Residues from the production of biofuels for transportation: Characterization and ash sintering tendency

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A B S T R A C T

The continuously growing demand for fuels in the transportation sector has led to the increased use of liquid biofuels, with a corresponding increase in the amounts of production residues. With energy recovery, these residues could become a source of biomass fuels. The current work investigated the behaviour of four potential biomass fuels during combustion. Fermented sewage sludge (FSS) is the residue from biogas production via anaerobic fermentation; distillers’ dried grains with solubles (DDGS) are a residue from barley bioethanol production; and rapeseed cake (RC) and palm kernel cake (PKC) are both oil extraction residues from first generation biodiesel production plants. Since the main challenges during biomass combustion are related to ash behaviour, this paper focuses on the ash-forming matter in the fuels and its effect on the ash sintering tendency. Three different types of tests were applied to study ash sintering: compression strength, microsample sintering, and standard ash sintering. The latter was carried out using hot stage microscopy and computer aided image analysis, and the results were compared with those from the compression strength and microsample tests. To obtain additional information about the nature and extent of the sintering, ash samples before and after sintering were examined with a scanning electron microscope equipped with energy dispersive X-ray (SEM/EDX) technology and a stereomicroscope incorporating a digital camera. To make it possible to study the ash-forming matter, chemical fractionation were performed accompanied by fuel proximate analyses by means of thermogravimetric analyzer. The results clearly showed that the lowest initial sintering temperatures were below 800 °C for RC and DDGS in all the sintering tests, while PKC and FSS did not exhibit any significant sintering below 900 °C. This could be interpreted to mean that when the combustion temperature is below 900 °C, no significant ash-related problems will occur. The chemistry of the fuel ashes investigated is dominated by phosphorus, and the shift between alkali metal and alkaline earth metal phosphates governs the sintering behaviour. The FSS sintering tendency is dominated by the iron oxide chemistry.

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1. Introduction

One of the key targets set by the European Council is an increase in the renewable energy share to 20% of European Union (EU) energy consumption by 2020 [1]. This can be achieved only if a portion of the fossil fuels are replaced by biomass. As suggested by the European Environment Agency (EEA) data for 2007, the present proportion of renewables in primary energy consumption is 8% [2], which implies that member countries will have to make extraordinary efforts to meet the target. Because energy demand is constantly growing, new fuels are required, so in recent years, increased attention has been paid to energy recovery from biomass or waste-derived fuels.

The transportation sector can become an important source of new biomass fuels. The constant escalation of energy demand in the transportation sector, oil import dependence, and climate change are the most significant factors driving legislation to enforce an increase in the proportion of biofuels in the transportation fuel market. European Directive 2009/28/EC imposes a reference value of 10% for the use of biofuels in this sector by the year 2020 [1]. According to EEA data [3], the proportion of biofuels in the EU-27 transportation sector reached 3% in 2007; in 2006, it was below 2%, so the biofuels market is growing and must do so rapidly. The increased amounts of production residues will then be available for energy recovery.

The literature has reported extensively on the combustion of biomass and related operating problems [4–11]. The main challenges during biomass combustion are related to ash behaviour and before new biomass fuels can be put into use, ash properties need to be determined.

The aim of this paper is to investigate the ash sintering tendency of potential biomass fuels in terms of their behaviour during combustion. Four solid residues from the production of liquid and gaseous biofuels are described: fermented sewage sludge (FSS) from biogas production via anaerobic fermentation; dried distillers’ grains with solubles (DDGS) from barley bioethanol production; rapeseed cake (RC); and palm kernel cake (PKC). The last two are oil extraction residues from first generation...
biodiesel production plants. The same fuels were described in detail by Giuntoli et al. [12], who investigated the fate of fuel nitrogen.

The sintering tendency of biomass fuels was studied in the laboratory by several authors, e.g., [13–16], while Bartels et al. conducted a review of available laboratory methods for bed sintering prediction in term of fluidized beds [17]. Steenari et al. [13] investigated rapeseed cake, among other fuels. However, the samples had lower sodium content than those used in the present work. The sintering of sewage sludge ash was studied by Wang et al. [16], who found that, for sludges treated with Fe₂(SO₄)₃ at a wastewater treatment plant, sintering started at 1000 °C. This result will be compared with those obtained in the current study for fermented sewage sludge. The sintering tendency of the two other fuels presented here has not been reported elsewhere.

Ash sintering was studied using three different tests: standard ash sintering, compression strength, and microsample sintering. The results from the fuel proximate analysis and chemical fractionation are presented along with those from ash sintering tests as will be demonstrated in Section 3. Ashed fuel samples were analyzed using a scanning electron microscope equipped with energy dispersive X-ray (SEM/EDX) technology and a stereomicroscope incorporating a digital camera.

2. Materials and methods

2.1. Fuel and ash characterization

The FSS used in this work came from a plant operating an anaerobic fermentation process for biogas production (Ab Stormossen Oy). The DDGS originated from a barley bioethanol production plant (Abengoa), while both the PKC and RC are residues from oil seed biodiesel production (E. On and Emmelev A/S, respectively).

The fuel proximate analysis was performed by means of thermogravimetric analysis (TGA). The samples were pre-dried and ground to obtain a mean particle size less than 1.0×10⁻³ m. First, each fuel sample was heated to 105 °C at a heating rate of 0.33 °C/s and kept at a constant temperature until the mass stabilized to allow complete drying. Next, the temperature was increased to 550 °C at the same heating rate to determine the volatile content. When the mass stabilized, only char remained. During both stages, an inert gas (N₂) flow was maintained at the level of 1.7×10⁻⁶ m³/s. To determine the ash content, the N₂ was replaced by synthetic air (a mixture of 20%vol. O₂ and 80%vol. N₂) to allow complete combustion of the organic residue. This method was adapted from Mayoral et al. [18]. To assess the repeatability of the tests, they were carried out in triplicate. Five repetitions were performed for the FSS sample.

Additionally, chemical fractionation was applied to all the fuels to determine the chemical compounds which contain the ash-forming matter. Chemical fractionation is based on selective consecutive leaching by water (H₂O), 1 M ammonium acetate (NH₄Ac), and 1 M hydrochloric acid (HCl) [19–22]. Subjecting the untreated fuel samples to the increasingly aggressive solvents produces a series of four fractions. The untreated samples, the three liquid fractions, and the remaining solids were analyzed by an external laboratory according to Swedish standards.

Standard ash was prepared according to CEN/TS 15403 to determine the ash content. A fuel sample was ground to a mean particle size less than 1.0×10⁻³ m (more than 90%) and, for FSS, less than 0.25×10⁻³ m (more than 80%). Then, it was placed in a laboratory furnace in such a way that the sample loading did not exceed 1.0 kg/m². The furnace was heated to 250 °C at a rate of 0.083 °C/s. The sample was left at this temperature for 1 h to allow devolatilization before ignition. Afterwards, the furnace was heated at 0.083 °C/s to 550 °C. The sample was maintained at this temperature for 2 h, removed from the furnace, cooled in ambient air for approximately 5 min, and then transferred to a desiccator where it was stored for later use in a sealed container.
Fig. 4. Chemical fractionation results. In the graph of fermented sewage sludge (top left), the scale on the Y-axis is different to accommodate the higher ash concentration.

Fig. 5. Composition of fuel standard ash prepared at 550 °C according to CEN/TS 15403, analyzed with SEM/EDX. Bar plots present the average of three samples and triangles show values for each sample.
than 1.0×10^3 m/s. Three pellets were prepared for each temperature, except 1050 °C. After preparation, the samples were subjected to heat treatment for 4 h at various temperatures in the range 350°–950 °C in a tube furnace with a constant synthetic air flow of 3.3×10^−3 m3/s. Three pellets were prepared for each temperature. After heat treatment, the pellets were removed and cooled to room temperature in desiccators. Before compression strength measurements were performed, the size of each pellet was measured to make it possible to calculate the compression strength per mm². The compression strength was measured with a standard crushing device.

Table 1

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>RC</th>
<th>DDGS</th>
<th>PKC</th>
<th>FSS</th>
</tr>
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<tbody>
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<td>550</td>
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<td>0</td>
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<td>*</td>
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<tr>
<td>850</td>
<td>*</td>
<td>*</td>
<td>x</td>
<td>x</td>
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<tr>
<td>950</td>
<td>**</td>
<td>Molten</td>
<td>**</td>
<td>***</td>
</tr>
<tr>
<td>1050</td>
<td>***</td>
<td>n/a</td>
<td>**</td>
<td>***</td>
</tr>
</tbody>
</table>

n/a—data not available.

2.2. Sintering tendency

The ash sintering tendency of the fuels was investigated using three different tests: microsample sintering, pellet sintering, and standard ash sintering according to CEN/TS 15370. As discussed in Section 2.1, prepared standard ash was used in the pellet sintering and standard ash sintering tests, while the original fuels were used for microsample sintering test. The sintered ash particles were analyzed by means of SEM/EDX.

The microsample sintering test of fuel samples was investigated using a thermogravimetric analyzer (TGA) and an optical microscope equipped with a digital camera. The fuels were ground to a mean particle size less than 1.0×10^−3 m to ensure the homogeneity of the samples. Approximately 15.5±0.3×10^−3 kg of the fuel sample was placed in the hot reactor at a stabilized temperature of 550 °C, 750 °C, 850 °C, 950 °C, and 1050 °C. The air flow was kept constant at 0.3×10^−3 m/s. Three samples were tested for each fuel at each temperature (except 1050 °C). The sample was removed after 25 min, and a picture was taken with the optical microscope at three different magnifications: 1.6, 3.2, and 5.0. Based on the pictures, the ash samples were classified according to the four stages of sintering introduced by Moilanen et al. [23] (Fig. 1). Unsintered ash residue that resembles the original fuel particles is marked “0”. There are two classes of partly sintered ash particles. The first, labelled with one asterisk, describes a sintered sample in which individual particles of the original unsintered sample can still be observed, so that the ash sample forms a sort of cake. In the second, labelled with a double asterisk, individual particles of the original sample can no longer be distinguished. Completely sintered ash particles are labelled with three asterisks.

The pellet sintering test is based on compression strength measurements described in detail by Hupa et al. [24] and Skrifvars [25]. The method comprises three main stages: pelletizing, heat treatment, and crushing. The standard ash was pelletized into 8.0×10^−3 m-high cylinders with a diameter of approximately 8.3×10^−3 m. The pressure applied to all the pellets was the same (approx. 40×10^3 Pa); it was determined by finding the minimum measurable pressure necessary to pelletize the ash. After preparation, the samples were subjected to heat treatment for 4 h at various temperatures in the range 350°–950 °C in a tube furnace with a constant synthetic air flow of 3.3×10^−3 m3/s. Three pellets were prepared for each temperature. After heat treatment, the pellets were removed and cooled to room temperature in desiccators. Before compression strength measurements were performed, the size of each pellet was measured to make it possible to calculate the compression strength per mm². The compression strength was measured with a standard crushing device.

Standard ash sintering test was performed according to the procedure described in CEN/TS 15370. Ash pellets with a diameter equal to their height (3.0×10^−3 m) were subjected to heat treatment at a controlled heating rate up to 1500 °C; the heating rate between 500 °C and 1500 °C was 0.083 °C/s. Images of the pellet during heating were recorded.

Fig. 6. SEM/EDX point analyses of rapeseed cake (RC) after the microsample sintering test. Results are shown on oxygen and carbon free basis.
MATLAB, and they were used to identify the phases in the ash melting process, as described in Fig. 2. The transitions were determined based on the shrinkage of the pellet area. The initial shrinkage temperature corresponds to a 5% shrinkage of the cross-sectional area. The initial deformation temperature, defined in the standard as a 15% change in the shape factor, could not be observed for the square-like cross sections, so these are not included in the results (Section 3.2.). Three replicates were performed for each fuel.

3. Results and discussion

3.1. Fuel analyses

The proximate analyses performed for each fuel were averaged, and a summary of the results appears in Fig. 3. For all four fuels, the proportion of volatile matter was similar (approximately 80%), and so was the fixed carbon content (approximately 20%) on a dry and ash-free basis. However, there is a significant difference between fermented sewage sludge and the three other fuels in terms of ash content: that of FSS is much higher, nearly 50% of the dry fuel. The origin of these samples accounts for the difference. While RC, DDGS, and PKC come from plant seeds, FSS originates from human waste. Very good reproducibility was achieved for both biomass residues and biowaste (±2% for FSS and ±1% for the other fuels).

The chemical fractionation results are shown in Fig. 4. This analysis gives some indication of the constituents with which the ash-forming elements in the fuel are combined. For example, the ash-forming matter of FSS occurs mainly in the form of iron phosphates, which are likely present because iron sulphate is used during wastewater treatment processes for the precipitation of phosphorus. The presence of aluminium silicates in the form of zeolites may also be indicated; the aluminium in the hydrochloric acid soluble fraction most probably originates from the dealumination of zeolites in the HCl solution.
Compared to the ash-forming matter of the other fuels, that of FSS is not highly soluble. The ash-forming matter of DDGS is mainly leached in water, indicating the presence of highly soluble salts of metal phosphates and chlorides. In addition, some mostly insoluble silicon is detected. The origin of the silicon might be explained by contamination with sand. Some silicon could also have accumulated in the barley grain during plant growth, most probably in soluble form. The presence of sulphur in the unleached residual fraction indicates that it is covalently bound to organic matter. In PKC, insoluble aluminium silicates, probably contaminants or residues from the production process, occur together with highly soluble potassium, phosphorus, and chlorine. Low concentrations of silicon are found in RC, in which the ash-forming matter consists of alkali metals, phosphorus, sulphur, and chlorine; they appear mainly in the fraction leached by water, indicating the presence of simple salts like alkali metal chlorides, sulphates, and phosphates. A substantial amount of sulphur was found in the residual fraction, suggesting that RC also contains covalently bound sulphur. Acid and ammonium acetate soluble phosphorus is assumed to occur in the form of phytic acid salts together with alkaline earth metals.

Depending on how it is combined with other constituents, ash-forming matter undergoes different transformations in combustion, such as oxidation (e.g., the oxidation of organic sulphur to SO2); chemical
reactions of, for example, reactive species with bed material [7]; and thermal decomposition (e.g., the calcination of calcium carbonates or loss of structural water from minerals or crystals). Consequently, how an element is combined in the fuel typically differs from how it is combined in the ash. Nonetheless, an understanding of the ash-forming matter in fuels serves as a starting point for understanding its subsequent transformations. Fig. 5 shows the composition of fuel ash prepared at 550 °C (described in Section 2.1). Despite the visible differences in the ashes, there is a common feature: the high phosphorus content. The FSS ash is dominated by iron, probably in the form of oxide, while the phosphorus could be in the form of calcium phosphates. The DDGS ash has the highest potassium and silicon content. When potassium is available for reaction with silica, it is likely that potassium silicates will form. However, the high affinity of phosphorus for potassium is expected to result in the formation of potassium phosphate [26]. The main element in both PKC ash and RC ash is phosphorus, most probably in the form of different phosphate salts, whereas in the fuels, it is organically bound. While PKC ash has high silicon and aluminium content, RC ash has the highest concentration of sodium and chlorine (approximately 9 wt.% and 1 wt.%, respectively). The ash composition of the fuels probably determines their sintering tendency, as discussed in Section 3.2.

3.2. Sintering tendency

For each fuel, the sintering tendency as determined by the microsample tests is shown in Table 1. The images used for the evaluation are included in an appendix. The first indication of FSS ash sintering was observed at 850 °C. At 950 °C, particles of the original unsintered sample could not be clearly observed, while at 1050 °C, the sample was completely sintered (labelled with 3 asterisks).

Based on Table 1, PKC exhibits the lowest sintering tendency of all the fuels considered in this work, whereas DDGS exhibits the highest sintering tendency. Already at 950 °C, the molten sample cannot be removed from the crucible. For RC, cake-like sintering could first be observed at 750 °C. However, further progression of the sintering could be observed at 950 °C. Since the tests were performed with ΔT = 100 °C, it is not possible to determine whether the change occurred at lower temperatures. Since the results are based on microscopic visual inspection, they might be somewhat subjective.

Figs. 6–9 present the SEM/EDX analyses of ash samples after the microsample sintering tests. It can be observed that the sintered FSS ash is dominated by iron oxides, whereas no large sintered particles can be seen for the palm kernel cake in the temperature range investigated. The SEM/EDX analyses of PKC samples indicate a greater presence of aluminium silicate particles and silicate particles than of alkali metal phosphate particles. The two biomass residues with the highest sintering tendency, RC and DDGS, have the highest phosphorus concentration. At 950 °C, DDGS already formed a molten amorphous phase. This sample consists mainly of potassium phosphate salts, with hardly any earth alkaline. The concentration of (Ca + Mg) in RC is much higher than in DDGS, so the further progression of sintering could be observed at 950 °C. The SEM/EDX analyses indicate that the sintering tendency of these two fuels is driven principally by the presence of alkali metal phosphate particles, as opposed to earth alkaline phosphate particles. The melting behaviour of alkali phosphates is different from that of earth alkali phosphates, which is why the shift between the two types of phosphates is of great importance during the combustion of phosphorus-rich fuels. The melting behaviour of the two kinds of phosphate was discussed by Lindström et al. [27], who studied the slagging characteristics of phosphorus fuels with and without limestone addition. She concluded that lime, as a source of calcium, contributes to the formation of high-temperature melting calcium potassium phosphates. The formation of high melting phosphates was also investigated by Barishić et al. [28], who reached a similar conclusion. Steenari et al. [13] improved the sintering tendency of rapeseed cake with the addition of kaolin as well as of limestone. The high K/Ca ratio for phosphorus-rich fuels was associated with low temperature ash sintering and melting.

The results of the pellet sintering tests are shown in Fig. 10. For each fuel, the dependence of the compression strength on the temperature is plotted. The curves have different shapes, indicating the differences in the sintering mechanisms. The leftmost points at 25 °C refer to standard ash pelletized and crushed with no prior heat treatment. This is the reference compression strength, corresponding to the unsintered area on the graphs. To determine the initial sintering temperature, the last unsintered temperature point was chosen. Changes in the compression strength below 1 N/mm² are considered to be negligible and are assumed to have no significant influence on the sintering of the ash pellets, and thus on boiler operation. The DDGS sintering curve starts to increase slowly after 450 °C, with a sharp rise at 650 °C. The sintering curve for RC shows an increase after 400 °C, and after 600 °C, there is a dramatic increase. For both FSS and PKC, no heavy sintering was observed. The sintering of FSS begins after 900 °C. The small changes in the shape of the curve before 900 °C could be the result of ash transformation, which probably does not have a major impact on the sintering of ash during boiler operation. Interestingly, PKC exhibits hardly any sintering tendency, as shown by the low peak at 900 °C.

Fig. 11 presents the standard ash sintering test results. The characteristic temperatures are defined in terms of the shapes in Fig. 2 (Section 2.2). Very good reproducibility was obtained for the triple replicates. The initial shrinkage temperature is taken to be an indication of the onset of sintering of the ash since the shrinkage is the result of a decrease in porosity, which could be caused by partial melting, viscous flow, or chemical reactions. The lowest initial shrinkage temperature, that recorded for RC, was approximately 650 °C. For DDGS, it was a little higher, approximately 720 °C, and for PKC and FSS, it was much higher, approximately 900 °C and 920 °C, respectively. The trend exhibited by the four fuels is in agreement with that for the pellet sintering tests, with the initial sintering temperature increasing in the following order: RC < DDGS < PKC < FSS. However, the pellet sintering tests suggest that the onset of sintering takes place at lower temperatures for RC and DDGS. The sintering temperatures for FSS and PKC are in good agreement with those obtained with pellet sintering. Based on the microsample sintering tests, the onset of sintering for PKC and FSS is expected to occur between 850 °C and 950 °C, which is in good agreement with the results from the other types of sintering tests performed on standard 550 °C ash. The initial sintering temperature for RC and DDGS (Table 1) is 750 °C; however, the microsample sintering tests were not performed between 550 °C and 750 °C, so it is not possible to determine whether sintering occurred at lower temperatures. Nevertheless, the results for DDGS are inconsistent: the hemisphere and flow temperatures from the ash sintering tests are significantly higher than those obtained with the microsample sintering tests. The two fuels with the lowest sintering temperatures, DDGS and RC, have the highest concentrations of water-soluble alkali metals and phosphorus. The water-soluble fraction is considered to be the reactive part of the fuel [7]. The composition of palm kernel cake is similar to
that of RC. However, their sintering tendencies differ significantly, which could be attributed to the smaller ratio of water-soluble alkali metals to earth alkaline metals in PKC; another possibility is the influence of the Al-Si in the fuel sample. As pointed out by Steenari et al. [13], phosphate species can interact with the silicate phases, but the interaction needs to be further clarified. The chemistry of FSS is dominated by iron oxides and, as concluded by Wang et al. [16], the appearance and disappearance of Fe$_2$O$_3$ in ash was the leading factor affecting the sintering of sewage sludge ash when Fe$_2$(SO$_4$)$_3$ was used at a wastewater treatment plant to precipitate phosphorus.

4. Conclusions

This work analyzed four residues from biofuel production: fermented sewage sludge (FSS); distillers' dried grains with solubles (DDGS); rape-seed cake (RC); and palm kernel cake (PKC). Chemical fractionation revealed the diversity of the fuels. The major element in all of them is phosphorus, but the combinations in which the ash-forming matter occurs are different for each fuel. The inorganic matter in FSS is dominated by iron phosphates and zeolites, while in DDGS, it is dominated by potassium phosphates and silica. The composition of RC is complex, most likely dominated by alkali chlorides, alkali phosphates, and phytic acid salts. In addition to phosphates, PKC contains aluminum silicates and iron. Differences in the ash sintering tendency arise from differences in the ash-forming matter content and the way it is combined. The lowest initial sintering temperatures were observed for RC and DDGS, for the three sintering methods, it is below 800 °C, which suggests that these fuels should not be combusted alone, without precautions against ash-related problems, no matter what the combustion technology. The low initial sintering temperatures can probably be attributed to the very high concentration of alkali metal phosphates in the ash. The PKC and FSS samples do not exhibit significant sintering below 900 °C, which could be interpreted to mean that when the combustion temperature is below 900 °C, no significant ash-related problems will occur.

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Appendix A

Micro-sample sintering test results (crucible diameter is 4 mm).
References


