

Evaporation of Biomass Fast Pyrolysis Oil: Evaluation of Char Formation

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Evaporation experiments of biomass fast pyrolysis oil and its aqueous fractions at low (TGA–10°C/min, Glass tube–100°C/min) and high (atomization ~10°C/min) heating rates are performed. Slow heating of pyrolysis oil produced ~28% char (on carbon basis), whereas atomization of oil droplets (~117 μm) produced ~9% char in the temperature range of 500–850°C. Aqueous fractions and glucose solutions also produced less amount of char by evaporating at higher heating rates (~3% char) when compared with slower heating (~24% char). The results obtained show that not a single lumped components class in pyrolysis oil can be identified that is primarily responsible for the char formation. At low heating rate, higher concentrations of organics in the bioliquids result in higher char yields, which reveals that a certain fraction in the oil produce char with a reaction order higher than one (polymerization reactions). The measured trends in char yield can be described by a model in which certain fraction of oil is converted by two parallel reactions to char and gas/vapor. © 2009 American Institute of Chemical Engineers Environ Prog, 28: 410–417, 2009

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INTRODUCTION

In gasification, reforming and combustion of pyrolysis oil, evaporation of the oil is the first step. For these applications, the oil is usually introduced as a fine spray (atomization) into a hot environment

(≥500°C). Atomization of pyrolysis oil into a hot environment is a complex process involving a vigorous phase change and a multi-components reaction network leading to gas/vapor and char (particulate matter), all in a very short period of time (milliseconds). Char formation leads to blockage and wear and tear problems in the atomizer and downstream applications. Therefore, char formation has to be minimized or dealt within the process by combustion, gasification or separation/recovery. However, char can also be a useful byproduct that can be combusted to generate the energy required for, e.g., gasification and reforming. The current understanding (both qualitative and quantitative) of char formation during atomization of pyrolysis oil is not sufficient to improve the design of the evaporation section in various applications.

There are only a few publications dealing with the evaporation of pyrolysis oil. Branca *et al.* [1] studied evaporation in a TGA (at low heating rates of 5–20°C/min up to 327°C) and focused on the evaporation pattern of the “light” components and the reactivity of the char residue. They reported that for the low heating rates applied, the char yield of pyrolysis oil evaporation was in the range of 25 to 40% for four different oils (on weight basis). To describe the evaporation they proposed a model of 8 parallel first-order reactions of lumped component classes to vapors. In this model it was assumed that a fixed fraction of pyrolysis oil reacted to char. Hallet *et al.* [2] used a furnace holding single droplets of *ca.* 1.6-mm diameter at 750°C (estimated heating rate ~6 × 10³°C/min above 120°C) and developed a model based on continuous thermodynamics and a

decomposition reaction of “lignin” to gas and char. Also in this study it was found that the char formation was severe during evaporation (*ca.* 25% on weight basis). Wornat *et al.* [3] and García-Pèrez *et al.* [4] studied the combustion of pyrolysis oil droplets by visualization techniques and analysis of the char residue. Wornat *et al.* [3] did experiments at 1375°C with droplets of 320 μm . With respect to formation of particulate matter, they concluded that soot was produced by vapor-phase pyrolysis reactions and liquid-phase polymerization reactions yielded char. García-Pèrez *et al.* [4] were able to produce very fine droplets of *ca.* 60 μm and injected them in a heated tube of 700 to 800°C. By a sophisticated measurement technique of the droplet diameter in a hot environment, they could show that the droplet size first decreased and then increased again as a function of residence time. Lederlin *et al.* [5] developed a model for evaporation of pyrolysis oil droplets based on oil with an artificial composition. This model included no char-forming mechanism.

To the best of our knowledge, quantitative information is not yet available in the open literature on the product distribution (gas, vapor and char) of pyrolysis oil evaporation when using small droplets (<2 mm). Recently, we submitted a paper on this subject using an atomizer that produces droplets of maximally 117 μm [6]. This work showed that these 117- μm droplets of pyrolysis oil injected into an inert environment of 500 to 850°C yielded significantly less char than oil slowly evaporating in a TGA (8 *vs.* 30% on carbon basis).

The present investigation deals with the product distribution of pyrolysis oil, its fractions and glucose solutions using the same atomizer. These feedstocks have been evaporated at different temperatures (500–850°C) and heating rates (TGA: 10°C/min, vaporization from a tube: 50°C/min and atomization: $\sim 1 \times 10^6$ – 8×10^6 °C/min) to clarify the char formation mechanism. To investigate the reaction order of the char formation reactions, glucose solutions of different concentration and pyrolysis oil aqueous phases of different dilution are atomized at *ca.* 510°C. In the discussion, it is evaluated which of the proposed char forming mechanisms is able to predict our experimental observations.

EXPERIMENTAL PROCEDURES

Materials

The pyrolysis oil used in this study was produced by VTT (Finland) from forest residue [7]. Before each experiment, the pyrolysis oil was filtered using a 10- μm filter. The aqueous and heavy fractions of this oil were prepared by adding demineralized water according to the schemes shown in Figure 1. The aqueous fractions ii, iii and iv represent a well-defined dilution series because they contain exactly the same organic molecules. This series (ii, iii and iv) and glucose solutions of different concentration were used to study the effect of the concentration of organics on the evaporation. Aqueous fraction (v) was prepared in a similar way as that by Czernik *et al.* [8], which was widely used for aqueous phase

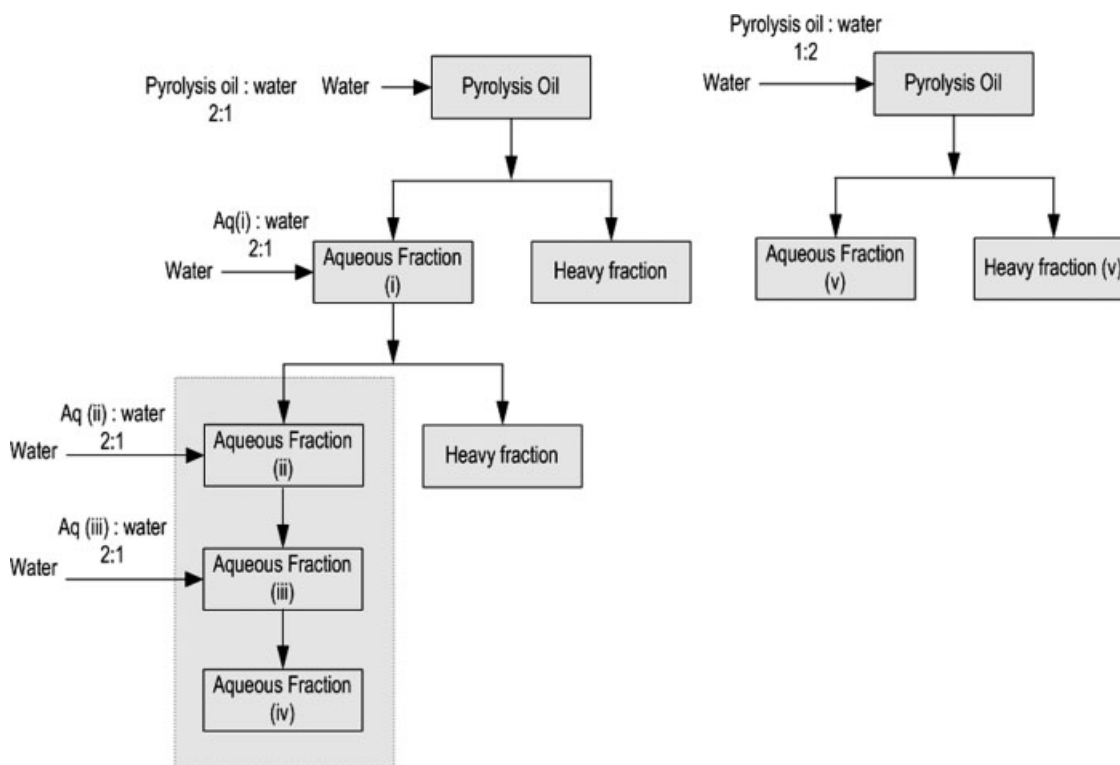


Figure 1. A Schematic process diagram of water addition in different amounts to the pyrolysis oil.

reforming. Glucose was obtained from Sigma Aldrich (St. Louis, MO). Pyrolytic lignin was prepared by adding the pyrolysis oil into ice-cooled water as described by Scholze *et al.* [9] The elemental composition and water content of the feedstocks are presented in Table 1.

Table 1. Elemental analysis and water content determination of pyrolysis oil and its fractions

Feedstock	C (wt %)	H (wt %)	Rest (wt %)	Water (wt %)
Pyrolysis Oil	40.6	7.6	51.8	23.9
Aqueous fraction (i)	24.4	7.2	68.5	48.5
Aqueous fraction (ii)	16.1	10.7	73.2	67.3
Aqueous fraction (iii)	10.8	10.8	78.4	79.2
Aqueous fraction (iv)	7.2	10.9	81.9	87.3
Aqueous fraction (v)	9.5	10.2	80.9	82.1
Heavy fraction (v)	46.5	5.9	47.6	13.5
Pyrolytic lignin	61.2	6.1	31.7	n.d

The rest is mainly oxygen with also other elements like sulfur and nitrogen. Ash is not determined. (n.d = not determined).

Continuous Pyrolysis Oil Atomization Set-up

To quantify the distribution of pyrolysis oil during evaporation between the gas, vapor and char phase, a dedicated continuous pyrolysis evaporation set-up was constructed. A schematic overview of the set-up is given in Figure 2. Pyrolysis oil (FR 100 ml/hr, duration *ca.* 1 hr; C_{in_oil}) was sprayed into an empty electrically heated stainless steel tube (\varnothing 40 mm, length 400 mm) using two different externally cooled atomizers. Two thermocouples were placed inside the reactor to record the actual temperatures in the middle of the reactor during evaporation experiments. The reported reactor temperatures are averaged values of the two thermocouples over the whole experiment. The reactor temperature was varied between 499 and 847°C. The droplet size was measured by pictures taken with a high-speed camera (Photron Fastcam SA1). An ultrasonic atomizer (Lecher US1, spraying angle 30°) created a droplet size distribution of which of the largest droplets were measured to be 88 to 117 micron (assisting gas N_2 4.0 Nl/min). However, the majority of the droplets was much smaller and below the resolution limit of the camera. The atomizer was specified for water to have a Sauter mean diameter of 30 micron. For pyrolysis oil, it is expected to be somewhat higher because of the higher viscosity. The heating rate of the droplets

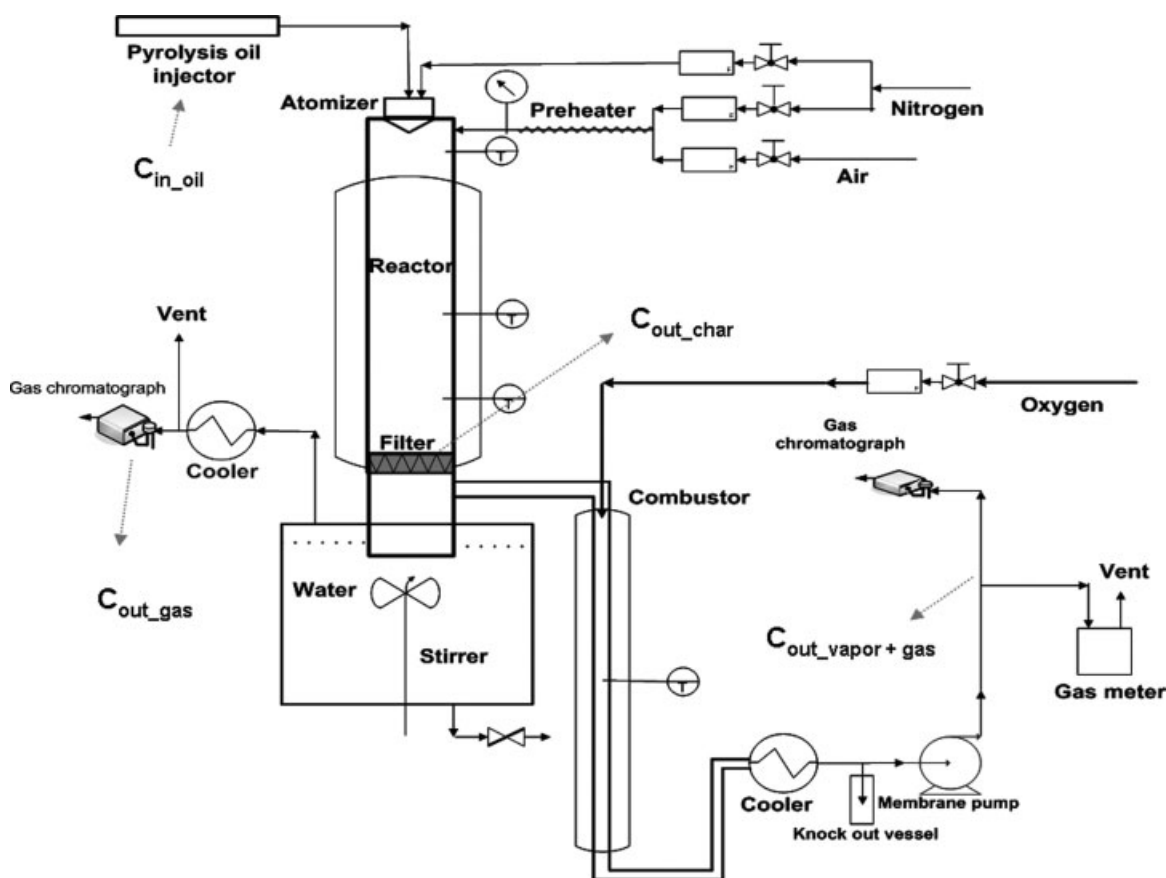


Figure 2. Schematic overview of the continuous pyrolysis evaporation set-up for measuring the carbon distribution from the oil to the gas, vapor and char. The amount of gas char are measured directly, the vapor amount is calculated by difference.

above 120°C was estimated to be in the range of $1 \times 10^6 - 8 \times 10^6 \text{C/min}^6$.

Additional preheated N_2 was added directly under the atomizer in a circular way to avoid vapor condensation on the cooler of the atomizer and to keep the residence time of the gases around 2 to 3 s over the temperature range measured. At the end of the evaporation chamber, a filter (mesh size 5 micron) was placed together with a small sand layer. This resulted in a pressure drop of maximally 0.3 bar. The filter temperature was always lower than the reactor temperature (T 498–665°C). After the filter, the stream was split into two streams. (i) Was going to a combustor where the produced gas/vapor mixture was totally combusted with pure oxygen producing CO_2 and H_2O . This gas flow was kept constant with a membrane pump that was placed after a condenser. (ii) Was directly fed to a quenching water bath that was mechanically stirred to quickly cool the gas/vapor mixture and trap the condensables. Two micro-GCs (2x Varian CP-4900; detecting N_2 , H_2 , CH_4 , CO , CO_2 , C_2H_4 , C_2H_6 , C_3H_6 and C_3H_8) measured the gas composition of the combustor ($C_{\text{out_vapor+gas}}$) and of the quench stream ($C_{\text{out_gas}}$). The integral carbon balance was made based on nitrogen as an internal standard that was fed to the evaporator. After an experiment, the collected char was combusted ($C_{\text{out_char}}$) to make a total carbon balance over the system. The carbon to gas and char conversions are measured directly and the carbon to vapor conversion is calculated by the difference between the combustor and quench stream according to:

$$C_{\text{out_vapor}} = C_{\text{out_gas+vapor}} - C_{\text{out_gas}}$$

Distribution:

$$\text{Gas} \equiv Y_G(\%) = 100 \frac{C_{\text{out_gas}}}{C_{\text{in_oil}}}$$

$$\text{Vapor} \equiv Y_V(\%) = 100 \frac{C_{\text{out_vapor}}}{C_{\text{in_oil}}}$$

$$\text{Char} \equiv Y_C(\%) = 100 \frac{C_{\text{out_char}}}{C_{\text{oil_in}}}$$

The carbon closure of the three different sections was found to be adequate: (i) Gas only: $101 \pm 1\%$ based on methane addition and recovery in both the combustor and gas + vapor line; (ii) gas + vapor: acetic acid was evaporated and partially thermally cracked (T \sim 720–750°C, S/C \sim 2.5–5.0). Here, no char is being formed: carbon recovery $96 \pm 1\%$; (iii) solid: wood pyrolysis char was combusted with a carbon recovery of $97 \pm 2\%$. The carbon recovery of all the pyrolysis oil and aqueous fraction evaporation experiments (gas + vapor + solid) was $98 \pm 4\%$.

Batchwise Pyrolysis Oil Evaporation

A fixed amount of pyrolysis oil (1.4 g) was added to the bottom of a glass tube (\varnothing 10 mm). The glass tube was placed inside a narrow fitting electrically heated oven and the temperatures were measured inside the oil itself and inside the oven (between the glass tube and alumina oven element). A heating rate of the oven of $\sim 50^\circ\text{C/min}$ was applied, which resulted in liquid heating rate of $\sim 100^\circ\text{C/min}$ at temperatures above 120°C. A small nitrogen flow was placed just above the oil to avoid direct contact with air and to remove the vapors released during evaporation. The remaining char was weighed and analyzed for its elemental composition.

Thermogravimetric Analysis

Heating experiments were performed in a Mettler Toledo thermogravimetric analyzer (TGA). The sample cups were heated to 800°C at a rate of 10°C/min in argon (60 ml/min). Additional to the TGA balance, the samples' overall weight loss was quantified with a very accurate external balance because some weight loss was already observed during the stabilization time of the TGA. The weight rate loss is defined:

$$r_{wt} \equiv \frac{dX}{dt} = - \frac{(m_\tau - m_{\tau+1})}{m_0(t_\tau - t_{\tau+1})} \text{ (1/s)}$$

Where τ and $\tau+1$ are logged times, T ($^\circ\text{C}$) the temperature of the sample cup and m_0 (mg) the initial amount of pyrolysis oil as weighted with the external balance. The overall char weight conversions (X) and carbon to char conversions were calculated using the external balance.

RESULTS AND DISCUSSION

TGA

Figure 3 shows the TGA curve of evaporating pyrolysis oil at 10°C/min up to 800°C. This curve is typical and in good agreement with the evaporation curves earlier reported [1]. At temperatures below 200°C, water and light components evaporate. Van Rossum *et al.* [6] showed that above 100°C, besides evaporation also polymerization reactions are already taking place in the liquid phase. In the range of 100 to 350°C, polymerization and cracking reactions proceed next to evaporation. Solvent solubility tests of the liquid at different temperatures [6] showed that the first actual char (THF insoluble material) is formed around 200°C and only char remains above 500°C. The low, but measurable, weight loss rate above 500°C (see Figure 3) shows that the char produced is devolatilizing/degassing slowly.

Table 2 lists the measured char yields of the feedstocks evaporated in the TGA (10°C/min up to 800°C). It has been found that the whole pyrolysis oil containing 23.9 wt% water gives 28% char (on carbon basis). Pyrolytic lignin clearly produces higher amount of char (54%). Evaporation of a glucose solution of 40 wt% in the TGA results in 28 wt% char. Remarkably, aqueous fraction i (48.5 wt% water) also

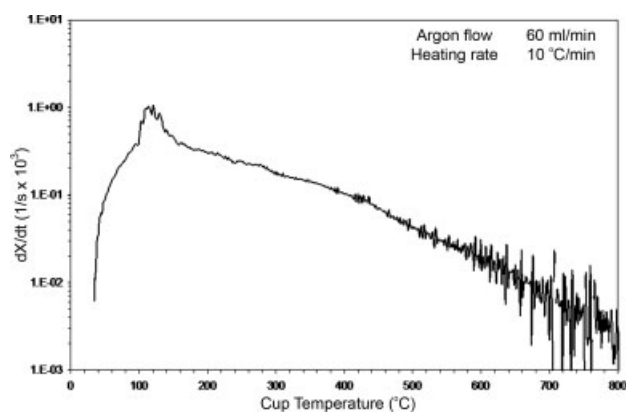


Figure 3. Thermo Gravimetric Analysis of pyrolysis oil at 10°C/min heating rate in inert (Argon) gas.

yields a high amount of char (24%). These results indicate that not a single lumped component class of pyrolysis oil (e.g., pyrolytic lignin) can be identified that is solely or predominantly responsible for char formation. Van Rossum *et al.* [6] has found that in the range of 1 to 100°C/min, the amount of char produced is not influenced significantly by the heating rate. This suggests that by performing TGA tests at such low heating rates, quantification of the maximum amount of char that can be produced during evaporation is possible. The components in the oil possibly leading to char are in this case not identified but are only quantified as a fraction of the feedstock. In a practical model (mechanism) for the evaporation of pyrolysis oil, the fraction of the feed susceptible to char formation can then be assumed to be the TGA char yield. This fraction can then be converted to char, gas and vapor in the model.

Continuous Evaporation by Atomization

The effect of reactor temperature on the amount of char, gas and vapor produced during the atomization of pyrolysis oil and its aqueous fractions is illustrated in Figure 4. The error bars in this figure are based on triple measurements, which show that the reproducibility is good. A series of atomization experiments were performed in the temperature range between 500 and 850°C, with a gas/vapor residence time of 2 to 3 seconds. The amount of the char produced from the pyrolysis oil is independent or slightly dependent on the temperature. This indicates that for pyrolysis oil, vaporization and the majority of the cracking reactions are completed before 500°C, which is in agreement with the TGA results (showing only low rates of char degassing above 500°C). The char yield from pyrolysis oil obtained with the atomizer is significantly lower compared with TGA results (8–9 *vs.* 28% char, carbon basis). This dependence on the heating rate (1–100°C/min for TGA *vs.* 1×10^6 – 8×10^6 °C/min for the 117- μ m droplets) cannot be predicted by the proposed models for pyrolysis oil evaporation that are based on fixed char yields [1, 2]. The char formation model proposed by Baert [10] for heavy fuel oil, which basi-

Table 2. Char productions using TGA of pyrolysis oil and related fractions/compounds

Feedstocks	Char wt %	Y _c (%)
Pyrolysis Oil	15	28
Aqueous fraction	7	24
Heavy fraction	21	33
Glucose solution	7	28
Pyrolytic lignin	43	54

The amounts are given both on weight and carbon to char basis. The sample was heated to 800°C with a heating rate of 10°C/min and an Argon flow of 60 ml/min.

cally consists of two parallel reactions of a certain fraction of the feed to char and vapors/gases, is able to predict this trend. To predict the trend of decreasing char formation for higher heating rates the activation energy of gas/vapor production reaction needs to be the highest; Baert [10] used 100 kJ/mol for polymerization and 270 kJ/mol for the reaction to gas/vapor. Their model predicted that although increasing the heating rate from 6×10^4 to 6×10^7 °C/min, the char production decreases from 12 to 0.5 wt% (on feed basis) for heavy fuel oil.

It is important to notice that the heating rate of pyrolysis oil evaporation by atomization is a function of the temperature of the droplet. When injected to the hot environment, the droplet is heated to 100–120°C, at which temperature it stays for a certain time (because of water and lights evaporation), where after it is heated again with a reasonably fixed rate. In this latter part of the heating trajectory (>120°C) char precursors and char are formed and, consequently, this heating rate is used in this study for comparison.

The char yield of the aqueous fractions is lower than the char yield of pyrolysis oil. Probably the aqueous fractions produce less char because of their low or zero content of pyrolytic lignin, which produces over 50% char in TGA (See Table 2). This may also explain why at 500°C aqueous fractions ii, iii and iv produce less char than fractions i and v (i and v still contain some heavies, see Figure 1). The char produced from aqueous fractions decreases from 500 to 650/700°C and hereafter remains constant. This char yield decrease may be ascribed to faster gasification reactions of char and/or char precursors (relative to polymerization) of the aqueous fraction of pyrolysis oil compared with the whole oil.

Our results show that when using the aqueous fraction of pyrolysis for steam reforming at temperatures around 850°C, as described by Czernik *et al.* [7], only a limited amount of char is produced (1–2% on carbon basis) in the atomization stage when producing small droplets of 117 μ m. Such low char yields can most likely be dealt with within the evaporator and/or downstream equipment, especially when a fluidized bed is being used and will only have a minor impact on the overall efficiency. When the whole oil is used for steam reforming under

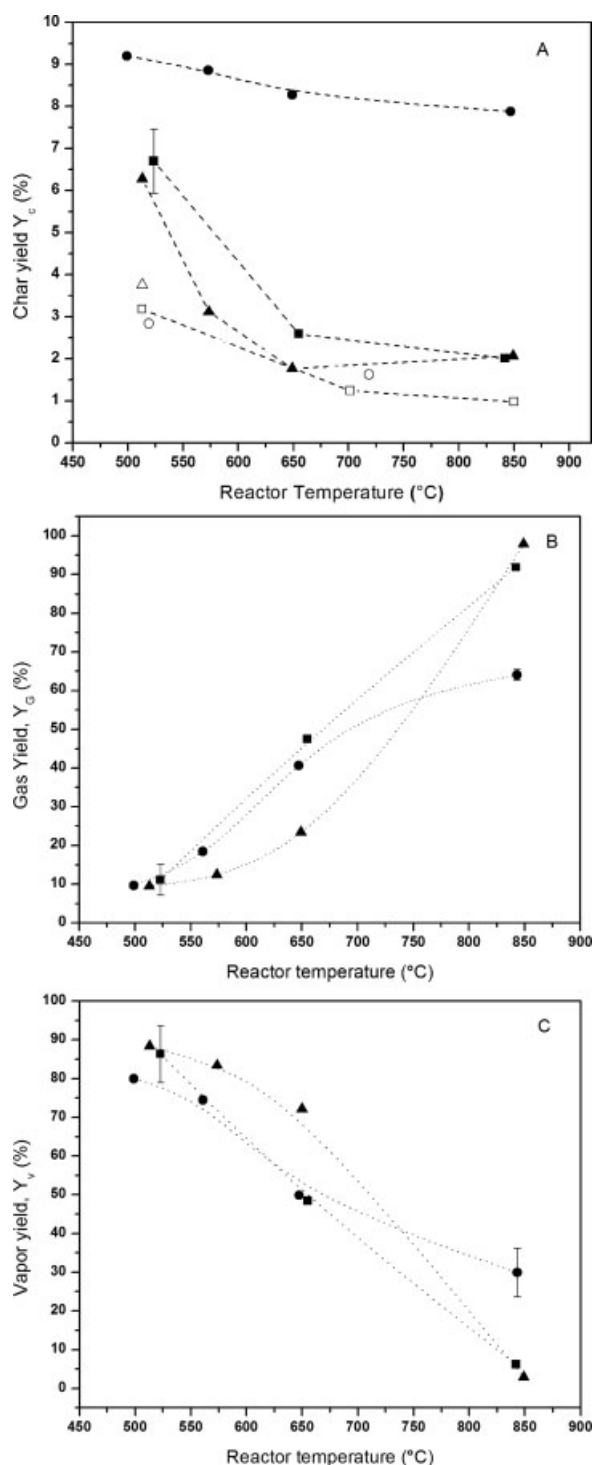


Figure 4. Carbon distribution over A. Char, B. Gas, and C. Vapor during the evaporation of pyrolysis oil and aqueous fractions. —●— Pyrolysis oil, —■— aqueous fraction (i), —▲— aqueous fraction (v) —△— aqueous fraction (ii), —□— aqueous fraction (iii), —○— aqueous fraction (iv).

otherwise identical conditions, as practiced by Van Rossum *et al.* [11], considerably more char is produced (8–9%), which makes the design of the evaporator more complex. At the moment of writing, we

are testing a new atomizer that produces droplets of less than 5 μm to investigate whether it is possible to further reduce the char production from the whole pyrolysis oil.

Figures 4B and 4C show that at increasing temperature, the gas yield increases and the vapor yield decreases, which is a result of thermal cracking reactions of the vapors. At 500°C, 70% to 90% of the carbon in the oil is recovered as vapors, whereas at high temperature (850°C), the vapor yield is 30 to 40% for pyrolysis oil and only 1 to 5% for the aqueous fractions.

The carbon-to-gas conversion is as low as 10 to 20% at 500°C and increases up to 60 to 65% at 850°C for pyrolysis oil, whereas for the aqueous fractions, a carbon-to-gas conversion of 90 to 95% is achieved at 850°C. It is not possible to ascribe the higher carbon-to-gas conversion for the aqueous fractions compared with the whole oil (difference is 30% on carbon basis) only to the difference in char yield (difference is 6–7%). It is therefore concluded that, overall, the vapors from the aqueous fractions are easier to crack than vapors from the whole oil.

Effect of the Organics Concentration on the Char Yield

Figure 5 shows the effect of the organics concentration in the bioliquid (10–40 wt%) on the char yield for both fast heating with the atomizer (1×10^6 – 8×10^6 °C/min) and slow heating in the batch evaporation tube (100°C/min) up to 510°C. As a feedstock, both glucose solutions and aqueous fractions ii, ii and iv were used. Both feedstocks are well-defined dilution series in which the organic molecules type does not change—only their concentration. In the batch evaporation tube, the aggregation state of the glucose solution was checked at temperatures above 100°C to exclude effects of complete evaporation of the water. In the range of 100 to 200°C, the samples appear as a boiling liquid, suggesting that some water is present or that glucose has already been partly converted.

Under slow heating conditions, the results clearly show that the char yield increases for higher concentration of organics in the bioliquids. This result indicates that the reactions of char precursors to char are of a reaction order higher than 1, which would be expected for polymerization reactions. For glucose solutions, such concentration effect has also been observed under hydrothermal conditions (350°C, 200 bar) by Knezevic *et al.* [12]. Using the atomizer, the char yield is lower and the effect of the concentration is not observed or, if present, falls within the error margins of the experiments. The absence of a concentration effect may be ascribed to the vigorous nature of the evaporation under very high heating rates. It is reasonable to think that with extremely high heating rates or diluted solutions, compounds remain isolated and end up in the gas/vapor phase before they can fully react in the liquid phase. With this “evaporation,” the density of the reactive compounds is lowered significantly (factor $\sim 10^3$), which will result in less polymerization.

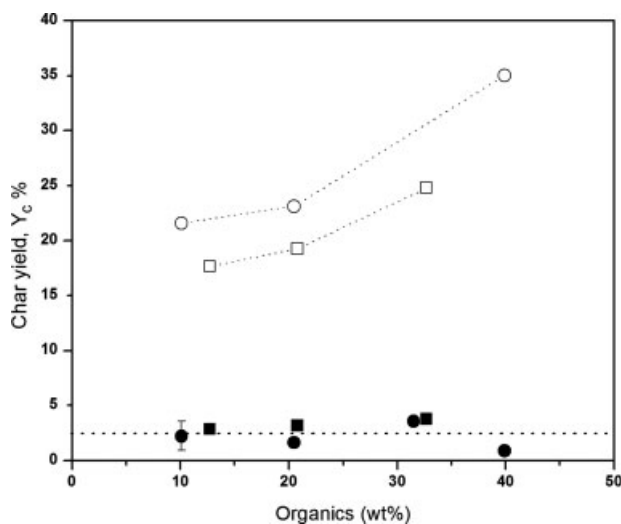


Figure 5. Effect of organics on char yield by different heating rates. reactor temperature = $510 \pm 10^\circ\text{C}$. —●— Glucose atomization; —■— Aqueous fraction atomization; —○— Glucose (glass tube - $100^\circ\text{C}/\text{min}$); —□— Aqueous fraction (glass tube - $100^\circ\text{C}/\text{min}$).

Char Formation Model

To the best of our knowledge, the only two proposed models for char production in evaporating pyrolysis oil are actually assuming that a fixed value of the oil is converted to char. These models cannot predict the trends we measured of decreasing char yield at increasing heating rate and higher char yields for more concentrated bioliquids. Models proposed for heavy fuel oil, in which a certain fraction of oil is converted by two parallel reactions to char and gas/vapor, can describe these trends (see Figure 6).

The cracking reaction is presumably first order, whereas our results with diluted feeds have shown that the reaction to char is of the order higher than one. To correctly predict the effect of the heating rate requires that the activation energy of the gas/vapor reaction is considerably higher than the activation energy for char production. For a practical model, it is proposed to assume that the fraction of oil that reacts to gas/vapor and char equals the char yield obtained in a TGA under slow heating conditions ($10^\circ\text{C}/\text{min}$).

CONCLUSION

The char yield of pyrolysis oil evaporation in a hot environment depends strongly on the heating rate. A char yield of 28% (on carbon basis) is measured under slow heating conditions in a TGA ($10^\circ\text{C}/\text{min}$ to 800°C), whereas using an atomizer producing droplets of *ca.* $117 \mu\text{m}$ results in 8 to 9% char in the temperature range of the environment of 500 to 850°C . Aqueous fractions of pyrolysis oil and glucose solution can be atomized ($117 \mu\text{m}$), yielding only 1 to 2% char for environment temperatures of 650°C and higher. Next to pyrolysis oil and its aqueous fractions (with different compositions), pyrolytic lignin and

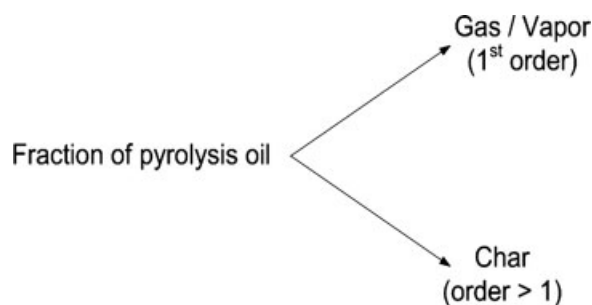


Figure 6. Model (mechanism) for char formation during pyrolysis oil evaporation.

glucose solutions also produced char upon heating, which shows that not a single lumped components class in pyrolysis oil can be identified that is predominantly responsible for char formation. Experiments with low heating rates using aqueous solutions with different concentrations of the same organics have revealed that the char producing reactions are of order higher than one (a higher organics concentration results in higher char yields). The measured trends in char yield can be described by a model in which a certain fraction of oil is converted by two parallel reactions to char and gas/vapor, with the reaction to char having an order higher than one and the activation energy of gas/vapor production being highest. For a practical model, it is proposed to use the char yield obtained in TGA under slow heating conditions (*e.g.*, $10^\circ\text{C}/\text{min}$) to define the fraction of pyrolysis oil that can react to char, vapor and gas.

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