



This is an author produced version of a paper published in *Fuel*.

This paper has been peer-reviewed and is proof-corrected, but does not include the journal pagination.

Citation for the published paper:

Gunnar Eriksson, Alejandro Grimm, Nils Skoglund, Dan Boström & Marcus Öhman. (2012) Combustion and fuel characterisation of wheat distillers dried grain with solubles (DDGS) and possible combustion applications. *Fuel*. Volume: 102, Number: December, pp 208-220.
<http://dx.doi.org/10.1016/j.fuel.2012.05.019>.

Access to the published version may require journal subscription.
Published with permission from: Elsevier.

Standard set statement from the publisher:

NOTICE: this is the author's version of a work that was accepted for publication in *Fuel*. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in *FUEL*, 102, December, (2012). <http://dx.doi.org/10.1016/j.fuel.2012.05.019>

Epsilon Open Archive <http://epsilon.slu.se>

**COMBUSTION AND FUEL CHARACTERISATION OF WHEAT DISTILLERS DRIED GRAIN
WITH SOLUBLES (DDGS) AND POSSIBLE COMBUSTION APPLICATIONS**

Gunnar Eriksson^{1,2}, Alejandro Grimm², Nils Skoglund,³ Dan Boström³, and Marcus Öhman²

¹Department of Forest Resource Management, Swedish University of Agricultural Sciences, S-901 83 Umeå, Sweden,

Tel. +46-90-786 84 29, fax +46-90-778 116, mobile+46-70-21 97 432

Gunnar.Eriksson@srh.slu.se

(corresponding author)

²Energy Engineering, Department of Engineering Sciences and Mathematics, Luleå University of Technology, SE-971 87

Luleå, Sweden,

³Energy Technology and Thermal Process Chemistry, Department of Applied Physics and Electronics, Umeå University, SE

SE-901 87 Umeå, Sweden.

ABSTRACT

The present transition to a sustainable global energy system requires that biomass is increasingly combusted for heat and power production. Agricultural fuels considered include alkali-rich fuels with high phosphorus content. One such fuel is wheat distiller's dried grain with solubles (wheat DDGS) from wheat-based ethanol production. Further increases in ethanol production may saturate the current market for wheat DDGS as livestock feed, and fuel uses are therefore considered. Fuel properties of wheat DDGS have been determined. The ash content (5.4 ± 1.6 %_{wt d.s.}) is similar to many agricultural fuels. In comparison to most other biomass fuels the sulphur content is high (0.538 ± 0.232 %_{wt d.s.}), and so are the contents of nitrogen (5.1 ± 0.6 %_{wt d.s.}), phosphorus (0.960 ± 0.073 %_{wt d.s.}) and potassium (1.30 ± 0.35 %_{wt d.s.}). To determine fuel-specific combustion properties, wheat DDGS and mixes between wheat DDGS and logging residues (LR 60 %_{wt d.s.} and DDGS 40 %_{wt d.s.}), and wheat straw (wheat straw 50 %_{wt d.s.}, DDGS 50 %_{wt d.s.}) were pelletized and combusted in a bubbling fluidised bed combustor (5 kW) and in a pellets burner combustor (20 kW). Pure wheat DDGS powder was also combusted in a powder burner (150 kW). Wheat DDGS had a high bed agglomeration and slagging tendency compared to other biomass fuels, although these tendencies were significantly lower for the mixture with the Ca-rich LR, probably reflecting the higher first melting temperatures of K-Ca/Mg-phosphates compared to K-phosphates. Combustion and co-combustion of wheat DDGS resulted in relatively large emissions of fine particles (<1 µm) for all combustion appliances. For powder combustion PM_{tot} was sixteen times higher than from softwood stem wood. While the Cl concentrations of the fine particles from the mixture of LR and wheat DDGS-mixture in fluidised bed combustion were lower than from combustion of pure LR, the Cl- and P-concentrations were considerably higher from the wheat DDGS mixtures combusted in the other appliances at higher fuel particle temperature. The particles from powder combustion of wheat DDGS contained mainly K, P, Cl, Na and S, and as KPO₃ (i.e. the main phase identified with XRD) is known to have a low melting temperature, this suggests that powder combustion of wheat DDGS should be used with caution. The high slagging and bed agglomeration tendency of wheat DDGS, and the high emissions of fine particles rich in K, P and Cl from combustion at high temperature, mean that it is best used mixed with other fuels, preferably with high Ca and Mg contents, and in equipment where fuel particle temperatures during combustion are moderate, i.e. fluidised beds and possibly grate combustors rather than powder combustors.

Keywords: biofuel; combustion; ash transformations; alkali; phosphorus

1. Introduction

The present transition to a sustainable global energy system requires that potentially problematic types of biomass with unfamiliar properties are increasingly combusted for heat and power production. One such fuel is residues from wheat-based ethanol production, known as wheat distillers dried grains (wheat DDGS), which may become available in considerable quantities for fuel uses. The worldwide ethanol production of 38.2 million cubic metres in 2006 (216 TWh), is modest

compared to the annual energy use within the transport sector of more than 10 000 TWh, of which 95 percent is fossil [1]. Apart from sugars, directly fermentable to ethanol, the main source of ethanol is currently starch from corn (maize) and wheat. Wheat grain is the most common feedstock for ethanol in the EU, with a production capacity of 1.51 million cubic metres annually, and 1.16 million cubic metres under construction [2]. The installed capacity in Canada is 0.382 million cubic metres [3]. Only about 50 percent of the energy in the wheat grain can be converted into ethanol. About 30 %_{wt a.r.} of the grain feedstock is converted to wheat DDGS, and is mainly used as a source of protein and energy for ruminants. Further increases to replace a more substantial fraction of the world's transport fuel use may saturate this market, and uses like combustion or anaerobic digestion to biogas may therefore be considered. Combusting it to supply heat for the ethanol production process would contribute to the net environmental benefits of ethanol as a transport fuel. Ethanol production can also be a way to utilise part of the heat from combined-heat and power production as recommended by the US Environmental Protection Agency (EPA) [4]. In the US, where expanded production has lowered the prices, the use of maize-based DDGS for process heat production has been studied by Morey et al. [5]. In Canada, supply of DDGS will exceed the demand for livestock feed at an ethanol production of about 11 TWh (including maize-based production which also generate livestock feed) [3]. In Sweden, the demand of wheat DDGS for livestock feed will be exceeded at an ethanol production of 2-3 TWh (about 5 percent of current gasoline use) [6].

To produce ethanol, wheat grains are ground to meal, which is mixed with water and enzymes. The starch, (60 %_{wt d.s.}) is hydrolysed to sugars. Yeast is added, fermenting the sugars into ethanol at a theoretical yield of 51 %_{wt}. The ethanol is separated from the slurry through distillation. The solid material in the ethanol-free slurry (whole stillage) is separated through centrifugation from the liquid (thin stillage), which is filtered and concentrated through evaporation of moisture. After remixing and drying the resulting distillers' dried grains with solubles (DDGS) are pelletised. The amount of DDGS produced is roughly equivalent to 30 %_{wt a.r.} of the wheat grain feedstock [7, 8]. Removing the starch concentrates the inorganic elements, and wheat DDGS has high concentrations of K [9, 10], known to contribute to ash-related operational problems, e.g. fouling and high-temperature superheater corrosion [11]. Wheat DDGS also has high concentrations of P [12, 13], which is known to interact with K, e.g. reduce the risk of high temperature corrosion [14] and form potassium phosphates with low melting points which may cause slagging [15]. Several phosphorus-rich fuels have been found to have problematic properties, including meat and bone meal [16, 17], chicken litter [18], sewage sludge [19] and peat [20]. Very little work has been devoted to alkali-rich fuels with high phosphorus content, as most combustion studies concern agricultural residues where silicon forms the main anions, e.g. straw and most short-rotation energy crops. Among the exceptions are meat and bone meal [16, 17], sewage sludge [21], cereals [22], rape seed cake [23], rapeseed meal (RM) [24, 25] and barley DDGS [26]. Phosphorus may be present either in inorganic/mineral form (e.g. meat and bone meal, sewage sludge) or in organic form (e.g. RM, cereals, DDGS).

Lindström et al. measured slag formation from the combustion of cereals (wheat, barley, ray and oats) in a small-scale horizontal burner, with wheat combustion resulting in more slag than the other fuels [27]. Rapeseed meal, with high

concentrations both of P and of K, was not unduly problematic in grate and fluidised-bed combustion, as its reasonably high concentrations of Ca and Mg raised the first melting temperatures of ashes. On the other hand, powder combustion of rapeseed meal resulted in K- and P-rich compounds with amorphous structure (from previous melting), suggesting likely fouling problems from use at high combustion temperatures [25]. Wheat DDGS differ from rapeseed meal as it has much lower concentrations of Ca and Mg, and compared to wheat cereals, it contains more S as well as having far higher total concentrations of ash-forming elements.

The interaction between P and K is complex. The affinity to P may mean that the mass fraction of K that either forms coarse particles or is retained in the furnace (e.g. in the bottom ash) is increased. Phosphorus may cause problems in the furnace as many K-phosphates have low first melting temperatures which could lead to slagging and bed agglomeration, a risk which may be reduced if they react with CaO/MgO to K-Ca-Mg-phosphates with higher melting points [28]. The interaction of K, Ca and P in a ternary system has been studied by Novakovic et al. [29], who found that a decrease in the Ca/P-ratio lead to a decrease in the K-release rate. Wheat DDGS also have high S-concentrations [13]. The presence of SO₃ in the flue gas may lead to the sulphatization of KCl. Elled et al. combusted municipal and paper mill sludges in a fluidised bed, the former fuel having far higher P-concentration. They found that phosphorus increased the emissions of SO₂, as Ca-phosphates were formed rather than calcium sulphates [30]. Regarding P-rich fuels, another consideration is the limited supply of soluble phosphorus, which is an essential nutrient. As some reuse of phosphorus-rich agricultural residues will probably be required [31], the feasibility of phosphorus recovery from the ash will be an important issue, requiring improved knowledge of its ash transformations.

Thermal gasification experiments with wheat DDGS have been performed by Tavasoli et al. [12], in a fixed-bed micro reactor. Removal of fibers (about 12 percent of the mass) from corn-based DDGS has been attempted experimentally to increase its nutritional value and digestibility for pigs and poultry [32]. Biogas production through anaerobic digestion has also been used [33]. Thus, only a limited number of studies have previously been published on combustion and gasification of DDGS and of these only Tavasoli's study concerns wheat DDGS. There are no studies known to the authors about ash transformations in combustion of wheat DDGS.

The objective of this work was therefore to

- (i) determine the fuel and combustion properties of wheat DDGS, including gaseous emissions, particle emissions, ash transformations and risks of ash-related operational problems;
- (ii) identify suitable uses of wheat DDGS in mixes with other biomass fuels or as additives to other fuels.

2. Method

2.1. Characterisation of fuel properties of wheat based DDGS.

The ETDE [34] and the Web of Science databases were used. The only fuel analysis found was the work by Tavasoli et al. [12], which did not include concentrations of ash-forming elements. Several published feed analyses were found and in addition an ethanol producer in northern Europe provided feed analyses (including moisture content, ash content, concentrations of P, K, Ca, Mg, Na, As, Cd, Hg and Pb). From these analyses the ranges of variation in fuel-/feed analyses properties were determined.

2.2. Fuel used for combustion tests. A relatively typical wheat DDGS sample from an ethanol producer in northern Europe was selected for the present study. The sample was analysed for moisture content (SS-1871 70), volatile content (ISO-562), ash content (SS-18 71 71), lower heating value (SS-ISO 1928), elementary composition (C, H, O, N), sulphur content (SS-18 71 77) and chlorine content (SS-18 71 54). Contents of main ash-forming elements (including Si, K, Na, Ca, Fe, Mg, Al, P and Mn) were determined using inductively-coupled plasma-atomic emission spectroscopy (ICP-AES). Contents of trace elements were determined using ICP-AES for As, Cd, Co, Cu, Hg, Ni, Pb, B, Sb and Se and using inductively-coupled plasma mass spectroscopy (ICP-MS) for Ba, Cr, Mo, Nb, Sc, V, W, Y, Zn and Zr.

Handling and feeding of biomass fuels may be problematic. To determine the risk of DDGS powder forming bridges, a test designed by Paulrud et al. was employed [35], using vertical funnels of different opening sizes, with a minimum of 60 mm. Thermo-Gravimetric Analysis (TGA) of DDGS was performed to compare the devolatilisation rate with the one of typical softwood stem wood powder [25]. A heating rate of 20 °C per minute was used. The purge gas was nitrogen (100 ml/min). The sample mass used was 14 mg for wheat DDGS and 5-6 mg for wood.

In two of the three combustion experiment series with a fluidised bed and an underfed pellet burner, respectively, pelletised fuel was used. In the third, pulverised DDGS fuel was used, with softwood stem wood powder [25] used for comparison. Pellets (8 mm diam.) of wheat DDGS as received were used for the combustion tests. In addition, tests were made with pelletised (8 mm diam.) mixtures of DDGS and two other biomass fuels. These were logging residues (LR) and wheat straw. DDGS was mixed with LR at 40 %_{wt d.s.} and with wheat straw at 50 %_{wt d.s.} For the combustion experiment with DDGS pellets in the underfed pellet burner, combustion could not be sustained due to severe slag formation, and therefore a mixture of DDGS pellets and 50 %_{wt a.r.} of wood pellets was used (the DDGS contributing to 90 percent of the ash content of the mix).

For the powder combustion tests, ground DDGS pellets were used. Sieving showed that the resulting DDGS powder was slightly finer than wood powder, with particles with diameters below about 260 µm making up 50 percent of the mass. The composition of the raw materials used (before pelletisation) and of the fuels used in the combustion experiments is shown in tables 1-2 and 3, respectively.

2.3. Combustion tests in a fluidised bed. Each of the pelletised fuels was combusted in a bench-scale fluidised bubbling bed (5 kW) (figure 1). The bed material consisted of quartz sand (at least 98 %_{wt} SiO₂) with grain diameters between 200 and 250 µm. All fuels were first combusted at a bed temperature of 800 °C for 8 hours (corresponding to a total amount of 5 kg fuel/experiment) or until bed defluidisation occurred. For fuels containing wheat straw, a bed temperature of 730 °C instead of 800 °C was used. During combustion of DDGS and wheat straw-DDGS bed defluidisation occurred after 2 hours and 1 hour, respectively. The temperature in the freeboard was 800±15 °C. The temperatures were controlled via individual regulation of the wall heating sections. During combustion the oxygen content in the dry gas was 8-10 percent and the CO concentration was below 100 ppm. The fluidising velocity was 1 m/s, corresponding to ten times the minimum fluidising velocity. Bed agglomeration tendencies of the fuels were quantified using a method developed and evaluated by Öhman and Nordin [36]. The reproducibility of the initial defluidisation temperature measured with this method has previously been determined to be ± 5 °C (SD) [36]. After the combustion had been completed, the bed temperature was raised at a constant rate of 3 °C per minute by heating of the primary air and of the bed section walls. Combustion of propane gas in a chamber prior to the primary air distributor plate was started to keep the temperature uniform and provide realistic combustion atmosphere during the temperature staging. Four bed temperatures and four differential pressures were recorded to detect initial bed agglomeration. After each experiment, all bed material/agglomerates were collected for further chemical analysis. During the combustion period, flue gas of about 200 °C was sampled after the cyclone (cut-off size 10 µm) and concentrations of O₂, CO and NO were continuously measured using a Testo XL 350 gas analyser (electrochemical sensors). The concentrations of SO₂ and HCl were continuously monitored using Fourier transform infrared spectroscopy (FTIR).

Total particulate matter (PM_{tot}) mass concentrations were measured through isokinetic sampling from the flue gas at about 160 °C using conventional equipment with quartz fiber filters. The PM mass size distribution was determined in a 13-stage low-pressure cascade impactor (LPI) from Dekati Ltd, which separates particles according to their aerodynamic diameter in the interval of 0.03-10 µm. The impactor was heated to around 120 °C during the sampling. Aluminum foils (not greased) were used as substrates in the impactor.

An air-cooled deposition probe with test rings of stainless steel, simulating super heater tube surfaces, was used to collect deposits in the freeboard. The metal temperature of the steel rings was measured by thermocouples and regulators controlled the flow of cooling air on the inside the test ring. During all experiments, the ring surface temperature was set to 450 °C and the exposure (sampling) time was 6 h. The temperature around the deposition probe was 800 °C at all tests. The residence time of the flue gas from the bed section to the deposit sampling point was about 12 s. Particles for PM_{tot} and impactor measurement were collected at a lower temperature, at a distance further downstream corresponding to a difference in residence time of 1 s at most.

2.4. Combustion experiments in an underfed pellet burner. An underfed residential pellet combustor was used to simulate conditions in a large-scale grate combustor (figure 2). For the combustion tests, a typical underfed pellet burner (Eco-Tech A3, 20 kW), was selected. The burner was installed in a reference boiler (Combi fire) used for the national certification test of residential pellet burners in Sweden. For combustion of LR, LR-DDGS and DDGS/wood pellets, the experiments lasted approximately 24 h with continuous operation at a constant fuel power of 12 kW. For the wheat straw and the wheat straw-DDGS mixtures, initial slagging occurred approximately 20 minutes from the start of the experiments and they were terminated due to severe slagging after 4h and 4h 20 minutes, respectively.

Three thermocouples of type N were situated on different levels above the burner grate. By continuous measurements during the experiments, the maximum combustion temperature in the region where the slag was formed, i.e. on the burner grate, was estimated to be about 1200 - 1250 °C. For wheat straw and wheat straw-DDGS the temperature may have been lowered during the later part of the experiment due to slagging, otherwise these temperatures did not vary for the different fuels used. The air flow was set to a level corresponding to 9-10 percent O₂ in the dried flue gas for all tests. The flue gas CO concentration was on average below 500 ppm in all experiments, but due to slagging there were periods with higher CO concentrations. The procedure for analysis of flue gas composition, flue gas particulate matter content and size distribution of the particles, was similar to the other combustion tests (described in the previous section) except that the flue gas temperature was 150 °C. For the DDGS/wood pellets fuel mixture, the flue gas composition, flue gas particle matter content and size distribution of the particles were not analysed because of the potential influence of the inhomogeneous fuel composition.

The residual matter after full conversion of fuel pellets in an underfed pellet burner was distributed between:

- molten ash (slag) deposited in the burner or pushed over the burner grate edge down to the bottom of the boiler
- non-molten ash at the bottom of the boiler (bottom ash) and
- fly ash.

All molten particles greater than 3 mm were removed from the bottom ash by sieving and characterised as slag. The amount of deposited matter in the burner as well as in the boiler (i.e. bottom ash and slag) was quantified after each experiment and the products were collected for analysis, described in section 2.6. A previous study has shown that the variation in the slag formation between replicate combustion experiments is minimal [37].

2.5. Combustion tests in a powder burner. Combustion of wheat DDGS was tested in a 150 kW VTS swirling powder burner with three sets of air vanes with separate flow control. A reference test with commercial wood powder was done for comparison [25]. The outer diameter of the burner was 130 mm. Fuel was transported pneumatically along the axis of the burner, with three annular sets of swirl vanes. The average fuel flow was 21 kg per hour and the air flow was adjusted for an oxygen concentration of 3.5 to 4 percent in the dried flue gas. The respective airflows as percentage of total flow were

transport air (10 percent), primary air (20 percent), secondary air (30 percent) and tertiary air (40 percent). The internal cross-section of the furnace was 550 times 550 mm, and its inner length was 3 100 mm. The measured furnace temperature was 1 100 °C (T1 and T2) which was lowered to 950 °C at the end of the furnace (T4). The locations of the thermocouples used are shown in figure 3. Oil was used to heat up the combustion chamber. At a temperature of 900 to 950 °C the oil flow was cut off and the powder feeding was started.

The procedure for analysis of flue gas composition, flue gas particulate matter content and size distribution of the particles was similar to the previous combustion tests (described in section 2.3). An air-cooled deposition probe, similar to the one used for the fluidised bed tests was mounted at the end of the combustion chamber (position shown in figure 3). Again, the ring surface temperature was set at 450 °C, and the exposure time was 6 h. After the end of the powder burner tests, ash from the burner and ash from the bottom of the furnace and ash from the boiler were collected for further analysis.

2.6. Analysis of bed material, -agglomerates, slags, bottom ashes and particles. Bed material and agglomerates from the fluidised bed, slags/bottom ashes from the underfed pellet burner, slags/bottom ashes from the powder combustor and the downstream boiler were studied with analysis methods described below. Particles collected in all impactor tests and deposits on all tests rings were also analysed. Morphologies were studied with scanning electron microscopy (SEM) and elemental compositions analysed using EDS (energy-dispersive X-ray analysis) spot- and area analyses (100x100 µm). For all combustion tests, fine-mode fly-ash particles from impactor plates 4, 5 and occasionally 6, with geometric mean diameters (GMD) of 0.19, 0.32 and 0.52 µm respectively, were analysed with SEM/EDS. For the fluidised bed tests (which resulted in bi-modal particle size distributions), the coarse particles collected on impactor plates 10 (GMD 3.3 µm) and in some instances plate 12 (GMD 8.7 µm) were also analysed by the same method.

Bed samples and agglomerates from the fluidised bed were mounted in epoxy, cut, polished and analysed with SEM/EDS to determine their morphology and elemental composition. From the deposit probes, lee- and wind-side deposits were analysed with SEM/EDS. Slag and bottom ashes from the grate combustion and from the powder combustion were also analysed using SEM/EDS. Qualitative measurements of crystalline phases in slag and bottom ash from the grate combustor tests and bottom ash from the powder burner were made using X-Ray Diffraction (XRD). XRD was also used for the fine-mode and coarse-mode particles from the fluidised bed tests, the grate combustion tests and the powder burner tests, with the same impactor stages selected as previously. Finally, lee-and wind side materials from the deposition probes used in the fluidised bed tests and powder burner tests were studied with XRD.

3 Results

3.1. Characterisation of fuel properties. The literature data and the analysis of the samples used for the experiments [41] show that the moisture content of wheat DDGS is 6.2-14 %_{wt} (with an average of 9.7 %_{wt} and a stdev. of 2.2 %_{wt} [13, 38, 39]

and that the ash content varies from 3.6-8.4 %_{wt d.s.} (av. 5.4 and stdev. of 1.6 %_{wt d.s.}) [7, 9, 13, 39, 40]. As feed analysis usually concerns protein, fat and other nutrients, elementary distributions are usually not reported. Tavasoli reported a distribution among C, H, O and N of 45.1 %_{wt d.s.}, 7.0 %_{wt d.s.}, 42.5 %_{wt d.s.} and 5.1 %_{wt d.s.}, respectively [12]. This may be compared to the values obtained from the analysis of the experimental sample which were 48.0 %_{wt d.s.}, 6.9 %_{wt d.s.}, 33.5 %_{wt d.s.} and 5.9 %_{wt d.s.}, respectively. The sample used for experiments had a volatile content of 77.6 %_{wt d.s.} and a calorific heating value of 20.6 MJ/kg _{d.s.}, and no data for these properties were found in other sources.

For main and ash forming main elements, the analyses of wheat DDGS (for the experimental sample and from other sources) are summarised in table 4. DDGS had high contents of nitrogen (5.5 %_{wt d.s.} ± 0.6). Among the main ash-forming elements, the phosphorus content was high (0.960 %_{wt d.s.} ± 0.073), while the calcium content was relatively low (0.159±0.094). The potassium content of 1.30 %_{wt d.s.} ± 0.35 was also relatively high. The magnesium concentration reported in the feed analysis were 0.40-0.60 %_{wt d.s.}, above the experimental batch (0.278 %_{wt d.s.}) [9, 10]. The sulphur content was mostly high, with an average of 0.538 and a stdev. of 0.232 %_{wt d.s.}. The sulphur content reported by Tavasoli [12], 0.3 %_{wt d.s.}, is far below the concentration in the experimental batch which was 1.03 %_{wt d.s.} and below all other data found. Silicon concentrations were not mentioned in the feed analyses reported but were relatively low in the used sample in the experiments (0.100 %_{wt d.s.}). The chlorine concentration in the batch used for the experiments was 0.22 %_{wt d.s.}. The most common trace elements in the batch used for the experiments were zinc and copper, with concentrations of 68.5 and 12.1 mg/kg, respectively.

The feeding properties of DDGS according to the funnel test were good. DDGS passed through a 60 mm opening without any tendency to bridging, while wood powder has been reported to form bridges at this diameter [35]. TGA measurements showed that the pyrolysis of DDGS has a characteristic temperature of 330 °C. Devolatilisation starts at about 135 °C (at a lower temperature than for wood powder), and proceeds to a conversion of about 67 % of the dry matter.

3.2. Gaseous emissions. The NO concentrations were generally high for combustion experiments of DDGS and DDGS-mixtures compared to LR, wheat straw and wood, reflecting the high nitrogen concentration in the fuel (see table 5).

Emissions of SO₂ from fluidised combustion of DDGS were very high compared to the co-combustion fuels. The emissions from LR-DDGS- and wheat straw-DDGS mixtures were lower although still more than a factor of hundred higher than the emissions from LR and wheat straw combustion. Grate combustion of the LR-DDGS mixture produced emissions which were two orders of magnitude higher than from LR combustion. Emissions from grate combustion of the wheat straw-DDGS mixture were a factor of six higher than from grate combustion of pure wheat straw. Fluidised-bed combustion of DDGS converts more than 45 percent of the sulphur content of the fuel into SO₂, while for the LR-DDGS- and wheat straw-DDGS-mixtures, only about 40 and 30 percent, respectively, are converted. For grate combustion of LR-DDGS, about 50 percent of

the sulphur is converted into SO₂. For powder combustion, a fraction of about 80 percent of the sulphur resulted in emitted SO₂. The SO₂ emissions from the experiments are shown in table 6.

For fluidised-bed combustion, the HCl emissions from DDGS (100 mg/Nm³ at 10% O₂ concentration in dry flue gases) were more than twice as large as the emissions from wheat straw. The mixed fuels (LR-DDGS and wheat straw-DDGS) had comparable HCl emissions to wheat straw but about 100 times higher than for LR combustion. For grate combustion, the HCl emissions from the LR-DDGS and the wheat straw-DDGS mixtures were lower compared to the fluidised bed (14 and 13 mg/Nm³, respectively), which is comparable to wheat straw combustion but three times as high as for LR combustion. From powder combustion of DDGS, the HCl emissions were below 3 mg/Nm³ at 10% O_{2 d.g.}

3.3. Particle emissions. From fluidised-bed combustion, the total particle emissions from the mixture of LR-DDGS were slightly higher than for pure LR. The total particulate matter mass concentrations are shown in table 7. The particle mass size distribution (shown in figure 4, upper) consisted mainly of fine-mode particles (aerodynamic diameters below 1 µm) and for the co-combustion fuels LR and wheat straw and for the LR-DDGS mixture, there were also coarse-mode fractions (diameters above 1 µm). A comparison between the size distributions of the particles produced from fluidised-bed combustion of LR and of the LR-DDGS mixture shows that there is a large increase in the mass concentration of finer particles as DDGS is added to the fuel. The total particulate matter emissions from the fluidised-bed combustion of wheat straw-DDGS and pure DDGS were not analysed due to fast defluidisation in the experiment. In addition, impactor sampling was not done for the straw-DDGS experiment due to total defluidisation within 1 hour.

Grate combustion of the LR-DDGS mixture resulted in emissions of total particulate matter which were more than three times higher than from combustion of unblended LR (figure 4, middle). Again, as the particle size distribution showed an increase in finer particles for combustion when DDGS was added to LR (although a superimposed peak around 0.1 µm which is probably caused by soot particles should be taken into account, the effect is still evident). Compared to grate combustion of wheat straw, combustion of the wheat straw-DDGS mixture leads to a slight reduction of fine mode particles as well as of the total particle emissions. No coarse mode fraction was present in the flue gas from the experiments in the pellets burner.

For powder combustion, particle emissions for DDGS were 16 times higher than for wood, with a particularly large increase of the amount of fine-mode particles. Particles from powder combustion were mainly of sizes below 1 µm. The particle mass size distributions of the particles from the combustion tests are shown in figure 4 (lower).

The fine-mode particles from fluidised-bed combustion of LR pellets consisted mainly of the elements K, Cl and S (apart from O). Adding DDGS results in particles with very low Cl concentrations, which mainly contain K and S. For LR-DDGS, XRD analysis showed that the fine-mode particles contained K₂SO₄, with some K₃Na(SO₄)₂. The fine-mode particles from

pure DDGS also contained mainly potassium and sulphur, with K_2SO_4 detected with XRD. The coarse-mode particles from fluidised-bed combustion of LR are mainly composed of Ca, Si and K (apart from O), with $Ca_3MgSi_2O_7$, MgO, $MgSiO_3$ and $Ca_5(PO_4)OH$ as the major phases detected with XRD. The coarser particles from the LR-DDGS mixture are mainly composed of Ca, S, Si, P and K (apart from O), with $CaSO_4$ and $CaMg(SiO_3)_2$ as the only phases detected with XRD.

As no impactor measurements were made for the mixture of wheat straw and DDGS due to fast defluidisation, SEM/EDS and XRD analyses were made for the larger particles separated in the cyclone from the wheat straw-DDGS flue gas, which consisted mainly of Si, K, P, Mg and S (apart from O) with K_2SO_4 and $CaK_2P_2O_7$ detected with XRD.

Grate combustion of LR resulted in particles with K, S and Cl (apart from O) as main elements, with K_2SO_4 and $(K, Na)_2SO_4$ detected with XRD. The LR-DDGS mixture produced particles with nearly the same composition when combusted, except that a significant amount of P was present. Unlike fluidised-bed combustion, the Cl concentration was slightly increased. Wheat straw pellets combustion resulted in particles with mostly K, Cl and S. Phases identified using XRD were KCl and K_2SO_4 . Addition of DDGS to the wheat straw will enhance the P concentrations and reduce the particle Cl concentrations, although the remaining Cl concentration is much higher than for fluidised-bed combustion of the same fuel. Detected phases with XRD in Wheat straw-DDGS combustion were K_2SO_4 and KCl.

Both the fine- ($< 1 \mu m$) and the coarse ($> 1 \mu m$) mode particles from combustion of pulverised DDGS contained K, P, Cl, Na and S (apart from O). Phases identified using XRD were KPO_3 , KCl and $(K,Na)_2SO_4$ in both the fine- and coarse-mode particles. Particles from combustion of wood powder consisted mainly of K, S and Na.

3.4. Bed agglomeration. DDGS and the mixture of wheat straw and DDGS had very high bed agglomeration tendencies. The mixture of LR and DDGS had a considerably lower bed agglomeration tendency than the DDGS fuel. The determined initial defluidisation temperatures for the different fuels are listed in table 8. More detailed information about the bed agglomeration processes during these experiments have been reported elsewhere [41].

3.5. Slag formation. The slagging tendencies of the combusted fuels, expressed as the fraction of in going amount of fuel ash that forms slag, is shown in table 9. The DDGS pellets mixed with wood pellets and the wheat straw pellet had a relatively high slagging tendency. By mixing the DDGS with logging residues the slagging tendency was decreased but still moderate. The wheat straw-DDGS mixture had a slagging tendency which was slightly lower than that of the unblended wheat straw.

The slag from combustion of DDGS pellets (mixed with wood pellets) contained, apart from O, mainly K, P and Mg and also some Na, Si and Ca. Phases detected with XRD from DDGS/wood combustion were $CaK_2P_2O_7$, $KMgPO_4$, $K_2MgP_2O_7$ and

CaKPO₄. Slag from the LR-DDGS mixture contained (apart from O) mainly Si, P, K, and Ca with some Mg and Na. Phases detected with XRD in the slag from LR-DDGS were CaKPO₄, KMgPO₄ and (Na, Ca)Al(Si, Al)₃O₈.

The elements detected in slag from combustion of the wheat straw-DDGS-mixture were K, Si, P and smaller amounts of Mg, Na and Ca (apart from O). Compared to the DDGS-wood pellets combustion, the mixture with wheat straw had higher concentrations of Si, and lower concentrations of P and Mg, while the K-, Ca- and Na-concentrations were roughly the same. Phases detected with XRD in the slag from wheat straw-DDGS were CaKPO₄ and KMgPO₄. The slag produced during combustion of wheat straw contained mainly (apart from O) Si, K and Ca. In combustion of logging residues a slag rich in Ca, Si, K and Mg was produced.

Combustion of ground DDGS pellets in the powder combustor resulted in the formation of hard glass-like slag on the bottom of the furnace, and less hard slag on the burner cone. The slag from the furnace bottom and the burner cone contained (apart from O) mostly K, P, Na and Mg. Phases identified with XRD were KMgPO₄, CaK₂P₂O₇ and Mg₃(PO₄)₂.

3.6. Deposit formation. Deposits on the lee-side of the cooled probe from fluidised bed combustion of the LR-DDGS mixture contained mainly K and S (apart from O). K₂SO₄ was detected with XRD, and so were smaller amounts of K₃Na(SO₄)₂, CaSO₄, Ca₃Mg(SiO₄)₂ and CaK₂P₂O₇. The wind-side deposits from LR-DDGS combustion contained mainly S, Ca and K (apart from O). In the wind-side deposits from LR-DDGS, the most common phases detected with XRD were CaSO₄, K₂SO₄ and K₃Na(SO₄)₂. Compared to deposits from LR-combustion, the Cl-concentration in the lee deposits from the mixture is much lower i.e. K and S are dominating elements.

The lee-side deposits from LR combustion were mostly composed of K, Cl and Ca (apart from O). The main phases detected with XRD from the LR lee side deposits were KCl, CaCO₃, CaSO₄, K₂SO₄ and K₃Na(SO₄)₂. LR combustion resulted in wind-side deposits of Si, Ca and K, with the phases CaCO₃, NaAlSi₃O₈, CaSO₄, KAlSi₃O₈, Ca₃Mg(SiO₄)₂ and Ca₅(PO₄)₃OH detected with XRD.

Lee-side deposits from the fluidised combustion of pure DDGS were not found in sufficient quantities for separate analysis, due to the fast bed defluidisation causing premature shutdown of the experiment. The wind-side deposits contained (apart from O) mainly K, P, Mg, Si, Na and S. The phases detected with XRD from pure DDGS on the wind side included CaK₂P₂O₇, K₂MgP₂O₇, (K,Na)₂MgP₂O₇ and β-K₂SO₄. Deposits on the lee-side of the probe from wheat straw-DDGS-contained mostly K and S (on an O-free basis), and phases detected with XRD were K₂SO₄, K₃Na(SO₄)₂, CaK₂P₂O₇ and Ca₃Mg(SiO₄)₂. The wind-side deposits from wheat straw-DDGS contained mainly the elements K, Si, P and Mg, with the phases CaK₂P₂O₇, K₂SO₄, KMgPO₄ and NaAlSi₃O₈ detected with XRD. During wheat straw combustion the lee-side

deposits contained mostly K, Cl and S i.e. the Cl concentration was higher than for the wheat straw-DDGS combustion. More detailed information about the deposit formation from the experiments in the fluidised bed have been reported elsewhere.[41]

The lee-side deposits from combustion of pulverised DDGS contained (apart from O) mainly K, P and also some content of Na, S and Cl. Phases detected with XRD of the lee-side deposits were K_2SO_4 , KCl, $KMgPO_4$ and traces of SiO_2 . The wind-side deposits from combustion of pulverised DDGS contained (apart from O) mainly P, K, Mg and also some content of Ca and Si. On the wind-side, $KMgPO_4$ and $CaK_2P_2O_7$ were detected.

4. Discussion

4.1. Fuel properties. Ground wheat DDGS can be fed without bridging problems. TGA did not indicate any difficulties regarding combustion stability, and combustion of pulverised fuel in the powder burner worked without difficulties, regarding combustion stability. The sulphur concentration of 0.3 %_{wt d.s.} reported by Tavasoli [12] is far below the concentration in the experimental sample, 1.03 %_{wt d.s.} and is also lower than the other published sulphur concentrations. Compared to barley DDGS [26], the studied sample of wheat DDGS had similar concentrations of K, Ca and P, higher concentrations of Mg and lower concentrations of S, Si and Cl. The HHV and the contents of moisture, ash, sulphur and chlorine for DDGS can be compared with those of other biomass fuels in table 10. The HHV of 21.6 MJ/kg d.s., of the DDGS used in this work, is typical of biomass fuels. The moisture content of 6.2-14 %_{wt} is sufficiently low for combustion without further drying of the fuels. The ash content of 5.4 ± 1.6 %_{wt d.s.} is higher than for most forest fuels and in the same range as for many agricultural fuels.

The concentration of nitrogen in DDGS of 5.1-5.9 %_{wt d.s.} is high in comparison to many other biomass fuels and also high in comparison to grain, which has a nitrogen concentration of 1.0-2.9 %_{wt d.s.} (average 1.86 %_{wt d.s.}) [43]. As the starch is converted into sugars which are dissolved, the other grain components like proteins and fat remain in the solid material. This will tend to increase the nitrogen concentration in the solid. Another possible source of nitrogen is residual enzymes.

The sulphur content of 0.538 ± 0.232 %_{wt d.s.} for wheat DDGS is higher than for most forest and agricultural fuels. Several waste fuels have comparable or higher sulphur concentrations, e.g. sewage sludge, forest industrial wastes, manure and waste leather. As the sulphur content of grain is 0.08 to 0.2 %_{wt d.s.} (0.126 %_{wt d.s.} average) [43], there is thus a considerable addition of sulphur in the ethanol production process, probably from the enzymes. The chlorine content is in the same range as in many other agricultural fuels as shown in figure 5.

A comparison of the ash-forming main elements in the DDGS used in this work and other biomass samples is shown in figure 5. The potassium concentration in the fuel is comparable to typical wheat straw and rapeseed meal fuels but in comparison to these fuels the $([Ca]+[Mg])/[K]$ ratio is relatively low in the fuel. This could potentially (as shown in this

work) lead to ash related problems such as slagging and bed agglomeration, as observed for barley DDGS despite its corresponding ratio being slightly higher [26]. The phosphorus concentration in the fuel ash of wheat DDGS is relatively high in comparison with many other biomass fuels but at the same level as in rapeseed meal.

4.2. Gaseous emissions. The high emissions of NO, SO₂ and HCl (in fluidised bed combustion) suggest that DDGS should preferably only be used as a fuel/co-combustion fuel (in significant amounts) in combustion applications with proper flue gas cleaning.

The fraction of the fuel S which was converted to SO₂ was 45 % during fluidised bed combustion and 80 % during powder combustion, which indicates higher interaction with other ash-forming elements in fluidised-bed combustion, e.g. formation of sulphates which are more stable at lower temperature. The HCl emissions during fluidised bed combustion of DDGS were about twice as high as during wheat straw combustion suggesting that less K was available for KCl formation in DDGS combustion. This difference was observed despite the two fuels having similar molar ratios of potassium and chlorine, [K]/[Cl] being close to four in both cases. A likely explanation is the high phosphorus content of the DDGS, resulting in capture of potassium to different phosphates.

The high HCl emissions during DDGS and DDGS-mixture combustion are probably caused by the strong affinity of phosphorus to potassium i.e. potassium is captured to different phosphates and is therefore not available for KCl-formation.

4.3. Particle emissions. Adding DDGS to either logging residues or wheat straw during fluidised bed combustion strongly reduced the Cl concentration in the fine particles. Despite the high chlorine content of this fuel, the potential risk for Cl-induced high temperature corrosion could thus be reduced. The coarse particle mode that was formed during combustion at relatively low temperature in the fluidised bed, consisted mainly of different Ca-K-Mg phosphates/silicates for the DDGS and DDGS mixtures. Compared to LR, there was an increased P-concentration in the coarse particles.

The fine particles from grate combustion of the DDGS mixtures had considerably higher Cl- and P-concentrations, compared to the fine particles from fluidised bed combustion of the same fuels. The HCl emissions were also significantly lower in the pellets burner experiments than in the fluidised bed experiments. The reason is probably the higher process temperature (fuel particle temperature) during combustion in the pellet burner, causing evaporation of K and P from the potassium rich melt formed. The small quantities of coarse particles detected may be caused by the relatively low gas velocities in the pellet burner equipment compared to commercial grate boilers, with coarser particles being deposited in the furnace or the boiler rather than entrained in the flue gas. It is worth comparing wheat DDGS with rapeseed meal (RM), a fuel which has K and P concentrations similar to wheat DDGS but with higher Ca and Mg concentrations. For RM grate combustion, using the same experimental methodology as in this study, no significant concentrations of P and Cl were found in the particles [25].

The abundant particles from powder burner combustion of DDGS contained high concentrations of potassium and phosphorus, while the HCl emissions were low, again suggesting evaporation of K and P at high combustion temperature.

4.4. Bed agglomeration. As reported elsewhere [41], the DDGS and the wheat straw-DDGS fuel had high bed agglomeration tendencies in comparison with many other biomass fuels (see table 11), including RM which has higher concentrations of Ca and Mg [24]. Co-combustion of DDGS with the relatively calcium rich LR reduced the bed agglomeration tendency significantly [41].

4.5. Slag formation.

Wheat DDGS has a high slagging tendency compared to most forest fuels as shown in figure 6. A mixture of fresh logging residues and wheat DDGS has a considerably lower slagging tendency than pure wheat DDGS.

DDGS combustion produces slag with high K concentrations and low Ca and Mg concentrations, consisting mainly of phosphates. If the DDGS is mixed with LR a slag with relatively higher Ca concentration is formed. Compared to the slag from unblended DDGS, the resulting slag from LR-DDGS contains more silicates and less phosphates.

In combustion of RM, with higher concentrations of calcium and magnesium, smaller amounts of slag were produced during the experiments. Compared to the slag formed during RM combustion, the slag from wheat DDGS combustion contained less Ca and Mg. [25]. The probable cause of this difference is the higher first melting temperatures of the Ca-Mg-K-phosphates formed from this fuel, compared to the K-phosphates formed from wheat DDGS combustion. K-phosphates could have first melting temperatures below 600 °C but calcium addition to these phosphates could significantly raise these first melting temperatures [28].

4.6. Deposit formation. For fluidised bed combustion, the fine particles (< 1 µm) from DDGS combustion mainly contain sulphates of potassium, and therefore the risk of problems caused by deposit formation should be moderate. It is known from previous work that sulphur addition reduces harmful deposit formations [45]. It is also known that the partially molten particles are most likely to stick to cool surfaces, and that the presence of chlorine increases the risk of corrosion. The lower Cl concentration in particles produced from combustion of DDGS mixtures, compared to the co-combustion fuels LR and wheat straw used in this study, is therefore an advantage. However during combustion in the pellets burner the addition of DDGS to the fuel did not result in any similar reduction in the Cl concentration in the fine particles.

Potassium phosphates abundant in the fine particles from powder burner combustion of DDGS have low first melting temperatures, which makes them sticky under common operating conditions and may result in deposits. Their abundance in the fine particles is a reason not to use DDGS as a fuel for powder combustors. The high fuel particle temperatures typical of

powder combustion probably cause the evaporation of potassium and phosphorus from the initially potassium phosphate rich melt formed as has also been discussed in 4.2 and in a previous work [25]. The presence of Cl in the particles is consistent with the low HCl emissions during DDGS powder combustion.

4.7. Possible applications of wheat DDGS. Compared to many other fuels, the phosphorus and potassium contents are high in wheat DDGS, as discussed in 4.1. From the combustion/co-combustion results of wheat DDGS in fluidised bed and grate firing processes, our preliminary interpretation is that K and P in the fuel will initially react during the burnout of a fuel particle, which is gradually converted into a K-phosphate rich bed ash particle. If Ca and Mg are present in the fuel/fuel mix, they will initially form CaO (s) and MgO (s) during the particle burnout phase, and these oxides will react with the K-phosphate rich melt, causing a rise in first melting temperature. Since highly stable alkaline earth metal phosphates exist, the presence of CaO and MgO could probably enhance the release of K from the formed melt/phosphates.

However, at high process temperatures, e.g. as found in powder combustion appliances, potassium and phosphorus evaporates, resulting in the formation of large quantities of fine, sticky particles rich in K and P. Consequently, wheat DDGS is unsuitable for use in powder combustors, and equipment where the combustion temperatures are lower, like fluidised bed combustors or possibly grate combustors, are preferable.

The high slagging and bed agglomeration tendencies of wheat DDGS are caused by melting of potassium-rich phosphates and silicates. This can be improved by the addition of Ca- and Mg-rich fuels resulting in phosphates and silicates with higher first melting temperatures. For this reason, if wheat DDGS is to be used as a fuel, it should be mixed with large quantities of other fuels, preferably ones which are rich in Ca and Mg.

The particle matter emissions from wheat DDGS combustion are high, and combustion facilities with advanced filtering capabilities are therefore required (a multi-cyclone is not sufficient as large fractions of the particle mass have aerodynamic diameters around and below 1 μm). The fuel composition of wheat DDGS results in large amounts of SO₂ and NO_x being produced, requiring use in combustion facilities equipped with sulphur and NO_x removal, i.e. large-scale facilities.

5. Conclusions

Fuel properties of wheat distiller's dried grain with solubles (wheat DDGS) from wheat-based ethanol production have been determined. The ash content (5.4 ± 1.6 %_{wt d.s.}) is higher than for most forest fuels and in the same range as for many agricultural fuels. In comparison to most other biomass fuels the sulphur content is high (0.538 ± 0.232 %_{wt d.s.}), and so are the contents of nitrogen (5.1 %_{wt d.s.} ± 0.6). Like several other agricultural fuels, the potassium concentration of wheat DDGS is high (1.30 %_{wt d.s.} ± 0.35). Unlike most other agricultural fuels previously studied, wheat DDGS has a low concentration of silicon (0.10 %_{wt d.s.}), and high concentration of phosphorus (0.960 %_{wt d.s.} ± 0.073 %_{wt d.s.}). This, together with the relatively

low concentrations of calcium ($0.159 \text{ \%}_{\text{wt d.s.}} \pm 0.094$) and magnesium ($0.28 \text{ \%}_{\text{wt d.s.}}$) gives wheat DDGS ash-chemical properties very different from rapeseed meal, another phosphorus- and potassium-rich fuel previously studied.

To determine fuel-specific combustion properties, wheat DDGS and mixes between wheat DDGS and logging residues (LR 60 \%_{wt} and DDGS 40 \%_{wt}), and wheat straw (wheat straw 50 \%_{wt} , DDGS 50 \%_{wt}) were pelletised and combusted in a bubbling fluidised bed combustor (5 kW) and in a pellets burner combustor (20 kW). Pure wheat DDGS powder was also combusted in a powder burner (150 kW).

Wheat DDGS had a high bed agglomeration and slagging tendency compared to other biomass fuels, although these tendencies were significantly lower for the mixture with the Ca-rich LR, probably reflecting the higher first melting temperatures of K-Ca/Mg-phosphates compared to K-phosphates. Combustion and co-combustion of wheat DDGS resulted in relatively large emissions of fine particles ($<1 \text{ }\mu\text{m}$) for all combustion appliances. For powder combustion PM_{tot} was sixteen times higher than from softwood stem wood. While the Cl concentrations of the fine particles from the LR-wheat DDGS-mixture in fluidised bed combustion were lower than from combustion of pure LR, the Cl- and P-concentrations were considerably higher from the wheat DDGS mixtures combusted in the other appliances at higher fuel particle temperature. The particles from powder combustion of wheat DDGS contained mainly K, P, Cl, Na and S, and as KPO_3 (i.e. the main phase identified with XRD) is known to have a low melting temperature, this suggests that powder combustion of wheat DDGS should be used with caution. The high slagging and bed agglomeration tendency of wheat DDGS, and the high emissions of fine particles rich in K, P and Cl from combustion at high temperature, mean that it is best used mixed with other fuels, preferably ones which have high Ca and Mg contents and in equipment where fuel particle temperatures during combustion are moderate, i.e. fluidised beds and possibly grate combustors rather than powder combustors.

Acknowledgements. The authors would like to thank Rikard Öhman and Henry Hedman, Energy Technology Centre at Piteå, Sweden, for their contribution to the powder combustion experiments, Prof. Rainer Backman at ETPC, Umeå University for performing TGA measurements, and Ulf Nordström and Erica Lindström, ETPC, Umeå University for help with fluidised bed and pellet combustor experiments, Gunnar Kalén, Håkan Örberg and Mikael Thyrell at the Unit of Biomass Technology and Chemistry, Swedish University of Agricultural Sciences at Umeå, for valuable contributions to the experimental work. Financial support from Värmeforsk, Ragnar Sellbergs Stiftelse, Stiftelsen Bengt Ingeströms Stipendiefond, the Swedish Research Council and the national (Swedish) strategic research program Bio4energy is gratefully acknowledged.

References

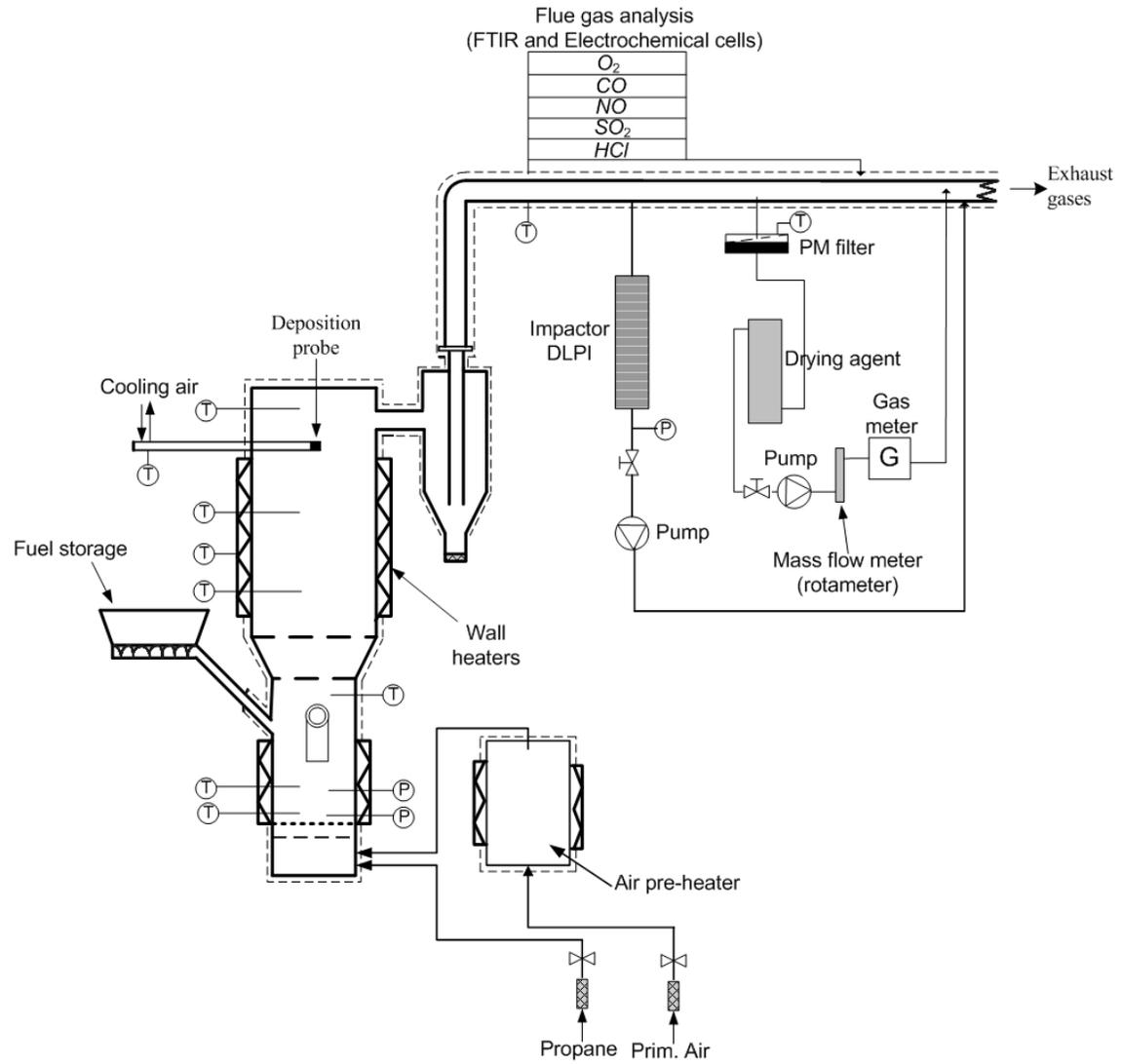
- [1] Kahn Ribeiro, S Kobayashi S, Beuthe M, Gasca J, Greene, D, Lee DS, Muromachi Y, Newton PJ, Plotkin S, Sperling D, Wit R, Zhou PJ, Transport and its infrastructure. In: Climate Change 2007: Mitigation. Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change (Metz B, Davidson OR, Bosch PR, Dave R, Meyer LA, editors, Cambridge University Press; 2007.
- [2] European Bioethanol Association, <http://epure.org/theindustry/statistics>, accessed November 2, 2011.
- [3] Canadian Renewable Fuels Association, Ethanol: Canadian Production List as at November 4 2010, available at: http://www.greenfuels.org/uploads/documents/ethanol_production_list.pdf (Accessed November 2, 2011).
- [4] www.epa.gov/chp/markets/ethanol.html (accessed November 2, 2011).
- [5] Morey RV, Tiffany DG, Hatfield DL, Biomass for electricity and process heat at ethanol plants. *Applied Engineering in Agriculture*, 2006; 22 (5), 723-728.
- [6] Börjesson P, Ericsson K, Di Lucia L, Nilsson LJ, Åhman M. Sustainable biofuels - do they exist? (in Swedish), Lund university, Environmental and Energy System Studies, Report 66, 2008.
- [7] Mustafa AF, McKinnon A, Christensen D. The nutritive value of thin stillage and wet distillers' grains for ruminants: a review. Department of Animal and Poultry Science, University of Saskatchewan, Saskatoon, Canada. Available at www.pound-maker.ca/pdf/WetDistillersGrain.pdf, accessed November 2, 2011.
- [8] Distiller's dried grains with solubles (DDGS) Agrodrank 90, Lantmännen Agroetanol, available at www.agroetanol.se, accessed November 2, 2011.
- [9] Market assessment of ethanol co-products, potential for Manitoba, 2006, January 30, prepared by Tyrchniewicz Consulting, available at http://www.tyrchniewicz-consulting.com/PDFs/Market_Assessment_of_Ethanol_Co-products.pdf (accessed November 2, 2011), 2006.
- [10] Schingoethe DJ. Utilization of DDGS by cattle. In: Proc. 27th Western Nutrition Conference, Winnipeg, Manitoba, Canada, September 19-20, pages 61-74. available from University of Minnesota, Department of Animal Science, <http://www.ddgs.umn.edu/> (accessed November 2, 2011), 2006.
- [11] Novakovic A, van Lith SC, Frandsen FJ, Jensen PA, and Holgersen LB. Release of potassium from the systems K-Ca-Si and K-Ca-P. *Energy & Fuels*; 2009, 23:3423-3428.
- [12] Tavasoli A, Masoumeh G, Chirayu S, Dalai AK. Production of hydrogen and syngas via gasification of the corn and wheat dry distiller grains (DDGS) in a fixed-bed micro reactor, *Fuel Processing Technology* 2009; 90:472-482.
- [13] Nuez Ortín WG, Yu P. Nutrient variation and availability of wheat DDGS, corn DDGS and blend DDGS from bioethanol plants, *J Sci Food Agric* 2008; 89:1754-1761.
- [14] Elled AL, Davidsson KO, Åmand LE. Sewage sludge as a deposit inhibitor when co-fired with high potassium fuels, *Biomass and Bioenergy* 2010; 34:1546-1554.
- [15] Lindström E, Sandström M, Boström D, Öhman M. Slagging characteristics during combustion of cereal grains rich in phosphorus, *Energy & Fuels* 2007; 21:710-717.

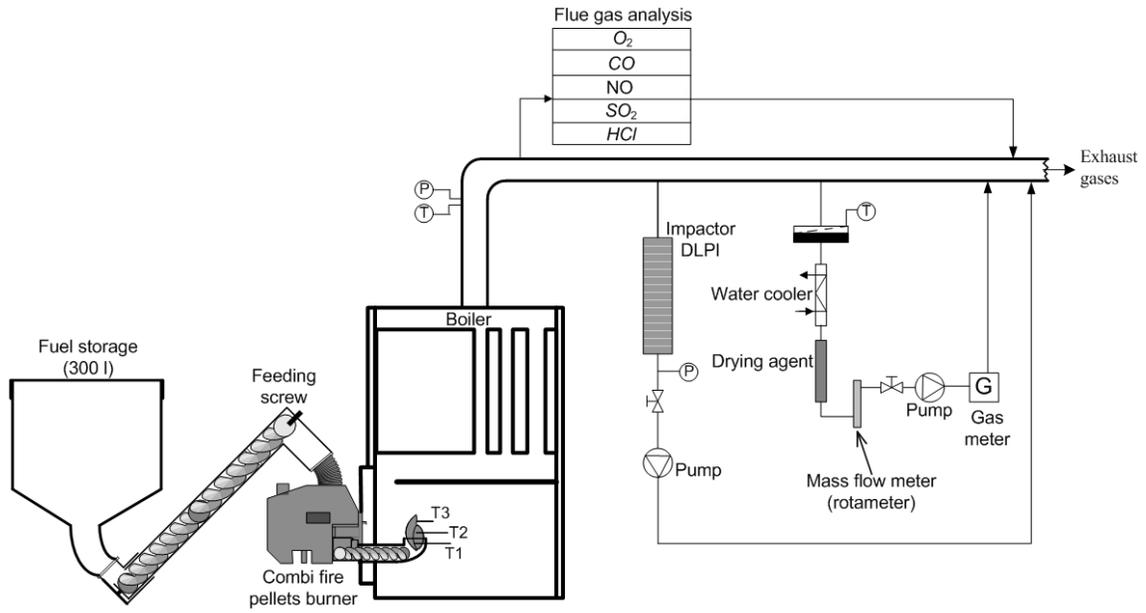
- [16] Fryda L, Panopoulos K, Vourliotis P, Pavlidou E, Kaaras E. Experimental investigation of fluidised bed co-combustion of meat and bone meal with coals and olive bagasse, *Fuel* 2006; 85:1685-1699.
- [17] Öhman, M., Nordin, A., Lundholm, K., Boström, D., Hedman, H. et al.. Ash transformations during combustion of meat-, bonemeal and RDF in a (bench-scale) fluidized bed combustor, *Energy & Fuels*, 2003; 17, 1153-1159.
- [18] Annamalai K, Sweeten J, Mukhtar S, Thien B, Wei G, Priyadarsan S. Co-firing coal: feedlot and litter biomass (CFB and CLB) fuels in pulverized fuel and fixed bed burners. Final report, Texas Engineering Experiment Station, Texas A&M University, US Dept of Energy National, Energy Technology Laboratory; 2003.
- [19] Zhang L, Masui M, Mizukoshi H, Ninomiya Y, Kanaoka C. Formation of submicron particulates (PM1) from the oxygen-enriched combustion of dried sewage sludge and their properties, *Energy & Fuels* 2007; 21:88-98.
- [20] Heikkinen R, Laitinen RS, Patrikainen T, Tiainen M, Virtanen M. Slagging tendency of peat ash, *Fuel Processing Technology* 1998; 56:69-80.
- [21] Beck J, Unterberger S. The behaviour of particle bound phosphorus during the combustion of phosphate doped coal, *Fuel* 2007; 86, 632-640.
- [22] Båfver LS, Rönnbäck M, Leckner B, Claesson F, Tullin C. Particle emission from combustion of oat grain and its potential reduction by addition of limestone or kaolin, *Fuel Processing Technology* 2009; 90:353-359.
- [23] Piotrowska P, Zevenhoven M, Davidsson K, Hupa M, Åmand L-E, Barisic V et al.. Fate of alkali metals and phosphorus of rapeseed cake in circulating fluidized bed boiler, Part 1: Cocombustion with wood. *Energy & Fuels* 2010; 24:333-345, 2010.
- [24] Boström D, Eriksson G, Boman C, Öhman M. Ash transformations in fluidized-bed combustion of rapeseed meal, *Energy & Fuels*, 2009;23:2700-2706.
- [25] Eriksson, G, Hedman H, Boström D; Pettersson E, Backman R, Öhman M. Combustion characterization of rapeseed meal and possible combustion applications, *Energy Fuels* 2009; 23:3930-3939.
- [26] Piotrowska P, Zevenhoven M, Hupa M, Giuntoli J, de Jong W. Residues from liquid and gaseous biofuels production - fuel characterization and ash sintering tendency, *Proceedings, Impacts of Fuel Quality on Power Production and Environment*, August 30-September 3, 2010, Saariselkä, Finland.
- [27] Lindström E, Sandström M, Boström D, Öhman M. Slagging characteristics during combustion of cereal grains rich in phosphorus, *Energy & Fuels* 2007;21:710-717, 2007.
- [28] Znamierowska T. Phase equilibriums in the system calcium oxide-potassium oxide-phosphorus(V) oxide. Part III. The partial system calcium dipotassium pyrophosphate-potassium pyrophosphate-potassium metaphosphate. *Pol J Chem* 52 1978;10:1889-1895.

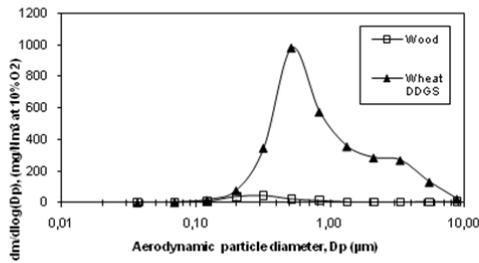
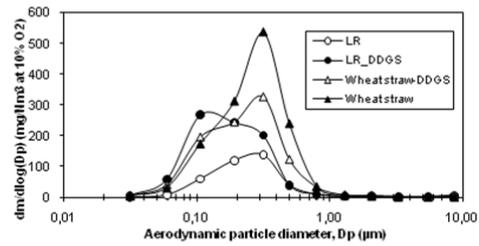
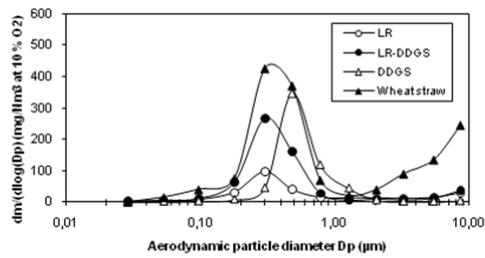
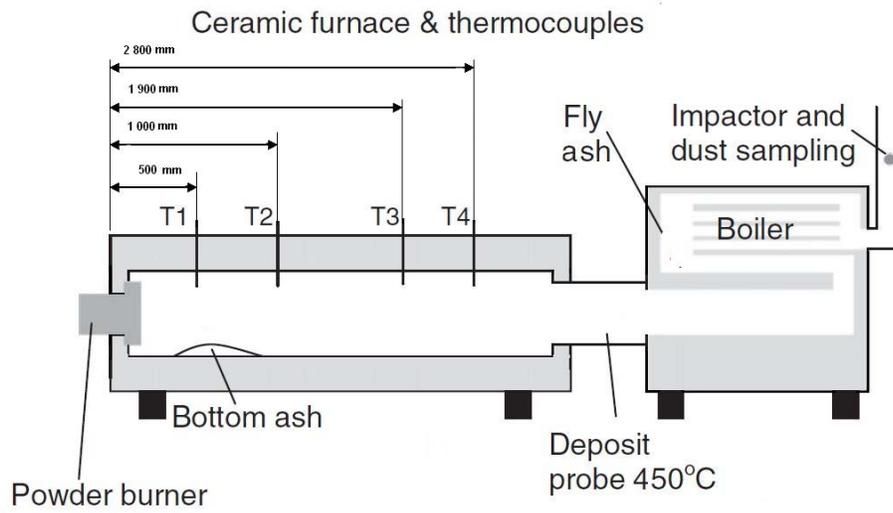
- [29] Novakovic A, van Lith SC, Frandsen FJ, Jensen PA, Holgersen LB. Release of potassium from the systems K-Ca-Si and K-Ca-P. *Energy & Fuels* 2009;23:3423-3428.
- [30] Elled A-L, Åmand L-E, Leckner B, Andersson B-Å. Influence of sulphur capture during co-firing of sewage sludge with wood or bark in a fluidised bed, *Fuel* 2006; 85:1671-1678, 2006.
- [31] Cordell D. Sustainability implications of global phosphorus scarcity for food security, PhD thesis, Linköping University, Department of Water and Environmental Studies, Sweden/University of Technology, Inst. for Sustainable Futures, Sydney, Australia; 2010.
- [32] Srinivasan R, Moreau RA, Parsons C, Lane JD, Singh V. Separation of fiber from distillers dried grains (DDG) using sieving and elutriation, *Biomass and Bioenergy* 2008;32:468-472.
- [33] Martin, M, Eklund, M. Improving the environmental performance of biofuels with industrial symbiosis, *Biomass and Bioenergy* 2011;35:1747-1755.
- [34] Energy Technology Data Exchange, www.etde.org. (accessed 2 November 2011)
- [35] Paulrud S. Upgraded biofuels - effects of quality in processing, handling characteristics, combustion and ash melting. PhD dissertation, Swedish Agricultural University, Umeå, Sweden, 2004.
- [36] Öhman M, Nordin A. A new method for quantification of agglomeration tendencies - a sensitivity study. *Energy Fuels* 1998;12(1):90-94.
- [37] Gilbe C, Öhman M, Lindström, E, Boström D, Backman R, Samuelsson R, Burvall J. Slagging characteristics during residential combustion of biomass pellets. *Energy Fuels* 2008;22:3536-3543.
- [38] McKinnon J, Beliveau R, McAlister T, Gibb D, Hao X. Impact of bio-fuel industry on beef industry: Use in growing & finishing rations, In: *Capturing feed grain & forage opportunities 2007 Proceedings - "Farming for feed, forage and fuel"*, Red Deer, Alberta, Canada, December 11,-12, available at [http://www1.agric.gov.ab.ca/\\$department/deptdocs.nsf/all/crop12129](http://www1.agric.gov.ab.ca/$department/deptdocs.nsf/all/crop12129) (accessed 2 November 2011), 2007.
- [39] Rasco BA, Dong FM, Hashisaka AE, Gazzaz SS, Downey SE, San Buenaventura ML. A research note - Chemical composition of distillers' dried grains with solubles (DDGS) from soft white wheat, hard red wheat and corn, *Journal of Food Science* 1987;52(1):236-237.
- [40] Emiola IA, Opapeju FO, Slominski BA, Nyachoti CM. Growth performance and nutrient digestibility in pigs fed wheat distillers dried grains with solubles-based diets supplemented with a multicarbohydase enzyme, *Journal of Animal Science*, 87 2009;2315-2322.
- [41] Grimm A, Skoglund N, Boström D, Öhman M, Bed agglomeration characteristics in fluidized quartz bed combustion of phosphorous rich biomass fuels. *Energy&Fuels* 2011, 25, 937-947.
- [42] Strömberg B. VÄRMEFORSK-971. Project Värmeforsk-F4-324. Värmeforsk, Stockholm, Sweden, 2006.
- [43] Hadders G, Arshadi M, Nilsson C, Burvall J. On the fuel quality of cereal grains - impact of soil composition, cereal species and variety, Swedish Institute of Agricultural and Environmental Engineering (JTI), report 289 (Lantbruk och industri). In Swedish, 2001.

[44] Skrifvars BJ, Öhman M, Nordin A, Hupa M. Prediction bed agglomeration tendencies for biomass fuels fired in FBC boilers - a comparison of three different methods, *Energy & Fuels* 1999;13:359-363.

[45] Henderson, P.; Andersson, C.; Kassman, H. *VGB PowerTech* 2004;6:58-62.







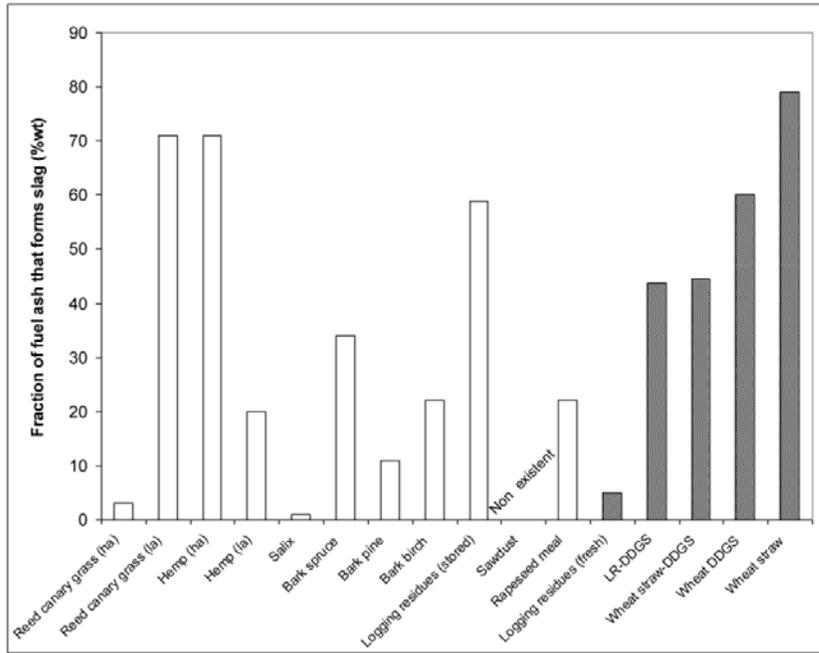


Fig. 1. Schematic view of the bubbling fluidised bed used.

Fig. 2. Schematic view of the underfed pellet combustor used.

Fig. 3. Schematic view of the powder combustor used.

Fig. 4. Particle mass size distribution in dry flue gases from fluidised bed combustion (upper), grate combustion (middle) and powder combustion (lower).

Fig. 5. Contents of main ash-forming elements of wheat DDGS used in this work and comparison with other fuel samples.

Fig. 6. Comparison of slag formation tendency in grate combustion for the pelletised fuels used in this study (dark) and some other biomass fuels combusted in similar conditions in previous studies (white) [37].

Table 1. Proximate analysis of the raw material used

	DDGS	Logging residues	Wheat straw
Moisture content, % _{wt a.r.}	11	10	12
Volatile content, % _{wt d.s.}	77.6	n.a.	n.a.
Ash content, % _{wt d.s.}	4.4	2.4	5.7

HHV, MJ/kg % _{wt d.s.}	20.6	20.7	18.5
LHV, MJ/kg % _{wt d.s.}	19.2	n.a.	n.a.

Table 2. Ultimate analysis and concentrations of main ash-forming elements in the used raw materials (values represent weight percent of dry substance)

	DDGS	Logging residues	Wheat straw
C	48	51.2	46.2
H	6.9	5.8	5.6
N	5.9	0.4	0.9
O	33.5	40.4	40.7
Cl	0.22	0.010	0.26
S	1.03	0.041	0.19
Si	0.10	0.29	0.80
Al	0.00127	0.036	0.006
Ca	0.109	0.51	0.40
Fe	0.0102	0.024	0.005
K	1.05	0.17	1.25
Mg	0.278	0.06	0.11
Na	0.0987	0.014	0.03
P	0.825	0.046	0.13

Table 3. Properties of the fuels used in combustion tests. Values represent weight percent of dry substance unless otherwise stated

	DDGS pellets/powder	Logging residues pellets	Wheat straw pellets	Logging residues-DDGS pellets	Wheat straw- DDGS pellets
Moisture content % _{wt a.r.}	11	10	12	10	10

Ash content. % _{wtd.s.}	4.4	2.4	5.7	3.2	5.1
C	48.0	51.2	46.2	49.3	47.1
H	6.9	5.8	5.6	6.46	6.25
N	5.9	0.4	0.9	3.7	3.4
O	33.5	40.4	40.7	36.3	37.1
Cl	0.22	0.01	0.26	0.136	0.240
S	1.03	0.041	0.19	0.634	0.610
Si	0.100	0.290	0.80	0.176	0.450
Al	0.00127	0.036	0.006	0.0152	0.0036
Ca	0.109	0.51	0.39	0.266	0.255
Fe	0.010	0.024	0.005	0.0157	0.00761
K	1.05	0.17	1.25	0.701	1.15
Mg	0.278	0.061	0.11	0.191	0.189
Na	0.0987	0.014	0.031	0.115	0.0643
P	0.825	0.046	0.130	0.513	0.477

Table 4. Ultimate analyses and main ash-forming elements of wheat distillers dried grains with solubles (DDGS).

Values represent weight percent of dry substance

	Min.value	Mean value	Max. value	Standard deviation
C	45.1	46.6 (n=2)	48.3	2.1
H	6.9	6.95 (n=2)	7.00	0.1
N	5.1	5.5 (n=2)	5.9	0.6
O	33.5	38.0 (n=2)	42.5	6.3
Cl	0.22	0.22 (n=1)	0.22	
S [10, 12, 38]	0.30	0.54 (n=8)	1.03	0.2
Si	0.10	0.10 (n=1)	0.10	
Al	0.00127	0.00127 (n=1)	0.00127	
Ca [9, 10, 38]	0.086	0.159 (n=15)	0.30	0.09
Fe	0.011	0.011 (n=1)	0.011	
K [9, 10]	0.75	1.30 (n=9)	1.70	0.35
Mg	0.230	0.277 (n=8)	0.290	
Na [9, 10]	0.030	0.120 (n=10)	0.230	0.10
P [9, 10, 13, 38]	0.60	0.96 (n=16)	1.05	0.07

Table 5. NO emissions (average values from the experiments given in mg/Nm³ at 10 % O₂ concentration in dry flue gas)

		Fluidised bed	Grate combustion	Powder burner
Pellets	Logging residues	340	350	
	Wheat straw	340	450	
	DDGS	710		
	Logging residues -DDGS	420	700	
	Wheat straw -DDGS	480	340*	
Powder	Wood			60
	DDGS			720

*The combustion temperature may have been lowered due to slagging, which may have influenced the results.

Table 6. SO₂ emissions (average values from the experiments given in mg/Nm³ at 10% O₂ concentration in dry flue gas)

		Fluidised bed	Grate combustion	Powder burner
Pellets	Logging residues	<1	<1	
	Wheat straw	<1	80	
	DDGS	965		
	Logging residues -DDGS	290	430	
	Wheat straw -DDGS	n.d	440	
Powder	Wood			<1
	DDGS			1 600

Table 7. Total particle matter mass concentration (mg/Nm³ at 10 % O₂ concentration in dry flue gas) from fluidised-bed combustion

		Fluidised bed	Grate combustion	Powder burner
Pellets	LR	140	100	

	Wheat straw	320	460
	LR-DDGS	180	310
	Wheat straw-DDGS	n.a.*	340
Powder	Wood		50 [25]
	DDGS		800

*) not analyzed due to fast defluidization during the experiment.

Table 8. Resulting initial de-fluidization temperatures for the fuel used.*

	Temperature of initial defluidization (°C)
LR	1 030 °C
Wheat straw	750 °C
DDGS	Total def. during comb. at ~ 800 °C
LR-DDGS	950 °C
Wheat straw-DDGS	Total def. during comb. at ~ 730 °C

*) From Grimm A et al [41]

Table 9. Fraction (%_{wt}) of fuel ash that formed slag during combustion in the underfed pellet burner.

	Fraction of fuel ash that formed slag (wt-%)
Logging residues (LR)	4
Wheat straw	79
DDGS-wood	60
LR-DDGS	44
Wheat straw-DDGS	45

Table 10. Fuel properties of distillers grain (DDGS) compared to other biomass fuels [42]

Fuel	Moisture content. % _{wt}	Ash % _{wt} d.s.	S % _{wt} d.s.	Cl % _{wt} d.s.	HHV, MJ/kg (d.s.)
Wood (dust. chips. powder)	8-60	0.4-0.6	0-0.3	0-0.05	16-18
Wood (pellets. briquettes)	9-10	0.4-0.8	0-0.3	0-0.05	19-21
Logging residue	35-55	1-5	0.02-0.05	0.02-0.05	19-21
Wood waste	3-50	3-16	0.04-0.3	0.04-0.2	20-24
Salix	25-50	1-5	0.005-0.03	0.01-0.1	16-20

Bark	21-65	2-6	0-0.1	0-0.02	20-25
Hardwood	20-40	0.3-1.7	0.01-0.04	0.005-0.06	19-21
Straw	10-20	4-10	0.05-0.2	0.05-1.5	18-20
Reed canary grass	10-15	3-7	0.05-0.2	0.1-0.2	17-20
Hemp	15-75	1.6-6.3	0.03-0.07	0.04-0.1	19
Grain	14	2-4	0-0.5	0.02-2.3	17-22
Crop residues	12	10	0.2	0.2	20
Olive residues	0-21	0.4-16	0.01-0.3	0-0.4	19-25
Cocoa beans and shells	7	5	0.3	0.02	30
Citrus pulp	8-10	4-7	0.2	0.02	21
Shea nuts	3.3-7.6	6-7	0.3	0.1	23
Sewage sludge	53-77	35-50	0.2-5	0.05-1.5	15-24
Waste. forest industry	41-84	2-60	0.1-2.4	0.01-0.3	17-23
Manure	4-92	15-42	0.3-1.1	0.6-2.4	19-21
Paper-wood-plastics	10-55	5-13	0.07-0.5	0.01-1.5	18-31
Tires. processed	0.6-4.3	5-26	1.3-3.3	0.06-0.9	36-43
Waste leather	54	2.5	2.6	1.2	19
Recycled carton	42-64	10-27	0.03-0.2	0.07-0.6	12-20
Meat and bone meal	7	30	0.7	0.5	23
Animal fat	0.1-0.6	0.1	0.02	0	39
Vegetable fat	0-1.2	0-0.1	0	0	39
Tall oil pitch	0.1-0.3	0.2-0.4	0.2-0.3	0	40
Peat	38-58	2-9	0.1-0.5	0-0.1	19-27
Peat (briquettes/ pellets)	10-15	2-8	0.25		20-27
wheat DDGS (present study)	6.4-14	3.6-8.4	0.30-1.03	0.22	19.2

Table 11. Temperatures of initial defluidization for the fuels tested and nine other biomass fuels

Temperature of initial defluidization (°C)	
Distillers Dried Grain with Solubles (DDGS)	Defluidization during combustion at 800 °C
LR-DDGS	950
Wheat straw-DDGS	Defluidization during combustion at 730 °C
Rape seed meal	1020 [24]
Bark	> 1015 [24]
Olive flesh	930 [44]
10% RM in Bark	965 [24]
30% RM in Bark	930 [24]

Peat	>1020 [44]
RDF	990 [44]
Bagasse	995 [44]
Alfalfa	670 [44]
