ABLATIVE FAST PYROLYSIS – PROCESS FOR VALORIZATION OF RESIDUAL BIOMASS

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Abstract

The direct use of pyrolysis condensates is hindered by unwanted properties of the liquid, especially if herbaceous biomass is used. Ablative fast pyrolysis simplifies the conversion process as no heat carrier material is necessary and for herbaceous biomass briquetting can be applied instead of energy-intensive grinding. To avoid phase separation of the primary liquid product staged condensation can be applied. Pyrolysis condensates collected as fractions from three-staged condensation can be used for energetic applications (bunker fuel or heavy heating oil) on one side but also as substitute for fossil resources in phenol-formaldehyde resins as adhesives in wood industry or polyurethane foams in sandwich boards for building insulation.

Introduction

Production of wood and food inevitably produces several residues like branches and tops from forestry, bark and saw dust from wood processing and straw, stems and leaves from agriculture. The utilization of these biomass resources does not imply any ethical conflict, neither for material utilisation nor fuels production. Fast pyrolysis is a conversion step to get a first intermediate product called pyrolysis condensate or bio-oil which has a higher volumetric energy density than the raw material, especially if herbaceous biomass is converted. This concentrated liquid intermediate product is worthwhile transporting over much longer distances than the original biomass residue to be further processed in a large industrial factory to a finished product[1]. The liquid product has several undesirable properties like high acid and water content and high viscosity[2]. For several feedstock even phase separation between an aqueous and a tarry phase occurs[3].

Several ways of utilising the primary liquid product(s) have been suggested[4]:

- Energetic use in boilers, diesel engines or gas turbines
- Gasification for the production of SNG, Fischer-Tropsch fuels, methanol or gasoline (MTG)
- Food ingredient after water extraction (“liquid smoke”)
- Substitution of phenol in phenol-formaldehyde resins as wood glue
- Reaction with compounds containing nitrogen to get a long-term fertiliser
- Reaction with calcium hydroxide to get a NO_x/SO_x-removing agent for coal fired power stations (“bio-lime”).

The majority of these applications require a physical or chemical upgrading of the primary liquid products[2]. The following sections will describe the principle of ablative fast pyrolysis, its advantage especially for herbaceous biomass and give examples for the utilisation of low-grade straw-based pyrolysis condensates after an easy upgrading step.

Principle of Ablative Fast Pyrolysis

Pyrolysis processes in general operate at elevated temperatures under air exclusion and generate two primary products: solid char and gaseous vapours. Parts of the vapours are condensable at ambient conditions, so that the primary vapour stream from the pyrolysis reactor can be further separated into a liquid product and permanent gases. While slow pyrolysis processes with long residence times of biomass and vapours aim at maximising char yield (up to 35 %), fast pyrolysis processes are meant to maximise the yield of liquid products (up to 75 %)[2]. To achieve this aim, the resulting vapours must be removed quickly from the heated area (to avoid secondary cracking reactions to permanent gases) and condensed in a downstream cooling section. Fast pyrolysis depends on high heating rates which usually require small particle sizes[2] in the range of 1 mm, sometimes even below. Grinding biomass to such small particle sizes is energy consuming, especially for herbaceous biomass[5]. Additionally, the majority of fast pyrolysis processes apply a solid heat carrier in direct contact with the biomass particles in order to achieve the necessary high heating rates[4].

As herbaceous biomass, especially when applied with low moisture content, has a low heat conductivity high heating rates can be achieved by introducing heat from an end face of a cylinder while securing good contact with the heating surface by mechanical force. This set-up is schematically shown in Figure 1. By applying such a principle biomass briquetting to certain dimensions (e.g. 50 mm diameter) is appropriate instead of grinding to below 1 mm. This set-up also eliminates the use of a heat carrier material and by that the later necessity to separate the char from the heat carrier, if the char is not used for heating the process.

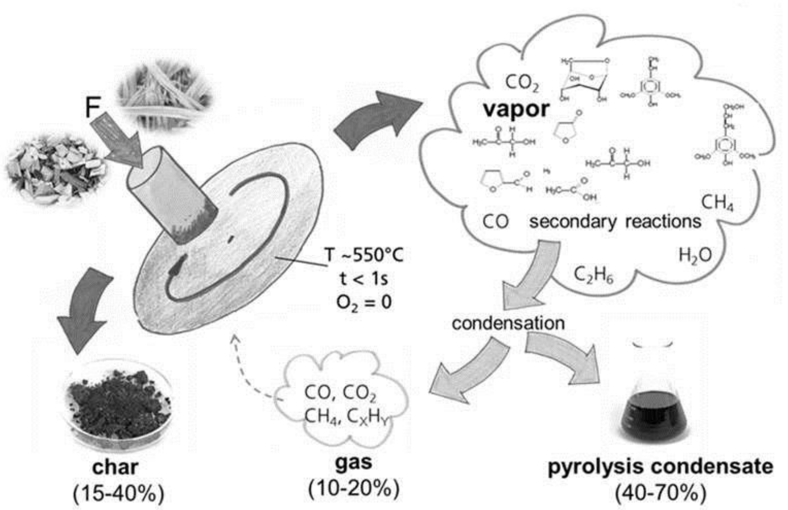


Figure 1. Schematic diagram of fast pyrolysis principle

Results and discussion

The pyrolysis plant used for the production of bio-oil samples uses the described principle of ablative fast pyrolysis. A rotating plate is heated by electrical resistance heaters from the rear side. Straw briquettes with a diameter of 50 mm were pressed against this plate by means of hydraulic pistons with a pressure of 30 barg. Coarse char particles directly fall out of the reactor due to gravity while fine char particles are removed from the primary vapours within a cyclone. Condensable components are received as liquids from a double effect cooler (coil and jacket cooling) and remaining aerosols are collected using an electrostatic precipitator. The permanent gases are burnt in a post-combustion chamber and released to stack. The pilot plant is described in more detail elsewhere[6,7].

Figure 2 shows the yield of solid, liquid and gaseous products for three different pyrolysis temperatures (as represented by the measured temperature of the rotating plate). Char yield is strongly decreasing and gas yield is slightly increasing with increasing temperature. The liquid, which is made of water and organic substances, shows a maximum yield of 49.6 % at a temperature around 540 °C. Although the liquid undergoes instantly phase separation into an aqueous phase and a tarry phase the shown distribution into water-free condensate and water condensate in figure 2 is only done by calculation. The tarry phase still contains a considerable amount of water and the aqueous phase dissolves lots of organic compounds as described later.

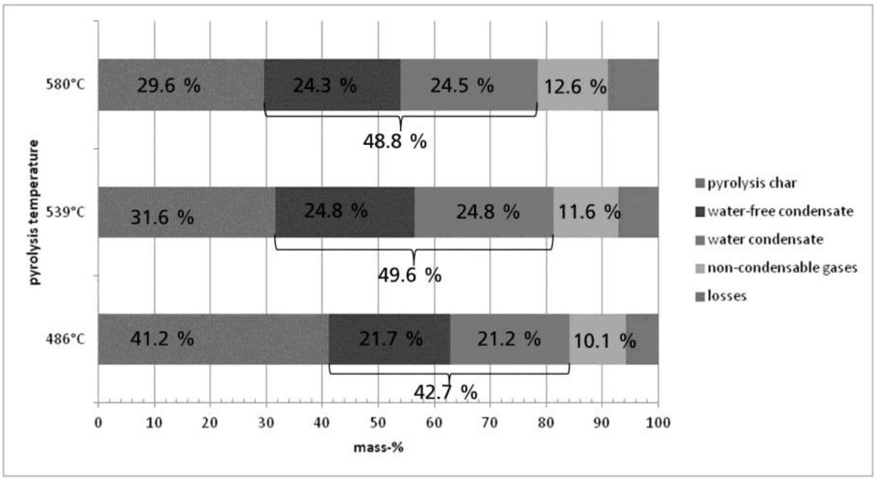


Figure 2. Mass balance of fast pyrolysis of straw at different pyrolysis temperatures

As the liquid is the target product it is analysed in greater detail using GC-MS/FID method by Thuenen-Institute for Wood Research in Hamburg[8]. The analysis revealed more than 150 individual organic compounds identified and quantified by this method. The individual substances were lumped to groups of categories and reported in table I together with the water content, which was determined by Karl-Fischer-Titration. The content of each category is analysed in both phases and calculated for the total amount of liquids by mass average. The overall water content slightly increases with pyrolysis temperature while the amount of heavy organics, which are not detectable with GC, decreases gradually due to further decomposition at more severe pyrolysis conditions. The tendencies of the organic categories are irregular. The yield of some categories increases with temperature (e.g. acids, alcohols, ketones and heterocyclic compounds), others reveal a maximum yield at 539 °C (e.g. phenols), while the remaining one shows a minimum yield (sugars). As the overall liquid yield shows a maximum at the medium temperature, a setpoint of 550 °C was selected for all following experiments.

Table I

Lumped composition of pyrolysis condensates for three different pyrolysis temperatures

Pyrolysis temperature	486 °C	539 °C	580 °C
Total water [%]	49.4	49.9	50.3
Nonaromatic acids [%]	6.1	6.9	10.7
Nonaromatic alcohols [%]	0.9	1.1	2.1
Nonaromatic aldehydes [%]	0.4	0.4	0.4
Nonaromatic ketones [%]	5.5	6.3	10.9
Phenols [%]	4.1	4.7	4.4
Sugars [%]	1.8	1.6	2.0
Heterocyclic substances [%]	1.8	1.9	2.1
Not GC-detectable compounds [%]	30.5	26.7	22.8

Pyrolysis condensates produced from a mixture of wheat and barley straw (50 weight-% each) instantly undergo phase separation into two liquids in the catch tank: an aqueous liquid in the upper part and a highly viscous, tarry liquid with a density of about 1.2 kg/ltr. in the lower part. In contrary to that behaviour the pyrolysis condensates produced from beech wood stay as single phase in the catch tank. Table II shows the lumped composition of both aqueous and tarry phase of pyrolysis condensates based on straw as well as the overall composition of the total liquid on a mass average and in comparison the composition of condensates produced from beech wood at the same setpoint for the pyrolysis temperature of 550 °C.

Table II

Lumped composition of two phases resulting from straw pyrolysis with single phase liquid from beech wood

	wheat / barley straw			beech wood
	aqueous	tarry	overall	
Mass ratio [%]	67.5	32.5	100	100
Total water [%]	61.7	25.3	49.9	28.7
Nonaromatic acids [%]	7.4	5.9	6.9	10.4
Nonaromatic alcohols [%]	1.5	0.3	1.1	0.2
Nonaromatic aldehydes [%]	0.0	1.1	0.36	3.5
Nonaromatic ketones [%]	5.9	7.1	6.3	5.5
Phenols [%]	1.2	12.0	4.7	7.7
Sugars [%]	1.6	1.5	1.6	6.0
Heterocyclic substances [%]	1.4	2.9	1.9	2.7
Not GC-detectable compounds [%]	19.1	42.4	26.7	34.8
Lower heating value LHV [MJ/kg]	7.9	22.3	12.6	15.4

As can clearly be seen the overall water content of straw based pyrolysis condensates is much higher compared to pyrolysis condensates produced from beech wood, although the moisture content of straw and beech wood was comparable (around 8 % for straw mixture[9] and 5 % for beech wood[10]).

Due to the unwanted properties of direct pyrolysis condensates (high polarity, high acidity, high corrosivity, low storage stability) the direct utilisation, especially that of phase separated condensates from straw pyrolysis, is at least challenging. Therefore different types of upgrading are introduced. One possibility is the esterification of acids and acetalisation of ketones and aldehydes, which masks said active groups in the mixture. This results in a reduced acidity and hence corrosivity as well as reduced polarity and thus lower water content[7]. The product is a single phase liquid, which might be then used as boiler fuel without any modification. A second possibility discussed in literature is hydrotreatment of the condensates under high hydrogen partial pressure (up to 100 barg) and elevated temperatures (up to 400 °C). This approach aims at the removal of oxygen from all reactive groups within the mixture and saturation of C-C double bonds[11]. A concept for only mild hydrotreatment of pyrolysis condensates based on herbaceous biomass was presented at this conference[12].

An alternative possibility to increase liquid properties for higher value added applications is the condensation of primary vapours in several stages and collection of fractions of condensates differing in dew point. The setup for a staged condensation in a side stream of the laboratory ablative fast pyrolysis plant comprises three series of double effect cooler and electrostatic precipitator (ESP)[13]. The vapours coming from the pyrolysis reactor enter the cooler of the first stage above 300 °C and leave the ESP at a temperature of 115 °C. The remaining vapours leave the second ESP at 87 °C and the third stage after total condensation is left with a temperature of 12 °C. Figure 3 shows the lumped composition of the three single phase liquids collected in these separators in comparison with the overall composition of the condensates of single stage total condensation. As can clearly be seen the water content of the first two fractions is greatly reduced in comparison to the total condensate and also the acid content of the first condensate is very low. On the other hand the amount of heavy organic compounds that are not detectable in GC is greatly increased in the first stage thus increasing the lower heating value of this condensate. The condensate collected from the second stage is enriched in phenolic compounds.

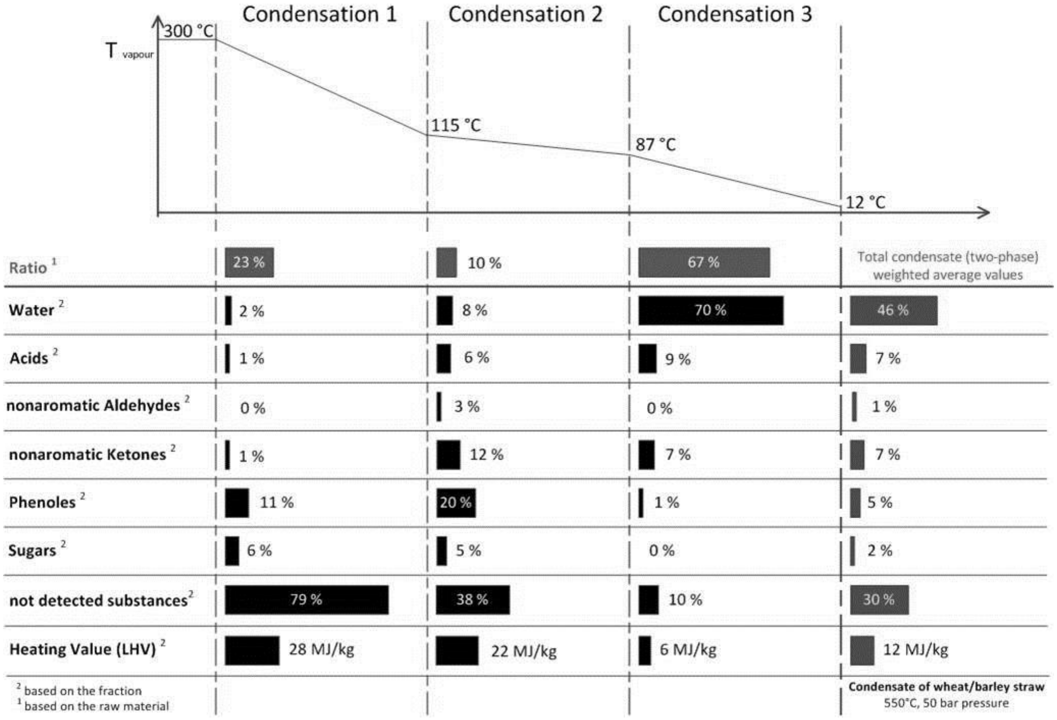


Figure 3. Lumped composition of liquids collected from three stage condensation.

The condensate collected from the first stage is virtually free of water and acids. Due to its high average molecular weight it appears solid at room temperature. When heated to around 70 °C it is easy to be pumped and due to its low corrosivity and naturally low sulphur content it might be applicable as bunker fuel in ECA zones like North Sea or Baltic Sea.

The condensate collected from the second stage was used in a detailed study to produce phenol-formaldehyde resins and characterised following DIN EN 205: “Adhesives - Wood adhesives for non-structural applications - Determination of tensile shear strength of lap joints”. Compared with data published earlier[13] the degree of substitution was further increased. This means, the phenol content in the original recipe for phenol-formaldehyde resin was substituted by weight with the pyrolysis condensate resulting from fraction two without any further treatment. As can be seen from figure 4 the free formaldehyde content always stays below 0.8 %, which is acceptable in comparison to 0.3 to 0.5 % in commercial resins. The most crucial value is the tensile strength of specimen glued together with the resin. For non-structural applications the threshold is defined as 10 N/mm^2, which is exceeded by the vast majority of samples. Also in nearly all samples the rupture occurred within the wood fibres and not within the glued joint. The increasing viscosity with increasing degree of substitution renders the application of such glues more difficult but not impossible. Also the lower reactivity revealed by the decrease of peak area in DSC tests indicates the necessity of longer curing time in application. The condensate collected in the third stage mainly consists of water and organic acids of which acetic acid is most abundant. One possibility to valorise this fraction is the recovery of pure acetic acid, but a more pragmatic approach is its application in agricultural biogas plants to increase methane yield[13].

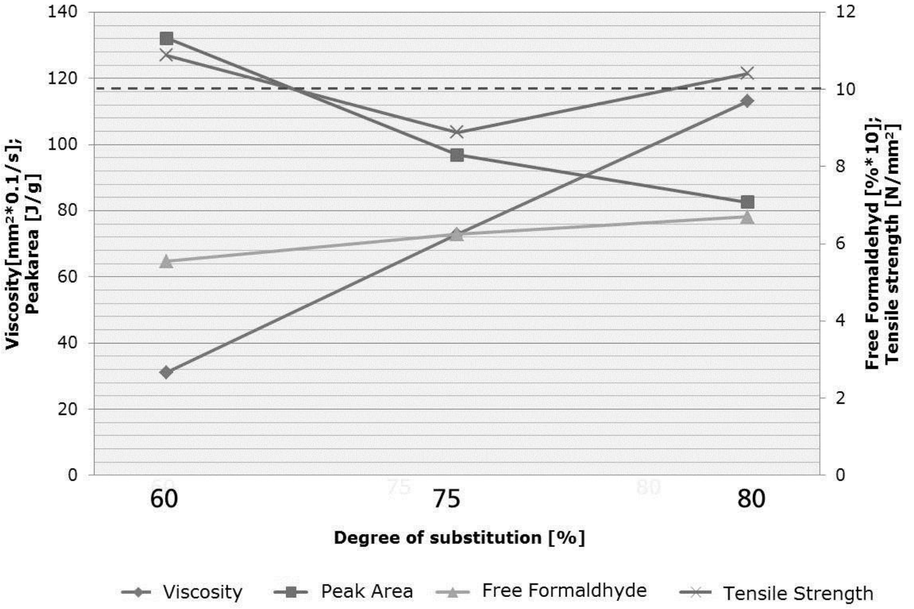
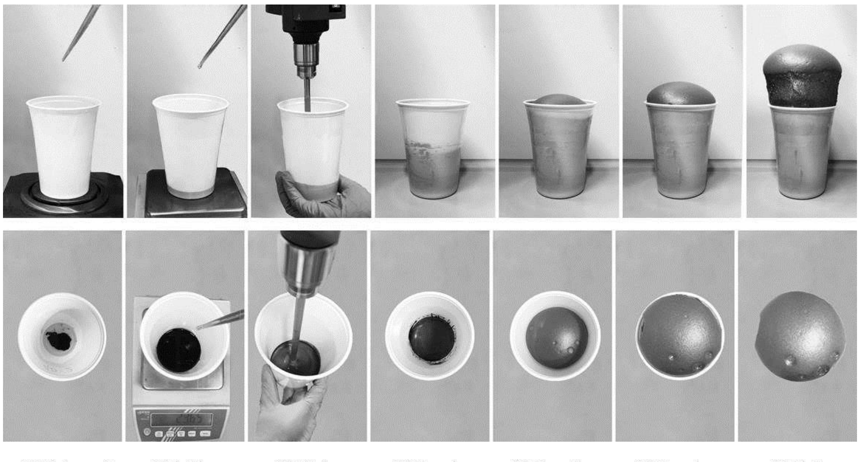


Figure 4. Variation of characteristic properties of phenol-formaldehyde resins over degree of substitution.

Alternatively the condensates from first and second stage can be combined to give a pyrolysis condensate low in water and acids and rich in organic compounds containing many OH-groups. Such material can be used to substitute the poly-alcohol component A in 2-component recipes for rigid polyurethane foams. Component B typically is a pure di- or poly-isocyanate like methylenediphenyl diisocyanate (MDI), which was used in its polymerised form (PMDI). Apart from polyalcohols as the main reactive compound in component A also catalyst, foaming agent and stabiliser are present. For the study polyethylenglycol with an average molecular weight of 400 Da (PEG400) was used in component A together with water as foaming agent (4 %), tin octanoate (1.5 %) and 1,4-Diazabicyclo[2.2.2]octane (0.5 %) as catalyst and Dow Corning® 2938 Additive (2 %) as stabiliser/surfactant. PEG400 was partly substituted on mass basis with pyrolysis condensates from 0 to 80 %. Figure 5 shows the process of production of polyurethane foam samples with a sample mass of 40 g each. The ratio component A/component B was set to 100:145. For intensive mixing of all compounds of the recipe a propeller stirrer was used at a speed of 700 rpm.



(1)Mixture of component A
(2)Adding component B
(3) Mixing
(4) Foaming beginning
(5) Foaming
(6) Foaming
(7) End

Figure 5. Production process of polyurethane foam samples with pyrolysis condensates.

A potential application for rigid polyurethane foams is the production of sandwich boards for building insulation. The most critical property for such application is the thermal conductivity. Measured values for thermal conductivity range from 0.03314 W/mK for pure PEG400 in component A and decrease with increasing content of pyrolysis condensate to 0.0283 W/mK for 80 % pyrolysis condensate as part of component A. A sample cut from commercial sandwich board as reference material exhibited a value of 0.0282 W/mK, which is similar to the value achieved with the sample with highest degree of substitution. Other properties like density or compressive strength of the substituted foam samples will be analysed in the near future.

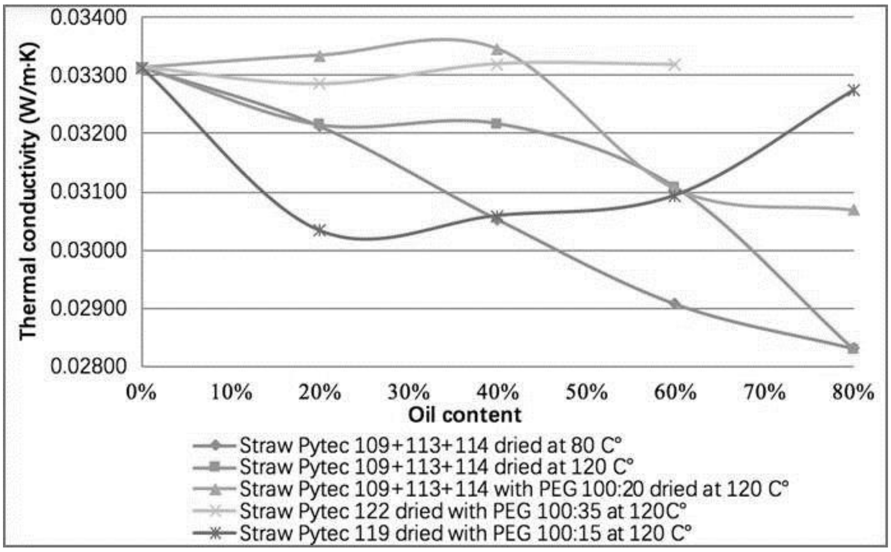


Figure 6. Thermal conductivity of polyurethane foams produced with straw-based pyrolysis condensates.

Conclusion

Staged condensation of primary pyrolysis vapours represents a first upgrading method for a preliminary separation of compounds according to their dew point. Component groups with similar characteristics are not fully separated but enriched in one fraction while depleted in the others. This enables an efficient processing of the separated fractions and opens up pathways to material utilization of (parts of) the pyrolysis condensates with potentially higher added value compared to energetic use. Especially material utilisation for phenol-formaldehyde resins in non-structural applications (adhesive in OSB or MDF) or polyurethane foams seems very promising. The main advantage of such separation method is that the remaining fractions are still utilisable for energy recovery (e.g. bunker fuel for high boiling compounds) or chemical production (e.g. acetic acid from third fraction).

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