Controlling the Water Content of Biomass Fast Pyrolysis Oil

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Several methods to control the water content of pyrolysis oil from fast pyrolysis of biomass were evaluated experimentally. Parameters varied were the operating temperature of the condenser, the gas load of the condenser, and the moisture content of the feedstock. Experiments were performed in a continuous bench scale plant (1 kg/h intake) equipped with a fluidized bed reactor. Pine wood with moisture contents between 0 wt % and 20 wt % (as-received basis) was used as feedstock. The mass balance closure was between 94 wt % and 102 wt %, and the reproducibility of yields of identical experiments was good. Increasing the condenser temperature (15−90 °C) and increasing the gas load (2.0−4.1 kg of gases/kg of vapors in the condenser feed) of the condenser are both well suited to control the water content. However, decreasing the water content by these measures always results in a loss of organic vapors, leading to a lower oil yield in the condenser. Deep drying of the feedstock is beneficial; a lower moisture content of the feed results in less loss of organic vapors for the same water content of pyrolysis oil. Experimental results were compared with the predictions of an equilibrium flash condensation model. Predictions of this equilibrium model are in good agreement with the experimental results. All input parameters of the model (reactor yields and composition of the organics in pyrolysis oil) can be measured, or are known, with sufficient accuracy.

1. Introduction

Fast pyrolysis is a promising process to produce transportable oil with a high volumetric energy density from bulky and inhomogeneous biomass.[1−3] There are several applications foreseen for pyrolysis oil. It has been tested as a substitute for fuel oil or diesel in boilers, furnaces, engines, and turbines for heat and power generation[2,4−6] and has been considered as a precursor for transportation fuels and chemicals.[2,7,8] Water is the most abundant component in pyrolysis oil; typically it is present in the range of 15−35 wt %.[1,4,9] Probably all applications require different specifications with respect to the water content of pyrolysis oil. For fueling into a diesel engine, for instance, Oasmaa et al.[5] and Oasmaa and Czernik[10] reported that the water content should be below ca. 30 wt % to decrease emissions of particles and to prevent ignition delay and phase separation, but that there should be also a minimum amount of water present to limit NO_x emissions and to ensure a uniform temperature distribution in the cylinders. For co-feeding pyrolysis oil in a mineral oil refinery, nearly all water and most organically bound oxygen must be removed.[7,8] Generally, less water is beneficial for the energy density, transportation costs, stability, and acidity of pyrolysis oil.[10] Below 15 wt %, the viscosity (at 20 °C) increases exponentially. Oil containing 4 wt % water, for example, has a viscosity of ca. 80 000 cP (at 20 °C), which could cause problems in pumping and processing.

The objective of this paper is to evaluate several options, available within the pyrolysis process, to control the water content of pyrolysis oil. The temperature and gas load (kilograms of gases per kilogram of vapors in the condenser feed) of the condenser are tested as process variables to steer the water content of pyrolysis oil. Pine wood with moisture contents between 0 and 20 wt % is used as feedstock.

Pyrolysis experiments have been performed in a continuous bench scale pyrolysis plant (intake = 1 kilogram of biomass

Table 1. Composition of Pine Wood

biochemical composition (wt %, dry)	value
cellulose	35
hemicellulose	29
lignin	28
ultimate analysis (wt %, daf)	
C	46.58
H	6.34
O (by difference)	46.98
N	0.04
S	0.06
alkali metals (mg/kg, dry)	
K	34
Mg	134
Ca	768
total ash	2600

per hour) equipped with a fluidized bed reactor. The experimental results obtained are compared with the predictions of an equilibrium flash condensation model.

2. Experimental Section

2.1. Materials. Silica sand with a mean diameter of 250 μm and a particle density of 2600 kg/m³ (bulk density = 1600 kg/m³) was used as bed material.

Pine wood was purchased from Rettenmaier & Söhne GmbH, Germany. The pine wood particle density was 570 kg/m$_{particles}$³, and the number-average particle size was 1 mm (maximum size = 2 mm). The composition of the pine wood used is listed in Table 1.

The moisture content of the wood was adjusted by the following methods. To obtain 0 wt %, the pine wood was dried completely in an oven at 105 °C[11] for at least 24 h. To achieve a moisture content of 12 or 20 wt %, biomass was contacted with a demineralized water spray in a closed vessel. This method is described in detail by Diego et al.[12] Moisture contents within the following ranges could be realized: 12 ± 1 and 20 ± 1 wt %. All biomass feeds were analyzed for moisture content by drying in an oven at 105 °C for at least 24 h. Water contents are always reported on an as-received basis (ar).

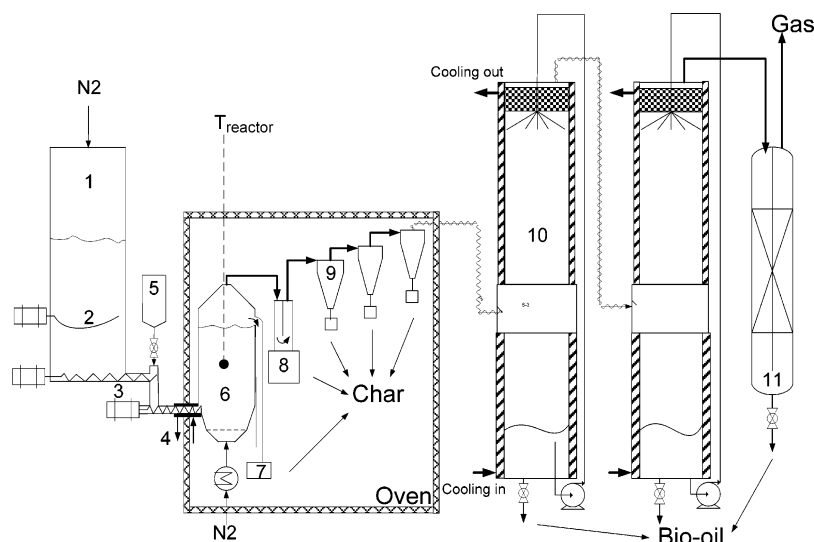* To whom correspondence should be addressed. E-mail: r.j.m.westerhof@utwente.nl.

Figure 1. Schematic drawing of the pyrolysis plant: (1) biomass storage hopper; (2) mechanical stirrer; (3) feeding system; (4) cooling jacket; (5) sand storage hopper; (6) fluidized bed reactor; (7) overflow tube + collecting vessel; (8) knock-out vessel; (9) cyclones; (10) countercurrent spray condensers; (11) intensive cooler.

2.2. Continuous Bench Scale Plant. A continuous fast pyrolysis bench scale plant with an intake of 1 kg/h biomass (ar) has been designed, constructed, debugged, and operated. This plant is schematically shown in Figure 1.

The biomass was stored in a hopper with a capacity of 4 kg. A slowly rotating stirrer inside this hopper prevented biomass particles from sticking together and forming bridges. A small nitrogen gas flow was fed to the biomass hopper, creating a slight overpressure, which prevented vapors and gases from flowing from the fluidized bed pyrolysis reactor to this hopper via the double screw feeding system. The first screw of this feeding system was used to transport the biomass from the biomass hopper and to mix this biomass with sand. Sand was stored in a second hopper and was fed to the screw with a calibrated valve. The second screw transported the biomass/sand mixture into the reactor. A water-cooled stainless steel jacket at the end of this screw (at the connection with the reactor) prevented biomass from pyrolyzing already inside it. Sand was added to control the char holdup in the fluidized bed. By feeding 2 kg of sand per kg of wet biomass, the char holdup in the reactor could be kept between 0.15 and 0.20 m^3 of char/m^3 of sand. The char holdup was measured by analysis of the reactor content after an experiment for the mass and density of char and sand. It is important to control and know the char holdup as char catalyzes the cracking of pyrolysis vapors leading to a lower oil yield[13] and influences the fluidization behavior.

The fluidized bed reactor was made from stainless steel 316 with a main diameter of 100 mm and a total height of 420 mm. It had a conical bottom part to ensure fluidization while minimizing the use of additional preheated fluidization gas (N_2), which was fed through a sintered metal plate. A mass flow controller was used to set the feed rate of the fluidization gas. The biomass was fed in the conical bottom (see Figure 1). Typical superficial gas velocities (fluidization gas, vapor, and produced gas) in the cylindrical part were in the range of 0.09–0.17 m/s. Other operating conditions and parameters are listed in Table 2.

In the fluidized bed, five thermocouples were installed at different heights to monitor the temperature. During a run, the difference in temperature between these thermocouples never exceeded 20 °C. The temperature at the center of the bed was defined as the reactor (fluidized bed) temperature, $T_{reactor}$ (see Figure 1). A solids overflow tube kept the bed level constant.

Table 2. Operating Conditions Fluidized Bed

parameter	value
experimental time	120 min
$M_{sand,initial}$	2.1 kg
bed height	0.250 m
bed diameter	0.1 m
U	0.09–0.17 m/s
U/U_{mf}	3–5
$\tau_{reactor}$	0.57–1 s
τ_{hot}	0.97–1.66 s
$T_{reactor}$	480 °C
$T_{cyclones}$	500 °C

Sand and char particles removed via this tube were collected in a vessel. The vapor/gas stream leaving the reactor contained sand fines and about 20 wt % of the produced char. In a knock-out vessel, all of the sand and most of the char particles were removed and collected. A downstream series of three cyclones, equipped with collection vessels, removed almost all residual char particles. The reactor, the solids overflow vessel, the knock-out vessel, and the cyclones were thermostated in the same oven. The fluidized bed temperature ($T_{reactor}$) was used as the set point for the oven's control loop.

The nearly particle-free hot vapor/gas stream was condensed in a jacketed countercurrent spray column (length = 1.68 m, diameter = 0.07 m). The temperature of this condenser could be controlled with an accuracy of 1 °C by pumping thermostated BP thermo-oil (Transcal SA) through the jacket. An on-line pressure indicator registered the pressure in the condenser during the run. The temperature was measured in the outgoing vapor/gas stream just after leaving the condenser. Shell Ondina 941 oil was used as spraying and startup liquid, because it has a low solubility in pyrolysis oil and therefore facilitated nearly full decantation of the pyrolysis oil produced. The circulation rate of Shell Ondina 941 oil was 5 L/min. The first condenser is hereafter referred to as the main condenser or simply as the condenser. With this condenser, the effects of operating temperature and gas load on the water content of pyrolysis oil have been investigated. The outgoing vapor/gas flow of the first condenser was led through another condenser (identical design to the first one) operated at 20 °C and an intensive cooler kept at 0 °C placed in series. These were installed to collect the remaining liquid in order to complete the mass balance. The volumetric flow rate of the gas leaving the intensive cooler was

measured with a dry gas flow indicator. A small sample of this stream was pumped through a gas analysis unit. On-line analyzers were used to measure CO, CO_2, CH_4, and H_2. A gas chromatograph was used to analyze C_2 and C_3 hydrocarbons off-line.

2.3. Analysis of Produced Pyrolysis Oils. The oils collected in the condensers and the intensive cooler were analyzed for water content by Karl Fischer titration (titrant: Hydranal-composite 5). On some oils, extraction experiments were performed by contacting demineralized water and pyrolysis oil at different phase ratios while stirring at room temperature. After agitation, the samples were allowed to settle for 2 h at room temperature in closed bottles to avoid evaporation of volatile components. Each of the phases was decanted in a separatory funnel, weighted, and analyzed for water content.

2.4. Mass Balance and Yield Calculations. Product yields Y were determined on both as-received basis (ar) and dry basis (dry). These yields are related by

$$Y_{dry} = \frac{Y_{ar}}{(1 - f_{w,biomass})} \quad (1)$$

$$Y_{dry} = \frac{\text{kg of product formed}}{\text{kg of biomass(ar) consumed} \times (1 - f_{w,biomass})} \quad (2)$$

Hereafter, only the formulas on dry basis are given. The amount of biomass fed to the reactor during a test was known by measuring the amount of biomass present in the hopper before and after the test. After an experiment, the char present in the reactor, the overflow vessel, the knock-out vessel, and the collecting vessels of the cyclones was collected and weighed. The char yield was defined by

$$Y_{char,dry} = \frac{\sum_{\substack{\text{reactor,overflow,} \\ \text{knock-out,cyclones}}} \text{kg of char collected}}{\text{kg of biomass(ar) consumed} \times (1 - f_{w,biomass})} \quad (3)$$

The amount of gas leaving the setup (after the intensive cooler) and its composition were measured continuously by a dry gas meter and on-line infrared and thermal conductivity detector (TCD) analyzers (CO, CO_2, CH_4, H_2), respectively. C_2 and C_3 hydrocarbons were measured at intervals of 15 min with a gas chromatograph (GC). On the basis of these data and the known flow rate of nitrogen fed to the fluidized bed, the gas yield was calculated:

$$Y_{gas,dry} =$$
$$\frac{\int_{t_0}^{t_{end}} \left(\left(\Phi_g \frac{P}{RT} \right)_{out} - \left(\Phi_g \frac{P}{RT} \right)_{in} \right) \times \sum_{\text{gas components}} (Y_{gc} M_{gc}) \, dt}{\text{kg of biomass(ar) consumed} \times (1 - f_{w,biomass})} \quad (4)$$

During an experiment, the condensed liquids remained in the condensers and intensive cooler. After an experiment, the liquids removed from the condensers and intensive cooler and the produced oil were separated from the Shell Ondina 941 oil. Hereafter the produced oils were weighed and analyzed for water content. These data provided the yields of pyrolysis oil, organics in pyrolysis oil, and produced water.

$$Y_{\text{organics in pyrolysis oil,dry}} =$$
$$\frac{\sum_{\substack{\text{condensers,} \\ \text{intensive cooler}}} \text{kg of liquid collected} \times (1 - f_w)}{\text{kg of biomass(ar) consumed} \times (1 - f_{w,biomass})} \quad (5)$$

$$Y_{\text{pyrolysis oil,dry}} =$$
$$\frac{\sum_{\substack{\text{condensers,} \\ \text{intensive cooler}}} \text{kg of liquid collected}}{\text{kg of biomass(ar) consumed} \times (1 - f_{w,biomass})} \quad (6)$$

$$Y_{\text{produced water,dry}} = Y_{\text{pyrolysis oil,dry}} - Y_{\text{organics in pyrolysis oil,dry}} - \frac{f_{w,biomass}}{1 - f_{w,biomass}} \quad (7)$$

The sum of $Y_{char,ar}$, $Y_{gas,ar}$, and $Y_{\text{pyrolysis oil,ar}}$ defines the mass balance.

The moisture content in the condensable feed stream of the first condenser ($f_{w,feed}$) is calculated from the amount and water content of the liquids collected in the first and second condenser and the intensive cooler:

$$f_{w,feed} = \frac{\sum [\text{kg of liquid collected} \times f_w]_{\substack{\text{1st condenser,} \\ \text{2nd condenser,} \\ \text{intensive cooler}}}}{\sum_{\substack{\text{1st condenser,} \\ \text{2nd condenser,} \\ \text{intensive cooler}}} [\text{kg of liquid collected}]} \quad (8)$$

3. Condenser Model

The condenser is modeled as an equilibrium flash separator. In this unit, the hot reactor effluent is cooled and partially condensed at constant temperature and pressure leading to phase separation. Because the qualitative and quantitative composition of pyrolysis oil is not known, the assumption of reaching equilibrium is a conjecture that is difficult to prove experimentally. However, whether the design of the condenser allows reaching equilibrium between the outgoing liquid and vapor stream can be checked by performing tests with model feeds. Nitrogen/steam and nitrogen/steam/ethanol vapor mixtures with flow rates corresponding to the ones in the pyrolysis experiments (steam and ethanol representing pyrolysis oil) were fed to the condenser at different temperatures. The amounts of water and liquid ethanol that were collected from the condenser after these tests corresponded well with the predictions of the model described below. This result shows that reaching phase equilibrium between the outgoing streams is possible for model feeds in the condenser. It is assumed further that this also holds for pyrolysis vapors.

The product compositions and flow rates of the vapor (y_i, V) and liquid (x_i, L) streams leaving the condenser are predicted with the so-called Rachford–Rice equation:[14]

$$f\left(\frac{V}{F}\right) = \sum_{i=1}^{C} \frac{z_i(1 - K_i(T,p))}{1 + \frac{V}{F}(K_i(T,p) - 1)} = 0 \quad (9)$$

Besides thermal ($T_L = T_V$) and mechanical ($p_L = p_V$) equilibrium, the model assumes phase equilibrium and ideal

Table 3. Organic Component Groups Used in the Condenser Model

group	normal boiling point [K]	components	vapor pressure component (Nbp [K])	molecular weight [g/mol]	appearance in organic condenser feed [wt %, daf]
IO1	250–300	formaldehyde, acetaldehyde	formaldehyde (253.9)	31.4	1.2
IO2	300–330	propionaldehyde, glycolic acid, glyoxal, acetone	propionaldehyde (322)	65.4	0.9
IO3	330–360	methanol, 2-oxobutanoic acid, ethanol, MEK, 2-propanol, (5*H*)-furan-2-one	ethanol (351.6)	48.4	3.3
IO4	360–390	formic acid, hydroxyacetaldehyde, 5-hydroxymethylfurfural	formic acid (373.9)	61.6	9.2
IO5	390–420	acetic acid, butanol, lactic acid, 4-propylguaiacol, propionic acid, acrylic acid, acetol	propionic acid (414.2)	71.0	18.0
IO6	420–450	isobutyric acid, 2-hydroxy-2-cyclopentene-1-one, 2-hydroxy-1-methyl-1-cyclopentene-3-one, 1-hydroxy-2-butanone, furfural, methacrylic acid, *n*-butyric acid, coniferylaldehyde	*n*-butyric acid (436)	105.8	2.9
IO7	450–500	phenol, crotonic acid, valeric acid, 3-hydroxypropanoic acid, *o*-cresol, tiglic acid, 4-methylpentanoic acid, *p*-creosol, *m*-cresol, hexanoic acid, guaiacol, 4-hydroxybenzaldehyde, 4-methylguaiacol, vinylguaiacol	*p*-cresol (475)	125.3	2.5
IO8	500–550	4-ethylguaiacol, 1,2-benzendiol, levulic acid, benzoic acid, eugenol, syringol, vanillin, isoeugenol (cis + trans)	eugenol (526)	150.9	2.4
sugar constituent					
1		levoglucosan, glucose, xylose, cellobiosan, hydroquinone, ...	hydroquinone (558)	160	17.3
2	∞	some components identified, no qualitative data on component level[a]	$p = 0$	320	17.3
LMM lignin	∞	some components identified, no qualitative data on component level[a]	$p = 0$	450	18
extractives	∞	some components identified, no qualitative data on component level[a]	$p = 0$	460	3
HMM lignin	∞	some components identified, no qualitative data on component level[a]	$p = 0$	1050	4

[a] From ref 16.

behavior of both vapor and liquid phases such that the partition ratios (K_i) are independent of composition:

$$K_i(T,p) \equiv \frac{y_i}{x_i} = \frac{p_i^0(T)}{p} \tag{10}$$

This is probably a reasonable assumption because the weight fraction of most individual components in the oil hardly exceeds 1%, as a result of which each component could behave as a diluted species in a bulk liquid that contains all the other components. For water, which is present up to 35 wt %, this reasoning does not hold. Nevertheless, it was assumed that water also behaves ideally.

In eqs 9 and 10, the molar composition (z_i) and molar flow rate (F) of the condenser feed as well as the condenser temperature (T) and pressure (p) should be specified. Temperature and pressure were measured. The amounts of water, fluidization gas (N_2), and the amount and composition of product gases in the condenser feed were known from the overall measured mass balance. Gases are defined here as species that cannot condense at the condenser temperatures tested (15–90 °C). The amount of organic vapors (species that can condense at the used condenser temperature range) in the condenser feed is also known from the mass balance, but the composition of this organic fraction is not measured. Our laboratory is not equipped with advanced liquid analysis apparatus. Therefore, the composition of the organic fraction in the condenser feed is collected from literature data. To fill in the organic fraction in the model, we have chosen pyrolysis oils from the literature that (i) represent almost all organics produced in the pyrolysis reactor (i.e., liquid condensed at low temperature in a condenser operating at equilibrium or the blend of liquids collected in several condensers), and (ii) were produced from the same feedstock (pine wood) in similar reactor configurations (fluidized/transported bed) under comparable operating conditions. About 40 wt % of the organics in pine wood pyrolysis oil produced by Dynamotive (fluidized bed, $T_{reactor}$ = 460 °C) have been identified on a component level by a round robin study.[15]

It should be mentioned here that the quantitative chemical analysis results at the level of individual components of the laboratories involved in the round robin were not very consistent. For the condenser model, the identified and quantified components are grouped into normal boiling point ranges; see Table 3.

A group is represented in the condenser model by its vapor pressure and molecular weight. For the vapor pressure curve a component in the middle of the boiling point range is selected; the group's molecular weight is the mass-average molecular weight of the components within the group. At the level of these groups the results of the round robin were more dependable. We used average values from laboratories 3 and 9 if available; if not, the results from laboratory 12 were taken.

The missing 60 wt % of the organics are defined as sugar constituents, extractives, low molecular weight lignin, and high molecular weight lignin as obtained from fractionation experiments done on pine wood pyrolysis oil produced by VTT (transported bed, $T_{reactor}$ = 520 °C, residence time of pyrolysis vapors is 1–2 s).[16] According to VTT analysis these component groups add up to about 65 wt % (daf basis) of the organics in pine oil. We copied their measured weight percent of extractives, low molecular weight lignin, and high molecular weight lignin. The average molecular weight of these groups is known[16,17] and is high enough to allow the assumption of a zero vapor pressure in the condenser. The sugar constituents fraction as measured by VTT is lowered by 5 wt % (making the total 100%) while assuming that some of these components are already present in the round robin list. These sugar constituents are split into two equal parts: one with the vapor pressure of hydroquinone and one with zero vapor pressure. In Table 3, the groups of organic components used in the condenser model together with their characteristics are listed.

4. Results

4.1. Mass Balance Closure and Reproducibility. In total, 41 experiments were performed without operational problems.
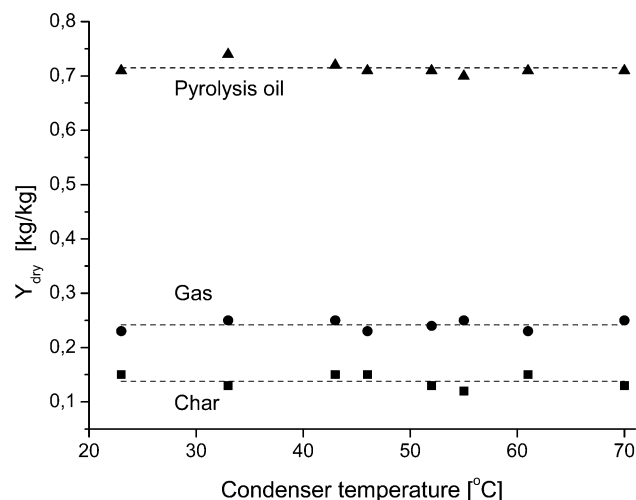
Figure 2. Yields of char, gas, and pyrolysis oil of nine identical experiments with respect to the reactor conditions, but different temperatures of the condenser. Conditions: $T_{reactor} = 480$ °C; $T_{cyclones} = 500$ °C; $\tau_{hot} = 1.32$ s; $\tau_{reactor} = 0.78$ s; $f_{w,biomass} = 0.12$. The dashed lines represent the average value of the nine experiments.

It was decided beforehand that the mass balance closure must be between 94% and 102% for proper interpretation of the results. Of the 41 experiments, 7 were outside the desired mass balance closure limits and have been rejected consequently.

Reproducibility was checked by repetition of nine experiments under identical reactor conditions and using the same feedstock (12 wt % moisture), but different operating temperatures of the first condenser.

Of these tests the average yields on dry basis are 14, 72, and 24 wt % for char, pyrolysis oil, and gas, respectively. These yields lie in the range of fluidized bed fast pyrolysis yields reported in the literature.[18] Our process conditions were, however, not optimal for maximizing the pyrolysis oil yield. Due to the fact that both the reactor and the char separation units (knock-out vessel + cyclones) were placed in the same oven, the temperature of these units was ca. 500 °C while the temperature in the fluidized bed was 480 °C. At 500 °C, cracking of pyrolysis vapors to gases can be significant,[19−21] lowering the pyrolysis oil yield and increasing the gas yield.

The statistics of the nine identical tests provides an estimate of the reproducibility of an individual experiment (see Figures 2 and 3). Table 4 lists the average yields, standard deviations, and the relative spread ($\sigma_{Y_{dry}}/\bar{Y}_{dry} \times 100\%$). The relative scatter on the char, gas, and pyrolysis oil yield is less than 8%, showing that the reproducibility of the experiments is good. The relative spread on the yield of produced water is somewhat larger (11%), but is still low enough for trend detection on the basis of single experiments. In this work, trends in yields based on single measurements as a function of the operating conditions are considered sound only if they exceed σ of the repetitive measurements reported in Table 4.

These nine experiments also show that the condensation train of two condensers and one intensive cooler in series works well: with this train we can collect all the products ultimately, under all conditions of the first condenser (see Figures 2 and 3).

4.2. Effect of the Operating Conditions on the Yields. The reactor yields of gas, organics in pyrolysis oil, and produced water are input parameters for the condenser model. In this section, it is reported if and how these yields are affected by the varied operating conditions.
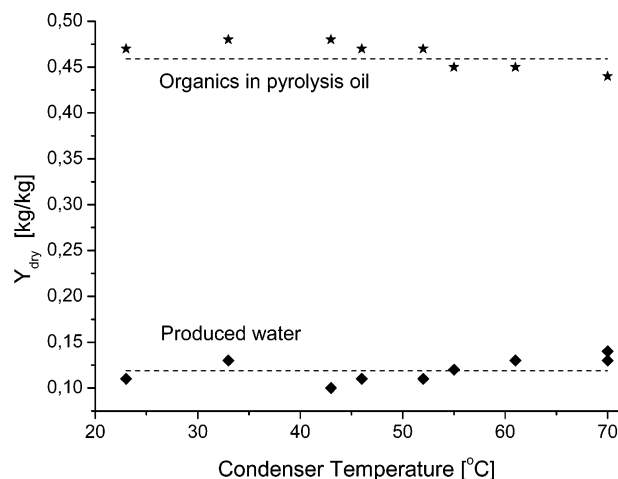

Figure 3. Yields of organics in pyrolysis oil and produced water of nine identical experiments with respect to the reactor conditions, but different temperatures of the condenser. Conditions: $T_{reactor} = 480$ °C; $T_{cyclones} = 500$ °C; $\tau_{hot} = 1.32$ s; $\tau_{reactor} = 0.78$ s; $f_{w,biomass} = 0.12$. The dashed lines represent the average values of the nine experiments.

Table 4. Reproducibility of Nine Identical Experiments, with Respect to the Reactor Conditions ($T_{reactor} = 480$ °C, $T_{cyclones} = 500$ °C, $\tau_{hot} = 1.32$ s, $\tau_{reactor} = 0.78$ s, $f_{w,biomass} = 0.12$)[a]

product	average yield, $\bar{Y}_{dry}$ [kg/kg]	std dev, $\sigma_{Y_{dry}}$ [kg/kg]	relative spread, $\sigma_{Y_{dry}}/\bar{Y}_{dry} \times 100\%$ [%]
char	0.14	0.010	7.6
gas	0.24	0.009	3.7
organic in pyrolysis oil	0.46	0.017	3.7
produced water	0.12	0.013	11.4
pyrolysis oil (organics + total water)	0.72	0.01	1.4

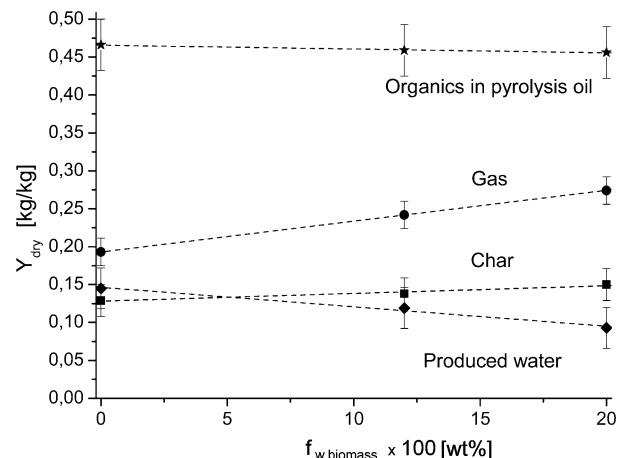[a] The condenser temperature varied from 15 °C to 70 °C.

Figure 4. Effect of moisture content of the feedstock on yields of char, gas, produced water, and organics in pyrolysis oil. Conditions: $T_{reactor} = 480$ °C; $T_{cyclones} = 500$ °C; $\tau_{hot} = 1.32$ s; $\tau_{reactor} = 0.78$ s; moisture content of the feedstock = 0−20 wt %. The condenser temperature varied between 15 and 90 °C. Condenser feed: 2.90−3 kg of gases/kg of vapors. Dashed lines represent trends.

4.2.1. Moisture Content of the Feedstock. The effect of the moisture content of the feedstock (range = 0−20 wt %) on the yields of char, gas, and pyrolysis oil, the latter subdivided into the organic fraction and produced water, is shown in Figure 4. All data points presented are averages of at least three experiments. In this experimental series, the reactor conditions were kept constant ($T_{reactor} = 480$, $\tau_{hot} = 1.32$ s), but the operating temperature of the condenser varied. It has been shown, however, that the latter variation does not affect the

yields (see section 4.1, "Mass Balance Closure and Reproducibility"). With increasing moisture content of the feedstock, it has been observed that the char and gas yield increase, the produced water yield decreases, and the yield of organics in pyrolysis oil remains constant (see Figure 4). Gray et al.[22] also observed that more moisture in the feed results in an increased char yield. The increase in char and produced water yield can be explained partly from the pyrolysis process at the particle level. Our single particle pyrolysis model[3] shows that the effective pyrolysis temperature of a biomass particle with a characteristic length between 1 and 2 mm and reacting at ca. 500 °C decreases upon increasing the moisture content, because of the energy consumption of water vaporization. The effective pyrolysis temperature is the volume-averaged value of the local temperature at which the reaction rate is maximal. If there are heat transfer limitations to or within the particle, the effective pyrolysis is lower than the reactor temperature. Kersten et al.[3] have shown that evaluation of the intrinsic kinetics at the effective pyrolysis temperature provides a good estimate of the yields predicted by a full model including, next to kinetics, also transport parameters. Several kinetic studies[23-25] have shown that, starting from a pyrolysis (fluidized bed) temperature of 480 °C, a lower temperature increases the char yield. Combining this trend of the intrinsic kinetics with the model predictions regarding the lower effective pyrolysis temperature for wetter biomass explains the measured increase of the char yield for feeds with a higher moisture content. However, the absolute effect predicted by the model is only half of the measured effect.

Bridgwater et al.[26] collected experimental data indicating that a decreasing temperature in the range of 500-400 °C results in a lower yield of produced water. The increase in gas yield and the constant yield of organics in pyrolysis oil cannot be explained unequivocally by the present knowledge of fast pyrolysis.

4.2.2. Vapor Residence Time. To steer the water content of pyrolysis oil, variation of the gas load (sweep gas) of the condenser is tested (see section 4.3.3, "Gas Load of the Condenser"). The additional gas was fed to the fluidized bed reactor which influenced the residence time of the produced pyrolysis vapors at high temperature. A higher residence time of vapors might influence the product distribution through cracking reactions (overall first order) of these vapors. In this experimental series the residence time of vapors varied between 0.97 and 1.66 s. From the results obtained, it can be concluded that within this range the yields are not affected by the vapor residence time (see Figure 5), especially when considering the scatter on individual data points (see section 4.1, "Mass Balance Closure and Reproducibility"). Also, Scott et al.[27] found that, at temperatures of 500 °C and below, the vapor residence time studied does not have a significant effect on the yield of pyrolysis oil.

4.3. Steering the Water Content of Pyrolysis Oil. Below, the results of the investigated methods to manipulate the water content of pyrolysis oil are reported and discussed.

4.3.1. Extraction of Pyrolysis Oil. As reference for the other methods investigated to remove water from pyrolysis oil, extraction of pyrolysis oil with water has been investigated experimentally. The conclusion concerning this method, though, could have been drawn also on the basis of phase diagrams of pyrolysis oil presented in the literature.[1,10] If single phase pyrolysis oil is extracted with enough water (ca. 30 wt % water in the total liquid), phase separation occurs. Just after decantation, the obtained hydrophobic phase contains 20 wt % water,
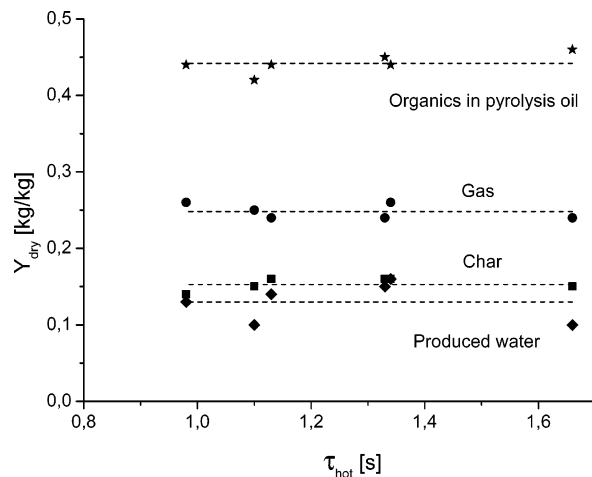

Figure 5. Effect of residence time on yields of gas, char, organics in pyrolysis oil, and produced water. Conditions: $T_{reactor}$ = 480 °C; $T_{cyclones}$ = 500 °C; $f_{w,biomass}$ = 0.12. Condenser temperature = 50 °C. Dashed lines represent average values.

independent of the initial water content, showing that the water content (can be up to 35 wt % initially) can be decreased by extraction.

However, from the offset of phase splitting, the organics in pyrolysis oil are distributed with a partition ratio that hardly depends on the amount of water added over the hydrophilic phase (containing ca. 45% of the organics) and hydrophobic phase (containing ca. 55% of the organics). Concluding, although the water content of pyrolysis oil can be lowered by extraction with water, it is not a feasible method because the pyrolysis yield decreases too much (50% of the organics end up in the water phase).

4.3.2. Varying the Temperature of the Condenser. Oasmaa et al.[17] reported some exploratory results on the effect of the condenser temperature on the water content of pyrolysis oil. We present a more detailed analysis covering a broad range of condenser temperatures from 15 °C to 90 °C. In Figure 6A the water content of pyrolysis oil is plotted versus the condenser temperature in the range 15-90 °C for various moisture contents of the feedstock (0, 12, 20 wt %). The used moisture contents in the feedstock correspond to 22.5, 35.7, and 42.9 wt % moisture in the condensable condenser feed ($f_{w,feed}$), respectively. All results described in this section were obtained with a gas load of the condenser of 2.90-3 kg of gases/kg of vapors in the condenser feed.

The water content of pyrolysis oil hardly depends on the condenser temperature in the range between 15 and 35 °C (see Figure 6A). Between 35 and 70 °C, the condenser temperature affects the water content significantly. Above 70 °C, the influence of the condenser temperature on the water content is minimal. The pyrolysis oil obtained at a condenser temperature of 90 °C (water fraction of 0.03) is very viscous (viscosity = 80 000 cP at) 20 °C. The agreement of the model predictions with respect to the moisture content of pyrolysis oil collected in the condenser is very good.

The average residence time of produced liquid in the condenser was ca. 1 h. Storage at elevated temperature for 1 h may affect the composition of pyrolysis oil. However, this has not been observed unequivocally in our study. The total yields of organics in pyrolysis oil and produced water are not affected by the condenser temperature (see Figure 3). Apparently, 1 h residence time of pyrolysis oil at temperatures of 90 °C and lower is not enough to have significant condensation (polymerization) reactions in the liquid phase, yielding water and
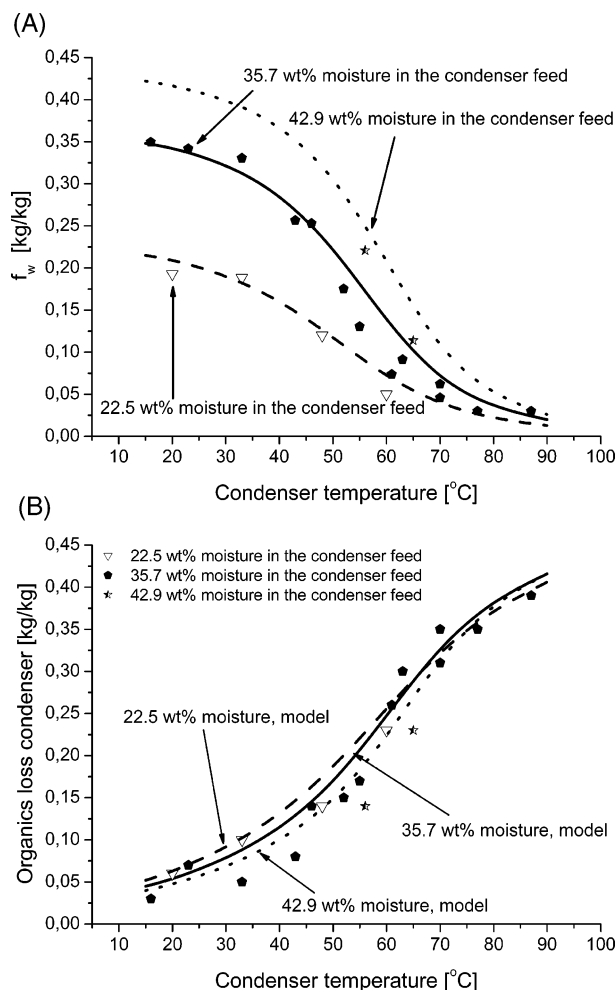
(A)

(B)

Figure 6. (A) Water content of pyrolysis oil obtained in the (first) condenser as a function of condenser temperature. Experimental results (presented by points) are compared with model predictions (presented by lines). Conditions: $T_{reactor}$ = 480 °C; $T_{cyclones}$ = 500 °C. Condenser temperature varied between 15 and 90 °C. (B) Loss of organics from the pyrolysis oil obtained in the condenser as a function of condenser temperature. Experimental results (presented by points) are compared with model predictions (presented by lines). Conditions: $T_{reactor}$ = 480 °C; $T_{cyclones}$ = 500 °C. Condenser temperature varied between 15 and 90 °C.

lowering the yield of organics. These results are in line with experimental results reported by Czernick et al.[28] concerning storage of pyrolysis oil at elevated temperature. They found only a slight increase in viscosity and molecular weight (~5%) after storage at 90 °C during 1 h. It is known that the main physicochemical changes of stored pyrolysis oil take place in the first 6 months after production and that water is formed as a byproduct of condensation reactions.[29] The pyrolysis oils produced in our study were analyzed just after production and after 6 months. Over this period no significant increase in water content is observed for all pyrolysis oils (see Table 5).

Obviously, starting with a wetter feedstock at otherwise identical operating conditions results in pyrolysis oil with higher moisture content (see Figure 6A). This effect is small at condenser temperatures above 70 °C, because then most water leaves the condenser in the vapor phase anyway. With increasing condenser temperature, not only water but also light organic volatiles are removed from the pyrolysis oil, thus decreasing the total amount of oil. The loss of these lights can be expressed as the fraction of total produced organic vapors in the condenser feed that is not collected in the first condenser. Figure 6B shows that, for different moisture contents of the feedstock, resulting
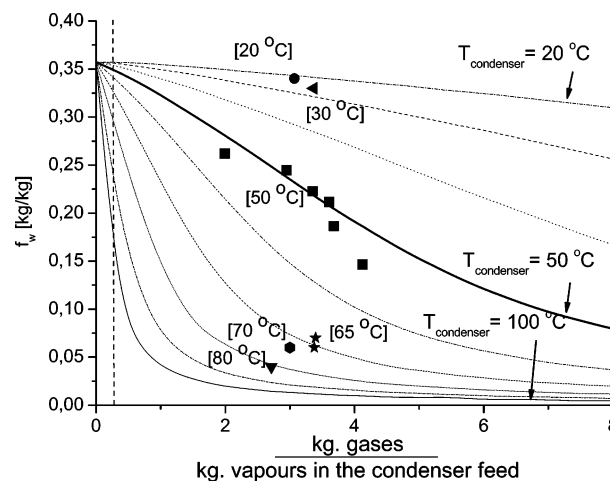

Figure 7. Water fraction of the pyrolysis oil obtained in the condenser as a function of gas load of the condenser. Experimental results (condenser temperatures are indicated near the data points) are compared with model predictions for condenser temperatures in the range of 20−100 °C. Conditions: $T_{reactor}$ = 480 °C; $T_{cyclones}$ = 500 °C; $f_{w,biomass}$ = 0.12.

Table 5. Water Content of Pyrolysis Oil as a Function of Condenser Temperature and Storage Time

condenser temperature [°C]	water fraction pyrolysis oil just after production, f_w [kg/kg × 100%]	water fraction pyrolysis oil after 6 months, f_w [kg/kg × 100%]
33	33.1	34.1
43	25.7	25.1
50	17.7	17.7
56	21.9	22.1
70	4.5	4.3

in different moisture contents of the condenser feed, this loss increases with increasing condenser temperature. Above 80 °C, the effect of the condenser temperature on the loss of organics diminishes, because most lights have left as vapors already and the heavy organics (e.g., heavy sugars, LMM and HMM lignin, extractives) still completely condense due to their high molecular weights. Also, for the loss of organic vapors from the condenser the agreement between the model predictions and the experimental data is good. At the same condenser temperature, it appears that the moisture content of the feedstock only has a slight effect on the organics fraction collected in the first condenser. In fact, below 70 °C at otherwise the same conditions, a higher moisture content of the condenser feed results in a lower loss of organics vapors in the condenser. This can be explained by a lower concentration of organic vapors in the condenser inlet at increasing steam load. From the list of compounds used in our condenser model (see Table 3), it can be seen that the organic compounds leaving condenser 1 are low molecular weight acids, aldehydes, and ketones. Etherification and esterification reactions between hydroxyl, carbonyl, and carboxyl groups are partly responsible for the aging reactions.[28] It has been suggested by Oasmaa et al.[17] that in removing these light compounds the pyrolysis oil becomes more stable.

Maintaining the same water content of pyrolysis oil when the condenser feed contains more water (wetter feedstock) requires a higher condenser temperature at otherwise identical conditions (compare Figure 6A and Figure 6B). As a result of this higher temperature, the loss of organics increases. Another method to maintain the same water content is to increase the gas load of the condenser. This is discussed in the next section.

4.3.3. Gas Load of the Condenser. In the experimental series, the temperature of the condenser was maintained at 50
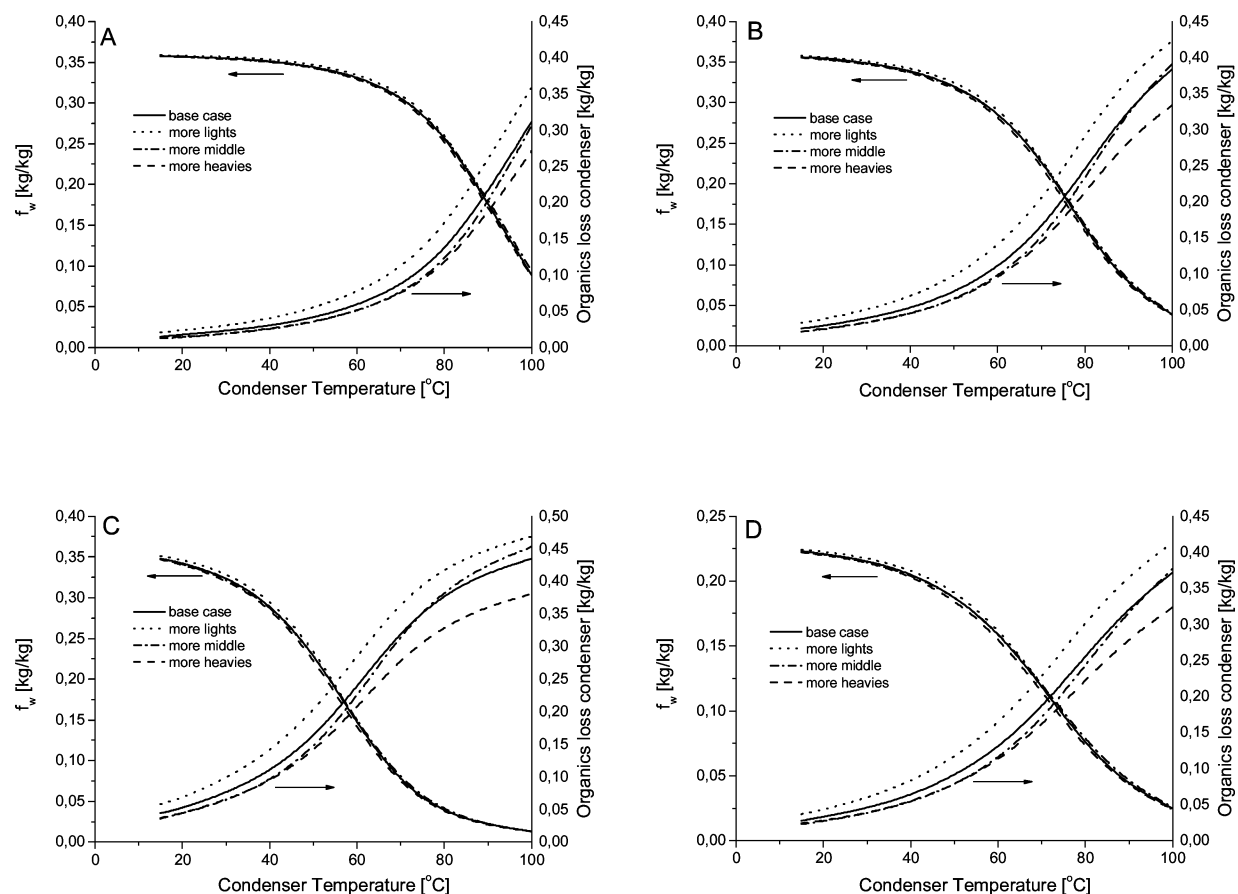
Figure 8. Model sensitivity: (A) gas load = 0.4 kg of gases/kg of vapors, water content of condenser feed = 35.7 wt %; (B) gas load = 1 kg of gases/kg of vapors, water content of condenser feed = 35.7 wt %; (C) gas load = 3 of kg of gases/kg of vapors, water content of condenser feed = 35.7 wt %; and (D) gas load = 1 kg of gases/kg of vapors, water content of condenser feed = 22.5 wt %.

Table 6. Composition of the Organic Condenser Feed in the Cases Used in the Condenser Model Sensitivity Study

	Composition (wt %, dry)			
component	base case	more lights	more middles	more heavies
lights (IO1−IO4)[a]	14.6	20	12	12
middles (IO5−IO8)[a]	25.8	23	31	23
heavies (IO9−IO13)[a]	59.6	57	57	65

[a] See Table 3 for details on IO1−IO13.

°C and the load of sweep gas was varied (2.0−4.1 kg of gases/ kg of vapors in the condenser feed). In the pyrolysis process this sweep gas can be (i) gas that is also led through the pyrolysis reactor (e.g., fluidization gas) or (ii) after further cooling, the gas stream leaving the condenser. In the latter recycle options further cooling of the recycle stream is required to lower the water vapor content of this gas relative to the equilibrium prevailing in the condenser. The experimental results are shown in Figure 7, together with model predictions. There is always a minimum amount of gas entering the condenser due to gas production in the pyrolysis process; this is indicated by the vertical dashed line in Figure 7. Clearly, the use of a sweep gas in the condenser lowers the water content of pyrolysis oil. However, as by increasing the condenser temperature, a decrease in water content also always results in a loss of light organics.

Next to the results at a condenser temperature of 50 °C, also model predictions for other condenser temperatures are included in Figure 7 together with individual data points. The model predictions show that at low gas loads (<1 kg/kg) a condenser temperature of at least 70 °C is needed to decrease the water content of pyrolysis oil significantly. At low gas loads and such

high temperatures, a small change in sweep gas load will largely affect the water content of the pyrolysis oil. This could lead to difficulties in controlling the water content. For high gas loads (>2 kg/kg), the water content can be decreased significantly at a relatively low condenser temperature of 50 °C.

5. Condenser Model Sensitivity

In this section, the condenser model sensitivity is evaluated. For this analysis, only the organic composition of the condenser feed is varied. Noncondensable gases and water in the condenser feed are (can be) known accurately enough. Gases follow from the mass balance and the water content can be estimated precisely by operating the condenser (first) at low temperature (<30 °C). Figure 6A shows that at such low temperatures the water content of the obtained oil in the condenser (first) is nearly identical to the water content of the condenser feed, if the condenser operation approaches equilibrium. The organic components in the condenser feed are divided in three groups according to their boiling points (lights, middles, and heavies). Three cases have been defined relative to the base case: more lights, more middles, and more heavies. Deviations relative to the base case are based on the maximum spread reported by the round robin study.[15] The weight fraction of the groups in the considered cases is listed in Table 6. Simulations are done for three different gas loads (0.4, 1, and 3 kg of gases/kg of vapors) and two different H_2O contents (22.5 and 35.7 wt %) in the condenser feed.

The model simulations show (see Figure 8) that the predicted water content of pyrolysis oil in the condenser (first) is almost independent of the (assumed) organic composition of the
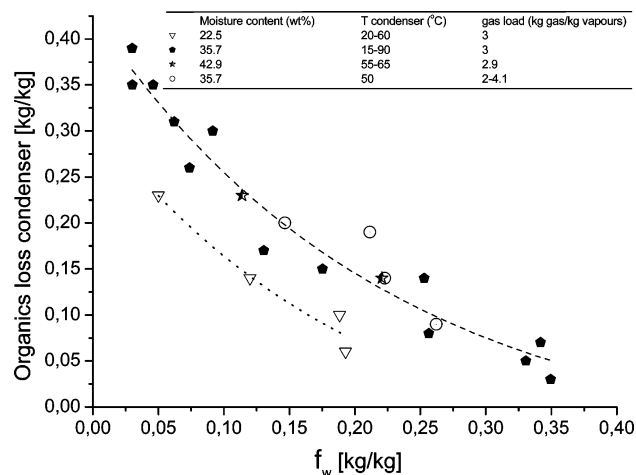
Figure 9. Operating regime map of the condensers on the basis of the water content of pyrolysis oil and the loss of organic vapors produced by pyrolysis. Results of varying condenser temperature for feeds with 22.5, 35.7, and 42.9 wt % H_2O at constant sweep gas load (kg of gases/kg of vapors) are compared with results of varying sweep gas load at otherwise identical conditions. Conditions: $T_{reactor} = 480$ °C; $T_{cyclones} = 500$ °C.

condenser feed within the ranges defined in Table 6 and for all considered gas loads and water fractions in the condenser feed. This can be explained by the fact that water is by far the major compound on molar bases (mole fraction = 0.77−0.82) present in the condenser feed in all cases. The absolute spread in loss of organics compared with the base case rises to maximal 0.05 kg/kg at higher condenser temperature.

6. Discussion and Conclusions

In this paper, several process options to steer the water content of pyrolysis oil are evaluated. Downstream extraction of pyrolysis oil with water does reduce the water content, but it is not a viable approach because the yield of pyrolysis oil is reduced too much. The temperature (15−90 °C) and the load of sweep gas (2−4.1 kg of gases/kg of vapors in the condenser feed) of the condenser are both well suited to lower the water content of pyrolysis oil. However, removing water is always accompanied by the loss of organic vapors in the condenser via entrainment with the outgoing gas stream. No negative effects with respect to yield and no increased aging of oil condensed at elevated condenser temperature have been observed at an average liquid residence time of 1 h. The influence of the operating conditions of the condenser on the water content of the collected pyrolysis oil and the loss of organic vapors can be predicted with sufficient accuracy for process design using a simple equilibrium model. This model assumes that the outgoing streams of the condenser are at equilibrium, which can be achieved in practice by providing enough contact area and contact time to condense the vapors. Inputs for the model are the yields of the pyrolysis products and the composition of the organic fraction of the pyrolysis oil. The yields can be measured, and from round robin studies in the literature sufficient accurate and reliable data on the composition of oils derived from various feedstock materials are available. In Figure 9 the loss of organic vapors in the condenser is plotted versus the obtained water content of pyrolysis oil. Results of varying the condenser temperature and water content in the condensable condenser feed (22.5, 35.7, 42.9 wt % corresponding in our process to a biomass feedstock moisture of 0, 12, and 20 wt %) at constant sweep gas load are compared with results of varying sweep gas load at otherwise identical conditions. Figure 9 shows that, for a condenser feed with 35.7 wt % H_2O, the

amount of organic vapors lost in the condenser to reach a certain water content of pyrolysis oil is fixed, irrespective of whether the water is removed by raising the temperature or increasing the gas load of the condenser (the data representing these scenarios are indistinguishable). In a practical pyrolysis plant, a well-considered combination of a sweep gas load and the condenser temperature can be used to control the water content.

The results of feeds with 35.7 and 42.9 wt % H_2O in the condenser feed are identical in view of the scatter in the experimental data. Drying the feedstock to very low moisture levels (approaching zero) leading to a low water content of the condenser feed (22.5 wt %) is beneficial, because it reduces the amount of organic vapors lost in the condenser over the whole range of desired water contents of pyrolysis oil. From a practical point of view such dry feedstock materials are, however, not realistic due to the high costs of the dryer.

Nomenclature

Roman Variables

M_{sand} = amount of silica sand, kg
U = superficial velocity, m/s
U_{mf} = minimal fluidization velocity, m/s
Y = yield, kg/kg
f_w = water content of the pyrolysis oil, kg of water/kg of liquid
$f_{w,biomass}$ = water content of the biomass, kg of water/kg of biomass(ar)
$f_{w,feed}$ = water content of the condensable condenser feed (given in terms of kg of water from the first and second condenser and the intensive cooler per kg of liquid from the first and second condenser and the intensive cooler, kg of water/kg of liquid)
t = experimental time, s
V = vapor flow that leaves the first condenser, mol/s
L = pyrolysis oil that leaves the first condenser, mol/s
F = condenser feed, mol/s
K = partition ratio
p = pressure, bar
z = fraction of a component in the first condenser feed
T_L = temperature of the pyrolysis oil in the first condenser, °C
T_V = temperature of the vapor that leaves the first condenser, °C
$T_{reactor}$ = reference reactor temperature, °C
$T_{cyclones}$ = reference temperature of the vapor/gas phase in the hot part of the pyrolysis plant, °C
y = mole fraction of a component in the vapor/gas phase
x = mole fraction of a component in the liquid phase
p_i^0 = partial pressure of a component, bar
l = length, m
d = diameter, m
c = number of components
M = molecular mass, g/mol

Greek Symbols

τ_{hot} = residence time of vapors and gases in the hot part of the setup, s
$\tau_{reactor}$ = residence time of vapors and gases in the reactor bed, s
ϕ_g = gas flow, m³/s
σ = standard deviation

Subscripts

dry = on a dry feedstock basis
daf = on a dry ash-free basis

initial = at the start of a experiment
0 = at time point zero
i = a single component that represents the average of a group
  of components used in the model
end = at the end of the experiment
gc = a single gas component
ar = as received

Terminology

LMM = low molecular mass
HMM = high molecular mass
Nbp = normal boiling point

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