

Characterization of biomass wood

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Abstract

Biomass is a renewable energy resource and can replace the use of fossil fuels, such as coal. Overgrown forests and fields are about to become a noticeable problem, because the rate of woodcutting is too low compared with the incremental growth of new forests. It is important to consider that there can be a time lag of many years related to the uptake of CO₂ in the new biomass. The time lag is caused by planting of new growing plants and a long growing period. Organic materials can be used as raw material for the gasification process in a biomass combined heat and power plant. Combined heat and power systems (CHP), produce electric energy and thermal energy far more efficiently and with lower emissions than systems where electricity and thermal energy is produced separately. Based on the measured HHV and the density of the different types of wood, the daily need of fuel in a 10 MW power plant was calculated. Oak corresponds to a need of 70.8 m³/day. Pine, birch and spruce correspond to 88.7 m³/day, 78.1 m³/day and 98.2 m³/day respectively.

Characterization of biomass from wood is studied. Chips from oak, birch, pine, and spruce were used as raw materials to find the gasification and the combustion properties of the wood. Analyses of pulverized wood chips from oak, pine, birch and spruce were performed in a bomb calorimeter, thermogravimetric analyzer and muffle furnace. Important factors that influence the gasification and the combustion properties of biomass are moisture, heating value, content of volatile components and ash residue. The heating values of oak, pine, birch and spruce were measured to 17.7 MJ/kg, 19.1 MJ/kg, 17.6 MJ/kg and 18.7 MJ/kg respectively. The thermogravimetric analyses of wood indicate that biomass is highly reactive due to the fast pyrolysis process. The volatile matter content varied from 73–79%. The ash content from samples with long residence time was almost the same as for samples with shorter residence time. The ash content is less than 1% for all samples.

Keywords: biomass, heating value, proximate analyses, gasification, combustion.

1 Introduction

Biomass is a renewable energy resource that can be converted into bio energy and replace use of fossil fuels [1]. Overgrown forest and fields are about to be a noticeably problem, because the woodcutting is too low compared to the increment of new forest. To utilize the wood that is not used as building materials will be profitable for the forest owners. Organic materials can be used as raw material for the gasification process in a biomass combined heat and power plant. In Norway productive forests are estimated to cover one fourth of the land area and the volume of timber increments every year [2]. In 2011 the timber accounted for a total volume of 878 million cubic metres and the annual growth was 25 million cubic metres. This means that more CO_2 are fixed in the trees [1, 2]. Biomass is referred to as a CO_2 -neutral fuel because CO_2 from combustion of biomass is part of a natural cycle. Figure 1 gives an illustration of the natural CO_2 cycle. When biomass is burned, CO_2 is released to the atmosphere. Growing plants will in turn absorb the released CO_2 through the photosynthesis [4, 5].

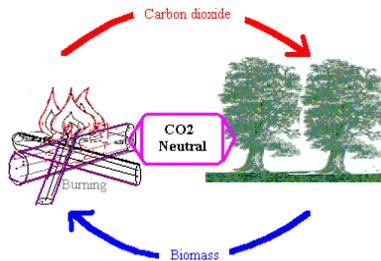


Figure 1: Natural CO_2 cycle during combustion of biomass [4].

It is important to consider that it can be a time lag of many years related to the uptake of CO_2 in the new biomass. The time lag is caused by planting of new growing plants and a long growing period [2]. The environmental advantages by using wood in production of heat and power, instead of coal or other fossil fuels, is dependent on whether the felling of timber exceeds the increment of the new forest, or not [2, 7].

Utilization of energy from biomass is available from three different thermo-chemical conversion processes, conversion of thermal energy (heat) directly from combustion or by upgrading to high quality products through pyrolysis or gasification. In Figure 2, the thermo-chemical conversion processes of biomass are shown [5, 7].

The end-product is in general thermal energy, and is used for heat production, to produce electricity, bio-fuel, and charcoal from biomass. Pyrolysis is the chemical decomposition of organic materials by heating in the absence of oxygen or any other reagents. The temperature is about 500°C and the reaction is irreversible [8]. The chemical process in gasification takes place in a reactor at temperatures higher than 700°C [8, 9]. In combustion the carbon and hydrogen in

the sample are respectively oxidized to carbon dioxide and hydrogen and energy is released.

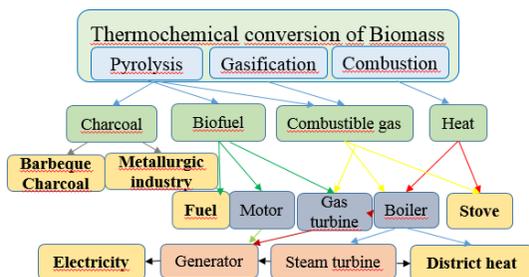


Figure 2: Thermochemical conversion of biomass.

In thermal conversion of biomass, proximate analysis is one of the most important characterization methods. Volatile matter and fixed carbon, together with ash residue and moisture content can be determined. This affects the combustion behaviour. The aim of this work was to characterize the gasification and the combustion properties of wood. Oak, birch, pine, and spruce were used as raw materials.

2 Experimental methods

Chips from oak, birch, pine and spruce were used as raw materials to find the combustion and the gasification properties of the wood. The chips were pulverized and calorific values, proximate characterization and ash residues were determined.

2.1 Measuring higher heating values

During combustion all fuels release energy due to breakage of chemical bonds. The released energy is referred to as heat of combustion, also known as the heating value or calorific value of the fuel and can be expressed as lower heating value, LHV or higher heating value, HHV. LHV is the heat released when a fuel undergoes a complete combustion and all the products remain in the vapour state. LHV is difficult to measure. HHV is the heat of combustion when all the water in the products has condensed to liquid. HHV is measured in a bomb calorimeter and describes the total release of energy when one unit mass of fuel is burned completely [10, 11].

HHVs of the wood were measured in a Leco AC-350 bomb calorimeter. In addition to these analyses, measurements of coal were performed. Samples of about one gram were prepared and analysed according to the user manual for the instrument [13]. Benzoic acid tablets were used to calibrate the instrument. To perform reliable results it was necessary to carry out three parallels of each type of wood. The results are presented as the average of all parallels with standard deviation.

2.2 Proximate characterization of wood with thermogravimetric analyses

Thermogravimetric analyses, TGA, is useful when it is necessary to study changes in sample weight while a sample undergoes a heating or a cooling process. TGA is used to characterize all kind of materials, for example polymer, plastic, food, petroleum, chemicals, biological and organic material. In a TGA it is possible to perform quantitative measurements of change in mass due to chemical reactions, decomposition, dehydration, Curie point transitions, oxidation, solvent and water evolution of a sample [17, 18]. The sample is heated in an inert atmosphere, a process called pyrolysis. The pyrolysis process of biomass usually starts at temperatures about 350°C. Pyrolysis involves both chemical and physical changes. The physical changes involve the samples potential to lose weight as well as the potential to change in thermodynamic properties [16].

Applying TGA to a particular problem is useful if change in mass due to heat is observed. If the change in mass is very small other techniques might be necessary [16]. TGA were performed with a Perkin Elmer TGA7 instrument with Pyris software. This standard furnace is operated at temperatures from 20°C to 900°C. One of the advantages of the standard furnace is the possibility of rapid heating and cooling rates [14, 15, 17].

During the analyses the samples were in an atmosphere of nitrogen with a purge rate of 20 ml/min. Weight changes were measured in the sample material as a function of temperature or time. In this atmosphere the sample only reacts to decomposition due to temperature, since nitrogen is an inert gas. Two different temperature programs were used to analyse the samples. The samples were gradually heated from 25°C to 900°C using 7 and 5 steps respectively. To evaporate all water content in the sample the temperature was kept at 110°C for 10 minutes. In the temperature range from 110°C to 550°C different forces will affect the chemical bonds and cause physical changes in the samples during the rise in temperature. Volatile compounds will be removed at a temperature of 550°C. The rest of the solid carbon is burned out at a temperature of 900°C. The residual matter is the ash content. Figure 3 shows the two different temperature programs.

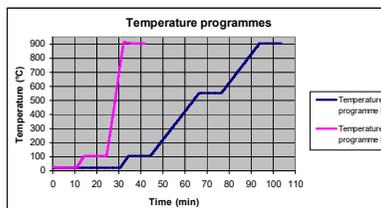


Figure 3: TGA using temperature program with 5 and 7 steps.

The total time of the two temperature programs was respectively 104 and 43 minutes. The three first steps were the same for both temperature programs. The system was kept isothermal at 25°C for 10 minutes. Then the temperature was increased to 110°C with a heating rate of 20°C/min and then was kept isothermal at 110°C for 10 minutes. In step 4 for temperature program I, the temperature was

increased from 110°C to 550°C with a heating rate of 20°C/min. and in step 5 it was kept isothermal for 10 minutes. In the sixth step the temperature was increased from 550°C to 900°C with a heating rate of 20°C/min. In the final step the temperature was kept at 900°C for 10 minutes.

2.3 Measuring ash residue in a muffle furnace

Ash is the solid residue from combustion process in air, produced from thermo-chemical or bio-chemical processes.

A Nabertherm muffle furnace was used in the analysis of ash residue. Six different methods were used to carry out measurements for the different types of wood. 2.0 - 4.0 gram of the sample material was weighed in a porcelain crucible. In two of the measuring methods the samples were first heated gradually from 20 to 900°C in 60 minutes and then burned isothermal at 900°C for 240 minutes and 2 minutes respectively. The samples were prepared from pulverized wood chips. Two parallels were prepared for all four types of wood. After ended program the samples were cooled to room temperature and the re-weighed.

In the last four measuring methods, the furnace was pre-heated to 900°C and the samples were burned under isothermal conditions with different time intervals, for 2, 5, 10 and 15 minutes respectively. These samples were from bigger wood chips. This procedure was applied to study how the different types of wood are affected by the time in isothermal conditions at a temperature of 900°C. The experiments are related to a real gasification process where the biomass enters the gasification zone at a temperature of 900°C.

3 Results

Characterization of the biomass were based on measurements of HHV, gasification properties and ash residues from oak, pine, birch and spruce. Results from the measurements of higher heating values of oak, pine, birch, spruce and coal are presented in Table 1.

Table 1: Results from analyses performed in bomb calorimeter.

Sample	HHV average (kJ/kg)	Standard deviation (kJ/kg)
Oak	17 682	± 33
Pine	19 099	± 183
Birch	17 551	± 164
Spruce	18 732	± 197
Coal	30 879	± 125

The HHV varied from 17.6 MJ/kg to 19.1 MJ/kg. Pine has the highest HHV, 19.1 MJ/kg. Birch has the lowest HHV, and the deviation between birch and pine is 1.6 MJ/kg. Compared to coal, which has a heating value of 30.9 MJ/kg, the heating capacity of wood is low. According to these results 1 kg coal produces nearly twice the heat compared to 1 kg of wood.



3.1 Thermogravimetric analyses, slow heating program

Thermogravimetric analyses were performed for oak, pine, birch and spruce under the same conditions using temperature program with a temperature raise from 25°C to 900°C for 104 minutes. The thermogravimetric thermal curve is displayed from left to right and are shown as an average of two parallels. The curve illustrates the variation in mass of a sample as a function of temperature and/or time. In Figure 4 the thermal curves from the analyses are displayed. Oak is displayed in blue colour, pine in pink, birch in yellow and spruce in red.

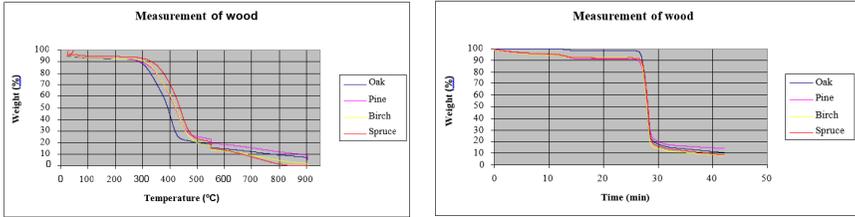


Figure 4: Weight/temperature and weight/time TGA thermal curve of wood.

For the first 62 minutes the curves representing pine, birch and spruce follow the same path. Oak deviates by losing weight more rapid in the temperature interval from 288°C to 455°C. This indicates that the pyrolysis process of oak starts at a lower temperature than for the other wood types. After 62 minutes the temperature has reached 455°C. Oak has reduced the weight to 22%, while the weight of pine, birch and spruce all have been reduced to 31%. During the final heating process the curves split. In the last 40 minutes, spruce had a more descending curve compared to the other wood types. Spruce is also the wood type that loses most weight in total, from the diagrams it is seen that spruce is burned completely. There is no sample left after 91 minutes, the temperature has then reached 850°C. Pine is the wood type that has the highest weight residue. At ended heating process pine has 5.6% left of its initial weight. Oak has marginal deviations from pine with a residue of 4.5%, while birch has a residue of 0.6% after ended heating process. The volatile matter content varied from 73–79%.

3.2 Thermogravimetric analyses fast heating rate from 110°C to 900°C

In this temperature program the sample is heated from 110°C to 900°C in during a time interval of 9 minutes. One parallel of oak, pine, birch and spruce were prepared. Figure 5 shows the thermal curves in temperature and time. Oak is displayed in blue colour, pine in pink, birch in yellow and spruce in red.

Pine, birch and spruce have approximately the same weight loss, with only marginal deviations, during the analysis. Oak takes another pattern in the first 27 minutes, where it has a slower weight loss than the others. After 27 minutes the temperature has reached 385°C. From 385°C to 900°C oak follows the other curves. At finished heating process the weight % of oak, pine, birch and spruce have only small deviations. Pine has a weight % of 14% and is the wood type that

has lost less weight. Birch has lost the most weight with 8% of its initial weight left. Oak has a residue of 10.5% and spruce 8.5%.

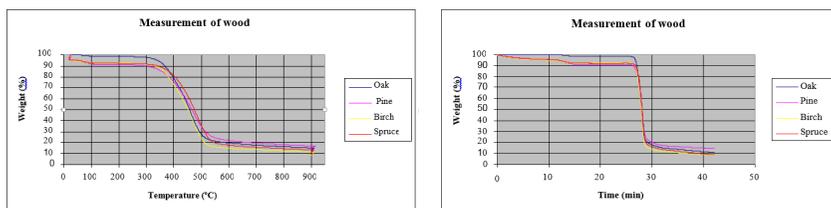


Figure 5: Weight/temperature and weight/time thermal curve of wood.

3.3 Results from ash residue, samples heated from 20°C to 900°C

In the two first measuring methods, the samples were heated gradually from 20–900°C in 60 minutes and then burned isothermal at 900°C in 240 minutes and 2 minutes respectively. The particulate matters that are left are grained finely, and that very small amounts of the samples are left as ash residue. Table 2 presents the results from the measurement of oak, pine, birch and spruce using methods I and II. The results are presented as average of two parallels.

Table 2: Results of analyses performed in muffle furnace.

Method	Oak	Pine	Birch	Spruce
Time, min.	Ash residue [%]	Ash residue [%]	Ash residue [%]	Ash residue [%]
240	0.58	0.46	0.48	0.24
2	0.81	0.54	0.44	0.29

There are some deviations between the different types of wood. Oak burns more slowly and has the highest ash residue in both of the methods. The ash residue results from oak also indicate that oak is more sensitive to time at isothermal conditions. It gives off a lot more weight in a period of 240 minutes compared to a period of 2 minutes at 900°C. Spruce is more easily burned and has the lowest ash residue in both of the methods.

3.4 Measuring ash residue in a preheated furnace with different time intervals

The samples were burned under isothermal conditions with different time intervals, for 2, 5, 10, and 15 minutes respectively and the samples were from bigger wood chips. Table 3 shows the results of the measurement. It was prepared one parallel of each type of wood.

Table 3: Results from ash residue performed in a preheated muffle furnace, different time interval.

(min)	Oak	Pine	Birch	Spruce
	Ash residue (%)	Ash residue (%)	Ash residue (%)	Ash residue (%)
5	0.90	0.39	0.53	0.28
10	0.77	0.23	0.43	0.14
15	0.73	0.24	0.23	0.23
2	0.91	0.82	0.45	0.76

Oak has the slowest burning rate compared to the other types of wood. Pine, birch and spruce have small deviations compared to each other. The variation between the different methods is also marginal. Method VI, which has a time interval of 2 minutes, distinguishes from the other methods. This method gives high percentage ash residue for all the four types of wood.

4 Discussion

Results from the experimental work are summarized and discussed

4.1 Heating value analyses

The heating value gives indication about the energy content in the samples. The higher heating value the more heat is produced during the combustion process. Combustion involves final oxidation of the combustible gases and the carbonated substances from the pyrolysis process. The result is a warm flue gas that can be utilized for electricity and for delivering heat to the district heating grid [19]. The experimental higher heating values, HHV, are listed in Table 4. This table also presents analyses results of HHV for certain wood types, carried out by Morten Grønli [19].

Table 4: Comparison of higher heating values.

Wood type	Experimental [MJ/kg]	Morten Grønli [19] [MJ/kg]
Oak	17.7 ± 0.03	
Pine	19.1 ± 0.2	19.7
Birch	17.6 ± 0.2	19.2
Spruce	18.7 ± 0.2	19.6

The HHVs of wood from forest indicate that energy content of the samples has relatively low variety. This can be seen from the small standard deviations. Table 4 shows that the experimental HHVs from this study are lower than the HHVs reported by Morten Grønli. The samples were not dried before the analyses, and this may be a reason for lower heating values. High water content in the samples gives lower heating value, since more energy will be used to evaporate the water. It is reasonable to believe that during combustion hardwoods like oak and birch produce less energy than softwoods like pine and spruce. If the density of the different wood types is taken into account, a different picture is drawn. According



to studies performed at Norsk Treteknisk Institutt in Oslo [20], hardwoods have higher weight per volume than softwoods [21]. This is shown in Table 5.

Table 5: Density and energy content per cubic meter wood with 15% moisture.

Wood type	Density [20] (kg/m ³)	HHV (MJ/kg)	Energy (GJ/ m ³)
Oak	690	17.7	12.2
Pine	510	19.1	9.7
Birch	630	17.6	11.1
Spruce	470	18.7	8.8

Oak has an approximate density of 690 kg/m³, while pine has an approximate density of 510 kg/m³. When these density values are known, it is possible to calculate the energy contents from the experimental HHV values.

$$\text{Energy} = \text{HHV} \cdot \text{Density} \quad (1)$$

Assuming a 10 MW CHP plant, the required volume of timber per day is estimated according to equation (2):

$$\text{Volume} = \frac{\text{Power}}{\text{Energy}} \cdot 3600 \cdot 24 \quad (2)$$

The density values obtained are from oak, pine, birch and spruce that contains 15% moisture. In Table 6, the density and the corresponding energy content for each type of wood are listed.

Table 6: Volume of wood required for production of 10 MW.

Wood type	Energy (GJ/ m ³)	Volume (m ³ /day)
Oak	12.2	70.8
Pine	9.7	88.7
Birch	11.1	78.1
Spruce	8.8	98.2

Coal has a HHV of 31.0 MJ/kg that is almost twice the heating value of oak, pine, birch and spruce. There are several advantages by replacing coal, and other fossil fuels (oil/gas), with fuel based on biomass. The major advantage is that biomass represents a renewable- and CO₂ reduced energy resource. The supplies of coal and oil are limited and therefore not renewable. For a 10 MW power plant, the need of coal can be calculated from equation (3):

$$\text{Mass} = \frac{\text{Power}}{\text{HHV}} \quad (3)$$

Assuming that the HHV of coal is 31.0 MJ/kg, the required amount of coal for a 10 MW power plant is then 0.32 kg coal/s that corresponds to 102000 ton coal/year. According to [30] 1 kg of coal produces about 2 kg CO₂ which corresponds a CO₂ emission of 19 000 ton/year. The ratio between amount of coal and the CO₂ emission depends on which type of coal that is used, but the value is normally between 1.8–2.5 kg. The use of bio energy has a great potential, partly

through higher production and utilization of biomass resources, and partly through efficient energy production due to research and development of technology. In 2011 the timber the annual growth in Norway was 25 million cubic metres. In principal it is possible to use the biomass that is available, and not refined, in energy production.

4.2 Thermogravimetric analyses

The thermogravimetric analyses of wood from forest in Norway indicate that biomass is highly reactive due to the fast pyrolysis process. In general, fuels with high content of volatile matters are flammable and easily burned. The combustion happens fast and gives a process that may be difficult to control. A controlled combustion process is important to achieve a complete combustion and regulated emissions. During the pyrolysis process the fuel is heated in an atmosphere free from oxygen. The products are bio fuel, combustible gasses and charcoal. The relative amount of these components depends on the heating rate and the temperature. Both the reaction mechanism and the production distribution are affected of these two factors [18].

It can be assumed from the TGA experiments that lower heating rates and temperatures improve the extent of decomposition. Oak, pine, birch and spruce were analysed under two different conditions. The residence time in a given temperature interval will be shorter for a sample that undergoes a rapid temperature program. It is therefore reasonable to think that in processes with high heating rate, the sample must reach a higher temperature to complete the overall reaction. Study of the TGA curves of oak, birch and spruce confirms this statement. For pine it shows a complete different pattern, the decomposition starts early and processes quickly. The difference may be due to decomposition of the extractive part of the sample. Pine contains relatively more extractives (resinous terpenes, light oils) compared to birch, oak and spruce [22].

To be able to draw any conclusions about how the heating temperatures and rates affect the pyrolysis process, it is necessary to have more knowledge about the structure and the composition of the wood types. The information from the TGA results is insufficient due to the thermal properties of the different types of wood. Implementation of Differential Scanning Calorimetry (DSC) will make it possible to generate both qualitative and quantitative data. Endotherm and exotherm reactions can be determined qualitatively at given temperatures. The amount of energy that is released from the on-going reactions can be quantified from the DSC thermogram.

4.3 Muffle furnace experiments

Deposition and sedimentation are often caused by ash residue. It is therefore important to have knowledge about the ash content of the samples. Biomass has small amounts of ash residue, and is therefore suitable even in small plants where the techniques for removing ash are manually and not well-developed. The experimental results are comparable to a set of ash residue measurements performed by Morten Grønli [21]. In Table 7, the results from the measurements



carried out by Morten Grønli are listed. The table also presents the results achieved by two of the experiments performed during this project.

Table 7: Comparison of ash residue.

Wood type	Gradually raise in temp.om 20°C to 900°C	Pre-heated furnace at 900°C	Morten Grønli [26]
Oak	0.58%	0.73%	
Pine	0.46%	0.24%	0.10%
Birch	0.48%	0.23%	0.23%
Spruce	0.24%	0.23%	0.14%

The procedure used by Morten Grønli corresponds to the experimental procedure where a gradually temperature raise was performed. During the experiments in this project the muffle furnace was heated to 900°C and kept isothermal for 2 hours, while Grønli during his experiment heated the furnace to 600°C and kept the temperature for 4–5 h. Results from Grønli gives lower ash residue results even if the temperature during his experiment was lower. By extending the heating time of the sample the burning process is affected, and the samples provides to burn out more of its carbonated residue. Comparison of the results with the experiment where the sample undergoes shorter heating time, in a pre-heated furnace at 900°C, shows that the ash residue is reduced. This might indicate that high pyrolysis temperatures gain the increase of pyrolysis gases, and decrease the gain of carbonated residue. Smoke emitted from the burning process was observed while the samples were burned. It was noticed that both softwoods and hardwoods have good burning properties and are easy to burn. It was observed that Softwoods have heavier smoke than hardwoods and starts to burn immediately while hardwood glows and gives good char quality.

5 Conclusion

Gasification and the combustion properties of wood are characterized. Oak, birch, pine, and spruce were used as raw materials. Analyses of pulverized wood chips from oak, pine, birch and spruce were performed in a bomb calorimeter, thermogravimetric analyzer and muffle furnace. Important factors that influence the gasification and the combustion properties of biomass are moisture, heating value, content of volatile components and ash residue. The HHV of oak, pine, birch and spruce were measured to 17.7 MJ/kg, 19.1 MJ/kg, 17.6 MJ/kg and 18.7 MJ/kg respectively. The thermogravimetric analyses of wood indicate that biomass is highly reactive due to the fast pyrolysis process. The volatile matter content varied from 73–79%. The ash content from samples with long residence time was almost the same as for samples with shorter residence time. The ash content is less than 1% for all samples. Analyses were performed with 2–3 parallels to check the repeatability. The standard deviations are small, which indicates that the results are reliable and representative.

Based on the measured HHV and the density of the different types of wood the daily need of fuel in a 10 MW power plant was calculated. Oak corresponds to a



need of 70.8 m³/day. Pine, birch and spruce correspond to 88.7 m³/day, 78.1 m³/day and 98.2 m³/day respectively. The heating value of coal is measured to 31.0 MJ/kg which is nearly twice the heating values of the wood. The advantage of replacing coal, and other fossil fuel, with fuel based on biomass is that biomass represents a renewable- and CO₂ neutral energy. The CO₂ emission from a 10 MW coal power plant is calculated to be about 19 000 ton CO₂/year, whereas a corresponding biomass plant will have a highly reduced net CO₂ emission. It is important to consider that it can be a time lag of many years related to the uptake of CO₂ in the new biomass. The time lag is caused by planting of new growing plants and a long growing period.

To be able to draw any specific conclusions about how the heating temperatures and rates affect the pyrolysis process, it is necessary to have more knowledge about the structure and the composition of the different types of wood. Biomass has small amounts of ash residue, and the influence of residence time in a heated atmosphere seems to be random. The ash content from samples with long residence time was almost the same as for samples with shorter residence time. Observations related to smoke emission from oak, pine, birch and spruce.

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