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# Characterization of pyrolysis products produced from different Nordic biomass types in a cyclone pilot plant

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ABSTRACT

Pyrolysis is a promising thermochemical technology for converting biomass to energy, chemicals and/or fuels. The objective of the present paper was to characterize fast pyrolysis products and to study pyrolysis oil fractionation. The products were obtained from different Nordic forest and agricultural feedstocks in a pilot scale cyclone pyrolysis plant at three different reactor temperatures. The results show that the main elements (C, H and O) and chemical compositions of the products produced from stem wood, willow, forest residue and reed canary grass are in general terms rather similar, while the products obtained from bark differ to some extent. The oil produced from bark had a higher $H/C_{eff}$ ratio and heating value which can be correlated to a higher amount of pyrolytic lignin and extractives when compared with oils produced from the other feedstocks. Regardless of the original feedstock, the composition of the different pyrolysis oil fractions (condensed and aerosol) differs significantly from each other. However this opens up the possibility to use specifically selected fractions in targeted applications. An increased reactor temperature generally results in a higher amount of water and water insoluble material, primarily as small lignin derived oligomers, in the produced oil.



## 1. Introduction

Increased utilization of renewable energy sources has gained particular interest in recent years due to environmental pollution, global climate change and depletion of fossil fuel resources. Biomass is an important source of renewable material and can be used to meet a wide variety of energy needs, including generation of electricity, heat and transportation fuels. The conversion of biomass can be achieved via thermochemical or biochemical processes. Pyrolysis is a promising thermochemical technology for converting biomass to energy, chemicals and/or fuels. Pyrolysis is basically thermal decomposition of organic materials in the absence of additional oxygen gas, which results in the formation of condensable vapor, gas and solid product (char, ash and particulate matter). The solid product is preferably separated directly after the pyrolysis step and the other products are rapidly cooled where pyrolysis oil is formed from the condensable vapors.

An opportunity for pyrolysis oil is that it can be produced from a variety of different low grade biomasses. The type of biomass is strongly dependent on the site location of interest for the pyrolysis production and in the Nordic countries possible biomasses include i.e. residues from the forest and agriculture, grass and short rotation coppice. Forest residues or residues from the forest industry are shown to be potential feedstocks for pyrolysis [1–3]. Furthermore, pyrolysis oil has been obtained from different kinds of straws [1,4,5], grass [1,4–7] and short rotation coppice [4,5] which exemplifies the broad range of possible feedstocks. According to Oasmaa et al. [1] forest residues (e.g. pine saw dust and forest residues) are the most feasible feedstock for pyrolysis in Scandinavia considering combustion application while agro-based biomasses (e.g. straws, timothy hay and reed canary grass) are more challenging, due to the high amount of alkali metals and nitrogen in these feedstocks. The pyrolysis principles used in these experiments [1] were a circulated fluidized bed pilot plant (20 kg $h^{-1}$) and a bubbling fluidized bed bench scale unit (1 kg $h^{-1}$), both operated in the temperature range 713–793 K. The pyrolysis of straw, perennial grasses and hardwoods, including willow short rotation coppice, in a bubbling fluidized bed laboratory scale reactor (1 kg $h^{-1}$) at temperatures between 778 and 798 K has also been investigated [4]. The aim was to characterize and compare the feedstocks and products by means of yields, quality and potential use and upgrading. The main conclusion found is that willow short rotation coppice is the energy feedstock that has the highest potential for fast pyrolysis processing if associated production costs and harvest yields can be maintained at the reported values [4]. Furthermore, it was also found that the bio-oil produced from switch grass has the highest potential regarding upgrading the oil for production of high value added chemicals [4].

When studying which particular feedstock that has the highest potential in pyrolysis processes, several aspects have to be considered. From an economical point of view, the obtained oil yield in the pyrolysis process is of importance but depending on the end application also the

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quality of the oil is of importance. If the oil is to be used in combustion applications, the crude oil is likely to be used directly. However, the quality is of importance since both the physical and chemical properties can adversely affect the related combustion properties and cause problems in storage and handling [8]. If the oil is aimed for more advanced applications, i.e. transportation fuels or chemicals, further upgrading is needed due to the relatively low energy content, high water and oxygen content, acidity and poor stability in the pyrolysis oil. Hence, in addition to the oil quality, the aspects of oil yield from the fast pyrolysis process and further upgrading steps have to be considered when the end application is chemicals or transportation fuels.

Regarding yields and quality of products from the fast pyrolysis process, these can be influenced by the process conditions (i.e. pyrolysis temperature, biomass heating rate and pressure) and the configuration of the reactor and condensation parts [9]. The fuel quality properties of the oil can be significantly improved by adding complementary upgrading processes, such as catalytic hydrotreatment and catalytic cracking, but with the main drawback that these upgrading technologies lead to a relatively low liquid oil yield [10] and possible use of the resulting byproducts will therefore be of importance for the overall economy.

Pyrolysis oil is a complex mixture of different compound groups, which makes further upgrading difficult since the different compounds react differently, e.g. cause coking [11]. If instead the oil can be fractionated and troublesome compounds removed (and further used) in an efficient and economical way before upgrading, the liquid yield during upgrading could be improved and other valuable components may be received. For instance, aldehydes and phenols tend to cause coking [12] and could perhaps therefore be removed from the oil before further catalytic upgrading to improve the efficiency.

The solid products from the pyrolysis process can also be used in a variety of applications, e.g. as energy source, carbon sequestration, improved soil fertility or activated carbon. In conventional pyrolysis technologies, sand (being the heat transfer media) is often mixed with the produced solids and hence complicate and limit the external usage of the solid product. The pyrolysis plant used in this work [13] utilizes a centrifugal ablative principle where biomass particles are rapidly heated by forced contact with an externally heated wall in a cyclone instead of in contact with hot sand particles. The solids formed in the reactor can therefore easily be separated from the other products and are not contaminated with sand.

This work was carried out under industrially relevant conditions using a novel pyrolysis oil cyclone reactor in pilot scale (20 kg $h^{-1}$) [13] in contrast to other studies comparing different feedstocks aimed for pyrolysis. Furthermore, the produced oil was sequentially fractionated by the principles of quench condensation and centrifugal separation into two separate fractions with different properties. Moreover, the objective of the present paper was to characterize fast pyrolysis products, in particular two oil fractions, produced from different Nordic biomass feedstocks in a pilot scale pyrolysis plant. The effect of reactor temperature on the product characteristics was studied for two forest feedstocks (stem wood and forest residue) and two agricultural feedstocks (short rotation willow (Salix) and reed canary grass). Complete mass- and energy balances for the different feedstocks will not be in focus in the current paper but will be presented elsewhere where the results presented herein will be used as input data. The results from this study will contribute to the existing knowledge of potential pyrolysis products from Nordic feedstocks and in addition propose potential applications of the oil fractions.

## 2. Experimental section

### 2.1. Pilot scale pyrolyzer

Below follows a description of the cyclone pyrolysis pilot plant, see Fig. 1. A complete description of the plant was reported recently [13]. The system can be divided into four main parts: feeding system, ablative cyclone reactor, oil separation system and gas furnace. In the feeding system fine-grained feedstocks (20 kg $h^{-1}$) are dispatched into a heated carrier gas (nitrogen, 750 $Ndm^3$ $min^{-1}$, 373 K) for further transportation through the system. In the ablative cyclone reactor the biomass particles are heated as the particles slide against the externally heated wall. The dimensions of the ablative cyclone reactor are based on a Stairmand cyclone [14] with adjusted inlet and gas outlet dimensions. The inlet was adjusted to fulfill the velocity recommendations for heavily loaded cyclones [15] while the gas outlet was reduced to reduce the gas residence time. The dimensions of the cyclone can be found in Fig. 1. The cyclone is constructed of different grades of stainless steel where the reactor is made of high temperature steel (253 MA) and the parts in contact with pyrolysis oil are made of acid-sustainable steel.

The reactor is jacketed and heated by using a mixture of air and hot gas produced in subsequent gas furnace. The wall temperature of the cyclone is monitored using one thermocouple of type K installed in direct contact with the wall located at the top of the cyclone. The temperatures in other locations of the reactor are also measured by additional eight thermocouples, at three different levels (top, middle and bottom, see Fig. 1). As reported earlier there is a temperature gradient at the reactor wall since the hot gas in the heating jacket enters at the top of the cyclone, the upper part of the reactor is about 40–120 K higher compared to the temperatures in the middle and bottom of the cyclone [13] which indicates that the reported wall temperature is somewhat overestimated.

The optimal pyrolysis temperature for liquid production is around 773 K depending on the feedstock [16]. In this study the term reactor wall temperature is used instead of pyrolysis temperature, which also is done in earlier ablative cyclone studies [17,18], due to difficulties measuring the true pyrolysis temperature. The experiments herein are carried out at different reactor wall temperatures (948, 1023 and 1048 K), a temperature range which is in good agreement with other ablative cyclone studies [17] used for optimum liquid production. An indication of the pyrolysis temperature is however given by the temperature of the gas leaving the cyclone which in this study varies between 723 and 803 K.

After the pyrolysis phase the produced volatile gases and solid residue are separated directly in the cyclone reactor. The solid residue is collected in a bin directly under the ablative cyclone and the gas, vapors and fine particles left through the top of the cyclone. The amount of fine particles is reduced in a second cyclone. The oil is thereafter collected in two separate steps. The first separation step is based on condensation in an indirect heat exchanger, resulting in a fraction here called condensed oil. The second step is based on aerosol collection in an oil mist separator, resulting in a fraction here called aerosol oil. The remaining gas is then preheated in a heat exchanger and combusted in a gas furnace. In Table 1 some operating conditions can be found for the experiments using different biomasses. The run times differ between the experiments but are not believed to affect the result to a high extent since the reactor operates at steady state during a major part of the experiments. The reactor reaches steady state very fast [13] and as soon as pressure changes due to buildup of deposits starts to occur the experiments are shut down.

Some improvements of the pilot plant have been made since previously reported tests [13]. The main change derives from an improved heat exchanger in the first oil separation step. The temperature of the gas after this step was in this work about 295 K and before it was about 313 K when operated with stem wood [13].

### 2.2. Description of the used feedstocks

In this paper five potential Nordic feedstocks were used: three forest feedstocks; stem wood (used as reference), forest residue and bark and two agricultural feedstocks; short rotation willow (Salix) and reed canary grass. The stem wood, delivered by Stenvalls Trä AB (Sweden),