Rotary kiln pyrolysis of straw and fermentation residues in a 3 MW pilot plant – Influence of pyrolysis temperature on pyrolysis product performance

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A B S T R A C T
The idea of co-firing biomass in an already existing coal-fired power plant could play a major contribution in the reduction of carbon dioxide emissions. Huge amounts of unused biomass in terms of agricultural residues such as straw, which is a cheap and local feedstock, are often available. But due to the high amount of corrosive ash elements (K, Cl, etc.), the residues are usually not suitable for co-firing in a thermal power plant. Therefore, the feedstock is converted by low temperature pyrolysis into gaseous pyrolysis products and charcoal. A 3 MW pyrolysis pilot plant located next to a coal-fired power plant near Vienna was set up in 2008. For the process, an externally heated rotary kiln reactor with a design fuel power of 3 MW is used which can handle about 0.6–0.8 t/h straw. The aim is to investigate the fundamentals for scale-up to the desired size for co-firing in a co-firing power plant. In addition to the desired fuel for the process, which is wheat straw, a testing series for DDGS was also performed. The high amount of pyrolysis oil in the gas had positive effects on the heating value of the pyrolysis gas. Chemical efficiencies of this pyrolysis pilot plant of up to 67% for pyrolysis temperatures between 450 °C and 600 °C can be reached. The focus of this work is set on the pyrolysis products and their behavior at different pyrolysis temperatures as well as the performance of the pyrolysis process.

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1. Introduction
The world energy demand is continuously growing. The International Energy Agency predicts an increase in global primary energy demand of about 45% from 2008 to 2030. The world energy outlook shows that the limit of 450 ppm CO2 equivalents in the atmosphere cannot be reached only by the OECD countries even if they cease all further production of CO2 equivalents [1]. The energetic use of biomass is basically neutral to the global carbon balance, because the same amount of carbon dioxide that is released during the combustion of biomass would be released by aerobic decomposition of biomass [2]. The difference between combustion and aerobic decomposition of biomass is the fact that for cultivating, harvesting, transportation and treatment, fossil fuels are usually used [3]. This means that extensively produced biomass (wood and residues like straw) has a much smaller CO2 footprint than those which are produced only for combustion (maize, rape, etc.). Also in this case extensively produced biomass is the designated fuel for the pyrolysis process.

A very effective way for utilizing biomass in power plants is co-firing in already existing coal-fired power plants. The benefit of this method is that large power plants operate at steam parameters that aim at high electrical efficiencies. Another advantage of substituting coal with biomass is that a lot of carbon dioxide emissions can be saved due to the relatively high output of CO2 emissions by burning coal even compared to other fossil fuels. Co-firing can be accomplished via three different modifications, which are direct, indirect and parallel co-firing. For direct co-firing, a mixture of the standard fuel and the additional fuel is burned together in the boiler, while for parallel co-firing, a separate boiler where only the additional fuel is burned would be required. In this case, indirect co-firing would be the aim as only the gaseous products made by pyrolysis or gasification would be burned in the coal-fired boiler. Co-combustion of biomass with coal is a matter of intensive research for different applications, and several comprehensive studies exist on this topic [4–9].

Co-firing of solid biomass into conventional hard coal or lignite-fired power plants is possible, but its use is limited to some boundary conditions. The fraction of biomass in the total thermal

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power of a conventional coal-fired thermal power plant is limited by the mass flow rate of biomass that can be burned without expecting significant drawbacks. Drawbacks could be corrosion of the boiler, higher emissions or disadvantages concerning the flow of the gases in the power plant. The possibility of co-firing is also dependent on the resulting flow rates of mass, volume and exhaust gas. Fig. 1 shows the influence on the parts of a plant in the co-firing of biomass.

To be competitive on the market, the feedstock for co-firing has to be cheap and available in huge amounts. Agricultural residues, like straw, are in many cases unused and are therefore cheap and locally available. However, as mentioned before, the composition of the biomass is essential and may cause problems. Corrosive components like chlorine or potassium can be harmful to the boiler of the coal-fired power plant, because these power plants employing pulverized coal firing are optimized for high efficiency. Therefore, the steam parameters (temperature and pressure) have to be as high as possible. At these high temperatures, the mentioned components (Cl, K, etc.) cause high temperature corrosion in the boiler especially at the super heater surface [11,12]. Some tests have shown that severe corrosion takes place at test probes with metal temperatures above 520 °C [12]. At the power plant at Dürnrohr/Austria, where co-firing is planned based on the investigations in this paper, the superheated steam has a temperature of 530 °C [13] at nominal load, so co-firing of straw would be dangerous for the durability of the parts of the power plant. Thus, there has to be an intermediate step for the co-firing of straw in coal-fired power plants.

Via pyrolysis, the feedstock can be split into gaseous pyrolysis products and charcoal. The aim of this process is to retain the corrosive elements in the char and to produce a highly calorific pyrolysis gas that can be co-fired in the power plant. Research in the area of biomass pyrolysis has shown that the release of chlorine and alkali metals during thermal utilization into gaseous pyrolysis products is quite promising for this case [14–17]. These investigations have shown that the first amount of chlorine is released between 200 °C and 400 °C, and most of the residual chlorine is released when temperatures increase from 700 °C to 900 °C. The entrainment of potassium starts at temperatures higher than 700 °C [16,17]. These facts have been strengthened by investigations at the pyrolysis pilot plant described in a previous study [18]. With this knowledge, the temperature boundaries for the pyrolysis process are given in this case; as temperatures above 700 °C should be avoided, the accomplished test runs were done between 450 °C and 600 °C. To fill the gap of the seasonal feedstock availability of straw, there could be used, in addition to conventional wood chips, the residues of renewable liquid fuel production to provide a significant contribution, as Austria’s largest bioethanol production plant is nearby the pyrolysis pilot plant. The waste products of bioethanol production are dry distiller’s grains with solubles (DDGS) that are often used pelletized as an animal feed for cattle due to the high protein content. The production of DDGS is batch-wise and due to the fact that it will be used as an animal feed, the requirements on sanitation are high. If a produced batch does not fulfill these regulations, it cannot be sold as an animal feed and has to be disposed, for example in a municipal waste combustor. Pyrolysis of DDGS has been investigated also by [19,20] with a focus on the high nitrogen content of this special fuel.

The type of reactor chosen here is an externally heated rotary kiln reactor. Basically also a fluidized bed reactor could be used for the operational temperature range and process parameters but rotary kiln reactors have advantages for solid fuels with different sizes and heating values that result in a different fuel mass flow [21,22]. Large knowledge about rotary kilns exists as this type of reactor is commercially used for incineration of fuels with a wide variety of size, heating value, water content or pollutants. The pyrolysis of wood, plastics and scrap tires in a rotary kiln pyrolysis reactor has been investigated widely by Li et al. [23,24], who reported the influence of the final pyrolysis temperature on the production of gas, oil and char. It turned out that the gas production increased and char production decreased by higher final pyrolysis temperature for all feedstock types, whereas the formation of pyrolysis oil decreased for wood and PE plastics but increased for waste tires at higher temperatures [23].

The experimental campaign carried out at the pilot plant for this paper sets a focus on the product yields and the pyrolysis oil contents for different pyrolysis temperatures. The 3 MW pyrolysis pilot plant, described later in this paper, is not connected to a coal-fired power plant yet. However, it provides information and results for a scale-up that could not be achieved with a small-scale lab testing rig.
11. Pyrolysis mechanisms and pyrolysis reactions

Biomass is a mixture of cellulose, hemicellulose, lignin and minor amounts of other organic components that each degrade at different rates and by different mechanisms and pathways. Most knowledge exists on the thermal decomposition of cellulose as it is the major part of the wood and as it not as complex as hemicellulose or lignin [25].

For pyrolysis of cellulose, the Broido-Shafizadeh model according to Bradbury et al. [26] has turned out to be the most adequate model for biomass pyrolysis. The pyrolysis of cellulose is characterized by a decreasing polymerization grade by splitting glycolic compounds between the glucose units by heat during two parallel reactions investigated by Bradbury Bradbury et al. [26]. If the condensable vapors produced by this reaction are not removed immediately out of the hot reactor, they can be cracked by a secondary reaction into char and gas. This reaction is undesired in the production of liquid products by fast pyrolysis [26–30]. The activation energy for the depolymerization reaction at higher temperatures is the highest, followed by the dehydration reaction that occurs at lower temperatures and the secondary cracking of the condensable gases which has the lowest activation energy [31].

Hemicelluloses and lignin are depolymerized by steaming at high temperatures for a short time. The majority of the pyrolysis products from lignin are char and tar, while only about 10% of the initial mass of lignin is converted to gas [32]. Kumar and Pratt [33] investigated the temperature range for the initiation of pyrolysis for cellulose between 275 °C and 350 °C, for hemicellulose between 150 °C and 350 °C and for lignin from 250 °C to 500 °C. The main sources for gaseous products for the pyrolysis process of biomass are cellulose and hemicellulose, whereas hemicellulose causes more non-condensable gases and less tar than are made by cellulose.

2. Material and methods

2.1. The pyrolysis pilot plant

Fig. 2 shows a flow sheet with the most important parts of the pilot plant. The delivery and handling of the unground biomass are carried out by agricultural vehicles. After cutting by a shredder, the material is stored temporarily in a hopper. In an indirectly heated rotary kiln reactor, pyrolysis takes place to produce combustible gases and char from biomass. The combustible gases are burned in a burner muffle located in the freeboard of the fluidized bed combustion chamber implemented as an afterburner. The fluidized bed combustion is not operated simultaneously with pyrolysis gas combustion but is dedicated for char combustion after a pyrolysis campaign. For the indirect heating of the rotary kiln reactor, flue gas from the afterburner is used. Charcoal is cooled and stored temporarily in a charcoal hopper. The exhaust gases from the afterburner are cooled in a spray type cooler by injection of water and cleaned in a spray absorber; the dust is removed in a fabric filter. Pyrolysis of biomass and burning of the temporarily stored char takes place periodically. If the charcoal hopper is full, pyrolysis is stopped and the char is burned in the fluidized bed combustion chamber.

The pyrolysis reactor is a jacked rotary kiln reactor that is externally heated. The heating medium is hot gas that is produced in the afterburner by combustion of the pyrolysis gas. The pyrolysis gas temperature at the outlet of the rotary kiln is between 450 °C and 630 °C. At this temperature, the main amount of undesired components, such as heavy metals, sodium and potassium salts, stay in the pyrolysis char. The feedstock is fed in via a lock system at the front wall of the rotary kiln. To transport the pyrolysis gas out of the rotary kiln and to provide optimal process conditions, a fan generates a pressure of a few millibar lower than the ambient pressure. To prevent the penetration of air, all locks and seals are pressurized with seal gas. As seal gas, nitrogen, oxygen-deficient recirculation gas or steam can be used. The heating jacket around the reactor is divided into three heating zones. This allows adjustment of the temperature and distribution of the heat along the kiln. The temperature of the hot gas is greater than 800 °C. At the inner wall of the rotary kiln reactor, temperatures greater than 650 °C can be achieved. Under these conditions, pyrolysis of the biomass occurs. In order to avoid condensation, the gas pipes to the burner muffle are equipped with a trace heating system that uses the used heating gas leaving the jacket of the rotary kiln reactor as a heating medium. At the discharge of the rotary kiln reactor, the pyrolysis char is transported via a lock system to an indirectly cooled screw conveyor and a water-cooled chain to cool it to storage temperature and conveyed to the charcoal hopper for storage.

For start-up and shutdown, as well as for necessary auxiliary firing, a gas burner in the freeboard of the fluidized bed reactor is available. The pilot plant is not designed for generating energy or heat so the hot flue gas after the combustion chamber has to be cooled for additional gas cleaning. Therefore, a spray-type cooler that injects water into the hot gas stream is used. As a result, the temperature after the spray-type cooler is below 400 °C. For gas cleaning, a spray absorber, a selective non-catalytic de-NOx and a fabric filter are provided. As an absorbent, calcium hydroxide is used to clean the gas of sulfur dioxide and hydrochloric acid. If the contents of HCl and SO2 in the flue gas are very low, it is often not necessary to use calcium hydroxide. In this case, pure water can be used in the spray absorber. For the reduction of nitrogen oxides, ammonia injection in the freeboard of the fluidized bed chamber is available, a so-called selective non-catalytic de-NOx (SNCR). This system is only used if the NOx emissions exceed limits. Table 1 summarizes general operational parameters of the plant.

2.2. Balance of the plant

For research and optimization of the pilot plant the parameters of all streams in the plant have to be known. There are many measuring points for temperature, pressure and flow at the plant. The composition of pyrolysis gas, feedstock and char are also measured, but there are some parameters that cannot be measured. Such a value is for example the volumetric flow rate of the pyrolysis gas. Due to the trace heating that is implemented by the pipe-in-pipe construction of the pyrolysis gas pipe from the rotary kiln reactor to the afterburner, the construction of a measuring orifice is not possible. In such a case, the value has to be calculated. This is done by a balance of the plant with the available data. For this purpose, the balance tool IPSEpro has been used. IPSEpro is a stationary, equation-oriented flow sheet simulation tool that has been
developed for power generating systems [34]. Detailed information about IPSEpro, its mode of operation and its utilization for biomass based energy systems can be found in [35].

2.3. Analytics

2.3.1. Gas measurement

The pyrolysis gas mainly consists of methane (CH₄), carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), water (H₂O) and small amounts of oxygen (O₂) and nitrogen (N₂). The applied measurement device for permanent gas measuring is an extractive gas analyzer (model S700, type S710) made by Sick–Maihak.

2.3.2. Pyrolysis oil measurement

The applied method is used to measure the dust, entrained char and tar content in a gas stream together with the water content. The main difference from CEN/TS 15439 which is a standard method for tar measurements is the utilization of toluene as the solvent, which allows for simultaneous measurement of the tar and the water content in the product gas. The scheme of the tar measuring system is shown in Fig. 3. The gas enters the heated sampling line, which consists of a cyclone and a glass wool filled filter cartridge, where dust is deposited. Afterwards, the gas is led through six washing bottles: five of them are filled with toluene. The washing bottles are situated in a cooling pond which is cooled to -10 °C by a cryostat. There, tar/pyrolysis oil and steam condense.

The liquid phases in the washing bottles are unified and the aqueous phase is separated from the toluene phase. GC-MS samples are taken from the toluene phase. The samples are analyzed by a Perkin-Elmer Autosystem XL GC with a PerkinElmer Turbomass mass spectrometer. The toluene is evaporated from the sample to determine the total mass of the pyrolysis oil. To analyze the oil in the filter cartridge, it is necessary to carry out a soxhlet extraction with isopropanol (IPA). Again, a GC-MS sample of the IPA phase is taken and analyzed. The filter cartridge is ashed in a muffle furnace for identification of entrained char and dust.

2.3.3. Feedstock and pyrolysis char analysis

The feedstock for the pyrolysis process, straw and DDGS, as well as the pyrolysis char are analyzed by the “Testing Laboratory for Combustion Systems” at the Vienna University of Technology. The sampling and preparation of the fuels is done according to DIN 51701. After determination of the water content, described in DIN 51718 (drying at 30 °C to constant mass, grinding of the dried sample to a maximum particle size of 1 mm and drying of this sample at 106 ± 2 °C in an inert atmosphere to constant mass), the ash content is determined according to DIN 51719 by burning the sample to constant mass. C, H, N and S are measured by an elementary analyzer EA 1108 CHNS-O made by Carlo Erba. This is done by burning the sample in an oxygen atmosphere. To make sure that a possible CO formation is avoided, the gas passes a tungsten catalyst that ensures complete oxidation. Afterwards the gas passes a layer of cooper at a temperature of 860 °C where free oxygen is bound. Here, also nitrogen oxides are reduced to N₂. As a result the gas consists only of the components CO₂, H₂O, N₂ and SO₂ that can be detected. Present chlorine in the gas is absorbed in an aqueous perhydrol solution (H₂O₂) which is analyzed afterwards by capillary electrophoresis.

3. Results

3.1. Operation with straw

For the balance of the operating points straw with the composition listed in Table 2 was used. The values are arithmetic mean values of four straw samples. The difference of the total sum of the elements to 100% is due to the fact that the oxygen content was not detected here. After pyrolysis, the elemental composition of the produced char was also detected. The values are arithmetic mean
values of three char samples. By comparing fuel and char analyses, the fundamental idea for the pyrolysis plant can be strengthened. The two most critical components, chlorine and potassium, were enriched in the pyrolysis char, which is the basic idea of this pyrolysis purpose. For the following balances, test runs at pyrolysis temperatures of 450, 500, 550 and 600 °C were performed. An interesting point for discussion is the output of gas, oil and char for the different pyrolysis temperatures. For comparison of the four operating points, the energy and mass contents of those three fractions were each converted to the reference of the sum of the energy and mass contents of gas, oil and char. The mass and energy contents were consequently calculated dry, so the water content in the gaseous products (gas and oil vapor) was not considered. In Fig. 4, it can be seen that by increasing pyrolysis temperature, the produced amount of pyrolysis gas increased significantly, whereas the amount of char slightly decreased and the mass of pyrolysis oil was heavily reduced. This graph strengthens the already known fact that a higher pyrolysis temperature forces the production of gas at the expense of the formation of pyrolysis oil. The higher temperature caused decomposition of oil to gas as it was explained before. The slightly lower mass of char results from the fact that more volatile compounds were stripped due to higher temperatures. Fig. 5 shows that increasing pyrolysis temperature caused an increase in energy delivered by pyrolysis gas and char and a decrease in the energy delivered by pyrolysis oil. Most of these effects were caused by the different amounts of the products that were generated (see Fig. 4). A further reason is that, due to different pyrolysis temperatures, the chemical composition of the products was slightly different. So, at lower temperatures in the rotary kiln reactor, there were more polyaromatic compounds with a high heating value formed that contributed to the pyrolysis oil yield.

At every operating point, several samplings of pyrolysis oil, particulate matter and water in the pyrolysis gas have been carried out. These results were validated by the mass and energy balance of the process. The validated results are shown in Figs. 6 and 7. Particulate matter that has to be removed for many downstream processes is divided here into dust and coke. Coke consists nearly completely of carbon that was detected by burning the dust sample and measuring of the weight difference. In this case, for the pyrolysis of indoor stored straw, the dust content decreased while coke increased with higher pyrolysis temperatures, but the total amount of particulate matter decreases slightly. As previously explained, the amount of

![Fig. 3. Tar/pyrolysis oil sampling system.](image1)

![Fig. 4. Mass fractions for the pyrolysis products of straw vs. pyrolysis temperature.](image2)

![Fig. 5. Energy fractions for the pyrolysis products of straw vs. pyrolysis temperature.](image3)
pyrolysis oil in the gas decreased with higher temperatures, and the water content also decreased slightly, because steam reforming reactions were forced by higher temperatures (Fig. 11).

3.2. Operation with DDGS

As mentioned in the introduction of this paper, the pyrolysis pilot plant has also been operated with a fermentation residue that occurs as a side product during ethanol production from wheat, corn and triticale. The production plant for bioethanol is located near the pyrolysis pilot, so DDGS from this plant would be also a regional available feedstock. The opportunity has been taken to test pelletized DDGS as a fuel for the pyrolysis process. The analyses of feedstock and char are pointed out in Table 3.

![Fig. 6. Yield of water and pyrolysis oil as a function of the pyrolysis temperature.](image)

Also for DDGS, the amount of chlorine and potassium was enriched in the charcoal. DDGS showed a completely different behavior during pyrolysis than straw. With this feedstock, test runs at temperatures of 450, 500 and 550 °C were performed. The results here show very interesting trends of the three produced components gas, oil, and char: Fig. 8 displays the mass fractions of the pyrolysis products of DDGS with temperature variation and Fig. 9 demonstrates the trends of the energy fractions of the pyrolysis products of DDGS with temperature variation. The mass of the pyrolysis gas had a significant contribution to the gaseous products and it increased for higher temperatures. There are distinctive trends for the mass fraction of pyrolysis gas and pyrolysis oil. While

![Fig. 8. Mass fractions for the pyrolysis products of DDGS vs. pyrolysis temperature.](image)

the produced amount of pyrolysis gas increased due to higher pyrolysis temperatures, the mass fraction of pyrolysis oil decreased. A special feature here is that for pyrolysis temperatures lower than 500 °C, the major part of the gaseous products was present in the form of oil, whereas for temperatures higher than 500 °C, pyrolysis gas represented the bigger part. Pyrolysis oil and water content of the pyrolysis gas were also measured for this testing period. Fig. 10 gives information about these datasets. The water content was reduced from 62.5 to 61.2 vol.% and the pyrolysis oil amount was reduced more significantly by an increase in the pyrolysis temperature.

![Fig. 7. Content of dust and coke in the pyrolysis gas as a function of the pyrolysis temperature.](image)

![Fig. 9. Energy fractions for the pyrolysis products of DDGS vs. pyrolysis temperature.](image)

![Fig. 10. Elemental analysis of DDGS and char from DDGS pyrolysis at 550 °C (db ... dry basis).](image)

Table 3

<table>
<thead>
<tr>
<th>Element</th>
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<th>DDGS char</th>
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</thead>
<tbody>
<tr>
<td>Water content</td>
<td>wt.%</td>
<td>6.5</td>
</tr>
<tr>
<td>Ash content (550 °C)</td>
<td>wt.%db</td>
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</tr>
<tr>
<td>Carbon content</td>
<td>wt.%db</td>
<td>49.04</td>
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<td>Hydrogen content</td>
<td>wt.%db</td>
<td>7.05</td>
</tr>
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<td>Nitrogen content</td>
<td>wt.%db</td>
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<td>Sulfur content</td>
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</tr>
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</tr>
</tbody>
</table>

![Fig. 11. Yield of water and pyrolysis oil as a function of the pyrolysis temperature.](image)
If the results of the pyrolysis product mass distribution are compared with the results of rotary kiln pyrolysis of scrap tires, investigated by Li et al. [24], there can be seen that straw behaved completely different. The amount of pyrolysis gas made by straw ranged from 49.6 wt.% at 450 °C to 62.7 wt.% compared to a gas yield for pyrolysis of scrap tires of 13.1 wt.% at 450 °C to 18.0 wt.% at 600 °C. DDGS behaved up to 500 °C like scrap tires with a gas yield of 18.5 wt.% at 500 °C, but at higher temperatures the production of pyrolysis gas rapidly increased.

3.3. Gas composition

Due to the different composition of the two fuels, the gas composition was also different for straw and DDGS. By the plot of the permanent gas composition in relation to the prepyrolysis temperatures, it can be seen that the composition of the gas did not change significantly in the operated temperature range. For straw (Fig. 11), CO was present at a concentration of about 34 vol.%db, CO2 at 27 vol.%db, CH4 at 25.5 vol.%db and H2 at 10 vol.%db. For DDGS (Fig. 12), the amount of H2 was negligible, CO and CH4 were about 15 vol.%db and CO2 was up to 64 vol.%db. The gas composition made by DDGS has, compared to the gas made by straw, a much lower heating value. That goes along with the distribution of the energy contents of the pyrolysis products (Figs. 5 and 9) as it was shown that most of the energy content of the gaseous products was provided by pyrolysis oil. So, the lower heating value for dry pyrolysis gas without pyrolysis oil from straw ranged between 14.44 MJ/Nm3 at 450 °C and 14.97 MJ/Nm3 at 600 °C. In contrast to this, for DDGS, the lower heating value reached only 3.68 MJ/Nm3 at 450 °C and 3.84 MJ/Nm3 at 550 °C due to the high CO2 and low CH4 content in the pyrolysis gas.

3.4. Chemical efficiency

Chemical efficiency is the ratio of the chemical energy of the product to the chemical energy of the feedstock. The feedstock in the pyrolysis process is the biomass (straw or DDGS). The products are the gaseous products of pyrolysis that are used for co-firing. In this case, the gaseous products contain the pyrolysis gas and the pyrolysis oil including the water content in the fuel and in the pyrolysis gas. Fly char and entrained dust are unaccounted for here because those are only minor amounts, and the loading of solid fines depends very much on the fluid dynamic design of the reactor. Equation 1 shows how this was calculated. The lower hating value for the used straw was 17.26 MJ/kgdaf and for DDGS it was 22.84 MJ/kgdaf. According to the energy balance, the lower heating value of the pyrolysis oil was 38.5 MJ/kg.

Equation 1: chemical efficiency

$$\eta_c = \frac{\dot{V}_{\text{H}_2} \times \text{H}_{\text{LHV}} + \dot{m}_{\text{oil}} \times \text{H}_{\text{LHV}}}{\dot{m}_{\text{fuel}} \times \text{H}_{\text{LHV}}_{\text{fuel}}}$$

As shown in Fig. 13, the chemical efficiency for the pyrolysis of straw was up to 56%. The chemical efficiency for the pyrolysis of DDGS was higher (up to 67%) because of the high energy density of pyrolysis oil which was predominantly formed from DDGS. In
addition, Fig. 14 illustrates the energy balance of the rotary kiln reactor at a pyrolysis temperature of 550 °C during straw pyrolysis. The heat loss of the reactor is included in the cold gas stream.

3.5. Product yield per fuel input

A good overview of the influence of the pyrolysis temperature on the net production of gas and oil and the required energy for the process give the ratios of product and needed heat to the input of fuel. They show which quantity of the pyrolysis products was made by one kilogram of fuel input. As was shown before, the amount of pyrolysis oil decreased with higher pyrolysis temperatures. During the pyrolysis of straw, pyrolysis oil was yielded at an amount of 48.3 g at 600 °C to 131.2 g at 450 °C per kg straw. DDGS provided a higher oil yield than straw, as there were 171.0 g of oil formed at 550 °C and 340.2 g per kg DDGS at 450 °C (Fig. 15). Pyrolysis gas was produced at an amount from 0.57 Nm³/kg at 450 °C to 0.62 Nm³/kg at 600 °C per kg straw and 0.47 Nm³/kg at 450 °C to 0.71 Nm³/kg at 550 °C were made by 1 kg of DDGS (Fig. 16). So, the net production of gaseous pyrolysis products increased (Fig. 17). This strengthens the fact that higher temperatures activate secondary cracking reactions of the pyrolysis oil to produce mainly gas and only a very small amount of char. The gaseous products contain the pyrolysis gas (including water) and pyrolysis oil. That is because the products of this process that will be used for co-firing are all gaseous products. Cooling these gases to the point where the components of pyrolysis oil condense before firing in the boiler should be avoided, so the sum of the gas, oil and water amounts is crucial. In Fig. 18, the input power for the pyrolysis process in the rotary kiln reactor is shown.

For the pyrolysis of straw, it can be estimated that higher temperatures need more input power to keep the process running. This was calculated from the energy balance. Here, the power increased from 807 kW at 450 °C to 926 kW at 600 °C for an input of one kilogram of straw. Only for a pyrolysis temperature of 550 °C there was a small decrease in the input power. This decrease is considerable for DDGS as the input power also dropped from 960 kW to 670 kW per kg DDGS at 550 °C, so it can be assumed that in this range of pyrolysis temperatures, some exothermic processes take place.
4. Conclusion

The most important reason for the construction and operation of the indirect heated rotary kiln pilot plant was to gain fundamental information on the initiation of a pyrolysis plant that produces gaseous pyrolysis products that are suitable for co-firing at coal-fired power plants. Pyrolysis of agricultural residues in an externally heated rotary kiln pyrolysis reactor is a not extensively investigated process that has potential to be optimized. Further, the aim to retain as much of the undesired components, like chlorine, potassium or sodium, in the pyrolysis char to prevent the boiler from high temperature corrosion requires intelligent process management of the pyrolysis parameters. Fortunately, it has already been proven that this process technology is suitable for producing a gas whose combustion products do not cause corrosion, as shown in previous work at this pilot plant. But, with this work, there has been a focus on the energetic side of the process technology. It turned out that the operation, handling and control of the pilot plant, especially the pyrolysis reactor, can be done without serious problems with the current state of knowledge. The ruggedly designed rotary kiln reactor is also insensitive to contamination of the feedstock with soil or other small inorganic particles. The balance of the plant system can be done in an accurate way as there are many measured values available that are recorded by the process control system. This offers the advantage of clearing the uncertainties of the measurements so problematic values can be found and checked. The measured and calculated values in this paper show great promise for large-scale industrial application. The most important fact here is to bring as much energy as possible from the feedstock into the gaseous products (gas, oil and water) that can be burned in the boiler of a power plant without the risk of hot corrosion. This performance is pointed out by the chemical efficiency of the process that is, depending on the feedstock, between 0.55 for straw and 0.67 for DDGS at 450 °C. This shows that between 55 and 67% of the energy of the feedstock is transferred to combustible gases. A big advantage of using this system for co-firing is its flexibility with alternative fuels. The rotary kiln pyrolysis reactor is suitable for a wide range of fuels, and the power plant where the pyrolysis gas is burned is not as affected as feeding these fuels directly into the power plant.

So far, only less attention was given to the solid pyrolysis product, pyrolysis char or so called biochar. The pyrolysis char has a very high heating value and is nearly free of any water content. In addition to the combustion in corrosive resistant boilers, biochar could also be restored to the fields where the feedstock came from. Biochar is perfectly suitable for the improvement of soil and therefore it could be used as a soil amendment. Using the pyrolysis char as reducing agent in the non-ferrous metallurgy is also under investigation [36]. The application of biochar techniques to soil has rarely been investigated up to now. A very important point for the near future will be the sequestration of carbon. Biochar application to soil places carbon originated from atmospheric CO₂ into the soil to protect it from surface combustion by fires and to maintain it in relatively stable forms for a long period of time with opportunities for carbon trading. A better contact with soil minerals enhances the biochar stability and increases its mean residence time. Seques-
tration in subsoil may be an especially effective way to increase stability. A deeper application method may therefore be useful for increasing the carbon trading value of biochar [37,38].

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