that the appropriate range of papermaking sludge content for producing high quality wheat straw composite pellets ranges from 10% to 20%.

1. Introduction

The ever-increasing interest in producing energy from local sources of agricultural residues poses new challenges for the development of technologies and processes in the production of biofuels suitable both for large and small combustion plants. Agricultural residues represent a cheaper energy source than wood, but their use has some technical limitations. The use of straw-based fuels, especially in small scale boilers up to 100 kW$_t$, is troublesome due to the low softening and melting temperature of the ash [1]. Slagging and fouling problems frequently occur. There are two ways of eliminating the formation of slag. One is to reduce the temperature in the burner place. The other way is to alter the composition of the ash forming content. This can be achieved by using the right type of additive during the treatment of raw material before the pelletizing process [1–4].

The low ash-fusion temperatures of biomass are a serious disadvantage [5]. It is widely accepted that most of the severe deposit formation, slagging and fouling problems during biomass thermochemical conversion result from the low ash-melting temperatures [5–8]. It was found that the high concentrations of K-, Si-, P-, S-, Fe-, Na- and Mg-containing minerals (excluding the highly enriched in Si biomass varieties) and low contents of Ca-, Al- and Ti-bearing minerals are commonly responsible for decreased ash-fusion temperatures of biomass [8]. According to [5,8], the low ash-fusion biomass varieties normally have high slagging propensity due to formation of low-temperature melts and their subsequent intensive melt crystallization followed by abrupt glass generation during cooling at relatively low temperatures. The lower ash-fusion temperatures with short softening-melting range and high flow-dissolution rate seem to be the worst case for slagging and fouling [5,8]. A selection of optimal temperatures for thermochemical conversion is required to avoid the above problems. As the overviews in literature [5,8] describe, in additionally, a beneficial approach for problematic low ash-fusion biofuels or alternative bed materials for fluidized bed combustion is to use various additives, namely kaolinite, mullite, clinochlore, bentonite, K feldspar, plagioclase, olivine, quartz, lime, bauxite, gibbsite, diaspore, corundum,

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hematite, calcite, dolomite, magnesite, ankerite, sand, high alumina sand, limestone, diatomaceous earth, dicalcium phosphate, chalk, elemental sulphur, peat, coal and coal ash. The application of such additives is to prevent the agglomeration, sintering and slagging tendencies by achieving higher ash-melting temperatures.

The physico-chemical transformations of organic matter and inorganic matter during biomass combustion include various interactions between solid, gas and liquid phases with original and newly formed genesis in such multicomponent system [6]. General processes, namely: (1) combustion of organic matter (200–850 °C); (2) fragmentation (disintegration) of particles (500 °C); (3) initial (700–900 °C), significant (700–1100 °C) and extensive (700–1300 °C) agglomeration or occasionally swelling of particles; (4) initial (700 °C), extensive (900–1100 °C) and complete (1100–1500 °C) fusion of particles or minerals with different melting points; (5) various new phase crystallizations (500–1500 °C); and (6) melt/glass formation (700–1500 °C); were observed in biomass ashes [6,9].

The systematization of physico-chemical transformations during biomass combustion described in detail in literature [6] show that the original organic matter and inorganic matter in biomass transform: (1) initially to devolatilization of organic matter and burning of combustible gases and char with formation of intermediate and less stable oxalates, nitrates, chlorides, hydroxides, carbonates, sulphates and inorganic amorphous (non-glass) material; (2) subsequently to more stable silicates, phosphates and oxides; (3) then to melting accompanied by dissolution of the refractory minerals; with increasing combustion temperatures in the system; and (4) followed by crystallisation of melt and formation of glass accompanied by some salt condensation and hydroxylation, hydration and carbonation of newly formed phases during cooling of biomass ash. Finally, some post-combustion transformations of the newly formed minerals and phases to stable during weathering species among silicates, hydroxides, phosphates, sulphates, carbonates, chlorides and nitrates also occur due to their hydration, hydroxylation and carbonation by moisture and CO_2 in the air through storage of biomass ash [6].

Mean ash-fusion temperatures for seven tested types of straw are: initial deformation temperature 857 °C, spherical temperature 1061 °C, hemispherical temperature 1105 °C and flow temperature 1214 °C [9,10].

According to the studies [2,11–15], clay minerals and dolomite or lime-based additives were successfully used to increase the ash melting temperature. Kaolin also proved to be a very suitable additive [12]; when combustion of wheat pellets with kaolin, added to an equivalent of 20% of fuel ash content, showed an increase of fusion temperature by 250 °C. In the study [16], the reduction of slagging tendencies was observed by admixing kaolin and calcite in wood pellet production.

The large content of potassium compounds present in wheat and barley straw ash contributes to their low values of characteristic temperatures of ash melting behaviour. The ash components primarily formed are reactive [11]. Therefore, high-temperature reactions between straw ash and kaolin or dolomite were investigated in this study. Kaolin was found to be the more effective additive. Solid state reactions at temperatures above 800 °C lead to the formation of secondary products, such as oxides and silicates. Minerals, such as kaolin and dolomite, have been suggested as fuel additives to increase the ash flow temperature. The potassium capture by kaolin partly explains the higher flow temperature of the ash-additive mixture. The observed enhancement of the flow temperature caused by dolomite is probably an effect of dilution or adsorption.

The effect of kaolin on particle formation was tested in a 65 kW burner [17]. 3 and 6% by weight of kaolin was mixed to two ash rich raw materials – wheat straw and Reed Canary Grass – during the pelletizing process. The particles formed were measured as total particulate matter and as mass and number concentrations. The results show that particle formation and sintering tendency was reduced.

The results of the study [18] indicate that silicate-alkali chemistry may play a critical role in initiating and enhancing the barley straw and husk ash sintering at elevated temperatures. The formation of low temperature melting potassium rich phosphates may also be the cause of the low sintering temperatures of barley husk ash. Adding kaolin and calcite significantly increased the sintering temperatures of barley straw and husk ashes. With kaolin addition, new high melting temperature potassium aluminium silicates were identified from the sintered mixture of the ash-additive.

However, the above-mentioned inorganic additives admixed into phytomass fuel do not significantly contribute to increasing the mechanical quality indicators of this fuel, and they complicate the process of compaction. The research presented in this paper considers using a new effective additive – a by-product from paper recycling – papermaking sludge.

The present study integrates two main goals: (i) to reach higher ash melting temperature of straw pellets and, thus their better mechanical properties, and (ii) to apply papermaking sludge as an effective additive because of its chemical composition. Papermaking sludge, as a waste by-product of the paper recycling process, contains a high proportion (almost 50 wt% in dry state) of mineral fillers such as kaolin, calcium oxide and others, and approximately 50 wt% of cellulose fibres. At present, most of the paper sludge is landfilled and only a minor part is used to produce bricks or cement. Producers pay for its use in the same way as for land-filling.

The present investigation has been carried out with the aim of contributing to the understanding of the mechanisms that lead to higher melting points in straw ash and better mechanical quality properties of pellets upon the addition of papermaking sludge containing the above-mentioned mineral additives.

2. Materials and methods

2.1. Materials

The tested type of agricultural residues used in this study is wheat straw because of its high energy potential. Wheat growing is abundant worldwide, and straw is gradually being used for heat production by the combustion of pellets produced from it. However, according to the preliminary combustion tests and laboratory tests of wheat straw pellets, severe ash sintering and slagging occurred. Therefore, pellets of wheat straw were selected and tested as a reference fuel.

The effect of pure kaolin, calcite and other mineral additives on increasing the ash melting points has been proven by research, as mentioned in many sources. In this work, papermaking sludge as a waste by-product of the paper recycling process was selected and tested to investigate its ability to raise the fuels' ash sintering temperatures. Chemical analysis of the papermaking sludge used is shown in Table 1.

Table 1
Chemical analysis of papermaking sludge.

Test	Value	Unit
Ash content	56.4	%
Dry matter (105 °C)	51.9	%
CaO	27.7	%
Al2O3	3.211	%
SiO2	4.721	%
Arsenic	0.5	mg/kg
Chromium total	7.0	mg/kg
Cadmium	< 0.1	mg/kg
Copper	46.5	mg/kg
Molybdenum	2.71	mg/kg
Nickel	1.75	mg/kg
Lead	10	mg/kg
Mercury	0.010	mg/kg
Zinc	100.6	mg/kg
NEL-IR	2264	mg/kg