Annex 3:

Production of Pyrolysis Oil Based on Different Biomass Types

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Introduction

A novel method to provide a renewable liquid fuel is to use fast pyrolysis in which biomass is converted into a bio-oil. The bio-oil can be used for chemicals production or be utilized as a liquid fuel which recovers 40 – 80 % of the biomass energy content. Among the many forms of biomass: lignin, algae and sewage sludge are attractive materials for fast pyrolysis due to their abundance, low price and non-competitiveness with food crops.

Many different fast pyrolysis reactor types have been developed. The fast pyrolysis reactors typically achieve a heating rate of 700 – 1500 K/s [1] and this is believed to be a main reason for dramatically increasing the bio-oil yield when compared with that of fix bed reactors having low heating rates of 5 – 100 K/min [2].

The pyrolysis centrifugal reactor (PCR) has been developed at the CHEC center. By a high centrifugal force, biomass particles can gain a high heating rate. The main advantages of this concept compared to fluid bed reactors are a compact design that uses a low flow rate of gas carrier but can treat large biomass particles up to a size of 20 mm

In this study the pyrolysis properties of lignin residue collected from an ethanol plant, sewage sludge collected from a waste water treatment plant and algae, straw and wood are investigated. The lignin residue, algae and sewage sludge are known as materials with a higher lignin fraction and high ash content when compared with a wood and straw. The objective of this study was to investigate the pyrolysis products distribution, enenergy recovery and bio-oil properties obtained by fast pyrolysis of these materials. The results were compared with wood and straw pyrolysis that were considered the reference sources.

Experimental setup

The PCR is described in figure 1. The biomass was introduced into the reactor by a screw feeder. The pyrolysis of biomass is taken place inside the reactor, whereby char, bio-oil and gas are produced. The large char particles are removed by a change-in-flow separator, whereas the fine char particles are collected by a cyclone. The vapor products are condensed in a bubble chamber filled with isopropanol as a condensing solvent. Light oil fractions and aerosols are further condensed by a coalescer filled with rockwool. Recycled gas maintained a desired gas residence time by using pumped back to the reactor.

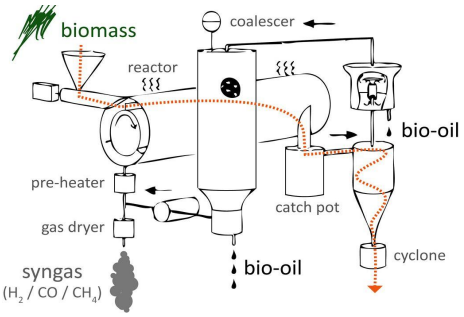

Fig. 1: sketch of the pyrolysis centrifugal reactor.

The collected liquid fraction is filtered through a filter paper of 5 µm. The char yield is determined from the chars collected in the char separator, the cyclone and the char left on the filter paper. The bio-oil yield is determined from the liquid that was passed through the filter paper. The gas measured from the gas meter is used to calculate the gas yield by the ideal gas equations.

Thermal Gravimetric (TG) analyses of the biomasses were carried out by a STA (Netzsch STA 449 F1). The bio-oils investigated have a water content of 25 – 28 wt%. The properties of the bio-oils were measured by the following methods: Water content by a karl fischer titration (Metrohm-701KT titrino), the higher heating value (HHV) by a bomb calorimeter (IKA C-200), the viscosity by a rotational viscosimeter (PAAR AMV 200), molecular mass by GPC and pH by pH meter (metro ohm).

Results

Thermal analysis of the biomasses (TG and DTG) was carried out at a heating rate of 10 °C/min. The samples were heated from room temperature to 950°C under N_2 flow, fallowed by cooling to room temperature. The sample was then heated up 950 °C with 90% N_2 and 10% O_2 flow. As can been seen in figure 2, the straw and wood experience maximum pyrolysis conversion in the temperature range of 200 – 400 °C while lignin, algae, and sewage sludge experience a broader pyrolysis conversion in the temperature range of 200 – 500 °C. The volatile yield is in the range of 84 - 76 % for wood and straw whereas yields of 67, 61 % and 45 % for algae, lignin and sewage sludge, respectively are determined by TGA (see table 1). The yield of ash and fixed carbon has an opposite trend. Based on the TGA data, the char yield of sewage sludge, algae and lignin residue could be predicted to be high in the PCR pyrolysis tests.

Table 1: the approximate analyses of the investigated biomass (dry basis)

Biomass	Volatile (% wt)	Fixed carbon (% wt)	Ash (% wt)
Wood	84.3	13	2.7
Straw	75.8	18.4	5.8
Lignin	61.2	26.7	12.1
Algae	67.1	10.3	22.6
Sewage sludge	45.44	3.02	51.54

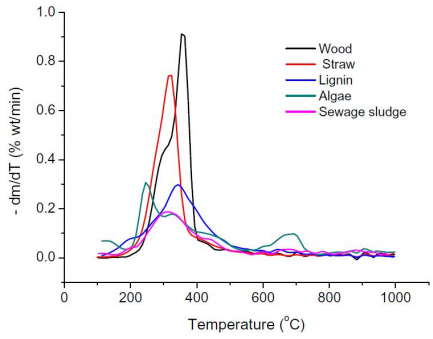

Fig. 2: TA for pyrolysis of the investigated biomasses

The pyrolysis in the PCR of biomasses were carried out in the temperature range of 550 - 575 °C, a total test time of 60-80 minutes and a feed consumption of 400 – 600g. The results are presented in figure 3. The largest liquid organic yield of 57 wt% on dry feedstock basis was observed for wood while the lowest liquid organic yield of 21 % appeared for sewage sludge. The organics yield of straw, algae and lignin residue feedstocks were in the range of 38 to 41 wt%.

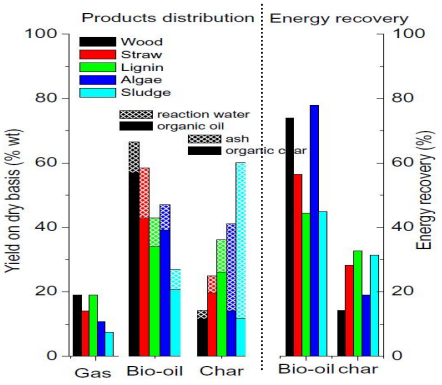

Fig. 3: product distribution and energy recovery

The reaction water yield at a level of 7 - 15 wt% was observed for the pyrolysis of the different biomasses. Since the ash is considered to remain totally in the char in fast pyrolysis, this leads to the high char yield for sewage sludge and algae (60 and 40 wt% respectively) when compared to that of wood and straw (14 and 25 respectively). Lignin shows a char yield of 36 wt% where it contains 26% organic char and 10 % ash. The gas yield varied from 8 to 20 wt% for the different biomasses.

The energy recovery was calculated based on the product yields and their heating values, and the results are shown in figure 3. Due to a high organic oil yield (57 %), wood oil gains 74 % energy recovered while straw, lignin and sewage sludge oils obtain 45- 56 % of feedstock energy content. An interesting result was found regarding the algae sample, the organic oil yield is 39 wt%, while the algae oil contains 78 % of the feedstock energy content. This gives a promising way to upgrade algae to liquid fuel with a high energy recovery efficiency.

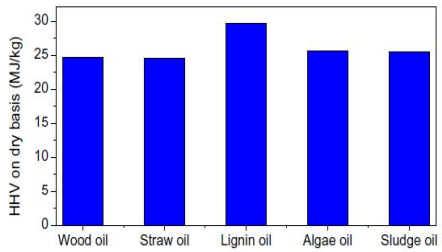

Fig. 4: HHV of bio-oils

The bio-oils properties were investigated with respect to higher heating value, molecular mass distribution, viscosity and pH. The higher heating value (HHV) of wood oil, straw oil, algae oil and sewage sludge oil obtain a similar value of 25 MJ/kg on dry basis. However the HHV of lignin oil show a higher value (30 MJ/kg) (figure 4). It is supposed that the oxygen content in lignin oil could be lower than that of other oils since lignin has a lower oxygen content.

As can be seen at figure 5, the molecular mass distribution shows two main peaks at around 165 and 398 g/mol for the bio-oils of wood, straw, lignin and sewage sludge that are corresponding to a water soluble fraction and water insoluble fraction (pyrolytic lignin) [3]. While the algae oil also has a third peak at around 1260 g/mol together with two main peaks at 165 and 398 g/mol. The average molecular mass for wood, straw, lignin, algae and sludge oil are 372, 272, 314, 442 and 440 g/mol, respectively. The results can partially explain the observed difference of oil viscosities in figure 6 where sludge oil and algae oil have a higher viscosity than that of wood, straw and lignin oil.

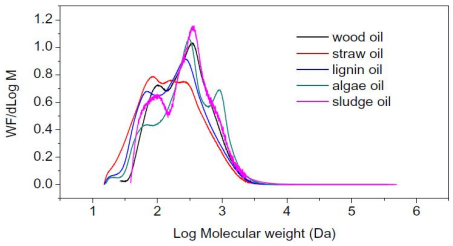

Fig. 5: the molecular mass distribution

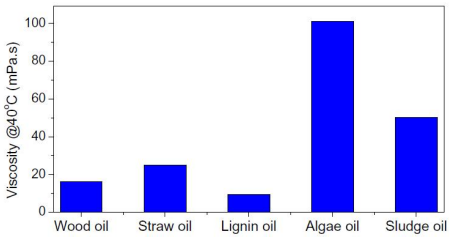

Fig. 6: the viscosity of bio-oils

As can been seen in figure 7 the pH of wood oil, straw oil, and algae oil vary from 3.1 to 3.8 whereas lignin oil and sludge oil have pH levels of 4.2 and 5.7, respectively. It is believed that some of the acid groups in lignin and sludge were removed during the treating in the ethanol plant or in the waste water treatment plant.

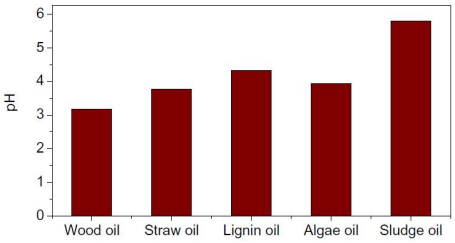

Figure 7: the pH of bio-oils

Conclusions

The highest liquid organic oil yield of 57 wt% on dry basis was produced by fast pyrolysis of wood while the lower yields of 34, 39 and 21 wt% for lignin, algae and sludge pyrolysis. The fast pyrolysis of algae showed a promising result with 39 % organic oil yield and 78 % of the algae energy value was recovered in the oil. Lignin oil obtains the highest HHV of 30 MJ/kg on dry basis when compared to others. The algae oil shows the highest average molecular mass of 442 g/mol, leading to a high oil viscosity of 101 mPa.s. Low pH value of oils from the virgin biomasses such as wood, straw, and algae were observed compared to that of the processed biomass such as lignin and sewage sludge.

References

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Acknowledgments

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