

Evaporation of Pyrolysis Oil: Product Distribution and Residue Char Analysis

Guus van Rossum

Thermo-Chemical Conversion of Biomass, Faculty of Science and Technology, University of Twente,
Research Institute IMPACT, Enschede 7500 AE, The Netherlands

Berta Matas Güell

Catalytic Processes and Materials, Faculty of Science and Technology, University of Twente,
Research Institute IMPACT, Enschede 7500 AE, The Netherlands

Ragavendra P. Balegedde Ramachandran

Thermo-Chemical Conversion of Biomass, Faculty of Science and Technology, University of Twente,
Research Institute IMPACT, Enschede 7500 AE, The Netherlands

K. Seshan and Leon Lefferts

Catalytic Processes and Materials, Faculty of Science and Technology, University of Twente,
Research Institute IMPACT, Enschede 7500 AE, The Netherlands

Wim P. M. Van Swaaij and Sascha R. A. Kersten

Thermo-Chemical Conversion of Biomass, Faculty of Science and Technology, University of Twente,
Research Institute IMPACT, Enschede 7500 AE, The Netherlands

DOI 10.1002/aic.12126

Published online January 6, 2010 in Wiley InterScience (www.interscience.wiley.com).

The evaporation of pyrolysis oil was studied at varying heating rates ($\sim 1\text{--}10^6\text{C/min}$) with surrounding temperatures up to 850°C . A total product distribution (gas, vapor, and char) was measured using two atomizers with different droplet sizes. It was shown that with very high heating rates ($\sim 10^6\text{C/min}$) the amount of char was significantly lowered ($\sim 8\%$, carbon basis) compared to the maximum amount, which was produced at low heating rates using a TGA ($\sim 30\%$, carbon basis; heating rate 1°C/min). The char formation takes place in the $100\text{--}350^\circ\text{C}$ liquid temperature range due to polymerization reactions of compounds in the pyrolysis oil. All pyrolysis oil fractions (whole oil, pyrolytic lignin, glucose and aqueous rich/lean phase) showed charring behavior. The pyrolysis oil chars age when subjected to elevated temperatures ($\geq 700^\circ\text{C}$), show similar reactivity toward combustion and steam gasification compared with chars produced during fast pyrolysis of solid biomass. However, the structure is totally different where the pyrolysis oil char is very light and fluffy. To use the produced char in conversion processes (energy or syngas production), it will have to be anchored to a carrier. © 2010 American Institute of Chemical Engineers AICHE J, 56: 2200–2210, 2010
Keywords: pyrolysis oil, evaporation, char, gasification, droplet

Correspondence concerning this article should be addressed to G. van Rossum at g.vanrossum@utwente.nl.

Introduction

Syngas production from biomass can play an important role for producing renewable fuels and chemicals especially when

Table 1. Elemental Analyses (wet) and Water Content Determinations of the Pyrolysis Oils and Related Fractions/Compounds Used

(wt %)	C	H	Rest	H ₂ O
Pyrolysis oil (PW)	41.1	7.4	51.5	24.5
Pyrolysis oil (FR)	40.6	7.6	51.8	23.9
Aqueous rich phase (FR)	23.3	9.4	67.3	52.1
Aqueous lean phase (FR)	48.8	7.5	43.7	12.3
Wood (PW)	45.6	5.8	48.6	6.8
Pyrolytic lignin (PW)	61.2	6.1	31.7	n.d.
Wood pyrolysis char (PW)	88.7	2.5	7.5	n.d.
Activated carbon (Norit)	85.9	0.6	13.5	n.d.

The rest is mainly oxygen with also compounds like sulfur, nitrogen, and ash. (n.d.) not determined.

waste streams are being considered. For logistics and processing advantages, pyrolysis oil is proposed to become an intermediate energy carrier as the new “crude oil” for refining.^{1,2}

To convert pyrolysis oil to syngas/hydrogen, which is the basis for the production and upgrading (hydrogen) of many fuels and chemicals, catalytic steam reforming is considered as a very attractive route because moderate process conditions can be applied and different scale sizes can be used as compared with high temperature entrained flow gasification.³

When pyrolysis oil is being catalytically steam reformed, it is always accompanied by thermal reactions such as gasification and cracking. Already during the evaporation of the pyrolysis oil, three different products can be identified, namely permanent gases, vapors, and a carbonaceous solid material (here called char). Especially due to char formation, a fluidized bed has been preferred^{3,4} to steam reform pyrolysis oil as clogging of the reactor can be avoided. The char particles are then evenly distributed into the bed or elutriated from the bed. The distribution between these products is likely to be influenced by the heating trajectory of the pyrolysis oil droplet and the final evaporation temperature.

Various groups^{3–6} have steam-reformed pyrolysis oil or its fractions in a single fluidized catalytic bed where in most cases a relatively clean fuel gas was being produced. However, irreversible catalytic activity loss (leading to increasing methane levels) was being observed, which has mostly been ascribed to attrition/sintering of the catalyst. Because of this, up till now, no long term operation of steam reforming (or its fractions) was feasible to see the influence of other impurities present in the pyrolysis oil (like sulfur) on the activity of the catalyst. Furthermore, optimization of the evaporation of pyrolysis oil is limited while using a single reactor because the reforming catalyst needs a high temperature to produce a methane free syngas at higher pressures due to the chemical equilibrium.⁷ To overcome these problems, which limits the applicability of the process, Van Rossum et al.^{3,7,8} proposed a staged reactor concept where the evaporation and catalytic conversion are decoupled using a fluidized bed for oil evaporation followed by a fixed bed which contains a steam reforming catalyst. In this way, optimization of both, essentially different, processes is possible. A clean syngas could be produced when both the fluidized and fixed bed were at a temperature $\sim 800^\circ\text{C}$. A decrease of the evaporation temperature showed promising results in such a way that the catalyst was able to actually “see” primary tars

(oxygenated pyrolysis vapors), which are easier to reform instead of a thermally cracked gas. A full carbon balance, however, could not be made since not all product streams could be analyzed; for instance formed char inside the fluidized bed was partly elutriated from both reactors and ended up in the condenser section. To have a high overall efficiency of the process, all char has to be converted in the process instead of partly being considered as a loss. For this, two options seem likely: (i) the char is either combusted in a separated combustor to supply heat for the endothermic steam reforming reactions and evaporation, (ii) or the char is kept in the reactor and gasified using steam and/or CO₂. An efficiency evaluation⁷ showed that internal gasification is preferable. Additionally, this option would also allow an easier process operation; external heating is easier to control than maintaining a heat carrier circulation especially at elevated pressures.

To get more insight in the evaporation of pyrolysis oil, the process is isolated and studied in this article. Initially, the effect of temperature, droplet size, and heating rate on the product distribution (char, vapor and gas) is studied. Second, the produced chars are evaluated on its general properties, reactivity, and shape. Finally, the implications will be discussed on designing a process for steam reforming of pyrolysis oil. In this article, the term “char” refers to char originating from pyrolysis oil evaporation unless clearly stated otherwise (e.g., char from fast pyrolysis).

Experimental

Materials

The pyrolysis oils were produced in the Process Development Unit of VTT, Finland.⁹ Two different biomass sources were used, namely pine wood (PW) and forest residue (FR). The forest residue oil was also separated into an aqueous rich and aqueous lean phase via water addition. Pyrolytic lignin was obtained by adding pine pyrolysis oil into ice-cooled water as described by Scholze et al.¹⁰ Activated carbon was obtained from Norit.

The corresponding elemental analyses and water determinations are given in Table 1.

Continuous pyrolysis oil evaporation

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 1. Pyrolysis oil (FR 100 ml/h, duration ca. 1 h; $C_{\text{in,oil}}$) 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 temperature 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 two different atomizers were used to create two different extremes of sizes of droplets, which were measured by pictures taken with a high speed camera (Photron Fastcam SA1). An ultrasonic atomizer (UA; Lecher US1, spraying angle 30°) created a droplet size distribution of which the

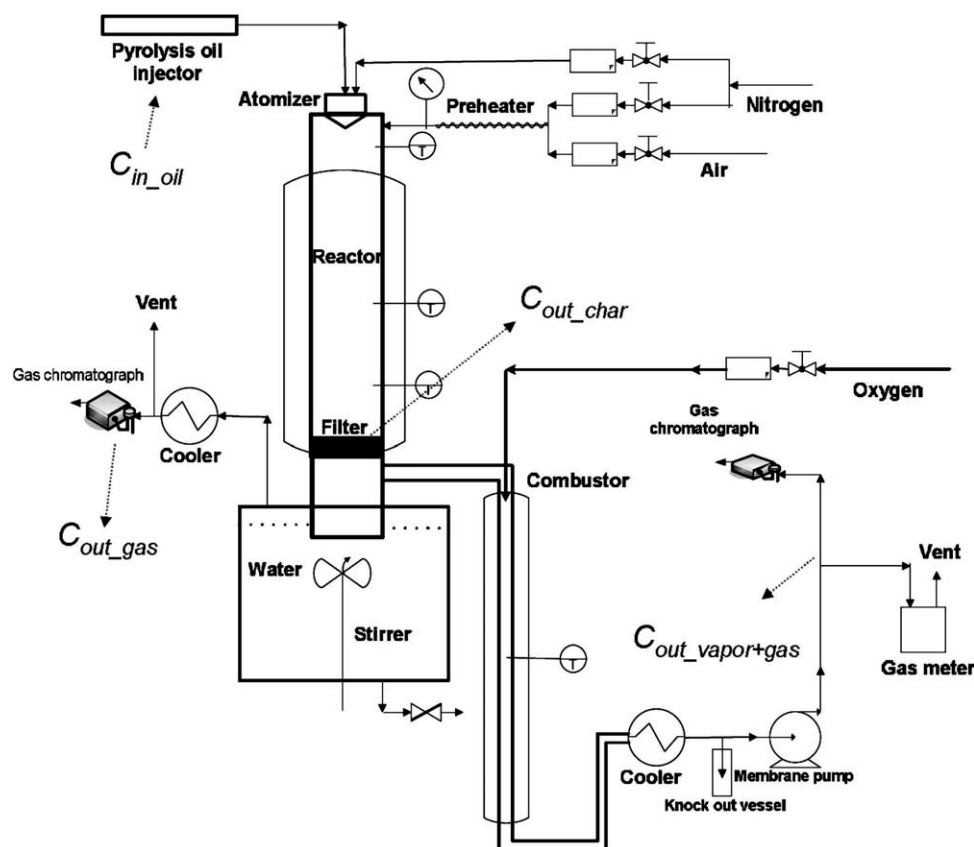


Figure 1. Schematic overview of the continuous pyrolysis evaporation set-up for measuring the carbon distribution from the oil to gas, vapor, and char.

The amount of gas and char are measured directly, the vapor amount is calculated by difference.

largest droplets were measured to be 88–117 micron (assisting gas N_2 4.0 Nl/min). However, the majority of the droplets was much smaller but 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 due to the higher viscosity. A house-made atomizer consisted (UT) of a needle, which was surrounded by an assisting gas (N_2 2.5 Nl/min). A uniform droplet was formed with a diameter of ~ 1.9 mm. 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 2–3 s over the temperature range measured. At the end of the evaporation chamber, a filter (mesh size 5 micron) was placed which together with a small sand layer and enough surface area resulted in a pressure drop of maximal 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) one 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, which was placed after a condenser. (ii) The other was directly fed to a quenching water bath, which was mechanically stirred to quickly cool the gas/vapor mixture and trap the condensables. Two micro-GC's (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

($C_{out_vapor+gas}$) and of the quench stream (C_{out_gas}). The integral carbon balance was made based on nitrogen as an internal standard, which was fed to the evaporator. After an experiment the collected char on the filter was either collected for analysis and reactivity testing or it was combusted (C_{out_char}) to make a total carbon balance over the system. The carbon to gas ratios 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:

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

Distribution:

$$Gas(\%) = 100 \frac{C_{out_gas}}{C_{in_oil}}, \quad Vapor(\%) = 100 \frac{C_{out_vapor}}{C_{in_oil}},$$

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

The carbon closure of the three different sections were 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 ($T \sim 720$ – $750^\circ C$, $S/C \sim 2.5$ – 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 evaporation experiments (gas + vapor + solid) was $98 \pm 4\%$.

Batch wise pyrolysis oil evaporation

A fixed amount of pyrolysis oil (FR, 1.4 ± 0.1 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). The oil was heated to the desired temperature and kept there (total time 1 h) and then either cooled down to room temperature or further heated to 550°C for additional 1 h and then cooled down. The remaining solid/liquid is called “Residue” and “Char”, respectively. A small nitrogen flow was placed just above the oil to avoid direct contact with air and to remove the vapors, which were released during evaporation. The remaining Residue/Char was weighed. The “Residue,” which was completely (or almost) soluble in tetrahydrofuran (THF), was analyzed with Gel Permeation Chromatography with THF as elutriation liquid and calibrated using polystyrene.¹¹

Thermogravimetric Analysis

Heating experiments (mainly pyrolysis oil) were performed in a Mettler Toledo thermogravimetric analyzer (TGA). The samples were heated to 800°C at a rate of 1, 10, or $100^\circ\text{C}/\text{min}$ in argon (60 ml/min). Combustion experiments were performed in the same system. In combustion mode, the samples were heated to 800°C at a rate of $5^\circ\text{C}/\text{min}$ in a mixture of air (20 ml/min) and argon (40 ml/min).

Additional to the TGA balance, the overall weight loss of the sample was quantified with a very accurate (± 0.1 mg) external balance as some weight loss was already observed during the stabilization time of the TGA. Two different weight rate losses are defined:

$$r_{\text{wt}} \equiv \frac{dX}{dT} = -\frac{(m_\tau - m_{\tau+1})}{m_0(T_\tau - T_{\tau+1})} \quad \text{at a constant heating rate} \quad (1/c)$$

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

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. The maximum estimated thermal lag (at a heating rate of $100^\circ\text{C}/\text{min}$ using water) using the fusion model¹² is 122°C .

Steam gasification of char

To gasify, a quartz tube ($\varnothing$ 4.5 mm, length 400 mm) was used, which was placed inside an electrically heated oven. A steam generator was used to create a steady steam flow ($\sim 300^\circ\text{C}$, 0.15–0.5 g/min) and preheated nitrogen ($\sim 200^\circ\text{C}$, 9 Nml/min) was added as an internal standard. The amount of steam added compared to the char sample (ca. 4–10 mg) was

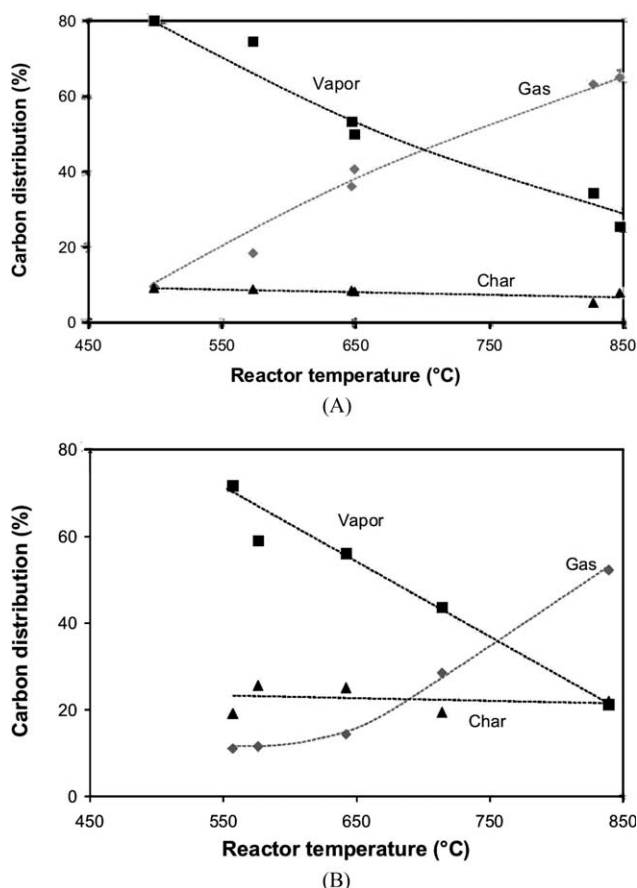


Figure 2. (A+B): Carbon distribution over the gas, vapor, and solid (char) phase during the evaporation of FR pyrolysis oil using an ultrasonic (A, UA) and needle (B, UT) atomizers at a pyrolysis oil feeding rate of 100 ml/h.

high enough that steam conversions below 1% were obtained. The char sample was placed at the end of the oven to ensure adequate preheating of the steam/nitrogen and allow isothermal gasification. The char sample to be gasified was premixed with quartz (0.2–0.6 g) to lower the pressure drop, which can be created due to the fine structure of the char. The mixed sample (ca. 1 cm in length) was held in the upper part of the heated quartz tube using quartz wool on both sides. Some pressure drop (0.2–0.5 bar) over the sample was being observed. The reactor outlet was cooled and all the steam was condensed out of the sample gas. A micro-GC (Varian CP-4900) was used to analyze the gas composition from which the carbon conversion was calculated. The gasification rate (r_{wt} , dX/dt) was assumed to directly correspond to the calculated carbon conversion rate, which introduces a small error since most of the char sample not only consists out of carbon (75% or more) but also some oxygen and hydrogen are present.

Results of Pyrolysis Oil Evaporation

Continuous pyrolysis oil evaporation: product distribution

Figure 2 shows the carbon distribution to permanent gas, vapor and solid phase for both the ultrasonic (UA) and the

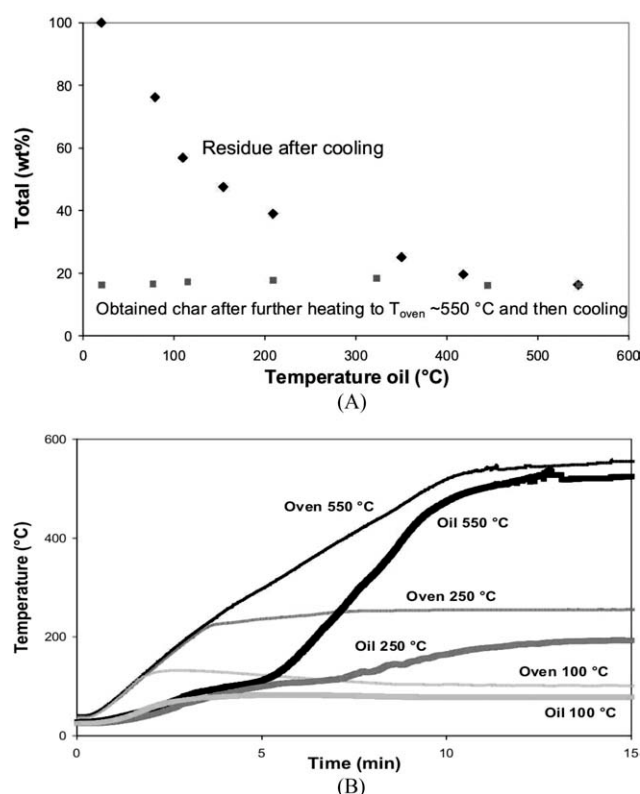


Figure 3. Results of pyrolysis oil evaporation done in glass reactor tubes.

(A) Residue after a heating-cooling cycle and char after a heating-further heating-cooling cycle. (B) Temperature profiles of both the oven (heating rate ca. $50^\circ\text{C}/\text{min}$) and the liquid/solid itself at three different oven set-points, namely: 100, 250, and 550°C .

needle (UT) atomizer using forest residue pyrolysis oil. Over the whole temperature range measured, the amount of char produced seems to be constant or a very slight decrease is being observed with increasing temperature. This indicates that the initial distribution between char and vapors/gases is apparently already attained in the temperature trajectory up to 500°C , an observation which is in line with earlier work.^{7,13} The vapor production decreases with increasing temperature and the amount of gases increases opposite to the vapor production. A big difference is seen in char production between the two atomizers where the ultrasonic atomizer gives much less char compared to the needle atomizer, ~ 8 and 22% on carbon basis, respectively. The vapor production seems more or less comparable. However, it is likely that initially more vapors are being produced using the UA atomizer leading to less char and that the main conversion pathway for gas production is via vapor cracking. Small droplets (UA) are much quicker evaporated than larger

droplets (UT) and in this way vapors have more time to be cracked to permanent gases.

Compared to the fluidized and staged reactor bed system used by Van Rossum et al.³ to study the gasification/steam reforming of pyrolysis oil, for the present set-up much more vapors are being measured (~ 20 – 30 wt % versus ~ 1 wt % on carbon basis at $T \sim 800^\circ\text{C}$, noncatalytic). This difference is probably caused by the longer residence time at high temperatures, which enhances thermal vapor cracking (~ 10 s versus 2–3 s).

Batch wise pyrolysis oil evaporation: residue analysis

Figure 3 and Table 2 shows the results of the pyrolysis oil evaporation carried out in glass reactor tubes, which are heated at $\sim 50^\circ\text{C}/\text{min}$ (oven) to different temperatures. The residue (Figure 3A) shows a steady decrease in amount with increasing temperature, which stabilizes around $T \sim 500^\circ\text{C}$. The amount of char shows more or less a constant production (~ 17 wt %, $\sim 32\%$ carbon basis) although the time-temperature trajectory has been totally different. The heating trajectory shows quite a difference between the measured oven temperature and the actual sample temperature. The oven temperature (Figure 3B), which is usually measured in heating experiments as for instance with a TGA, shows roughly a constant heating rate till its desired set-point temperature. However, the sample temperature strongly deviates from the oven heating trajectory and shows four heating stages as is best illustrated for the $T_{oven} = 550^\circ\text{C}$ experiment:

- 0–3 min: heating of the liquid, some vapor release can already be visually observed.
- 3–5 min: the liquid temperature increases very slow; this can predominantly be ascribed to water, which is evaporated together with some lights. The vapors, which are being released, are colorless and transparent. The difference in oven and sample temperature almost reaches 200°C .
- 5–9 min: the sample temperature increases at a constant heating rate. The vapors, which are being released, get more and more dark with increasing temperature, and at a sample temperature $\sim 220^\circ\text{C}$ a phase transition occurs and a solid is being formed, which is accompanied with a volumetric expansion ($\pm$ three times) that has also been described by Wornat et al.¹⁴ during the combustion of pyrolysis oil.
- 9 min–end: the sample temperature reaches a constant value/level and the vapor release stops. The produced char has a very porous structure and is brittle.

Figure 4 shows Gel Permeation Chromatography results of the residue samples 1 till 5 (Table 2), which were (almost) completely soluble in THF. The initial oil heating, which is accompanied with already some vapor release, did not result in a significant differences in the profile of the distribution of the higher fractions present in pyrolysis oil. This suggests that even though the oil was at 79°C for almost an hour, no

Table 2. Averaged Temperatures (at “Steady-State”) and Solubility of the Obtained “Residue” in THF (T, Totally; P, Partly; N, Not Soluble) from Forest Residue Pyrolysis Oil Glass Reactor Tube Heating Experiments

	1	2	3	4	5	6	7	8
T_{oven} ($^\circ\text{C}$)	–	101	152	203	254	368	452	556
T_{sample} ($^\circ\text{C}$)	20	79	110	154	209	350	418	544
Solubility in THF	T	T	T	T	T/P	P	P	N

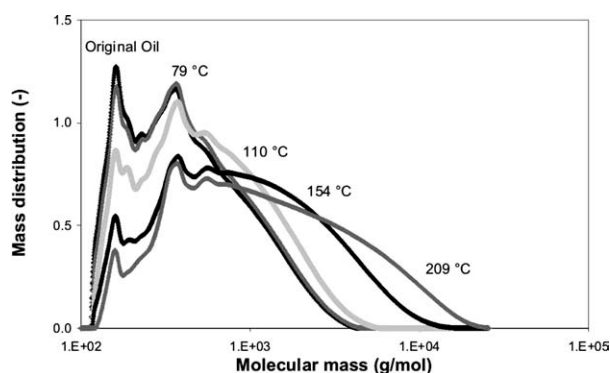


Figure 4. Gel Permeation Chromatography results of the original pyrolysis oil (sample 1) and of residues after heating (samples 2 till 5).

The displayed temperatures are of the actual liquid (at “steady-state”).

significant polymerization, which would result in heavier product formation, took place. Further heating of the oil created heavier fractions as seen in the increasing molecular weight measured with the GPC. This is also in line with the observation of lesser solubility in THF and the visual change from liquid to solid during the experiment. This suggests that polymer formation takes place in the liquid phase directly after water (and lights) evaporation ($T_{\text{liquid}} > 100^{\circ}\text{C}$). These polymers eventually react further to char (solvent insoluble) fractions, which were observed from 250°C (See Table 2).

TGA: evaporation

Figure 5 shows the evaporation of pyrolysis oil using TGA with increasing sample cup temperature. Table 3 shows the amounts of char (both weight and carbon basis) being produced with TGA for pyrolysis oil and related fractions/compounds. When the heating rate is varied, the following observations can be made:

- In the initial heating stage (up to 175°C), a clear peak of mass release (Figure 5B) can be identified. This is the evaporation of water and lights when the liquid temperature is almost constant similar to as can be seen in Figure 3B (region 3–5 min in the $T_{\text{oven}} = 550^{\circ}\text{C}$ experiment).
- The dX/dt profile (Figure 5C) shows that between the three experiments roughly a factor of $10\times$ change in conversion rate is being observed, which corresponds to the step change applied in the heating rates. This is an indication that the reactions/evaporation of the component groups seem to follow first order kinetic behavior, which has been the basis for modeling pyrolysis oil droplet evaporation.^{15,13}
- The dX/dt (Figure 5B) profiles are quite similar. The small differences observed are most likely caused by a difference in actual liquid sample temperature and sample cup temperature which is expected to be large at high heating rates (next to the first order behavior of the evaporation and reactions).
- The carbon to char conversion shows a slight trend of increasing char production with lower heating rates. The produced char amounts are similar to the glass tube heating

experiments and higher than the droplet evaporation experiments.

The heating of different fractions of pyrolysis oil and related compounds (Table 3) all resulted in the formation of considerable amounts of char. The aqueous rich fraction of pyrolysis oil, which is considered to be an important

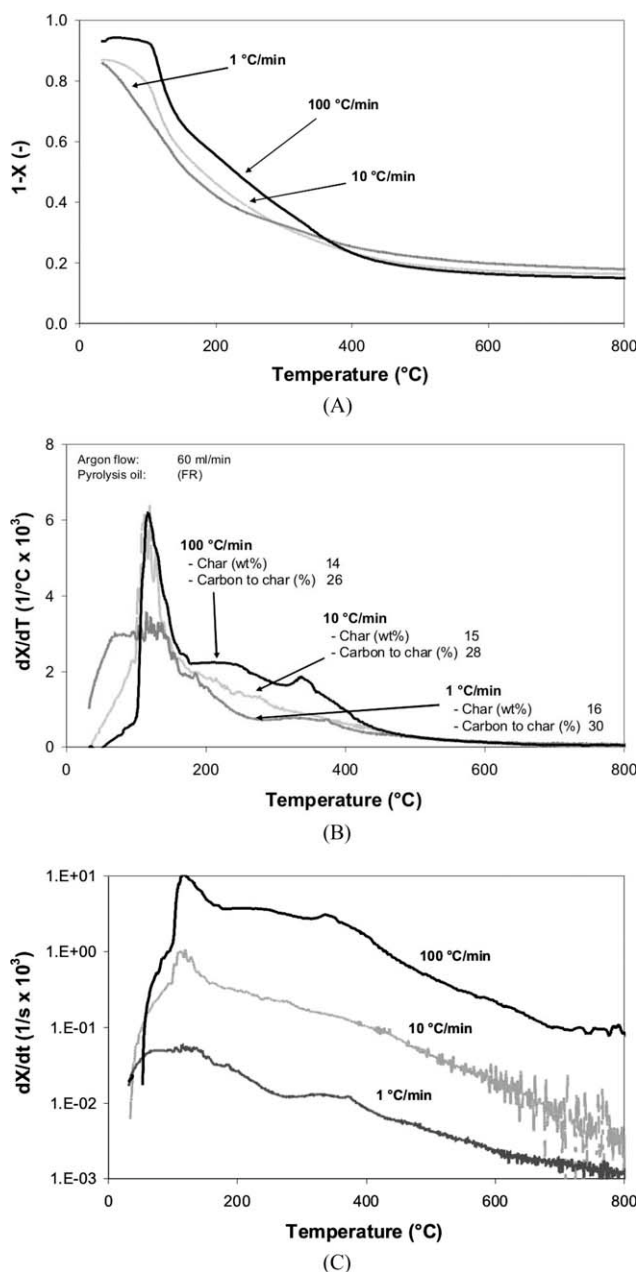


Figure 5. Thermo Gravimetric Analysis of pyrolysis oil at different heating rates (1, 10, and $100^{\circ}\text{C}/\text{min}$) in inert (Argon) gas.

(A) Weight conversion (X) versus temperature profile. (B) Reaction rate r_{wT} (temperature based) versus temperature. (C) Reaction rate r_{wT} (time based) versus temperature. The reported measured temperatures are of the sample cup, not of the actual liquid inside. m_0 is measured with an external balance since some weight loss is being observed during the stabilization time of the TGA; this results in that the starting point is always lower than 1.

Table 3. Char Productions using TGA of Pyrolysis Oil and Related Fractions/Compounds

(%)	Weight of Feed	Carbon to Char
Pyrolysis oil (FR)	15	28
Aqueous rich phase (FR)	7	24
Aqueous lean phase (FR)	21	33
Wood (PW)	15	25
Pyrolytic lignin (PW)	43	54
Glucose solution (40 wt %)	7	28

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.

hydrogen resource and easy to steam reform,^{4,5} still resulted in 24% of carbon which was converted to char. The heavier fractions of pyrolysis oil (aqueous lean phase and pyrolytic lignin) form high amounts of char. The amount of char formed with evaporating pyrolysis oil is under slow heating rates (1–100°C/min) similar to pyrolysis of solid biomass at ~500°C (25% carbon to char conversion, Table 3). It is striking that such high amounts of char are formed since the large molecular structures which were present in the original biomass are being depolymerized in the pyrolysis process to end up in the pyrolysis oil or are mainly concentrated in the char by-product. Char formation during pyrolysis oil evaporation seems to be mainly due to polymerization reactions of the oil as illustrated in Figure 4. However, some polymerization reactions and elutriation¹⁶ of heavier components already take place during the pyrolysis oil production/condensation directly leading to products, which cannot be re-evaporated. It is then interesting to see if these products can be readily gasified or that they always lead to the production of char.

It will be important to heat up quickly through the 100 → 350°C temperature zone where the polymerization takes place. The lower amount of char formation at higher heating rates shows clearly that steering is possible. Figure 6 shows heating rates for the TGA, heated glass tubes, and droplet evaporation. The “droplet evaporation” heating rates after “lights” evaporation when char formation starts were estimated with a heat balance over a droplet according to:

$$\frac{dT}{dt} = \frac{6Nu\lambda}{C_p\rho d_p^2} \Delta T \quad \text{with Nusselt (flow around sphere)}$$
$$Nu = 2 + 0.66Re^{\frac{1}{2}}Pr^{\frac{1}{3}} \approx 7$$

With d_p the droplet size of the pyrolysis oil, c_p the heat capacity of a liquid ~2000 J/kg/°C, ρ the density of the liquid ~1000 kg/m³, λ thermal conductivity of gas ~0.06 W/m/°C and ΔT the temperature difference ~500°C (a 50% spread over the calculated heating rate values is assumed in Figure 6). The estimated heating rates are in the same order of magnitude as estimated by García Pérez et al.¹⁷ Only very high heating rates ($\geq 10^5$ °C/min) results in significant reductions of char production. This shows that with widely used heating analyzing equipment such as TGA, an analysis can be made of maximum char production that is probable from a certain compound/oil. This can be useful to predict gasification behavior but it must be kept in mind that the

process of evaporation is most likely/essentially different between a TGA and an atomizer. Probably there is also a minimum amount of char, which will be formed. Glucose like compounds and heavier fractions are always present in the pyrolysis oil (both aqueous rich and lean phases), which tend to polymerize rather than to evaporate/decompose (see Table 3). However, it is possible that with extremely high heating rates or diluted solutions (e.g., water and methanol) compounds remain isolated and due to the vigorous nature of such evaporation 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 ~10³), which will result in less polymerization as polymerization has a reaction order higher than one.¹⁸

Results of Char Analysis

Char combustion

From the continuous pyrolysis oil evaporation set-up, char samples (called pyrolysis oil char) were collected from the installed filter (see Figure 1), which were produced at different temperatures and using the two different atomizers. Figure 7 shows the combustion experiments done in a TGA when the samples were heated in an air/argon mixture at a constant heating rate of 5°C/min. Two different types of carbon containing materials were initially heated to see the difference in the start and the peak of the combustion process (see Figure 7A), namely char from fast pyrolysis (wood pyrolysis char), which is known to have a high reactivity, and activated carbon, which is quite stable char. The difference in combustion peaks is significant; around 500°C for wood pyrolysis char and 645°C for activated carbon. The collected chars (Figure 7B) show reactivities more similar to char from wood fast pyrolysis than from activated carbon. This is different to what Branca et al.¹⁹ measured where the pyrolysis oil char reactivities were lower than those of wood pyrolysis char. This difference is most likely due to the different char production methods (cup heating versus atomization). The use of different atomizers shows a slight difference in

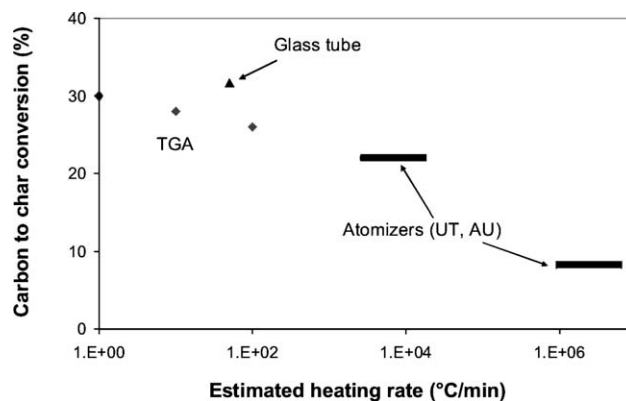


Figure 6. Carbon to char conversion of pyrolysis oil versus estimated heating rates of the following equipment: Thermo Gravimetric Analysis (TGA), heated glass tube, and droplet evaporation using two different atomizer types (UT and UA).

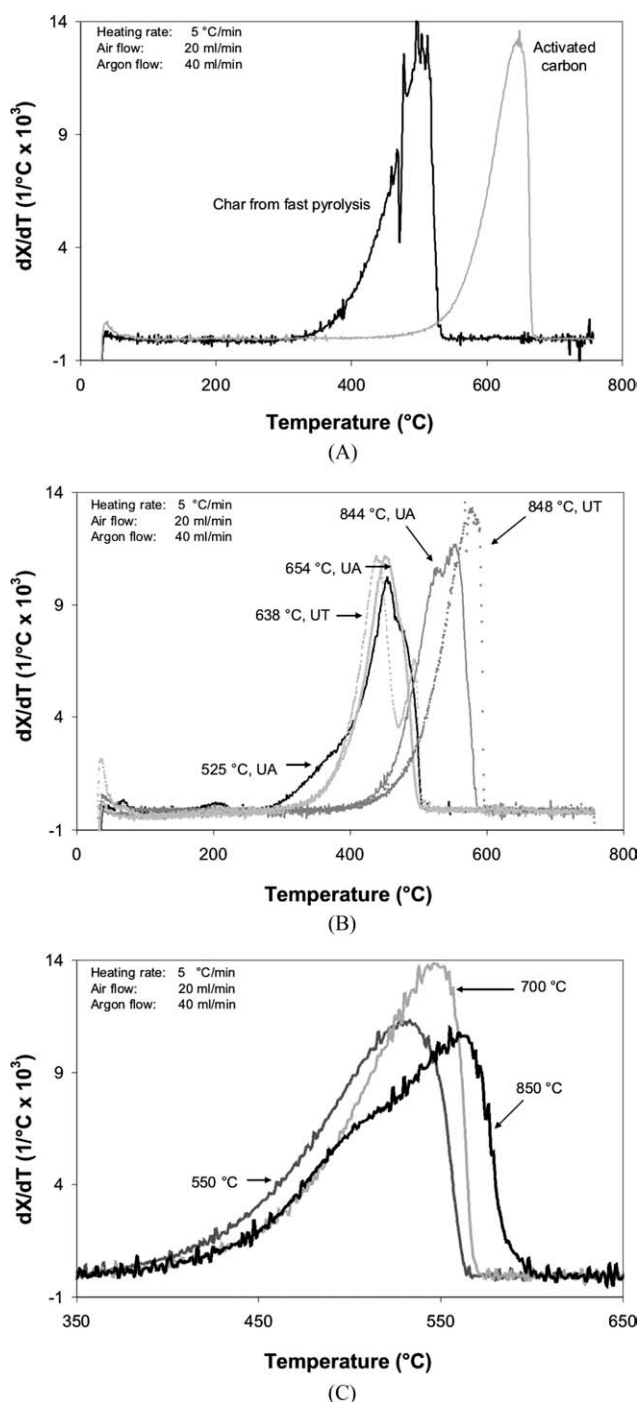


Figure 7. Thermo Gravimetric Analysis in an air flow.

(A) Shows combustion profiles during a constant heating of the sample for char produced during the fast pyrolysis of pine wood and of activated carbon. (B) Shows combustion profiles of chars collected from the continuous evaporation setup which was operated at different temperatures using two different atomizers. (C) Shows chars produced at a constant heating rate of $10^{\circ}\text{C}/\text{min}$ and then cured (15 min) at different peak temperatures (550, 700, and 850°C).

reactivity where UA (small droplets) is combusted at a lower temperature than UT (big droplets). This is remarkable because with small droplet evaporation the amount of char being produced is much less and one could think only a

lesser reactive fraction would remain. The reactivity is most likely determined by the composition of the char and the accessibility for gases. Besides this, the temperature, to which the char has been produced, seems to have an important influence on the activation and peak temperatures. When pyrolysis oil evaporation chars are being produced at high temperatures ($\sim 850^{\circ}\text{C}$), they are less reactive. Up till a temperature of 654°C , the reactivity seems similar. This was also confirmed when chars were produced at different final temperatures (heating rate: $10^{\circ}\text{C}/\text{min}$), kept at those temperatures for 15 min, and then cooled down. The reactivity of these chars increase with decreasing final temperature of production as is shown in Figure 7C.

Structural analysis of char

From the chars produced, one was selected for further analysis, namely the pyrolysis oil char produced at 525°C with the ultrasonic atomizer (UA, elemental analysis (wt %): C: 76.7, H: 3.4, Rest: 19.9). This choice was based upon (i) evaporation experiments showed the lowest char yields with this atomizer and (ii) combustion activity measurements showed that this char is among the most reactive. Figure 8 shows scanning electron microscope (SEM) photos of the char. The char shows to be consisting of mostly hollow spheres (wall thickness order magnitude of a few hundred nanometers), which have been ruptured. Onto and into these larger structures, smaller particles are deposited. The char is very light/fluffy as compared with char produced during fast pyrolysis of wood. This is believed to be the reason for the high carbon elutriation from an earlier used fluidized bed for steam reforming of pyrolysis oil.^{3,7,8} The largest sizes of the spheres (around 100 micron) are in the same size range as the largest pyrolysis oil droplets (88–117 micron), which were photographed with the high speed camera. The spheres seem to be similar to the glassy/cenosphere solids produced during pyrolysis oil evaporation and/or combustion.^{14,17}

Char steam gasification

Besides combustion reactivity, the reactivity of char toward steam gasification was also studied. A high surface area is seen using the SEM photo's (Figure 8), which promises a high reactivity since the steam should be able to penetrate deep into the char structure. Figure 9A shows measured reaction rates of the char for steam gasification at a char conversion (X) of 0.3. The steam gasification was always preceded by some devolatilization of the char, which is also expected when looking at TGA pyrolysis oil heating (Figure 5B) where above 525°C a small but significant amount of solid conversion is attained. At low temperatures (700°C), this effect is still significant but at higher temperature it is negligible compared to the steam gasification.

The gasification rate of pyrolysis oil char can be well described with an Arrhenius type of temperature dependence giving an activation energy (E_a) of $274\text{ kJ}/\text{mol}$, which is at the higher end compared to earlier measured activation energies of steam gasification of biomass originating chars (E_a : $105\text{--}271\text{ kJ}/\text{mol}$).²⁰

The reactivity profiles at the same temperature for pyrolysis oil char, wood pyrolysis char, and activated carbon show distinct behavior (Figure 9B). The activated carbon shows a

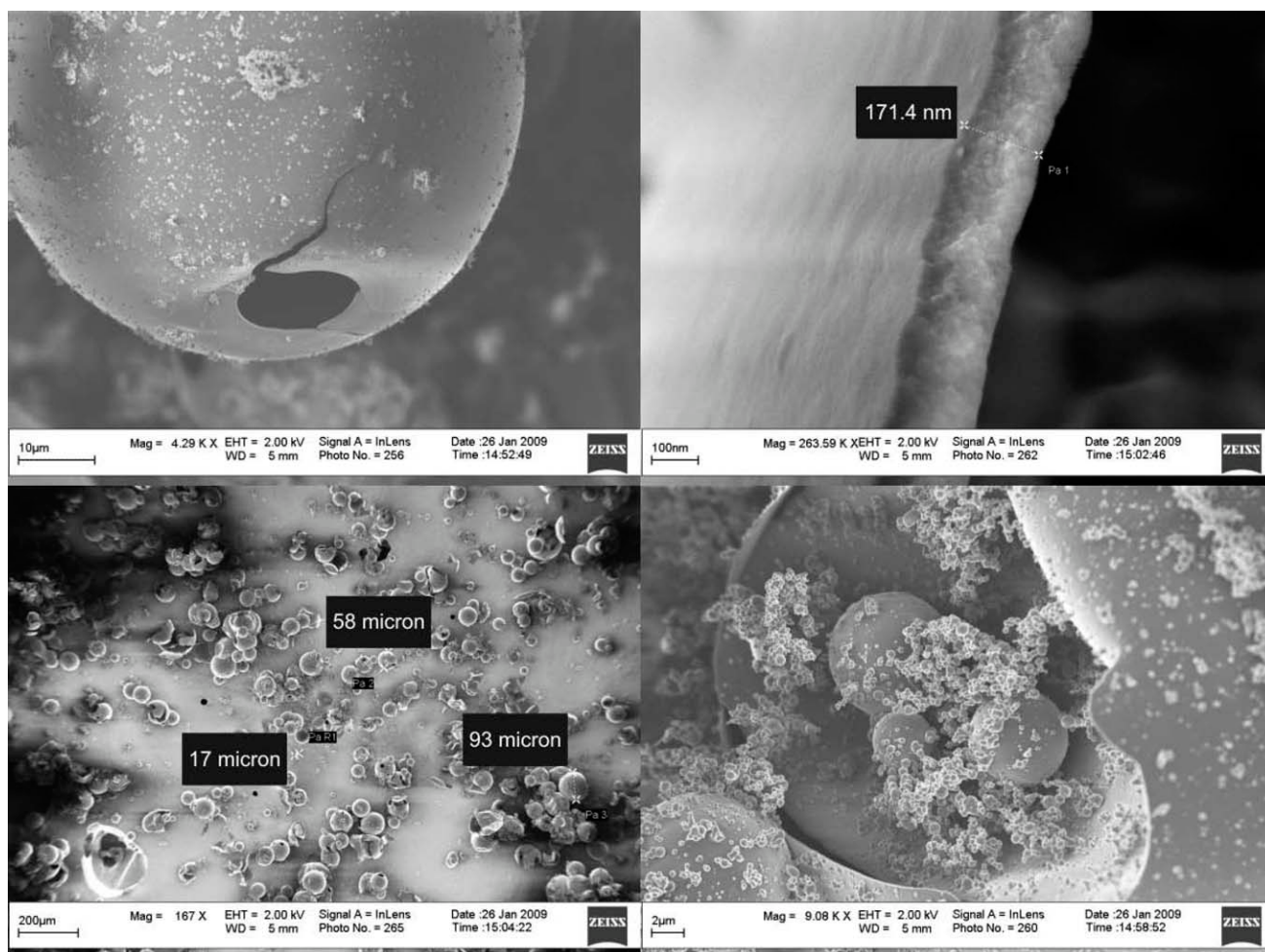


Figure 8. SEM photos taken of char from the continuous pyrolysis oil droplet evaporation set-up produced at 525°C using an ultrasonic atomizer.

constant activity over the whole conversion range measured, which can be interpreted as zero order gasification reactivity in char. The pyrolysis oil char and wood pyrolysis char show quite similar profile namely a readily decreasing reactivity with increasing conversion, which was also observed by Barrio et al.²⁰ The following explanation can be given for this change in reactivity: (i) the reaction order in char is not zero, (ii) there is inhibition (for instance hydrogen and carbon monoxide), (iii) the carbon structure changes/is less accessible, which results in an apparent different reaction order, and (iv) the char ages in time leading to less reactive chars. (iii) and (iv) are expected to be dominant in explaining this behavior. The carbon surface structure has been shown on SEM photos to be very complex (Figure 8) where big hollow spheres, which could be assumed to be reacting as a flat plate, and smaller deposits, which could react away as small porous spheres, are present. This complex structure could lead to a higher initial rate decreasing with increasing conversion. The char has shown “aging” (reactivity loss due to thermal exposure) behavior when it is subjected to elevated temperatures for a certain time (Figure 7C and Ref. 21) leading to a decreasing reactivity rate. The activated carbon giving its constant reactivity over time is then due to that the overall structure does not change (in the conversion

range measured) and does not undergo “aging” since it was already subjected to higher temperatures during production.

Mechanism of Pyrolysis Oil Evaporation

The temperature-time history of a pyrolysis droplet determines not only the amount of char being formed but also its reactivity as is illustrated in Figure 10. Our results show that a part of the pyrolysis oil seems to always evaporate, leading to gases and vapors, which can be reformed to create syngas. Another part can either be converted to char or similar to the aforementioned route generate gases/vapors, which is determined by the heating rate. With higher heating rates, the ratio of the rate of polymerization/gasification is lowered. The formed chars show “aging” behavior when they are exposed to higher temperatures (above 650°C, see Figure 7B and C). This aging behavior, together with the complex structure of the char, results in steam gasification rates, which decrease with increasing extend of conversion.

When the whole evaporation process would be pressurized, the evaporation curve (Figure 3 and 5) is expected to shift to higher temperatures. This will probably lead to more char formation as polymerization rates are higher.

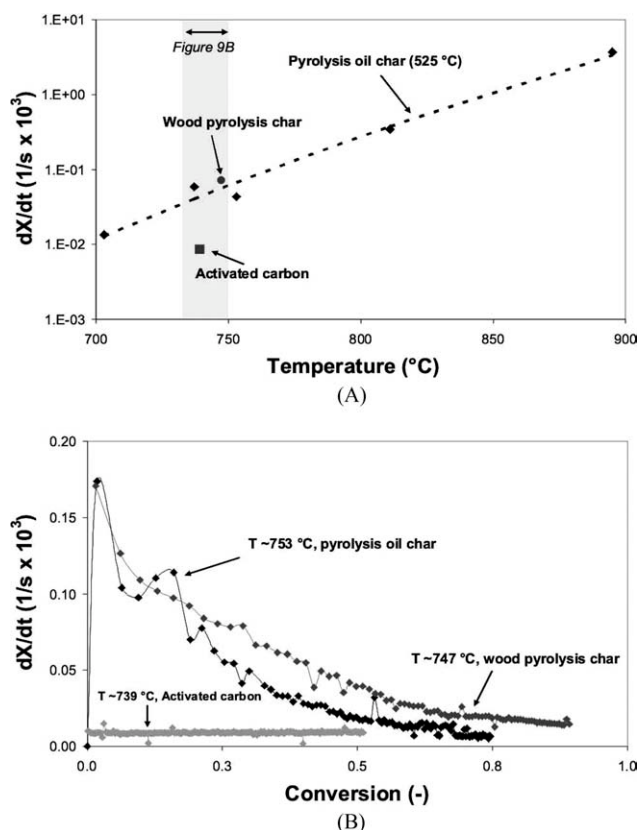


Figure 9. Steam Gasification of Chars.

(A) Steam gasification rate versus temperature (including devolatilization) of char produced from evaporation of pyrolysis oil at 525°C with the ultrasonic atomizer (UA) at a char conversion of $X = 0.3$.

The dotted line is the Arrhenius kinetic fit with an E_a of 274 kJ/mol. The steam gasification rates of wood pyrolysis char and activated carbon are added for comparison. (B) Gasification rate profiles (r_{wt}) of pyrolysis oil char, wood pyrolysis char and activated carbon at similar temperatures (T 739–753°C).

Implications for Steam Reforming of Pyrolysis Oil

The presented results have shown that with the evaporation of pyrolysis oil (or its fractions) always char will be formed. This has a large impact on steam reforming process of pyrolysis oil whether single or staged reactor concepts are

envisaged. This char amount can be considerable: a maximum of 32% on carbon basis was obtained using forest residue pyrolysis oil under slow heating conditions. This amount differs with varying types/qualities of pyrolysis oil.⁷ Char formation during slow evaporation is much higher than other possible reactions leading to solid carbonaceous species such as coke, which can be formed on the steam reforming catalyst (at sufficient high temperatures) and soot formed *via* vapor cracking. By applying very high heating rates, the amount of char formed can be significantly reduced where the underlying mechanism seems to be dilution of the reactive species ($\sim 10^3$ times with evaporation) and/or higher gasification rates of char precursors relative to polymerization. Specially designed atomizers create very small droplets, which can be evaporated quickly. The speed of evaporation can be further increased with the use of a fluidized bed, which has excellent heat transfer properties. However, not only the amount of char is important but also in which form it is being created. Droplet evaporation in a heated empty space leaves a very light/fluffy char residue, which easily elutriates from the reactor before it can be converted. It is therefore necessary to bind the char to a carrier. Sand³ has shown to not have enough binding capacity (fluidization scrapes char of its surface) and therefore more porous materials are probably preferred so that char formation takes place inside the carrier. How to contact the pyrolysis oil to such a carrier is not yet straightforward and has to be investigated further. The initial high temperature difference between the droplet and the carrier can limit the effectiveness of contacting. The Leidenfrost effect (which was shown to occur with large pyrolysis oil droplets on a hot surface) can let droplets bounce off the carrier and it has to be investigated what would be the ideal oil/carrier particle diameter ratio: a high ratio will cool down the carrier, which then would allow carrier soaking and a low ratio would instantly heat the oil. Another option could be to modify the shape of the steam/dry reforming catalyst in such a way that residual char which elutriates from the fluidized bed is bound to it in the secondary reactor. In this way the char could get sufficient residence time to react. Preliminary tests in a bubbling fluidized with a more porous bed material have shown higher carbon to gas conversions as compared to “inert” sand.²²

The char itself has combustion and gasification properties comparable to other biomass originated chars. When

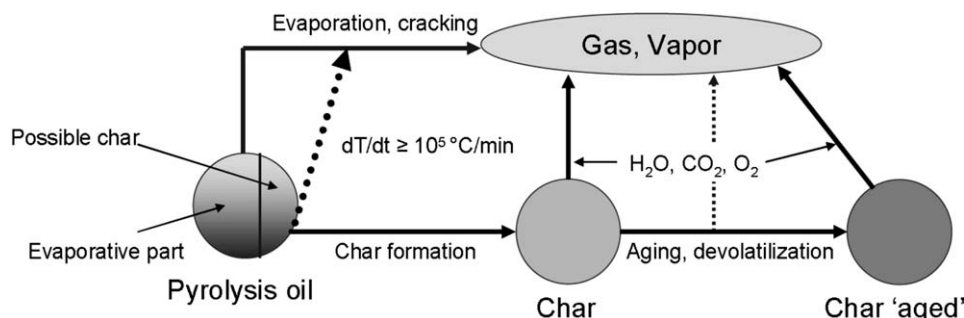


Figure 10. Evaporation scheme of pyrolysis oil leading to gases, vapors, and char.

The formed char can age to form a less reactive char. Both chars can be converted either by gasification (steam and CO_2) or combustion. The temperature-time trajectory will determine which pathways are more dominant.

pyrolysis oil steam/dry reforming is considered, the char can be combusted to supply heat for the endothermic reforming reactions and evaporation. However, direct internal gasification of the char is preferred from an efficiency and process operation point of view.⁷ Current steam gasification tests have shown that at the preferred temperature regime (< 700°C) for operating a fluidized bed for evaporation, the rate of char conversion is too low. Higher operating pressures will probably enhance this conversion rate but catalytic active materials seem to be necessary to change char gasification conversion times from hours to minutes.

Conclusions

Pyrolysis oil (and all its fractions) evaporation is always coupled with the formation of char, which is formed via polymerization reactions. The speed through which the pyrolysis oil liquid goes through the 100–350°C temperature zone determines the total amount of char that is formed. Very high heating rates ($\geq 10^5$ °C/min) which can be achieved with small droplets lead to much less char (~8%, carbon basis) than the “maximum” amount (~30%, carbon basis) which is measured with analytical heating equipment like TGA.

Char from pyrolysis oil evaporation has a very open structure, and it consists out of large hollow spheres onto which smaller particles are being deposited. The char has reactivities toward combustion and steam gasification comparable to char formed during the pyrolysis of biomass. The char shows aging behavior when subjected to higher temperatures (≥ 650 –700°C).

Acknowledgments

The work has been performed in the framework of a NWO-ACTS project (Sustainable hydrogen, 053.61.007). The authors would like to thank VTT (Finland) for supplying the pyrolysis oil and the Master student who contributed to this work: A. Teekman.

Literature Cited

- de Miguel Mercader F, Ardiyanti A, Gutierrez A, Khromova S, Leijenhorst E, Kersten SRA, Hogendoorn JA, Prins W, Groeneveld MJ. Upgrading of bio-liquids for co-processing in standard refinery units. In: Proceedings of the 16th European Biomass Conference and Exhibition. Valencia, Spain, June 2–6, 2008:2103–2106.
- Corma A, Huber GW, Sauvanaud L, O’Conner P. Processing biomass-derived oxygenates in the oil refinery: catalytic cracking (FCC) reaction pathways and role of catalyst. *J Catal.* 2007;247:307–327.
- van Rossum G, Kersten SRA, van Swaaij WPM. Catalytic and non-catalytic gasification of pyrolysis oil. *Ind Eng Chem Res.* 2007;46:3959–3967.
- Czernik S, French R, Feik C, Chornet E. Hydrogen by catalytic steam reforming of liquid byproducts from biomass thermoconversion processes. *Ind Eng Chem Res.* 2002;41:4209–4215.
- Kechagiopoulos PN, Voutetakis SS, Lemonidou AA, Vasalos IA. Hydrogen production via reforming of the aqueous phase of bio-oil over ni/olivine catalysts in a spouted bed reactor. *Ind Eng Chem Res.* 2009;48:1400–1408.
- Medrano JA, Oliva M, Ruiz J, Garcia L, Arauzo J. Hydrogen from biomass pyrolysis liquids. Catalytic steam reforming in fluidized bed reactor with Ni/Mg-Al catalysts. In: Proceedings of the 16th European Biomass Conference and Exhibition. Valencia, Spain, June 2–6, 2008:2158–2162.
- van Rossum G, Kersten SRA, van Swaaij WPM. Staged gasification/steam reforming of pyrolysis oil. *Ind Eng Chem Res.* 2009;48:5857–5866.
- van Rossum G, Potic B, Kersten SRA, van Swaaij WPM. Catalytic gasification of dry and wet biomass. *Catal Today.* 2008;145:10–18.
- Oasmaa A, Sipilä K, Solantausta Y, Kuoppala E. Quality Improvement of pyrolysis liquid: effect of light volatiles on the stability of pyrolysis liquids. *Energy Fuels.* 2005;19:2556–2561.
- Scholz B, Meier D. Characterization of the water-insoluble fraction from pyrolysis oil (pyrolytic lignin). I. PY-GC/MS, FTIR, and functional groups. *J Anal Pyrolysis.* 2001;60:41–54.
- Scholz B, Hanse C, Meier D. Characterization of the water-insoluble fraction from pyrolysis liquids (pyrolytic lignin). II. GPC, carbonyl groups, and ¹³C-NMR. *J Anal Pyrolysis.* 2001;58–59:387–400.
- Narayan R, Antal MJ. Thermal lag, fusion and the compensation effect during biomass pyrolysis. *Ind Eng Chem Res.* 1996;35:1711–1721.
- Branca C, Di Blasi C. Multistep mechanism for the devolatilization of biomass fast pyrolysis oils. *Ind Eng Chem Res.* 2006;45:5891–5899.
- Wornat MJ, Porter BG, Yang NYC. Single droplet combustion of biomass pyrolysis oils. *Energy Fuels.* 1994;8:1131–1142.
- Hallett WLH, Clark NA. A model for the evaporation of biomass pyrolysis oil droplets. *Fuel.* 2006;85:532–544.
- Daugaard E, Brown RC. The transport phase of pyrolytic oil exiting a fluidized bed reactor. In: *Science in Thermal and Chemical Biomass Conversion*. Newbury Berks, U.K.: CPL Press, 2006;2:1189–1202.
- García Pérez M, Lappas P, Hughes P, Dell L, Chaala A, Kretschmer D, Roy C. Evaporation and combustion characteristics of biomass vacuum pyrolysis oils. *IFRF Combust J.* 2006:200601.
- Knežević D, van Swaaij WPM, Kersten SRA. Hydrothermal conversion of biomass. I. Glucose conversion in hot compressed water. *Ind Eng Chem Res.* 2009;48:4731–4743.
- Branca C, di Blasi C, Elefante R. Devolatilization and heterogeneous combustion of wood fast pyrolysis oils. *Ind Eng Chem Res.* 2005;44:799–810.
- Barrio M, Gøbel B, Risnes H, Henriksen U, Hustad JE, Sørensen LH. Steam gasification of wood char and the effect of hydrogen inhibition on the chemical kinetics. In: Bridgwater AV, editor. *Progress in Thermochemical Biomass Conversion*. Cornwall: MPG Books Ltd, 2001;1:32–46.
- Chen G, Yu Q, Sjöström K. Reactivity of char from pyrolysis of birch wood. *J Anal Appl Pyrolysis.* 1997;40/41:491–499.
- Bleeker MF, Veringa HJ, Kersten SRA. Pure Hydrogen production from pyrolysis oil using the steam-iron process: Effects of temperature and iron oxide conversion in the reduction. *Ind Eng Chem Res.* DOI: 10.1021/ieq00530d.

Manuscript received July 7, 2009, and revision received Oct. 21, 2009.