

PRODUCING SINGLE PHASE FAST PYROLYSIS OILS FROM STRAW BY STAGED CONDENSATION

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ABSTRACT: Bio-oil produced from straw by means of ablative fast pyrolysis will separate into two phases due to high amount of water. This paper investigates the influence of staged condensation temperature on the water content of the condensates, with the aim of finding the minimum temperature at which the resulting bio-oil in the first stage will be a single phase liquid. The pyrolysis vapours were fractionated using a two-stage condensation system, each stage consisting of a cooler and an electrostatic precipitator (ESP) connected in series. The cooling medium temperature of the first stage was varied between 60 °C and 80 °C, whereas the temperature of the second stage was kept constant at 4 °C. The minimum vapour temperature at which the 1st stage condensate is a single-phase liquid was found to be 65.8 °C. The investigation showed that staged condensation is a possible way of producing single-phase bio-oils with a reduced water content and total acid number (TAN). Compared to the tarry phase of total condensates, the 1st stage condensates had an increased yield of organics.

Keywords: fast pyrolysis, biomass to liquid, upgrading, agricultural residues

1 INTRODUCTION

The thermochemical process of fast pyrolysis is a promising way to convert straw to liquids with better transport characteristics and higher volumetric energy density [1,2]. Loose straw has a density of 20-50 kg/m³, whereas by briquetting it using Hesston large bales, a density of 130 kg/m³ can be achieved [3]. Furthermore, during the pyrolysis process, complex lignocellulose structures (cellulose, hemicellulose and lignin) are decomposed (degraded) in short chain molecules that – after condensation to liquids – have a density of about 1,200 kg/m³. This main liquid product can be used with some restrictions as crude, untreated bio-oil or advanced (catalytically upgraded, mildly hydro-deoxygenated) bio-oil for further materials, fuels, and in the energy sector [4].

Fast pyrolysis crude bio-oil from straw spontaneously decomposes into two phases: a tarry-like phase at the bottom and an aqueous phase on top. The water content of the bio-oil plays a vital role in the phase separation process. Typically, fresh bio-oils with a total water content of more than 30 wt.% separate into two phases [5]. A correlation between the reaction water and the content of minerals in the biomass can be established. In their investigation, Oasmaa et al. [5] came to the conclusion that the bio-oil produced from feedstocks with an ash content below 1.0 wt.% have one phase and above 2 wt.% likely two phases. As agricultural residues have higher contents of catalytically active alkali metals compared to forest residues and soft woods [1], the bio-oils obtained from them will also have a higher water content, and thus a phase separation is not surprising.

For transport, storage, and further applications, single phase bio-oils have significant advantages. Biomass pretreatment (like leaching) for the prevention of phase separation is complex and partly expensive, whereas the water content in the bio-oil can be easily reduced by using staged condensation of vapours [2,11]. This investigation focuses on producing single-phase bio-oils from straw by varying the temperature of the 1st condensation stage.

2 METHODS

2.1 Feedstock characterisation

A mixture of barley/wheat straw (50 wt.% wheat and 50 wt.% barley straw) supplied by Erhard Meyer, Hude-Vielstedt, under the trade name “Strohfix – Gerste” was used as feedstock. Ultimate and proximate analyses were carried out at Fraunhofer UMSICHT, Oberhausen in accordance with standard test methods (DIN EN 15104 for CHN [6], DIN EN 15148 for volatile matter [7], DIN EN 14775 for ash content [8] and DIN EN 14918 for calorific value [9]). Minerals were analysed after microwave preparation by ICP-OES according to DIN 22022 [10]. The oxygen content was calculated by difference to carbon, hydrogen, nitrogen, and ash content.

2.2 Fast pyrolysis and staged condensation procedure

The experimental part was done in an ablative fast pyrolysis lab-scale (nominal feedstock throughput of up to 10 kg/h) reactor build by PyTrade GmbH, Hamburg. The pyrolysis conditions during the test series were kept constant at 550 °C pyrolysis temperature, 30 bar hydraulic pressure, 2.9 kg/h N₂-flow through the reactor, 440 °C hot vapour temperature and 17 s hot vapour residence time – mainly caused by the hot gas filter (Table I).

Table I: Experimental conditions

| | |
|---|-----------|
| reactor (surface) temperature | 550 °C |
| hot vapour temperature | 440 °C |
| hot vapour residence time | 17 s |
| hydraulic feeding pressure | 30 bar |
| biomass feed throughput | 4.1 kg/h |
| N ₂ mass stream | 2.9 kg/h |
| 1 st stage temperature | 4 – 80 °C |
| 2 nd stage temperature | 4 °C |
| ESP voltage (1 st and 2 nd stage) | 15 kV |

Fine char particles were removed using a hot gas filter. The cleaned volatiles (vapours and aerosols) were collected in a two stages condensation chain in a side stream (about 10 wt.% of the produced vapours), each stage consisting of an internally cooled condenser and an electrostatic aerosol precipitator (ESP) (Fig. 1).

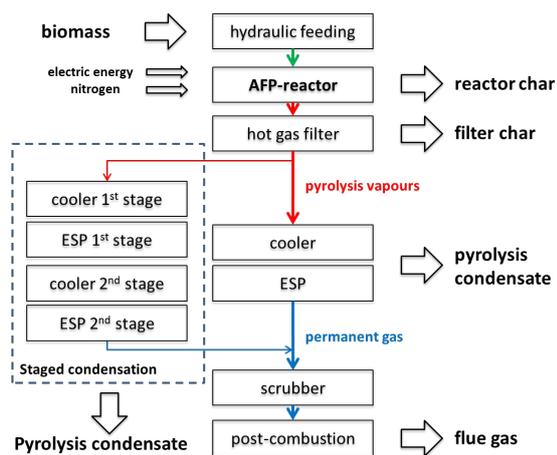


Figure 1: Schematic experimental setup

The vapour condensate and the precipitated aerosol from each stage (1st and 2nd stage) were collected together in a cooled flask. The reactor and condensation system are described in more detail in Schulzke et al. [11]. In the investigation, the condensation temperatures of the 1st stage (cooler and ESP) was varied by changing the cooling medium temperature from 60 °C, 65 °C, 70 °C to 80 °C. The temperature of the 2nd stage (cooler and ESP) was kept constant at 4 °C. The further reported vapour temperatures were measured using resistance temperature sensors PT100 in the gas stream after the ESP of each stage.

2.3 Product characterisation

The mass of the collected bio-oil liquids was measured with a mass balance Sartorius PC60 FEG-S. In case of two phase bio-oils, the tarry phase was separated from the aqueous phase by decantation. The analytical values for the whole bio-oil were expressed as mass weighted averages of its both phases.

The water content and total acid number (TAN) of the bio-oil fractions were analysed at Fraunhofer UMSICHT, Oberhausen. The water content was determined according to Karl Fischer (ASTM D6304 [12]) using Metrohm KFT 795 with Hydranal® Composite 5 (Fluka) as titrant and Hydranal® methanol rapid water-free (Fluka) as solvent. The total acid number (TAN) was measured according to ASTM D664 [13] using Mettler Toledo T50 with 0.1 mol/l KOH solved in isopropyl alcohol (KB Bernd Kraft) as titrant and a mixture of 50 vol.% toluene (Carl Roth), 49.5 vol.% isopropyl alcohol (Carl Roth) and 0.5 vol.% water as solvent.

The homogeneity of the bio-oil fractions was studied by using the microscope Keyence VHX 1000 at Fraunhofer UMSICHT.

GC-MS/FID analytics of bio-oil fractions were performed by Thuenen-Institute for wood research, Hamburg. The reported results of individual compounds were lumped together in groups of chemically similar compounds.

3 RESULTS AND DISCUSSION

The used straw feedstock had a moisture content of 6.8 wt.% and an ash content of 3.1 wt.%. The water from the feedstock and the reaction water that results from

primary and secondary pyrolytic reactions are mainly found in the condensed bio-oil; only a small part is probably carried out with the gas stream. The amount of reaction water is promoted by the presence of catalytically effective minerals (13,300 ppm K, 1,660 ppm Ca and 338 ppm Mg) (Table II).

Table II: Feedstock analysis

| Proximate analysis (wt.%) | |
|------------------------------|--------|
| water content (ar) | 6.8 |
| ash (mf) | 3.1 |
| volatiles (mf) | 73.1 |
| fixed carbon (mf) | 23.8 |
| Ultimate analysis (wt.%, mf) | |
| C | 47.6 |
| H | 5.6 |
| N | 0.4 |
| O ¹ | 43.3 |
| Inorganic metals (ppm, mf) | |
| Cl | 2,448 |
| K | 13,300 |
| Ca | 1,660 |
| Mg | 338 |
| Na | 187 |

mf – moisture free

ar – as received

¹ calculated by difference

The product distribution of three mass balance experiments, calculated from as received biomass, is as follows: 50.4 wt.% bio-oil, 27.6 wt.% char and 15.5 wt.% gases (Figure II). CO₂, CO and CH₄ were analysed continuously as the main gases during pyrolysis process. Other hydrocarbons (< C₆) and hydrogen were only present in trace amount, and thus can be neglected. The difference to 100 wt.% represents the cleaning losses, undetected gases, and vapour backflow through the biomass feeding channels.

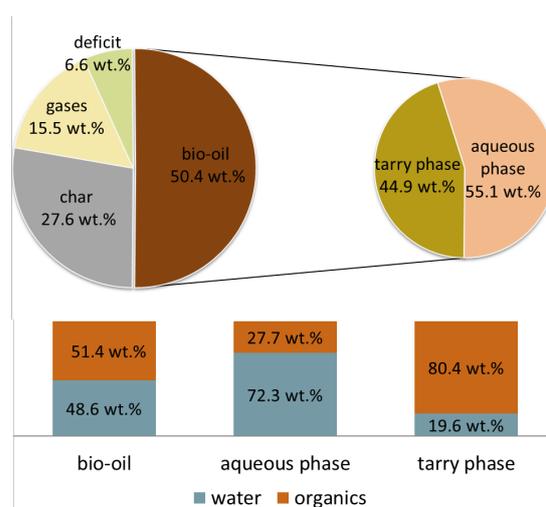


Figure 2: Mass balance of straw on as-received biomass basis (above); water and organics of bio-oil fractions (below)

The produced bio-oil decomposes into 44.9 wt.% tarry like bottom phase and 55.1 wt.% aqueous phase. The aqueous phase has a water content of 72.3 wt.% and the

tarry phase of 19.6 wt.%; this corresponds to a calculated water content of the whole bio-oil of 48.6 wt.% (Fig. 2). Based on these data a phase separation is not surprising.

For the most main applications, only the tarry phase is usable. Char, gases and the aqueous phase are considered as by-products, although they could also have useful applications. By-product pathways are not discussed further in this paper.

The obtained aqueous phase contains a significant amount of organics (27.7 wt.%), while the tarry phase still contains a significant amount of water (19.6 wt.%). In order to increase the process efficiency, the optimization approach aims to reduce the water content (and organic acids) in the tarry phase and the content of organics in the aqueous phase by condensing the pyrolysis vapours in two stages. The target end product is a single-phase high quality bio-oil which retains a maximum possible amount of organics. A vapour separation using staged condensation according to vapour pressure has the advantage that the water and acetic acid (main organic acid product) are in a similar temperature range compared to other middle and high boiling organics, and therefore they are easy to separate. In order to produce single-phase bio-oils, the condensation temperature must be adjusted in a way that the resulting bio-oil will have a water content below 30 wt.% (critical water content area for phase separation) [5]. The total water content of the 1st stage condensate decreases from 48.6 wt.% at 4 °C and about 35.9 wt.% at 62.8 °C to 6.3 wt.% at 71.0 °C. The collected bio-oil decomposed into two phases at and below 62.8 °C vapour condensation temperature. At and above 65.8 °C a single-phase bio-oil was produced. The area of phase separation was found between 62.8 °C and 65.8 °C which corresponds to a water content in the 1st stage condensate of 35.9 wt.% and 25.1 wt.% respectively. Fig. 3 describes the relationship between phase separation and water content of the whole 1st stage bio-oil.

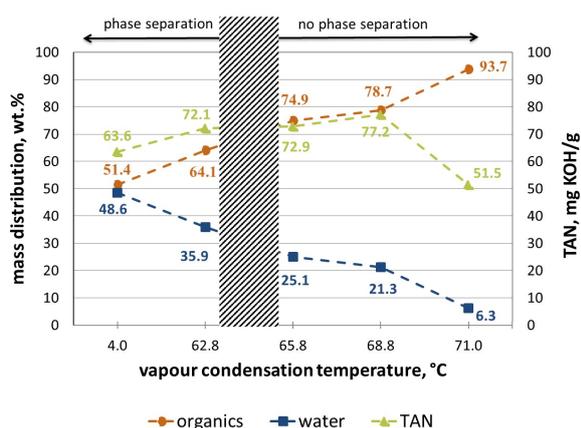


Figure 3: Phase separation depending on water, organics and total acid number (TAN) of the 1st stage condensate

The determined critical water content (25 – 35 wt.%) is in accordance with the literature (typically critical content of 30 wt.%) [5]. The TAN will significantly decrease from 77.2 mg/g (68.8 °C) to 51.5 mg/g (71.0 °C). Because the main component that determines the TAN has a slightly lower vapour pressure (acetic acid; 15.8 hPa at 20 °C) compared to that of water (23.3 hPa at 20 °C), a significant reduction of TAN will be observed at a higher condensation temperature.

Fig. 4 shows a two-phase bio-oil from a single stage condensation (left) and the liquids obtained from staged condensation at 68.8 °C (right). The 1st stage condensate with a water content of 21.2 wt.% is a single-phase bio-oil and the 2nd stage aqueous liquid has an organic layer on top.

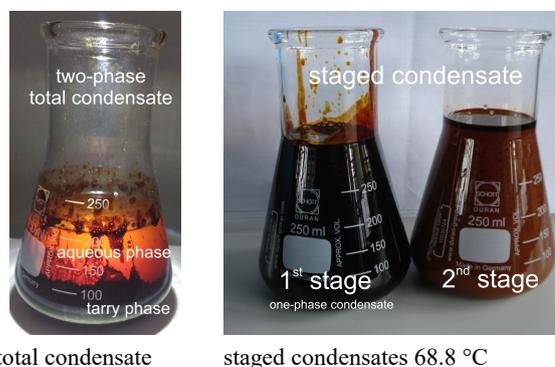


Figure 4: Two-phase total condensate (left) and staged condensates (right)

On one hand, the organics in the 1st stage tarry phase increase at the transition between the two-phase condensate (62.8 °C) and the single-phase condensate (65.8 °C) (Fig. 5). This can be explained by the fact that in the case of phase separation a significant part of organics will enter the aqueous phase.

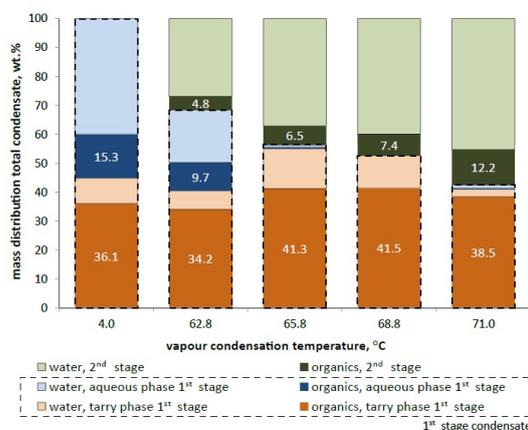


Figure 5: Distribution of water and organics on the tarry and aqueous phase from 1st and 2nd stage condensates

On the other hand, with increased condensation temperature more and more organics (starts with light organic compounds) will be lost to the second stage. Following the same logic, the water content of the tarry phase in two-phase condensations (62.8 °C) is lower than in single-phase condensates (65.8 °C). With increasing condensation temperature, the water content of single-phase 1st stage condensates decreases. The water content can be significantly reduced to 6.3 wt.% at 71.0 °C. However, the organics in the 1st stage condensate will also decline (Table III).

Compared to the tarry phase of the total bio-oil (4 °C), staged condensates (68.8 °C) with a similar water content showed more usable organics based on biomass in the target fraction. Furthermore, at higher condensation temperature a significant reduction in the water content

and TAN can be achieved at a small loss of organics (mainly caused by organic acids, aldehydes and ketones).

Table III: Comparison of the quantity and quality of the tarry phase, total condensates and one-phase 1st stage condensates

| | tarry phase | 1 st stage condensate | |
|--|-------------|----------------------------------|---------|
| cond. temperature | 4 °C | 68.8 °C | 71.0 °C |
| based on biomass (wt.%) | | | |
| organics | 18.2 | 20.9 | 20.1 |
| based on condensate fraction (wt.%) | | | |
| water | 19.6 | 21.2 | 8.6 |
| org. acids | 7.3 | 7.8 | 4.7 |
| org. alcohols | 0.4 | 0.9 | 0.9 |
| org. aldehydes | 0.7 | 1.4 | 0.2 |
| org. ketones | 11.8 | 11.0 | 7.4 |
| phenolics | 19.4 | 13.9 | 17.8 |
| sugars | 3.7 | 3.4 | 4.4 |

Both the bio-oil's tarry phase and the 1st stage condensate obtained at 68.8 °C have a macroscopic single phase appearance. However, due to complex chemical composition represented by both polar and non-polar compounds which are not completely mutually soluble, the liquids have in fact a microscopic multiphase structure. Fig. 6 shows the microscope images of the two liquids.

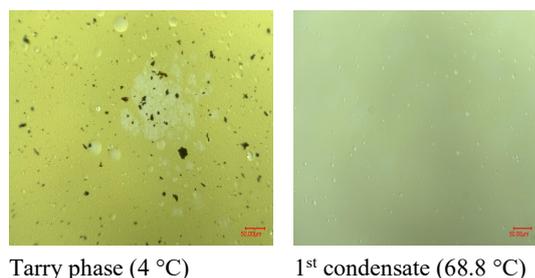


Figure 6: Microscope images of homogeneity of tarry-phase total condensate (left) and single-phase 1st stage condensate (right)

In the left image depicting the tarry phase, many droplets with a diameter up to 30 µm can be seen. Additionally, the tarry phase liquid was also observed to contain crystals with a diameter up to 20 µm which could be formed by polymerization process. The 1st stage condensate is more homogeneous, containing significantly less droplets with a smaller diameter (up to 10 µm) and no crystals.

4 CONCLUSION

The study demonstrated that staged condensation is an effective way of producing single-phase bio-oils from agriculture feedstock (straw) using staged condensation. Depending on the final application, bio-oils with different characteristics can be produced by a sound selection of condensation temperatures. The minimum vapour temperature at which the 1st stage condensate will be a single-phase bio-oil (or liquid) was found to be 65.8 °C. At higher temperature, the water content and TAN decrease significantly with a moderate loss of organics. Depending on the further application an optimum condensation tem-

perature for single-phase bio-oils regarding to the organics, water content and TAN can be determined.

5 REFERENCES

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7 LOGO SPACE

